The analytical chemist in nineteenth century English social history

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THE ANALYTICAL CHEMIST IN NINETEENTH CENTURY ENGLISH SOCIAL HISTORY

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by

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Abstract

Laws regulating the sale of poisons and the purity of foods and medicinals imply the existence of methods for detecting offences, and of persons qualified to employ them. The 1804 Stamp Duty Act named 453 proprietary medicines, many of extreme complexity . Synthetic drugs tended to diminish the polypharmacy of earlier days, and the rise of the health salt trade brought further simplification, but analysis was still made difficult by the practice of substitution. Advertising of nostrums was assiduously developed by Holloway and Beecham.

Chemical analysis had its roots in mining for metals. The blowpipe enabled metals to be detected in complex environments. Group analysis developed from the work of Klaproth, Thomson, Rose and Fresenius. The systematic use of H_2S is due to Berthollet and Gay-Lussac. Analysis of animal and vegetable products was slower to develop: significant stages were destructive distillation, solvent extraction, element tests, melting points, characteristic group reactions, and instrumentation. Positive identification was difficult to achieve.

Chemical evidence in poisoning trials was given usually by medical men: the consequent forensic disasters (Palmer case, 1856, Smethurst case 1859) brought chemical analysis into disrepute. Landmarks in chemical toxicology were Marsh's test for arsenic (1836) and the Stas-Otto method for extracting poisons from stomach contents (1852). Examples of social problems in the chemical detection of poisons were the easy confusion of oxalic acid with Epsom salt, and the prevalence

of opium-containing soothing syrups for infants.

Apothecaries, druggists and pharmacists concerned themselves with the adulteration of drugs. General chemical analysis was undertaken by such 'practical' chemists as F. Accum. Pharmacists acquired the right to be called chemists: chemistry was often made to appear as a frivolous science. The 1863Alkali Act and the 1860 Food Act paved the way for the professional analyst. The Society of Public Analysts was founded in 1874 and the [Royal] Institute of Chemistry in 1877.

The adulteration of food is not treated in this study.

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CHAPTER I

THE CAPABILITIES AND LIMITATIONS OF CHEMICAL ANALYSIS BEFORE 1800.

This study concerns the emerging and changing role of the chemical analyst in English public life during the nineteenth century. The function of the analyst impinges on the life of the ordinary citizen at a number of points, particularly in guaranteeing the quality of the goods that he buys, defending him from the worst excesses of quackery and protecting him from poisoning. In the course of this activity, the law has frequently been changed and new social habits have been formed. It is therefore necessary to begin by examining the social life of England at the end of the eighteenth century as it is reflected in contemporary attitudes to health and disease, popular medicine, food and drink, and to relate this to the resources and limitations of analytical chemistry at that time.

It is difficult to write about the last decades of the eighteenth century without obsessive use of the word revolution. In foreign affairs, in policies at home, in agriculture, commerce, and industry, as well as in science, the rate of change was increasing beyond the capacity of the corporate mind to assimilate it, so that at one point practice lagged behind theory, at another new skills outpaced the understanding of those who used them.

Chemical analysis was at this time in the former class, for the sweeping changes in chemical theory did not influence in any noticeable degree the practice of the laboratory. This is best shown by reference to the greatest theoretical change of all, the overthrow of phlogistonism by the introduction of the oxygen theory of combustion. During the second half of the seventeenth century air had been seen to be a material substance due to the experiments of Otto von Guericke, Robert Boyle and Evangelista Torricelli, and Johannes Baptista van Helmont had recognised two kinds of air, calling them by the new name of 'gas'. John Mayow in his Tractatus Quinque (1674) and Robert Hooke in his Micrographia (1665) examined the function of air in combustion and respiration but their work bore no immediate fruit. Instead, the course of chemistry was deflected by Becher and Stahl into the unprofitable paths of the phlogiston theory, phlogiston being the essence of combustibility: in order to make the theory fit the experimental facts ~~it was necessary to postulate~~ the property of anti-weight was postulated for phlogiston. Throughout the eighteenth century, the pioneers of pneumatic chemistry, Stephen Hales, Henry Cavendish, Joseph Priestley, and Carl Wilhelm Scheele patiently evolved methods for preparing and collecting a number of gases including oxygen, Joseph Black began to show quantitative relationships between gases and solids, and the work of Jean Rey (forgotten for a century) on the increase in weight of metals on heating was given a second hearing. It fell to Lavoisier to place the keystone upon this archway, bridging the apparently unrelated phenomena of combustion and respiration, demonstrating that both depended upon combination with oxygen.

Among the casualties in the demolition of phlogistonism was a whole system of chemical nomenclature. Clearly, if phlogiston did not exist, such names as "dephlogisticated marine acid" no longer had any meaning and had to be replaced. Further, the key position of oxygen in Lavoisier's thinking led to the introduction of an oxygen-based nomenclature in which a salt was given a binary name, one part denoting the metal or basic oxide and the other the acid.[1] A mere change in nomenclature would have had little significance, but the new names gave rise to a grammar of chemistry with its own "Sprachgefühl" of precision and solecism: a chemical sentence of the form

$$AB + CD \longrightarrow AD + CB$$

could be appreciated on linguistic grounds without the knowledge of the chemical properties of the individual salts concerned, whereas the older nomenclature had led to sentences of the form

$$E + F \longrightarrow G + H$$

which were beyond the range of linguistic criticism.

These new linguistic aids to classification and memory were not in general taken up by analysts (nor by their colleagues in the newly created chemical industry: the alkali trade abounded in such terms as "blackash", "red liquors", "Weldon mud", and the legacy of this latter reluctance is with us still in the form of "commercial names").[2] Thus as late as 1831, J.J. Griffin could write in his preface to Heinrich Rose's textbook of analytical chemistry "it is by no means a common opinion among chemical students in England that chloride of ammonium is synonymous with muriate of ammonia".[3]

This is not, however, to belittle the practical achievements of late eighteenth century analysis. Particularly in those countries where there was a long tradition of mining for metals, Sweden, Finland and Northern

Germany, minerals were investigated and new metals isolated with the aid of the blowpipe. This useful tool, long known to jewellers and goldsmiths, was introduced into metallurgical investigation by Johann Andreas Cramer, whose "Elementa Artis Docimasticae" was published in Leyden in 1739. The use of the blowpipe was extended to general chemical examination by Axel Frederic Cronstedt: his "Forsok till Mineralogie" appeared anonymously in 1758, the true authorship being revealed only when Engeström's translation was published in London in 1788.

There was no hint of our arbitrary division of elements into "common" and "rare" for teaching purposes. Everyday metals such as copper and iron shared the same mineral matrix with uranium and zirconium, and even the beginner in analysis was expected to work through such combinations. Not the complexity of the mixtures alone but also the sensitivity of the tests is noteworthy: Johann Gotlieb Gahn, for instance, could detect extremely minute traces of copper in writing paper by means of the blowpipe.

By the end of the eighteenth century a rich literature of the blowpipe had appeared. In addition to the works of Cramer and Cronstedt mentioned above, Bergman's important essay "De Tubo Ferruminatorio" was published in 1779, and the century closed with the comprehensive survey by C.E. von Weigel in 1790 and 1794. The subsequent history of this indispensable piece of equipment is discussed in Chapter III.

While the investigation of minerals and ores was proceeding, another fruitful line of research was beginning to occupy the minds of chemists, namely the composition of the various mineral waters at the increasingly fashionable watering places. As early as 1684 Boyle had described tests based on change of colour or on precipitation (which he called "inspissation") and formulated the beginnings of a systematic way of examining mineral waters.[4] In this work he drew upon some much earlier sources. For example, he reintroduced the use of papers impregnated with coloured reagents first prescribed by Pliny as a test for iron occurring as an adulterant in verdigris.[5] Further work on the use of coloured reagents was carried out by Tachenius and by Samuel Duclos (not Domenic Duclos, with whom he is often confused). The depth of the interest in the subject of mineral water analysis is shown by the fact that up to 1780 the Royal Society had published no less than thirty-four papers on the subject in its Philosophical Transactions. Books and pamphlets also proliferated, in the pages of which local doctors vied with each other in defence of the claims of the springs in their own districts.[6]

Urged on by miners and mineralogists on the one hand therefore, and by the medical interest in mineral springs on the other, we can say that by the end of the eighteenth century chemical analysis had advanced sufficiently to be able to detect all the then known metals in solid compounds, and the common acids in solution. In addition, many common gases could be recognized by the methods elaborated by the pneumatic chemists.

When we turn to the detection and recognition of materials of vegetable or animal origin, the position was not nearly so well consolidated. It is true of course that in antiquity many materials for everyday use had been prepared from plant and animal sources; these included gums, resins, oils, fats, colours and sweetsmelling essences. As distillation and crystallisation became commonplace operations, the number of such materials increased, although there was little corresponding increase in knowledge of their composition. As late as 1798 Fourcroy referred to them as "proximate principles".[7] The problem was of course fundamentally different from that of discovering the constitution of minerals. There, to detect all the elements present was the major difficulty: here, the elements were almost always the same, carbon, hydrogen, oxygen, nitrogen, perhaps sulphur or phosphorus, but in each case arranged in different proportions. To a generation conditioned to the blowpipe examination of minerals, the chemical behaviour of organic bodies must have seemed vexatious and capricious, and many took refuge in the notion of a "life force" which excused them from probing too deeply into organic chemistry.

Two further considerations delayed the evolution of the methods of organic analysis. Metals were usually isolated and weighed in a pure form; for example silver in an ore containing silver and lead had been burnt off or absorbed into the material of the crucible, leaving behind a bead or button of silver. Carbon and hydrogen however could not be isolated in this way and could be weighed only as their oxides, obtained by burning the organic material in some closed system. Clearly this involved first the recognition of oxygen and its place in combustion, and secondly some assumptions about the indestructibility of matter and the laws of stoichiometry. It is not surprising, and is indeed most appropriate, that the first successful analyses of organic compounds were made by Lavoisier. Before the end of the eighteenth century these methods had been revised by Fourcroy and Vauquelin but the subject was still in a rudimentary stage of development.[8]

Analysis as a tool of research is in general a simpler matter (at least in terms of the questions posed) than analysis applied to articles of trade and commerce. In this latter respect, the art of analysis was not equal to the tasks with which it was presented. The complete analysis of medicines, for instance, was quite beyond the bounds of possibility, the presence of organic ingredients complicating the otherwise straightforward recognition of mineral constituents. Although the mid-eighteenth century pharmacopoeias showed considerable simplification when compared with those of a century earlier, there were still many preparations of needless complexity. These were assessed (when assessment was demanded as it sometimes was by the apothecaries themselves or by the physicians) by appeals to taste and colour. It is obvious therefore that a preparation would stand or fall by the proportions of the most highly flavoured or highly coloured member, even if, in terms of weight or potency, this were a minor constituent. Thus, in the investigation of a complaint that Mithridate had been sold for Venice Treacle (both popular panaceas), an apothecary testified that both preparations were identical, basing his opinion on the fact that they tasted too strongly of aniseed, a minor constituent. It was urged that "Venice Treacle should be compounded of about One Hundred different Materials; and though it was impossible to discover whether everyone of such Materials were in the Medicine, yet a Person skilled in the Business of Pharmacy might easily distinguish the principal Ingredients by the Taste." Another preparation was dismissed as being " not black enough for Venice Treacle nor yellow enough for Mithridate".[9]

At the height of the popularity of Ward's drops and pills, physicians of the calibre of Sir Hans Sloane and Dr. Richard Meade claimed to have discovered the nature of the preparations, but their findings were based upon clinical observations of the results of taking the medicines and not upon any chemical evidence: they concluded that arsenic and mercury were present, though the pill and drop actually contained antimony.

At the very period when science was least able to protect the consumer of medicinal products, the quantities of such products consumed were abnormally high. Apothecaries were allowed to charge for the materials that they supplied but not for attendance or advice; it is not surprising therefore that from time to time complaints arose about over-prescribing. A bill for one patient for one day showed something of the scale of the provision of medicines when, as in this case, the patient was a wealthy merchant:-[10]

An emulsion	4s 6d
A mucilage	3s 4d
Gelly of Hartshorn	4s 0
Plaster for blister	1s 0
Emollient	2s 6d
2 Cordial boluses	5s 0
2 Cordial draughts	4s 8d
Another bolus	2s 6d
Another draught	2s 4d
Cordial Spirits	3s 6d
2 Blistering Plasters	10s 0
3 Boluses again	5s 0
2 Draughts again	4s 8d
Another emulsion	4s 6d
Pearl julep	4s 6d

The bolus and the cordial draught would certainly be of complex composition, many of the ingredients being themselves plant extracts of indeterminate constitution. The effect upon the consumer was two-fold; first there might be held out the inducement of some rare and expensive ingredient of peculiar potency without any possibility of the claim being checked; second even when no exaggerated claims were made, the substitution of a cheaper for a more costly constituent could easily be made.

The over-attentive services of the qualified apothecary were not the only threat to the patient, for there began in the eighteenth century the hey-day of the quack doctor which was to last until the end of the nineteenth century. The causes of this phenomenon are complex, but prominent among them must be counted the fear of falling into the hands of the surgeons. On a purely technical level, the manipulative skill and the anatomical and pathological knowledge of the surgeons had progressed to the stage at which a wide range of operations were possible, but the terrifying pain of pre-anaesthetic practice, and the probability of infection in the years before antiseptic surgery were a sufficient deterrent from the general resort to operative treatment. Anyone who could shout in a loud enough voice that his wares would render "amputation unnecessary, the knife superseded" was sure of a ready hearing. Added to this was the extraordinary appeal of the established quack, very often plying his trade under noble, or even royal patronage. "Crazy Sally", Mrs. Mapp the bonesetter, Chevalier John Taylor the trader in eye washes, and Joshua Ward ("Spot Ward") each enjoyed a tremendous vogue and prosperity even though the last two were dismissed by Dr. Johnson with the remark "Taylor is the most ignorant man I ever knew ..... Ward is the dullest."[11] Yet Ward's claims were supported by George II, Henry Fielding and Horace Walpole. His case is of particular interest to the central core of our thesis, for his medicines were compounded of simple and well-known ingredients, one of which (antimony sulphide) had been the subject of a vast quantity of chemical literature.[12, 13, 14, 15] A few decades later his claims would have been susceptible to chemical investigation.

Paradoxically it was at the very time when chemical analysis seemed powerless to combat the misrepresentations of trade and commerce, that trade gave rise to a new kind of chemical analysis. As early as 1756 Francis Home had published a work entitled "Experiments on Bleaching" in which he discussed methods for comparing the strengths of alkaline solutions. The only commercial alkali available to bleachers was the product from burning vegetable matter, known variously as "ashes", "kelp", or "barilla", being an impure form of sodium and potassium carbonates. Francis Home evaluated ashes from different sources by measuring the amount of nitric acid needed to quench the effervescence of the carbonate, using the number of teaspoons of acid as the measure of volume.[16] The heavy chemical industry grew out of experiments to increase the production of synthetic "ashes" and methods of evaluating products came to be developed to a high degree of precision: thus the new technique of titrimetric analysis was born. The major developments in this field did not occur until after 1806, and did not materially affect the proprietary medicine trade.

We must now ask what kind of people they were who needed the protection of chemical analysis when our period opens, and what conditions in their lives contributed to that need. This involves a consideration of the eating and drinking habits of the later Georgians, their attitudes to health and disease, and the methods of communication which conditioned their corporate outlook.

Between 1780 and 1800 the death rate fell from 28.8 to 23.1 per thousand while the birth rate remained fairly constant at about 23.1 per thousand.[17] These figures reveal an expanding population, one of the first of whose concerns would be with the sufficiency of food. The migration of workers from the small rural communities to form the large industrial communities of the towns brought a change to the nation's eating habits. It is easy to paint too rosy a picture of the conditions of

the agricultural labourer before enclosure became regular: nevertheless, the single man would have at least his main meal in the day at the farmer's table, and the married man would often have his pig, the produce of his garden and the occasional piece of game from the covert. The well-to-do in town as well as country fed lavishly and even grossly, and one whose position was merely comfortable could yet afford to allow food and drink to occupy a very large part of his life, as the descriptions of meals in Parson Woodford's diary show. Examples are:- "July 11th 1789. We had a very good dinner, a fine Piece of fresh Salmon, a Leg of Mutton rosted, fricasseed Rabit, a Couple of Ducks rosted and Peas, a currant Pye and Syllabubs etc. A good Desert of Fruit after Dinner, Strawberries, Cherries and Currants ......
May 29th 1702. We had for Dinner a fine Pike, Saddle of Mutton rosted, Cream Soup, Couple of boiled Chicken and a Tongue, Veal Collops and Patties. 2nd Course rost Pigeons, green Goose etc.".[18] The significant change brought about by the move to the towns was concerned with quality rather than with quantity. Food fresh from the field or garden was replaced by food from the purveyor, and immediately the way was opened to the falsifier and the adulterator. Scarce as it might have been in bad times, the countryman knew where his food came from: the town dweller had no means of knowing the frightful vicissitudes through which his food passed on the way to his table. This state of things was exacerbated by the near-famine and high prices of the first years of the new century.[19]

Here again we have to confess the inadequacy of chemical analysis to reveal the extent of a common evil. From time to time 'scare' books appeared, and rumour was rife about the possible ingredients of bread in particular:[20] but it was only in cases of adulteration with earthy matter recognisable as ash that chemical analysis could help. Beer, wines and spirits could be investigated for metallic contamination, but there were many other adulterants intended to increase the intoxicating power (cocculus indicus was common) which being of vegetable origin, could not be detected chemically.[21] The gin which caused such scenes as Hogarth depicted in "Gin Lane" was frequently strengthened with sulphuric acid: this additive would have been easily detected in a mineral water, but there was at that time no confidence in the test as applied to other liquids.

The food purchased in the towns was subject to a further hazard due to slow transport and unsatisfactory storage, so that butter became rancid, flour infested with vermin and meat putrescent, though none of these interfered with the sale of the article. In this connection it is of interest to observe that by 1800 Appert's experiments on food canning (at first bottling) were underway.[22]

The former high living, and the later poor eating each contributed a health problem of its own: the gout and chronic obesity of the middle years of the eighteenth century gave way to the diseases of malnutrition and overcrowding of the end of the century. Public health and preventive medicine, as subjects for study or legislation, scarcely existed.

In times of serious epidemic, communities large and small were sometimes driven to making improvements in towns or dwellings, but the foundation of such work was to remain insecure until the modes of transference of disease had been discovered. Popular belief, and enlightened opinion, held that miasmas from rivers and marshes and effluvia from dead bodies were the media by which infections were carried: within this context the great crusades of Edwin Chadwick (leading to the Public Health Act of 1848)[23] and of Florence Nightingale were waged. In spite of the clear direction pointed by the work of Leewenhoek (1632 - 1723) and Spallanzani (1729 - 1799), no further step was taken toward the understanding of infectious disease until the science of bacteriology was established by Louis Pasteur in the 1850s.[24]

In fact very little notice was taken of the patient scientific work that was laying the foundations of modem physiology and pathology. What seized the popular imagination instead was the exploitation and misrepresentation of the electrical discoveries of Galvani and Volta. A macabre lecture demonstration of wide appeal was the "galvanising" of a corpse, usually that of a felon newly cut down from the gallows: the twitching of the limbs and the contortions of the face both horrified and delighted the audiences. Ure described one such episode:"Every muscle in his countenance was simultaneously thrown into fearful action. Rage, horror, despair, anguish, and ghastly smiles united their hideous expression in the murderer's face, surpassing far the wildest representations of a Fuseli or a Keane. At this period several of the spectators were forced to leave the apartment from terror or sickness, and one gentleman fainted".[25]

The curative powers of electricity were extolled even by John Wesley, in an anonymous book entitled "*The Desideratum - or Electricity made Plain and Useful*. *By a lover of Mankind and Common Sense*". (1780). Among the conditions which electricity would allegedly cure were St. Anthony's fire (erysipelas), epilepsy, gout, palsy, sciatica and sore throat. Jean Paul Marat, during his stay in London, used the same means to treat painters' colic or lead poisoning. Perhaps more characteristic of the flamboyant claims of the galvanists, and also of the sensationalism to which the public was conditioned, was the case of James Graham whose Temple of Health in the Adelphi was graced by Emma Lyon (the future Lady Hamilton). Graham was perhaps influenced by the electrical experiments of Benjamin Franklin, whom he had met in America, or perhaps his sketchy and incomplete medical studies in Edinburgh had provided him with a little knowledge of electricity. In either case it is clear that many wealthy and aristocratic patients came to his rooms to hear his discourses (including one on mud-bathing) and to sit on the electrifield stools and thrones: for a time a certain number even paid fifty pounds to sleep in his 'celestial bed'. When we consider that such an enterprise as Graham's was furbished with all the attractions that music, painting, sculpture and perfumery could yield, it is easy to understand why the unspectacular achievements of scientific medicine were crowded out from the notice of the public.[26]

Not electricity alone, but the sister science of magnetism made its claim upon popular credulity, and much sound scientific fact was obscured by quackery and charlatanism. The greatest name in medical magnetism was that of Anton Mesmer (1733 - 1815), not a quack but a regularly qualified practitioner from Vienna. As early as 1600 William Gilbert had suggested a connection between magnetism and health, and both the Jesuit orientalist, Athanasius Kircher (1602 - 1680) and astronomer Maximilian Hell (1720 - 1792) had developed the practice of stroking the seat of pain with natural or artificial magnets. Mesmer discovered that similar results could be obtained by substituting the touch of his hand for the magnet. Here, clearly, was the germ of the notion of suggestion upon which so much later psychological treatment was to be based: unfortunately so far as Mesmer's work was concerned, this fruitful idea was lost in the more colourful elements of the magnetic passes the baguet or reservoir of magnetic fluid, the mirrors and the robe of purple and yellow silk. Mesmerism in fact came to be identified with showmanship until it was rescued by James Braid who in 1842 gave it the name of hypnotism, demonstrating the subjective nature of the phenomenon.[27] A profitable derivative of the craze for magnetic cures was the introduction by Elisha Perkins in 1798 of his metallic tractors. These large metallic forceps were sold in England for five guineas, on the understanding that if they were properly applied to the affected place the pain would be drawn out. The success of the tractors declined when John Haygarth, a physician in Bath, showed that patients would respond in the same way to tractors made of wood painted to look like metal.[28] It can thus be seen that the credulity and sensation-hunting of the age were bringing out the raw materials for the creation of the new sciences of human behaviour. Of Mesmer himself it was truly said that, like Columbus, he did not understand the true importance of his discovery.

Reference has been made to sensation-hunting, a feature of life which was encouraged by the newspapers. By the middle of the eighteenth century the informative Gazettes and Intelligencers had been joined by a host of popular papers written in the debased style of journalism so often derided by Dr. Johnson. Wonders were the order of the day: longevities, monstrous births, comets, travellers' tales, wagers, all combined to encourage a climate of opinion in which the sober virtues of commonsense and sound judgment were unlikely to thrive. Such a proliferation of printed matter, in itself, created a competition for the eye of the reader, and this competition was most fierce in the field of advertisement. The state of press advertising when our period begins can best be judged by the promise which William Cobbett thought it necessary to make when launching his paper "The Porcupine" in 1800; "Not a single quack advertisement will on any account be admitted into the Porcupine. Our newspapers have been too long disgraced by this species of falsehood, filth and obscenity."[29] In the closing decades of the eighteenth century there occurred the first signs of a change in advertising policy: hitherto, advertisements had been directed toward certain restricted classes of people, but now the aim was to provide something for everyone, and consequently everyone was subjected to commercial pressures of a new kind. This was the stream which grew to a flood in the early years of the nineteenth century when the extra shed of The Times was described in these terms: "Here, within the Compass of a single Newspaper, are above five hundred announcements of wants or superfluities - remedies for all sorts of ailments - candidates for all sorts of situations - conveyances for those who wish to travel, establishments for those who wish to stay at home - investments for him who has made his fortune, and modes of growing rich for him who has that pleasure yet to come - elixirs to make us beautiful, and balsams to preserve us from decay - new theatres for the idle, new chapels for the serious, new cemetries in pleasant situations for the dead".[30]

The scene is now set for the commencement of the century-long battle between the chemical analyst, examining and reporting with trust upon the materials of commerce, and those who had an interest in concealing that truth, a battle in which the consumer, as innocent bystander, did not always escape without injury.

CHAPTER II

POPULAR AND PROPRIETARY MEDICINES.

The first great challenge to chemical analysis during the nineteenth century arose out of the trade in proprietary medicines, placed before the public in such rich abundance. The appendix to the Stamp Duty Act of 1804 provided a list of 453 preparations held liable to duty, (Table 1) revealing the magnitude of the problem.[31] The list does not of course suggest that a new phenomenon had occurred: rather it represented the culmination of more than a century of panaceas and elixirs for all complaints together with specifics for particular diseases.

On the Continent, Dippel's Animal Oil (made by subjecting animal refuse to repeated distillation over potash) had made its appearance in 1711, and had been claimed by its inventor as a universal medicine.[32] Seven years later, the situation at home was summarised in a pamphlet dedicated, not without irony, to Dr. Bateman (not the author of "Cutaneous Diseases" but the president of the Royal College of Physicians) whose name was to be associated with a number of nostrums:- "For diseases of the Head and Brain we have Cephalick Tinctures and Head Pills of divers kinds: Apoplectick Spirits and Balsams: Vapour Drops and Drops for the Palsy and Convulsions; for the Eyes, we have Salves and Waters without Number, some of them as far fetch'd as Jerusalem, tho' they never travelled perhaps a Mile from the Exchange: not forgetting Goody Cater, the Oyster-Woman's most excellent Ointment, revealed to her Husband's great-Grandfather in a Dream .... lastly you have Mother Bedlicot's Drink for the Dropsy and Jaundice: she, good Woman, used to open the Pews at St. Sepulchres, when she could spare time from visiting her Patients".[33]

Table 1.

Schedule to 1804 Act.

All Foreign Medicines, except Drugs.

Adam's Solvent
Addison's reanimating European Balsam
Aethereal Anodyne Spirit
Ague and Fever Drops (by Wilson)
Amboyna Lotion
" Mouth Powder
" Tooth Powder
American Alterative Pills
" Salve
Andalusia Water
Anderson's Scots Pills
Angibaud's Lozenges of Blois
Anodyne Necklace
Antipertussis
Appleby's Tea
Arabian Balsam
Arnold's Drops
" Pills
Arquebusade Water
Aromatick Spirit of Vinegar
" " Condensed
Asiatic Bilious Pills
" Tonic Tincture
Austin's Chalybeate Pills
Balm of Mecca
Balsam of Iceland Liverwort
Barclay's Antibilious Pills
" Asthmatic Candy
Barlowe's Specific Medicine
Barron's Cachou de Rose Lozenges
Barton's Alterative Pomade
" Vital Wine
Bateman's Drops
" Golden Spirit of Scurvy Grass
" Plain Spirits of " "
Bayley's British Tooth Powder
Beasely's Family Plaister
Beaume de Vic
Beiker's Tincture
Bell's Restorative Pills
Bennet's Worm Powders
Benzoin, Essence of
Berry's Bilious Pills
Betton's British Oil
Birt's Martial Balsam
Blair's Cephalic Fluid
Boerhaave's Antiscorbutic Wine
Bolderson's Worm Cakes

Bollman's Specific
Bolton's Asthmatic Tincture
Bostock's Cordial
" Grand Elixir
Bott's Corn Salve
" Tooth Powder
Bourne's Aethereal Essence
Box's Magnesia Lozenges
Brazil Salts
Brodum's Botanic Pills
" Botanical Syrup
" Nervous Cordial
Browne's British Pills
" Rheumatic Powders
" Tincture of Yellow Bark
Bryant's Essence of Coltsfoot
Camphor, Aethereal Essence of
Cathcart's Edinburgh Ointment
" Water
Cephalic Snuff
Chamberlain's Ointment
" Pills
Chapman's Cerate
" Chilblain Water
Ching's Worm Lozenges
Chinner's Pills
Church's Anodyne Essence
" Chilblain Ointment
" Cough Drops
" Eye Salve
" Pectoral Pills
" Volatile Tincture
Clerval's Syrup
Clinton's Oil for Deafness
" Snuff
Clyde's Balsam
Collier's Assistant Pills
" Ointment
" Remedy for Fistula and Piles
Complin's Specific
Cordial Balm of Gilead
Cornwell's Fruit Lozenges
" Opodeldoc
" Oriental Vegetable Cordial
Costello's Cerate
" Collyrium
Cottier's Resolvent and Healing Plaister
Cox's Tincture
Coxwell's Castor Oil Medicine
Culpepper's Herb Cordial
Cundell's Balsam of Honey

Curtis's Syrup

Daffy's Elixir

Dalby's Carminative

Dalmahoy's Sal Poignant

" Tasteless Salts

Dawson's Lozenges

Deering's Drops

Delescot's Myrtle Opiate

De Velno's Pills

" Syrup

Dicey and Co's Bathing Spirits

" Daffy's Elixir

Dickenson's Cephalic Drops

" Red Drops for Convulsions

" Drops for Fits

Dixon's Antibilious Pills

Donavan's American Vegetable Syrup

Doranstorff's Opodeldoc

Dutch Drops

Earl's Remedy for the Hooping Cough

Edward's Ague Tincture

Edward's Nipple Ointment

Elixir of Longevity, or Swedish Preferative

Ellis's Aperient Pills

Falck's Cerate

" Universal Pills

Findon's Drops

Ford's Balsam of Horehound

Fordyce's Cooling Opening Pills

Fothergill's Pectoral Pills

" Restorative

Fraunce's Elixir

Freake's Tincture of Bark

Freeman's Bathing Spirits

Freeman's Eye Water

Friend to Man

Frith's Antibilious Elixir

Fry's Worm Pills

Fryer's Balsam

Gamble's Aromatic Snuff

Garaveni's Styptic

Gardener's Ointment

" Pills

German Corn Plaister or Salve

Gilbert's Roseate Lotion

Glasse's Magnesia

Godgold's Balsam

Godfrey's Cordial

" Rose Lozenges

Gowland's Lotion

Grand Specific or Infallible Antidote to
Consumption

Grant's Drops

" Lisbon Tonic Pills

Green's Honey Lozenges

" Oil, or Infallible Oil

Green's Tooth Ache Pills

Greenough's Tincture

" Tolu Lozenges

Grey's Lozenges

" Tooth Powder

Griffin's Asthmatic Tincture

Grubb's Fryar's Drops

Guest's Lotion

" Pills

" Powder

" Tooth Powder

" Welcome Guest

Haarlam's Drops

Hadley's Convulsive Powders

Hallam's Anima of Quassia

" Antibilious Pills

" Quassia Pills

Hamilton's Asthmatic Effluvia

" Cinnamon Drops

" Com Salve

" Vegetable Balsamic Tincture

Hannay's Wash

Harvey's Anti-Venereal Pills

" Grand Restorative Drops

Hatfield's Tincture

Hayman's Munedant's Drops

Hayward's Stomachic Lozenges

" Anti-Acid

" Samaritan Water

Hemet's Essence of Pearl

" Pearl Dentifrice

Heming's Pine Bud Lozenges

Henry's Aromatic Spirits of Vinegar

" Magnesia

Hewitt's Analambanic Pills

Hickman's Pills

Hill's Balsam of Honey

" Bandana Drops

" Canada Balsam

" Essence of Water Dock

" Gout Essence

" Tincture of Centaury

" " Sage

" Valerian

Hodson's Aromatic Nervine Tea

" Imperial Oil

" Persian Restorative

" Syrup

Holdsworth's Lozenges

Hooper's Female Pills

Homell's Powders for Epilepsy

Hunter's Elixir

Hunter's Pills

" Restorative

Jackson's Corn Salve

Jackson's " Ointment

" " Tincture

Jacobson's Cough Drops

James's Analeptic Pills

" Fever Powder

" Medicine for the Dropsy

Jebb's, Sir Richard Elixir

" " Pills

Jesuits Drops

Imperial Anodyne Opodeldoc

Infallible Restorative

Inglish's Scots Pills

Johnston's Essence of Horehound

Johntenocco's Tooth Powder

Jone's Rheumatic Tincture

Irvine's Fruit Lozenges

Juniper's Essence of Penny Royal

" " Peppermint

Kennedy's Corn Salve or Plaister

Keyser's Pills

Knight's Pills

Lammert's Balsam

Lancaster Black Drop

Leake's Cerate

" Chilblain Water

" Pills

" Purifying Drops

Leathe's Lotion

Le Cour's Imperial Oil

Lee's Lozenges

Lewis's Specific Pills

" Tincture of Angustura Bark

Liquid Shell for the Stone and Gravel

Lockyer's Pills

Lord's Corn Salve or Plaister

Lorraine's Consumptive Pills

Lourie's Eye Water

Lowther's Drops

" Nervous Powders

Lozenges Aniseed

" Benzoin

" Camomile

" Ginger

" Horehound

" Ipecacuanha

" Patirosa

" Peppermint

" Poppy

" Rose

" Roseated Liquorice

Lozenges Specific
" Spermaceti
" Tolu
Lucas Pure Drops of Life
Luzatte's British Pills
Lygnum's Antiscorbutic Drops
" Lotion
" Pills
Magnesia Tablets
Man's Cough Medicine
Mapoon's Sanative Salve
Marshall's Cerate
" Wort Dissolvent
Matthew's or Matthews's Alterative Medicine
" Chymical Tincture
" Remedies for curing Fistula and Piles without cutting or Pain
" Samaritan Restorative
Mayerbach's Balsamic Pills
Mayerbach's Mixture
" Restorative Powders
Medley's Aromatic Herb Snuff
Metallic Tractors
Military Drops
Millman's Itch Ointment
Monsey's Rheumatic Powders
Nailor's Corn Ointment
Newton's Restorative Tooth Powder
Norman's Syrup
Norris's Chalybeate Pills
" Drops
" Tonic Essence
Norton's Manedant's Drops
Oliverian Ointment for the Piles
Ormskirk Medicine for the Bite of a mad Dog
Palmer's Laxative Pills
Paraquay Lotion
Paschall's Teething Remedy
Pectoral Essence of Coltsfoot
Perkin's Metallic Tractors
Perrin's Balsam of Lungwort
Peter's Pills
" Tincture
Pidding's Balsam of Liquorice
Pike's Ointment
Pomade Divine
" Royal
Powell's Camphor Liniment
" Eye Salve
Price's Breast Salve
Prickett's Styptic

Pullen's Antiscorbutic Pills
" Purging Pills
Pyrmont Tablets
Radcliffe's Purging Elixir
" Rheumatic Tincture
Refined British Oil
Relse's Nipple Ointment
Richardson's British Corn Salve or Plaister
Riga Balsam
Robbend's Cough Drops
Robert's Worm Sugar Plums
Roche's Embrocation
Roe's English Coffe for Nervous Disorders
Roger's Antibilious Elixir
" Antiscorbutic Pills
Rook's Balsam
Rose Tablets
Ruspinis Styptic
" Tincture
" " for the Toothache
" Tooth Powder
Ryan's Essence of Coltsfoot
Rymer's Cordial and Nervous Tincture
" Detergent Pills
" Essence of Garlock
" Pectoral Medicine

Rymer's Tonic Pills
Schnid's Liquid Dentifrice
Schult's Vegetable Acid Air
Scot's Gout Pills
Senate's Aromatic Steel Lozenges or Lozenges of Steel
Sharpe's Hepatic Pills
Sibley's Lunar Tincture
" Solar "
Simson's Infallible Aethereal Tincture
Singleton's Golden Ointment
Sloane's, Sir Hans, Pills
Smart's Tincture of Cascarilla Bark
Smellome's Eye Salve
Smith's Antibilious Pills
Smith's Antihectic Balsam
" Cooling Opening Pills
" Drops
" Purifying Pills
" Restorative Medicated Wine
Smyth's Drops
" Restorative
Solander's Sanative Tea
Soley's Essence of Squills
Soloman's Abstergent
" Anti Impetigines
" Balm of Gilead

Speediman's Stomach Pills
Specific Convulsion Drops
" for the Yellow Fever
" Remedy (by Wessels)
" Tincture
Spencés Dentifrice
Spilsbury's Antiscorbatic Drops
" Compound Essence
Spinluff's Aromatic Bilious Cordial
Squirés Elixir
Squirrel's Drops
" Tonic Pills
" Powders
Steers Camomile Drops
" Camphorated Eye Water
" Convulsion Oil
" Nitre Drops
" Opodeldoc
" Panegoric Lozenges
" Purging Elixir
Siterne's Balsamic Ether
" Balsamic Stomach Tablets
" Tincture and Gout Drops
Storey's Worm Cakes
Stoughtons Bitters
" Elixir
Stringer's Essence of Myrrh
Stringer's Myrrh Dentifrice
" Panegoric Lozenges
Swedish Preservative or Elixir of Longevity
Swinsens Anti Acid
" Electuary
" Ointment
" Worm Sugar Cakes
Swiss Balsam
Tasteless Ague Drops
" Fever Drops
Thomas's Tolu Essence
Thompson's Ague Tincture
Tickell's Aether
Tincture for the Teeth and Gums
Tooley's Cordial
Tooth Ach Fluid (sic)
Tooth Powder Asiatic
" " Paraquay
" " Royal
Trotter's Asiatic Tooth Powder
Trowbridge's Golden Pills
Tuberosa Vitae, or Chilblain Water
Turlington's Balsam
Vandour's Nervous Pills
Van Swieten's Gout Cordial
Vegetable Embrocation

Vital Balm

Waitne's Worm Nuts

Walford's Pancreatic Powders

Walker's Jesuit Drops

" Specific Remedy

" Stomachic Wine

Walkey's Tooth Powder

Waller's Ointment

Walsh's Coltsfoot Lozenges

" Ginger Seeds

" Pills

Ward's Dropsy Pills

" Essence for the Head Ache

" Liquid Sweat

" Paste

" Powders

" Red Pills

" Sack Drops

" Sweating Powder

" White Drops

Ware's Asthmatic Drops

Warren's Analeptic Powders

" British Tooth Powder

Water's Artificial Mineral

Webster's Diet Drink

Welch's Female Pills

Wheatley's Ointment

" Fluid

Whitehead's Essence of Mustard

" " Horehound

" Pills

Williams Aperient Pills

" Essence of Benzoin or Pulmonick Drops

" Spa Elixir or Restorative Drops

Willis' Asthmatic Pills

Winch's Cough Drops

Wray's Ague Pills

Zimmerman's Stimulating Fluid

In 1748 there appeared in the Gentleman's Magazine a list of "Nostrums and Empiricks" under the name of "Pharmacopoeia Empirica"; nostrums were defined as "such medicines as are kept a secret for the use of the proprietor, tho' advertised (in the Newspapers etc.) for the benefit of the public", and empirics were "those persons who have by experience (εμπειρία) found the benefits of those medicines they administer". The list shows the categories of popular medicines on sale (Table II) and also indicates the names of shops where they might be obtained.[34]

The amateur in medicine had in fact enjoyed a great vogue, more particularly if he bore the additional stamp of respectability that came from his being a clergyman. Thus one of the oldest preparations in the 1804 list was the brainchild of the Rev. Thomas Daffy, rector of Harby in Leicestershire. His Elixir Salutis was well known in 1673 and became the basis of a family business, as it was advertised by his daughter Catherine and sold by his son Daniel at an apothecary's shop in Nottingham.[35] "Daffy's Elixir" later became a blanket name for a number of similar preparations made and sold by different firms. George Berkeley, Bishop of Cloyne, seems to have been actuated by a genuine care for mens wellbeing when he launched his crusade for Tar Water in 1744. He took as his test "As we have opportunity, let us do good to all men (Gal. IV.10)" and went on to say that nothing would have induced him to undertake the labour of writing, but the "firm belief that it would prove a valuable present to the public .... I never knew anything so good

Table II

Categories of Proprietary Medicines and Appliances in *Gentleman's Magazine List* 1748.

Balls
Balsam
Belts
Bitters
Boluses
Confections
Cordials
Drenches
Drinks
Drops
Electuaries
Elixirs
Essences
Fluids
Girdles
Juleps
Liniments
Liquid Shells
Liquors
Lotions
Lozenges
Medicines
Mixtures
Necklaces
Oils
Ointments
Opiates
Peas
Pills
Plasters
Plasters
Powders
Quintessences
Salts
Salves
Smell Bottles
Snuffs
Specifics
Spirits
Styptics
Sugar Plums
Tinctures
Tobaccos
Wash-balls
Waters

for the stomach as tar water: it cures indigestion and gives a good appetite. It is an excellent medicine in an asthma. It imparts a kindly warmth and quick circulation to the juices without heating, and is therefore useful, not only as a pectoral and balsamic, but also as a powerful and safe deobstruent in cachetic and hysteric cases".[36] Two years later the Gentleman's Magazine published a list of 140 complaints alleged to have been cured by tar water. One of the few sceptics in this matter seems to have been Mrs. Montagu who wrote "I find tar-water succeeded to Wards drop. Tis possible by this time that some other quackery has taken place of that; the English are easier than any other nation infatuated by the prospect of universal medicines, nor is there any country in the world where the doctors raise such immense fortunes".[37] The product must have contained only simple acids and alcohols as all else would have been insoluble in water: it was made by stirring wood tar with cold water and allowing to settle.

Among the clerical dabblers in medicine we must include John Wesley. In 1746 he opened a dispensary at the Foundlings Hospital in Moorfields, London, followed in the same year by a second at Bristol. A year later he published "Primitive Physic: or an easy and natural Method of curing most Diseases"; the book contained prescriptions which were subsequently published separately as "Receipts for the use of the Poor". Although Wesley was a scholarly theologian, the quality of his recipes for common ailments shows all the credulity of his age;

the cure for ague, for instance, was to "apply to the stomach a large onion, slit". In a later work, "Advices with respect to health" (1758) he included a treatment for erysipelas which consisted in applying warm treacle to the soles of the feet.[38]

The 1804 list of proprietary medicines, then, contains a number of categories, some being obscure names which would not have survived but for the accident of their being on sale when the Act was passed, and indeed many of these can no longer be identified. Others were old favourites such as Daffy's Elixir, Batemans Drops, Scotch Pills, Dutch Drops, Balm of Gilead, Opodeldoc, Friars Balsam, Godfrey's Cordial, Hooper's Female Pills, James' Powder, Jesuits Drops, Paregoric, Stoughton's Elixir and Ward's Pills and Drops. J.A. Paris, in his Pharmacologia, attempted to expose most of these established preparations. (See Appendix to this chapter).
It must be noted however that it is not possible to assign fixed compositions to these or any other preparations of that time. There are three reasons for this.

First, the practice of substituting one drug for another was both ancient and widespread, the name "Succedaneum" being coined to meet the need for a polite description for what was often a fraudulent act. Lord Herbert in 1643 wrote:- "It being the manner of Apothecaries so frequently to put in the Succedanea that no man is sure to find with them Medicines made with the true drugs which ought to enter into the Composition when it is exotique or rare".[39] The same situation was expressed more explicitly by Tobias Smollett in "Roderick Random" when speaking of the

French apothecary in London, Mr. Lavement:- "However, his expense for medicines was not great, for he was the most expert man at a succedaneum of any apothecary in London; so that I have been sometimes amazed to see him, without the least hesitation, make up a physician's prescription, though he had not in his shop one medicine mentioned in it. Oystershells he could invent into crab's eyes; common oil, into oil of sweet almonds; syrup of sugar, into balsamic syrup; Thames water, into aqua cinnami; turpentine, into capivi; and a hundred more costly preparations were produced in an instant, from the cheapest and coarsest drugs of the materia medica; and when any common thing was ordered for a patient, he always took care to disguise it in colour or taste or both in such a manner as that it could not possibly be known, for which purpose cochineal and oil of cloves were of great service".[40]

The second reason for variations in formulae was the alleged necessity to accommodate customers from the cheaper markets by providing a second-class product known to the trade as "non-verum". The Committee which met in 1747 to examine the grievances of the Society of Apothecaries revealed a curious state of affairs:-

"Mr. Edmund Stallard, being examined said, That he served an Apprenticeship to a regular Apothecary in London; and had acted as Operator, which he explained to mean Compounder of Medicines, first to Mr. Midgley a Chymist, then to Mr. Hall a Druggist, and was afterwards concerned in Partnership in the Chymical Business himself: That when he was employed by Mr. Midgley, he understood that Two Sorts of Medicines were made, which were distinguished by the Names of Verum and Non-verum; and had since discovered that to be the common Practice in above one Hundred Chymists and Druggists Shops; and, though he knew several Chymists and Druggists had compounded and vended the very best Sort of Medicines, yet he was of Opinion they were all under a Necessity of preparing the Non-verum Sort to supply Country Apothecaries and other Customers, who often asked for Medicines at such Prices as the genuine could not be afforded at."[41]

Further, Wesley had commented on the same unsatisfactory position in the preface to his work mentioned above, and indeed made this one of the justifications for writing the book. "One grand advantage which most of these medicines have above those commonly used is this - you may be sure of having them good in their kind, pure, genuine, unsophisticate. But who can be sure of this, when the medicines he use are compounded by an apothecary ? Perhaps he has not the drug prescribed by the physician, and so puts in its place 'what will do as well'. Perhaps he has it, but it is stale and perished, yet 'you would not have him throw it away; indeed he cannot afford it'. Perhaps he cannot afford to make up the medicine as the dispensatory directs, and sell it at the common price; so he puts in cheaper ingredients, and you take, neither you nor the physician knows what."[42]

The third factor was the changing social or political climate into which the medicines were projected. For example " Mother Winslow's Soothing Syrup" was advertised for more than eighty years with no indication that the ingredients had altered over that period: yet the original preparation had contained laudanum but by the end of the nineteenth century it had changed into a pleasant aniseed syrup with no soporific in its composition. Similarly, the "Daisy Powders" of recent years do not contain the dangerous acetanilide which was the sole constituent of this preparation at the close of last century.

The existence of popular remedies containing opium focusses attention onto the danger attached to the sale of medicines without any chemical check on the contents: in fact many preparations of opium were in use, both officinal and non-officinal. Laudanum, as a name, had been introduced by Paracelsus and applied by him to a solid compound of opium with spices. In 1669 Sydenham used liquid laudanum (the name meant 'praiseworthy'), compounded of opium saffron, cinnamon and cloves in canary wine. This he said "is the best of all cordials; indeed it is the only cordial we possess".[43] The formula was gradually simplified until it became the Tincture of Opium B.P. The next opium preparation to appear was Paregoric (named from the Greek word for 'soothing') and introduced by Le Mort, Boerhaave's successor at Leyden (1702 - 18). This was made from opium, honey, liquorice and "salt of tartar" (potassium sulphate), and found a place in the London Pharmocopoeia of 1721. The 1788 Pharmacopoeia showed it modified to a camphorated tincture of opium: meanwhile a "Scotch Paregoric" had arisen, being an ammoniated tincture of opium.[44]

The polypharmacy of the confections known as Venice Treacle and Mithridate, both containing opium, has already been mentioned in Chapter I. It might be noted that the popularity of Venice Treacle and similar confections led to the application, since the sixteenth century, of the word "Triacleur" to any quack medicine vendor in France.[45] Vinegar of opium, better known as Black Drops, was prepared by Edward Tunstall of Durham from sliced opium crabapple juice, nutmeg, sugar and yeast, the final product being much stronger than laudanum: another name for the same preparation was Quaker's Drops.[46] The acetum Opii of the B.P.C was similar, but not fermented. Thomas Dover, the buccaneer who rescued Alexander Selkirk and thus suggested the idea for "Robinson Crusoe", is remembered for his diaphoretic powder containing opium, ipecacuanha root and potassium sulphate.[47] It is said that apothecaries who dispensed this powder urged patients to make their wills.

The medicine proprietors had all these popular preparations to draw upon, with the addition of one more of great importance from the middle of the century. This was Collis Browne's Chlorodyne, first used in India in 1846 and put on the English market in 1853. It rapidly became a household remedy for colic, diarrhoea and coughs. The exact formula was not disclosed, but the basis was certainly opium in chloroform. Several London hospitals issued their own chlorodynes, that of St. Mary's containing chloroform, morphine, dilute prussic acid, tincture of capsicum, peppermint oil and treacle, a formula very similar to that of the B.P. 1885.[48]

The menace of these preparations was commented upon by A. Wynter Blyth in 1906, after recording that the deaths from opium poisoning in England and Wales during the ten years from 1894 to 1903 totalled 1,655: "The more considerable mortality arises, in great measure, from the pernicious practice - both of the hard-working English mother and of the baby farmer - of giving infants various forms of opium sold under the name of "soothing syrups" "infants friends" "infants preservatives" and "nurses drops".[49]

It is certain that such everyday remedies as "Atkinsons Infant Preserver" "Grinrod's Remedy for the Spasm" and the old-established "Godfrey's Cordial" enjoyed a widespread popularity among harassed mothers and nursemaids. Blyth's reference to baby-farming is borne out by an early report of the Society for the Suppression of Medicity, in 1839, when two women who have hired babies to go begging compare the costs from their respective farmers: "I only give sixpence for mine, and they feeds 'em and Godfrey's Cordials 'em and all, afore I take them, into the bargain".[50] That the easy accessibility of these preparations also played into the hands of those seeking self-destruction is shown by the fact that more than one third of the deaths quoted above were suicidal.

To satisfy the immense demand for this drug, much thought was given to its culture in England. The Rev. A. Swayne contributed papers on this subject, commending the culture of the poppy as an aid to the economy. "From the frequent paragraphs which have lately appeared in the public prints on the subject of opium, it should seem that the eyes of the British public are at length beginning to open to the prospect of those advantages which would be likely to accrue to the Community, from the introduction of an article of commerce, so much wanted at home, to supersede the abominably adulterated drug with which the guardians of our health are supplied from the Levant etc under that name".[51]

The earlier nostrums were almost all compounded from vegetable extracts and therefore more or less complex in their composition: by the middle of the nineteenth century however there had appeared on the market a new, and simpler, class of remedies, namely the health salts or fruit salts. It is significant for the subsequent history of pharmaceutical chemistry that the first two new salts ever to be discovered were aperients: these were Glauber's Salt (about 1640) and Epsom Salt (1695). This latter salt, indeed, constitutes the first patent medicine, for a patent for its manufacture was granted to Nehemiah Grew in 1698.[52] Both salts had been obtained by evaporation of waters from mineral springs, a fact which led to a reawakening of interest in mineral waters. When it is considered that the *Philosophical Transactions* of the Royal Society contained forty papers on this topic during the seventeenth and eighteenth centuries, and that these had to compete for room with accounts of comets, monstrous births and travellers' tales apart from the more vigorous scientific communications, some idea of the popularity of the subject is grasped. In addition to these papers, a vast literature in book and pamphlet form urged the claims of local springs throughout the British Isles. The great watering places grew up with their complex etiquette and rigid regimen taking their cue from Bath under Nash, and for a time the application of mineral waters, either internally or externally, became the current cure-all. Richard Kentish in 1787 attempted to rescue medicine from becoming "a base and iniquitous trade" by publishing a list of diseases and conditions which could be cured by bathing in or by drinking sea-water, the greatest mineral water of all: the list included "Leprous eruptions, Elephantiasis, Convulsions, St. Vitus's Dance, Hysteric Complaints, Giddiness, Headache, Toothache, Ruptures, Insanity, Melancholy, Epilepsy, Apoplexy, Rheumatism, Deafness, Gout, Cholera Morbus, Jaundice, Stone and Gravel, Thirst, Dropsy, Hectic Fever, Lethargy, Universal debility without any particular disease, Hydrophobia, Hiccough, Hoarseness, Profuse spittings, Violent Fits of Intoxication, Plague, Varicose swelling of the legs, Diabetes, Etc."[53]

There were some however who recognised that the strictly ordered life of the spas might be at least as valuable as the contents of the waters. Dr. Clanny of Sunderland, for example, suggested that many who entered hospital and there became accustomated to a lazy life at free quarters might with advantage be made to walk a few miles into the country, drink from a mineral spring and return home again: the exercise at least would benefit them and might help to sort out malingerers.[54]

Not everyone could go to the waters however, so some attempt was made to send bottled waters into the big towns. These had not the success of their Continental counterparts, Spa water and Vichy water, so the next step was to evaporate the waters and send only the residues to be reconstituted by the addition of ordinary water. Claims were made that these salt residues possessed not merely the virtues of one particular spa, but "combined those of the world famous medicinal spas of Carlsbad, Vichy, Marienbad, and similar waters".[56]

These evaporated waters were more popular for bathing in than for drinking, and would probably have remained so but for the invention, by Alfred Bishop in 1857, of "Granular Effervescent Citrate of Magnesia". This was a mixture of citric acid, sodium bicarbonate and Epsom salt, and did not contain any solid citrate of magnesium.[56] Chemists protested from time to time against the misleading description, but were answered by the trade in peremptory terms: "It is only the public analysts who are worried about the public not getting magnesium citrate - the business of the chemist and druggist is to give the public what it wants".[57] The public certainly did want the effervescing granules, with or without the small quantity of magnesium sulphate. Many shops found it worth while to make up and sell effervescent mixtures, with sugar in place of Epsom salt, as a pleasant summer drink, and one lemon-flavoured form became very popular as "Lemon Kali" "Al Kali" or "Sherbert". The more expensive citric acid was often replaced by the cheaper tartaric acid, and for really poor preparations all organic acids were dispensed with in favour of potassium hydrogen sulphate, known in a trade euphemism as "Tartroline".

As an example of the way in which the health salt trade developed we may take the case of Eno's Fruit Salt, which is still on the market. James Crossley Eno was born in Newcastle upon Tyne in 1820, his parents being grocers and general dealers in a very small way. After serving an apprenticeship to a druggist in the town, Eno became the Dispenser at Newcastle Infirmary. This post brought him into contact with

Dr. Dennis Embleton (said to have been the last man to test for sugar in urine by dipping in his finger and tasting it). Embleton was in the habit of prescribing an effervescent drink for his patients, and this prescription, consisting of sodium bicarbonate and citric acid, would have been made up in the hospital pharmacy.[58] After a few years, Eno left the Infirmary to commence a druggists business in the town, and there began to make and sell the hospital preparation as Eno's Fruit Salts. Bottles were given away to the ship captains who traded in the Tyne, and in this way the mixture was carried all over the world. The proceeds from this business enabled Eno to donate £10,000 to the new Infirmary in Newcastle.

Other medicine proprietors had their own ways of promoting sales. In fact, the development of commercial advertising during the nineteenth century changed the whole aspect of the proprietary medicine trade. The small firms who could not afford to advertise nationally gradually died out, leaving the field to a few giants. Of these, one of the first was James Morison (1770 - 1840) who began to make, and to use himself - vegetable pills in 1822. Three years later they were advertised as "vegetable universal medicine", and in a further three years were sufficiently well established to enable Morison to open his "British College of Health" in Hamilton Place, London. The magnitude of his turn-over in pills can be judged from the fact that he paid out in stamp duty no less than £60,000 between 1830 and 1840. This may have been helped by the fact that massive doses of 20 to 30 pills were prescribed.

The pills faded into obscurity soon after the death of their creator, though his writings continued to enjoy some popularity. It is said that Morison refused any other medical aid in his last illness and in fact died a martyr to his own treatment: there was nothing unusual about the composition of the pills which were simply purgatives containing gamboge, aloes and other resins. The extent to which the name had passed into current language can be seen from two diverse quotations: when Wöhler wrote to Liebig in 1843 counselling him against protracted battles with other chemists, he said "Du consumirst Dich dabei, argerst Dich, ruinirst Deine Leber und Deine Nerven zuletzt durch Morison'sche Pillen";[60] and Carlyle had cause to lament that there was no Morison's pill to heal a sick society (therein echoing Wesley's words of a century earlier about Ward's pill).[61,62]

Far more successful even than Morison was Thomas Holloway (1800 - 1883) who secured immortality for his name by endowing Holloway College, later to be dubbed "Royal" by Queen Victoria. His earliest essay in proprietary medicines was an ointment, said to have been filched from an itinerant Italian, but his name is particularly linked with the pills which began to appear in 1838. After an initial period of failure, the proprietors determined advertising gained him success, and in 1842 the tide turned. From that year until his death in 1883, the size of his annual advertising budget rose from £5000 to £50,000. His first premises stood in the Strand, on the site now occupied by the Law Courts, but he later moved to No. 78

New Oxford Street where one hundred hands were employed. Holloway was a man of advanced and liberal views as is shown by his requirement that the College, while imposing no religious tests - should have a simple daily service, and that degrees should be granted to women as soon as an act of Partliament could be obtained.[63] The Lancet in 1884 made acid comment under the heading "Apotheosis of the late Professor Holloway" on the fact that Holloway's portrait appeared in the London Illustrated News between those of Sir Joseph Lister and Sir William Browne, both knighted for their service to medicine, but in fact Holloway's name was probably at least as well known to the readers as were those of the other two, regular, practitioners.[64]

The advertising techniques of these pill vendors consisted in choosing always the bludgeon rather than the rapier, and was characterized by consistent, regular hammering at the same few ideas. Morison, for instance, was one of the first to exploit a now familiar trick of showing a picture of the imposing building in which his British College of Health was situated. [This trick was exploited fifty years later by the Coza Institute, a drunkenness-cure firm which inhabited three rooms in a prominent building in Chancery Lane]. Morison's other line of approach was to compare the cost of treatment by an imaginary firm of doctors ("Bleedem and Killem") with that of a box of his own pills.[65] Holloway also used a two-pronged attack. For those who liked a little culture with their advertising he would quote Dante:- "How little it was imagined that those celebrated lines of Dante 'And time shall see thee cured of every ill' would be literally fulfilled in England, and in the nineteenth century." Yet so it is. The disorders of man, however complicated they may be, are now subdued with surprising rapidity by that incomparable preparation "Holloway's Ointment" in combination with its powerful auxiliary "Holloway's External Disease Pill".[66] Yet all the while he kept in mind those who would not care for Dante, and for these he simply kept the name of Holloway constantly before their eyes: he would commonly fill a space in one of the daily papers with nothing more than the reiterated phrase "Holloway's Pills".

The techniques of advertising, viewed as the essential core to any commercial enterprise, received a fillip in the second half of the nineteenth century from the activities of the soap makers. It is not part of our study to trace this particular development, but only to notice that the lessons taught by Barratt of Pear's Soap were quickly learned by such men as Thomas . Joseph Beecham. The episode of H.M.S. Foudroyant stranded on the beach at Blackpool and emblazoned with the notice "England Expects Every Man to do his Duty and Take Beecham's Pills" shows how well the precepts had been absorbed. Obstinately different, however, were the advertisements of J.C. Eno who favoured a page closely packed with quotations from classical or contemporary authors, in which the connection with fruit salt was only rarely obvious. Lord Lytton was invoked:- "This life is a great schoolmaster and Experience the mighty volume"; and even less apposite was Tennysons"Not once or twice in our fair island story, the path of duty was the way to glory". Occasionally, news items were pressed into service, for example the erection of Cleopatra's Needle was the signal for an exhortation to every man to erect a more noble monument to himself by banishing want and disease (Plate I); and a retired general contributed little poems urging that no drop of the precious elixir be wasted.[67]

Lest it should be thought that proprietors invariably aimed their campaigns at the less literate and less critical section of the public, it should be remembered that the meeting of the British Association for the Advancement of Science in Newcastle (1889) was subjected to a special campaign, presumably tailored to its needs. The booklet of excursions carried an advertisement for "Epps Cura-cene or Wine of Ozone": after a long list of complaints, including "unfitness for study, society or business", which the compound would cure, the advertisement ends with the statement that "It nourishes the brain, sharpens the intellect, and removes excitement, confusion of ideas, dread, gloom, indecision, timidity, irritability, dullness of perception .... supplying at the same time, nerve, thought, and brain food and giving a great increase in intellectual power."[68] This meeting was attended by men of the calibre of Sir Oliver Lodge and Lord Rayleigh.

At the same time there was a campaign among those who profitted by publishing the advertisements for proprietary medicines to ensure that the truth about the nostrum trade was not published. Thus, the judge at an Edinburgh trial described the success of "Bile Beans" as based on "unblushing falsehood for the purpose of defrauding the public"[69]

Plate I

NOBILITY OF LIFE.

WHO BEST CAN SUFFER, BEST CAN DO.—*Milton.*

The Victorian Reign is unparalleled in the History of Great Empires for its Purity, Goodness, and Greatness!!!

WHAT ALONE ENABLES US TO DRAW A JUST MORAL FROM THE TALE OF LIFE?

Were I asked what best dignifies the present and consecrates the past; what alone enables us to draw a just moral from the *Tale* of Life; what sheds the *purest light upon our reason*; what gives the firmest strength to our religion; what is best fitted to *soften the heart* of man and elevate his soul,—I would answer with Lassus, it is

EXPERIENCE.—*Lord Lytton.*

"J. C. ENO. Queen's Head Hotel, Newcastle-upon-Tyne, June 4, 1877.

"Sir,—Will you to-day allow me to present you with this Testimonial and Poem on your justly celebrated Fruit Salt? Being the writer for several first-class London Magazines, and my occupation being a very sedentary one, I came here for a few weeks, in order to see what change of air would do for me, and at the wish of some *personal friends* of mine here, I have taken your Fruit Salt, and the good results accruing therefrom have been my reason for addressing you.—

"I am, Sir, yours truly, A LADY."

As sunshine on fair Nature's face,
Which dearly do we love to trace;
As welcome as the flowers in May,
That bloom around us on our way;
As welcome as the wild bird's song,
Which greets us as we go along;
As welcome as the flower's perfume,
That scents the air in sweet, sweet June,
Is Eno's Famous Fruit Salt!

Cool and refreshing as the breeze,
To Headache it gives certain ease;
Biliousness it does assuage,
And cures it both in Youth and Age.
Giddiness it will arrest,
And give both confidence and rest;
Thirst it will at once allay,
And what's the best in every way?—
Why, Eno's Famous Fruit Salt!

The Appetite it will enforce,
And help the system in its course;
Perhaps you've eaten or drunk too much?
It will restore like magic touch.
Depression with its fearful sway,
It drives electric-like away;
And if the Blood is found impure,
What effects a perfect cure?—
Why, Eno's Famous Fruit Salt!

Free from danger, free from harm,
It acts like some magician's charm;
At any time a dainty draught,
Which will dispel Disease's shaft;
More priceless than the richest gold
That ever did its wealth unfold;
And all throughout our native land
Should always have at their command
Eno's Famous Fruit Salt!

"This Life is the great Schoolmaster, and Experience the Mighty Volume. It is only through woe that we are taught to reflect, and gather the honey of wisdom not from flowers but thorns."—Lord Lytton.

AT HOME, MY HOUSEHOLD GOD; ABROAD, MY "VADE MECUM."

A GENERAL OFFICER, writing from Ascot on Jan. 2, 1886, says:—"Blessings on your 'FRUIT SALT'! I trust it is not profane to say so, but in common parlance, I swear by it. Here stands the cherished bottle on the chimneypiece of my sanctum, my little idol—at home my household god, abroad my 'vade mecum.' Think not this the rhapsody of a hypochondriac. No; it is only the outpouring of a grateful heart. The fact is, I am, in common, I daresay, with numerous old fellows of my age (67), now and then troubled with a tiresome liver. No sooner, however, do I use your cheery remedy than exit pain—'Richard is himself again!' So highly do I value your composition that, when taking it, I grudge even the sediment that will always remain at the bottom of the glass. I give, therefore, the following advice to those wise persons who have learned to appreciate its inestimable benefits—

When Eno's Salt betimes you take
No waste of this Elixir make;
But drain the dregs, and lick the cup
Of this, the perfect pick-me-up."

WRITING again on Jan. 24, 1888, he adds:—"Dear Sir,—A year or two ago I addressed you in grateful recognition of the never-failing virtues of your world-famed remedy. The same old man in the same strain now salutes you with the following—

When Time, who steals our years away,
Shall steal our pleasures too,
Eno's Fruit Salt will prove our stay,
And still our health renew."

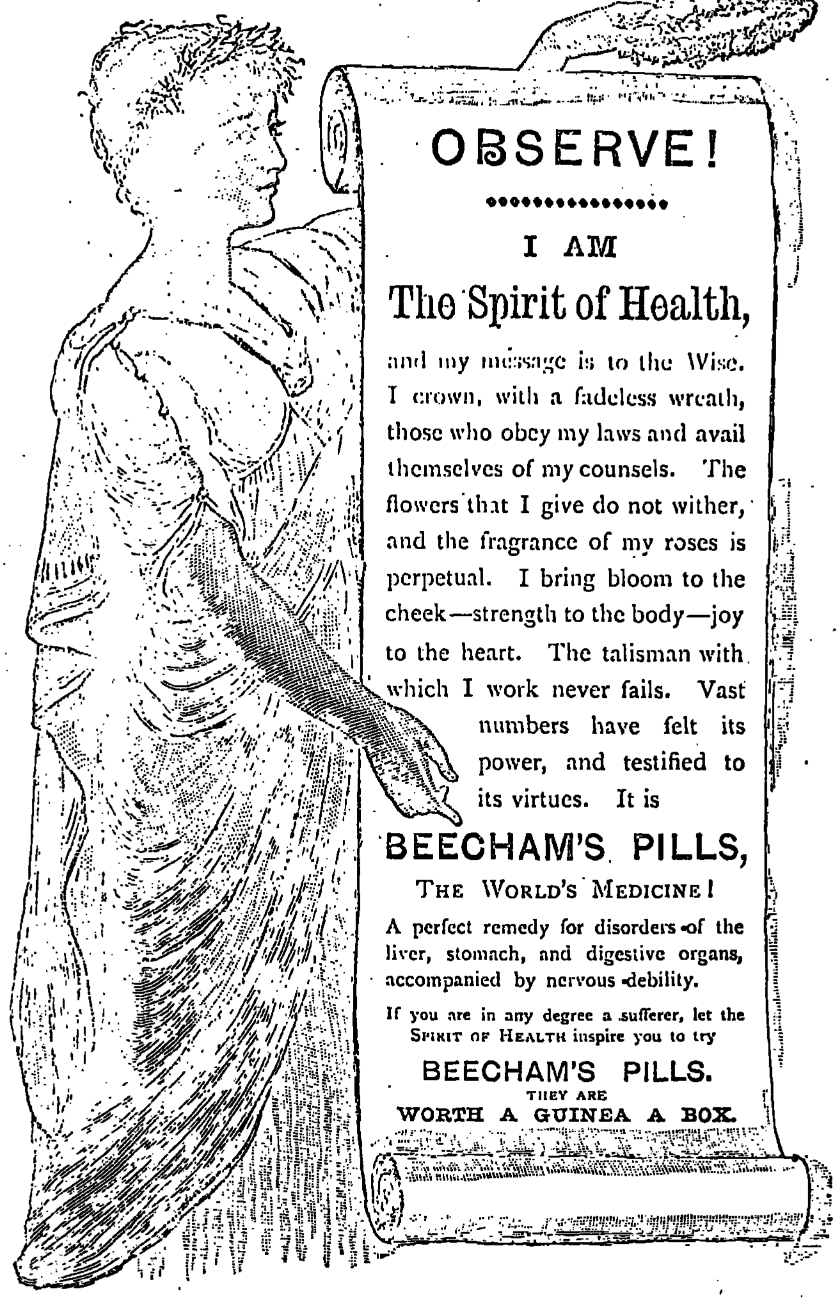
FEVERS, BLOOD POISONS, &c.—"Egypt, Cairo.—Since my arrival in Egypt in August last, I have on three occasions been attacked by fever, from which on the first occasion I lay in hospital for six weeks. The last attacks have been completely repulsed in a short time by the use of your valuable 'FRUIT SALT,' to which I owe my present health at the very least, if not my life itself. Heartfelt gratitude for my restoration and preservation impels me to add my testimony to the already overwhelming store of the same, and in so doing I feel that I am but obeying the dictates of my duty.—Believe me to be, Sir, gratefully yours, A Corporal 19th Hussars.—May 26, 1883.—Mr. J. C. Eno."

CAUTION.—Examine each bottle, and see the Capsule is marked "ENO'S FRUIT SALT." Without it you have been imposed upon by a worthless imitation. Sold by all Chemists.

PREPARED ONLY AT ENO'S "FRUIT SALT" WORKS, LONDON, S.E.

PICKWICK'S IMMORTAL DISCOVERY.

"There is an inscription here," said Mr. Pickwick. "Is it possible?" said Mr. Tupman. "I can discern a cross and a B." "This is important," continued Mr. Pickwick, "this is some very interesting inscription—it must not be lost." All admirers of the great Pickwick should pause and examine the stone, and they will find the words, "BEECHAM'S PILLS." Let them bear this in mind, and they may safely conjecture that on the other side of the stone, not reproduced by the artist, is added "WORTH A GUINEA A BOX."



OBSERVE!

I AM

The Spirit of Health,

and my message is to the Wise. I crown, with a fadeless wreath, those who obey my laws and avail themselves of my counsels. The flowers that I give do not wither, and the fragrance of my roses is perpetual. I bring bloom to the cheek—strength to the body—joy to the heart. The talisman with which I work never fails. Vast numbers have felt its power, and testified to its virtues. It is

BEECHAM'S PILLS,

THE WORLD'S MEDICINE!

A perfect remedy for disorders of the liver, stomach, and digestive organs, accompanied by nervous debility.

If you are in any degree a sufferer, let the SPIRIT OF HEALTH inspire you to try

BEECHAM'S PILLS.

THEY ARE

WORTH A GUINEA A BOX.

Tune .... "The Flowers that bloom, &c." .... *Mikado.*

For the pimples that bloom in the spring, tra la,
And make such a mess of your face,
A Beecham's the very best thing, tra la,
To cure them and leave not a trace, tra la,
So deal right away with the case.
And that's what I mean when I say and I sing
"Oh! pills for the pimples that come in the spring,
Tra la la la la! Tra la la la la!
Oh pills for the pimples of spring!"

Plate II

HEALTH, STRENGTH & ENERGY

Are quickly obtained by simply taking a few doses of

EPPS'S CURA-CENE ([illegible] of Ozone).

The greatest purifier [illegible]
Its effects are [illegible]

EPPS'S CURA-CENE ([illegible] of Ozone).

A guaranteed cure for nervous [illegible] and singing noises in the head and ears, [illegible] before the eyes, dizziness, failing appetite, [illegible] and fluttering, rising of food, and acidity of the [illegible] wind, wasting diseases, shortness of breath, kidney [illegible] coughs, asthma, and in the early stages of [illegible] of the blood with pimples, blotches, and eruptions, [illegible] exhaustion, melancholy and loss of memory, [illegible] and rheumatism, loss of energy, and unfitness for [illegible] a disease but what this medicine will reach, and [illegible] thousands of times before, even after everything else had [illegible] failed.

IT GIVES STRENGTH AT ONCE

and will give more strength in ten minutes than any other medicine will give in as many weeks, and is extremely pleasant to take.

IT PURIFIES THE BLOOD,

rendering the skin clear and transparent, [illegible] and eruptions. It produces new, rich, and pure blood, [illegible] muscle, flesh, bone, brain, &c., and contains the very [illegible] LIFE.

IT NOURISHES THE BRAIN,

sharpens the intellect, and [illegible] indecision, timidity, irritability, dullness of [illegible] exhaustion or overworked brain, supplying at the same [illegible] and giving a great increase in intellectual power.

This Grand RESUSCITATING ELIXIR

has been recommended by the most illustrious Physicians [illegible] Sir Erasmus Wilson, Sir Charles Locock, Physician to the Queen, [illegible] Sergeant-Surgeon to the Queen, who have given their Testimonials [illegible]. Copies of which, together with opinions of the Press, will be sent to anyone post free.

Sold in bottles at 2/9, 4/6, and 11/-, and most Chemists [illegible] any not having it in stock will procure it without extra charge, and there is a great saving in buying the larger sizes. Should, however, any difficulty be found in getting it the Proprietors will send it carriage free.

LONDON AGENTS:—BARCLAY & SONS, [illegible] Farringdon Street; EDWARDS & SON, 157, Queen Victoria Street; NEWBERY & SONS, [illegible] Edward Street, Newgate Street; THOMPSON, MILLARD & CO., Great [illegible]; [illegible] & SONS, 48a, Oxford Street; H[illegible] & SONS, [illegible] Street, [illegible] Street, W., and 91-95, City Road; SUTTON & CO., [illegible] Bow Church Yard; [illegible] & CRISPE, 4, Cheapside; LYNCH & CO., [illegible] Aldersgate Street; [illegible] ROBERTS & CO., 9, Clerkenwell Road, E.C.

EPPS & Co.,
366, Albany Road, Camberwell,
LONDON.

3.

BRITISH ASSOCIATION,

NEWCASTLE-ON-TYNE, 1889.

KING'S COLLEGE, NEWCASTLE
LIBRARY

SATURDAY.

EXCURSION TO

E—Durham, Finchale Abbey,

AND

USHAW COLLEGE.

Newcastle-on-Tyne:
TYNE PRINTING WORKS CO., PUBLISHERS, 26, SIDE.

1889.

Plate III

and this was not reported except in the medical press: similarly when H.G. Wells attempted to publish as a serial "Tono Bungay" (a story of the floating of a nostrum) several newspapers refused it, and it was eventually taken by the English Review in 1909. An uglier side to the pushing of proprietary medicines was to be seen in the existence of "Dupes Directories". A firm in Leeds, for instance, would supply names and addresses of sufferers from cancer, tuberculosis and diabetes at a small fee: these names and addresses were in turn obtained from answers to newspaper advertisementsor to handbills distributed in concentrated raids on a particular area.[70]

Apart from the health salts, most of the popular remedies had been compounded from vegetable extracts, resins, etc., and thus even the simplest were chemically complex. The nature of the medicines was however radically changed by the rise of the organic chemical industry: the separation from coal tar of such intermediates as benzene and phenol made available a range of new and powerful substances. Acetanilide (known as Antifebrin) came onto the market in 1887, its most famous for being the Daisy Powder. The makers of this product bought acetanilide by the ton, and packed it into papers containing about six grains. The advertisements carried "analysts' certificates" to say that the powders contained no harmful substance, although many people were susceptible to poisoning by acetanilide and deaths were reported in the medical press:[71] acetanilide was later put onto Schedule I of the Poisons List.

Distribution was almost exclusively through small grocers and general dealers in poor areas. As an uncompounded drug, Daisy Powders were not liable to stamp duty, but vendors of such substances needed a licence, annual value five shillings; the makers often paid all but a few pence of the licence fee.

The discovery by Dreser in 1893 of aspirin and its manufacture by the German firm of Baeyer at Leverkusen, brought a second and safer synthetic product to the field of pain-killers, but the use of acetanilide persisted. The significance, for our study, of these last few years of the 19th Century, lies in the fact that the formulae for proprietary medicines became drastically simplified, with the substitution of a few potent synthetics for a whole series of vegetable extracts.

It had been hoped, in many quarters, that the Stamp Duty Act, so far as it related to medicines, would limit and control the trade (though we must not lose sight of the fact that its primary end was to raise money). There were however too many opportunites for evasion. For instance, a preparation which was advertised as being good for a particular organ, without mentioning the complaints which might be associated with the organ, was exempt. So that "corn plasters" or "cough mixtures" paid duty whilst "foot plasters" or "chest mixtures" did not. Many manufacturers, however, were more than content to pay duty in exchange for the privilege of having the stamp on their containers. "Every genuine bottle of Beecham's Pills carries the Government stamp".[72] Thus, not unnaturally, the general public came to regard the stamp as a guarantee of purity and efficacy. Worse still, the Inland Revenue would allow the maker's name to be printed on the stamp on payment of the cost of the block, though the effect of this was partly offset at a later date by the addition of a reminder that the stamp was not a guarantee.

Almost the only voices raised against the situation were those of the medical profession, who of course were suspected of having an axe to grind. By the end of the century, the British Medical Association had set in motion a scheme for publishing the contents and real costs of a large number of proprietary medicines, and in such a scheme chemical analysis was obviously to play a key part. We must now turn to the development of analytical techniques in preparation for the great clash of arms.

Proprietary Medicines appearing in the 1804 list and exposed by Dr. J.A. Paris.

Ague Drops:	Liquor Arsenicalis (London)	274
Anderson's Pills:	Aloes, Jalap and Aniseed	44
Aromatic Vinegar:	Camphor, cloves, lavender and rosemary in vinegar	15
Barclay's Anti-bilious Pills:	Colocynth, Jalap, Almond Soap, Guaiacum, Antimony, oils of Juniper, Carraway, Rosemary and syrup of Buckthorn	194
Bateman's Pectoral Drops:	Tincture of Castor, Camphor and Opium, Aniseed and Cochineal	130
Beaume de Vie:	Decoct. Aloes comp. (London)	
Brodum's Nervous Cordial:	Tinctures of Gentian, Calumba, Cardamom, Bark, Wine or Iron and Spirit of Lavender comp.	221
Cephalic Snuff:	Powdered Asarum, diluted with other vegetable powder	408
Y Chamberlain's Pills:	Cinnabar, Sulphur, Sulphate of Lime and gums	247
Ching's Worm Lozenges:	Calomel with purging gums	244
Daffy's Elixir:	Tincture Sennae comp. (Edin.) with aniseed and Elecampane	433
Dalby's Carminative:	Magnesium carbonate, oils of Peppermint, Nutmeg and Aniseed, Tinctures of Castor, Asafoetida and Opium, Spirit of Pennyroyal, tincture of Cardamom comp. with Peppermint water	285
Dixon's Antibilious Pills:	Aloes, Scammony, Rhubarb and Antimony	44
Dutch Drops:	Turpentine, Guaiacum, Ethylnitrite, Amber and Cloves	418

Elixir of Longevity:	An aromatic tincture containing Aloes	45
Ford's Balsam of Horehound:	Horehound, Liquorice, Brandy, Opium, Camphor, Benzoin Squills, Aniseed and Honey	322
Fothergill's Pills:	Aloes, Scammony, Colocynth, Antimony (This is unlikely to be the "Pectoral" Pill)	44
Freeman's Bathing Spirits:	Linimentum Saponis comp (London) with various additions	269
Friar's Balsam:	Tincture Benzoini comp.	113
Godbold's Balsam:	usually Honey and Vinegar	328
Godfrey's Cordial:	Sassafras, Carraway, Coriander, Treacle, Aniseed and Opium (subject to much variation)	371
Gowland's Lotion:	Corrosive Sublimate in emulsion of Bitter Almonds	238
Greenough's Tincture for the Teeth:	Bitter Almonds, Brazil wood, Cassia, Iris root, Cochineal, Salt of Sorrel, Alum, Horse Radish and Spirit (contains poisonous oxalates!)	429
Hannay's Lotion:	Caustic Potash solution	280
Hatfield's Tincture:	Tincture of Guaiac and Soap	224
Henry's Aromatic Vinegar:	see Aromatic Vinegar	
Hooper's Pills:	Aloes, Myrrh, Iron Sulphate, Canella Bark and Ivory black	44
Jame's Powder:	Pulvis Antimonialis (Lond. and Edin.)	356
Jame's Analeptic Pills:	The powder made up with gum ammoniacum, aloes, myrrh and tincture of castor	356
Jesuit's Drops:	see Friars Balsam	
Keyser's Pills:	Acetate of Mercury with Manna	6

Marshall's Cerate:	Palm Oil, Calomel, Lead Acetate and Mercury Nitrate	136
Norris's Drops:	A tincture of Antimony	67
Norton's Drops:	Corrosive Sublimate	239
Peter's Pills:	Aloes, Jalap, Scammony and Gamboge	44
Radcliffes Purging Elixir:	A compound tincture of Aloes and Rhubarb	44
Riza Balsam:	Aqueous extract of Pine shoots	413
Roche's Embrocation:	Oils of olive, clove and amber	305
Rymer's Cardiac Tincture:	An infusion of Capsicum, Camphor, Cardamom, Rhubarb, Aloes, Castor with a small quantity of Sulphuric Acid	122
Singleton's Golden Ointment:	Arsenic sulphide in Lard; OR Ointment of Mercury nitrate (London)	92
Smellome's Eye Salve:	Basilicon Ointment (London) with oil and Verdigris	37
Soloman's Anti-impetigines:	Corrosive Sublimate	239
Solomon's Balm of Gilead:	Tincture of Cardamoms	430
Speediman's Pills:	Aloes, Myrrh, Rhubarb and Chamomile	44
Spilsbury's Anti-scorbutic Drops:	Tincture of Antimony, Mercury, Gentian, Orange Peel, Red Saunders	239
Squire's Elixir:	A compound tincture of Opium and Camphor	321
Steer's Opodeldoc:	An aromatic ammoniated spirit soap	268
Storey's Worm Cake:	Calomel and jalap coloured with cinnabar	245
Stoughton's Elixir:	An aromatic tincture of Gentian	221
Walker's Jesuit Drops:	Tincture of Guaiacum, Balsam of Copaiba, Oil of Sassafras	224
Ward's Essence for Headache:	Linamentum Camphorae comp. (London)	268

Ward's Paste:	Black Pepper, Elacampane, Fennel seeds in Honey and Sugar	335
Ward's Sweating Powder:	Veratrum and Opium [Paris is not accurate on Ward's preparations; see Page, J., "Receipts for preparing and compounding the Principal Medicines made use of by the late Mr. Ward," London, 1763; see also W.A. Campbell, Univ. Newcastle Med. Gazette, June 1964].	438
Whitehead's essence of Mustard:	Balsam of Tolu, with resin	380

The reference numbers refer to pages in Paris, J.A., "Pharmacologia"

II 5th ed., London, 1822.

Many of the index references in this work are inaccurate.

CHAPTER III

THE DEVELOPING TECHNIQUES OF CHEMICAL IDENTIFICATION.

About fifty common ingredients sufficed for the composition of the medicines "exposed" by J.A. Paris. It will be seen from Table III that these comprise a dozen metals, some plant extracts or parts of plants, a few oils, and a small collection of household materials used as solvents or bases. As the nineteenth century advanced, the number of plant extracts (especially alkaloids) increased, but at the same time the nature of the extracts became simpler. For instance "bark" was replaced by quinine, opium by morphine, and in general pure crystalline compounds took the place of vegetable matters of uncertain composition. The synthesis of organic drugs which had no place in nature did not become an important consideration until the 1870's.

The metals listed in Table III could be detected and determined with certainty. The founders of inorganic qualitative analysis had learned their trade in that most difficult field of the analysis of stones and minerals. Here the problems of grinding and pulverisation, of solubility, of separating large quantities of silica, and of distinguishing between pairs of very similar elements, were encountered and solved. The result was that schemes for inorganic qualitative analysis began to appear in book form in the first decades of the nineteenth century. They were not, however, schemes which relieved the analyst of personal responsibility. The contemptuous references to "test-tubing", and the frequently expressed doubts about the educational value of analytical work in schools (p. 180) would have been incomprehensible to Vauquelin, Klaproth, Thomson, Rose or Fresenius. To them, each analysis was a research in which the analyst drew upon his

Table III.

Common Constituents of XIXth Century Proprietary Medicines.

Metals

- Aluminium
- Antimony
- Arsenic
- Bismuth
- Calcium
- Copper
- Iron
- Lead
- Mercury
- Magnesium
- Potassium
- Sodium

Oils

- Carraway
- Castor
- Juniper
- Lavender
- Nutmeg
- Peppermint
- Rosemary
- Sassafras

Plant Parts or Extracts

- Aloes
- Ammoniacum
- Aniseed
- Balsam of Peru
- "Bark"
- Benzoin
- Camphor
- Canella
- Capsicum
- Cardamom
- Cloves
- Colocynth
- Elacampane
- Fennel
- Gamboge
- Gentian
- Ginger
- Guaiacum
- Horehound
- Jalap
- Liquorice
- Myrrh
- Opium
- Pennyroyal
- "Red Saunders"
- Rhubarb
- Squills

Bases and Vehicles

- Amber
- Brandy
- Honey
- Lard
- Resin
- Soap
- Treacle
- Turpentine
- Wine

Synthetics (after 1870)

- Acetanilide
- Aspirin
- Iodoform
- Phenacetin
- Phenols

general knowledge of chemistry at every point: such mechanical operations as grinding were not dismissed as menial preliminaries to the analysis, but were regarded as opportunities for the analyst to display his best qualities. Thomson tells a cautionary tale of two students to each of whom was given a Brazilian chrysoberyl for analysis. One was at great pains to powder his portion as finely as possible, and achieved complete solution, finishing the analysis in a few days: the other, less attentive to detail, did not spend long enough over his pulverisation and found that fusion and extraction were of no avail, so that "after spending a great many days in these disagreeable repetitions he was unable to render the mineral soluble in muriatic acid, and gave up the analysis in despair".[73] Vauquelin in his essay on the analysis of stones says "La pulverisation est donc le premier travail qui doit occuper l'artiste, et quoique mechanique, il exige les precautions assez grandes".[74]

Even the addition of reagents to solutions under test called for extreme skill and judgment. Thomson reminds us that "unless we add ammonia in excess, the precipitate which falls is apt to contain muriatic acid, and is in part redissolved again while we are washing it on the filter. But we should avoid a great excess of ammonia, because it might dissolve a portion of some of the substance at first precipitated".[75]

Nevertheless, systems of analysis did appear and became the stock in trade of chemists in general. It is not possible to assign the invention of group analysis tables to one person, but the steps by which the group tables emerged are clear enough. Bergman (in De Terra

Gemmarum 1779) had established the practice of fusing the powdered sample with sodium carbonate and separating the acid-soluble from the acid-insoluble part by filtration. Successive treatments with further portions of soda followed by acetic and sulphuric acids enabled him to deal with silica, iron, aluminium, magnesium, calcium and barium. Klaproth used in addition ammonia and caustic alkali, extending his range of metals to include strontium, beryllium, manganese and some rare earths.[76] (Table IV)

Although these schemes were of immense importance in a pioneering way, it will be seen that they make no provision for detecting the common metallurgical metals. To deal with these (later to be known as the Group II and Group IV metals) three different procedures were available.

The first of these required a universal reagent which was to make possible the immediate identification of the common metals, provided that they were encountered only one at a time. Such a reagent was thought to have been found in potassium ferrocyanide ("yellow prussiate of potash"), commercially available since Maquer had shown in 1752 how to prepare it by digesting prussian blue with potassium carbonate solution. W.T. Brande, at the Royal Institution, drew up a table of the colours which this reagent produced with various metals (Table V), from which it can be seen that a very high order of experience, and also of colour-perception, would be required to make it work. The precise distinction between "yellowish-white" and "pale yellow" would not be easy to establish. As a confirmatory test for a metal already characterised the table would be useful, though the stability of

Table IV.

Klaproth's System for Analysis of Stones.

Powder the sample finely.

Fuse with caustic potash.

Extract with hydrochloric acid.

Repeat these operations until everything except silica is soluble.

Dissolve in hydrochloric acid.

Filter.

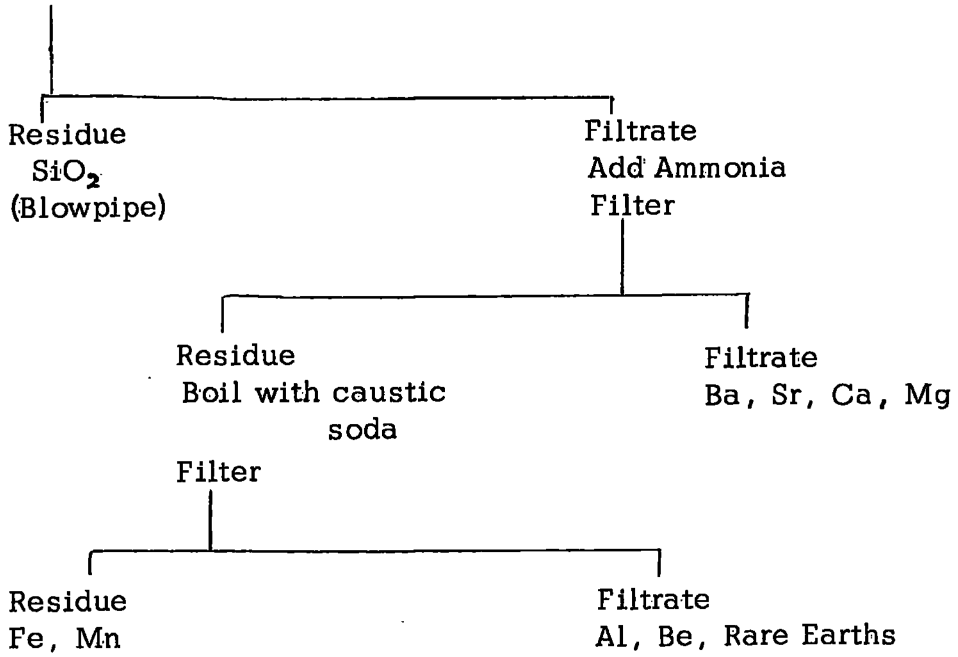


Table V.

Brande's Table of Ferrocyanide Colours.

Manganese	White
Iron (II)	Pale blue
Iron (III)	Prussian blue
Zinc	Yellowish white
Tin (II)	White, then yellow, then blue
Tin (IV)	Pale yellow
Copper (I)	Lilac
Copper (II)	Deep brown
Lead (II)	White
Cobalt	Pale green
Uranium	Deep brown
Nickel	Grey
Titanium	Deep blue
Mercury	Greenish white
Silver	Cream
Platinum	Yellow

some of the precipitates would be a limiting factor.

The second tool for the identification of metals was hydrogen sulphide, long known as the smell from liver of sulphur and studied systematically by Scheele as "stinking sulphur air" in his *Experiments on Fire and Air* (1777).[77] Mellor has suggested that the origins of the analytical use of this gas are to be found in a paper by Liebig in 1831,[78] but this paper (on the separation of some metal oxides) is not about hydrogen sulphide. Fourcroy had used the gas to detect lead in wine in 1787, but by then the main facts about metal sulphide precipitation were known.[79] A list of reactions of metallic salts with hydrogen sulphide solutions had been given by Bergman in his essay on the artificial production of mineral waters, in 1778. He included mercury, silver, lead (nigrescens dejicitur), zinc (album praebet sedimentum), copper (lente deponit sedimentum), iron, and arsenic (tandem auripigmenti indolem adquiret).[80] The fundamental paper is however that of Berthollet in 1798 (*Observations sur l'hydrogène sulfuré*), in the forty pages of which he describes carefully the precipitates and colours to be obtained from fourteen metals in acid or alkaline conditions, (Table VI).[81] Gay Lussac took up the matter of hydrogen sulphide precipitation in 1811. In a paper entitled "*Sur la precipitation des Métaux par l'hydrogène sulphuré*" he showed that some sulphides come down in acid solution, and others in the presence of ammonia.[82] M.P. Crosland points out that this was a decisive step in the establishment of group separations.[83]

OBSERVATIONS *sur les Oxides et les Dissolutions métalliques.*

	Eau de sulfure hydrogéné de potasse.	*Eau d'hydrogène sulfuré.*	*Hydrosulfure de potasse et d'ammoniaque.*	*Précipité par l'hydrosulfure et acide muriatique.*	*Précipité par l'hydrosulfure potasse pure.*
Sulfate de fer	Précipité noir qui devient jaune par le contact de l'air.	Point de précipité pour peu qu'il y ait excès d'acide.	Précipité noir.	Dissolution et dégagement d'hydrogène sulfuré.	rien
Oxide rouge, de fer		Devient noir. La liqueur reste fortement colorée s'il y a excès d'hydrogène sulfuré.	Devient noir. La base est éliminée.		
Sulfate de zinc.	Précipité blanc	Précipité blanc.	Précipité blanc	Dissolution complette et dégagement d'hydrogène sulfuré.	rien
Oxide de zinc.		L'odeur s'évanouit	La base est éliminée		
Acétite de plomb.	Précipité blanc qui, par une addition, devient noir.	Précipité noir	Précipité noir.	Disparution de la couleur et dégagement d'hydrogène sulfuré	rien
Oxide de plomb, rouge		Devient noir.	Élimination de la base		
Nitrate de bismuth.		Précipité noir	Précipité noir		
Oxide de bismuth.		Couleur noire	*D'Ammoniaque.* Élimination de l'ammoniaque		
Nitrate d'argent	Précipité noir	Précipité noir	Précipité noir.	Non décomposé.	
Sulfate de cuivre.	Précipité brun.	Précipité noir	Précipité noir.	Dissolution et dégagement d'hydrogène sulfuré, mais il reste du noir.	
Oxide vert de cuivre		Devient noir.	Élimination de la base		
Nitrate de mercure	Dans beaucoup d'eau, couleur brune.	Précipité noir brunâtre	Précipité noir brunâtre	Non décomposé à froid	
Muriate de mercure oxigéné.	Précipité blanc qui devient noir par une addition.	Précipité blanc, puis noir par une addition.	Blanc, puis noir par une addition.	Non décomposé à froid	
Oxide rouge de mercure.		Noirâtre.	*D'Ammoniaque.* Chaleur qui fait bouillir l'hydrosulfure. Élimination d'ammoniaque. Combustion d'hydrogène (*).	Point de dégagement.	
Muriate d'étain			Précipité noir.		
Muriate d'étain oxigéné.	Précipitation du souffre et de l'oxide	rien	Précipité d'oxide d'étain blanc, et dégagement d'hydrogène sulfuré.		
Oxide blanc d'étain.		rien	Élimination d'hydrogène sulfuré.		
Sulfate de manganèse.		rien	Précipité blanc	Dissolution et dégagement de l'hydrogène sulfuré.	rien
Oxide de manganèse noir		L'odeur disparoît. Un excès le dissout	*D'Ammoniaque.* Ammoniaque rendu libre. Chaleur et bouillonnement.	Dissolution et dégagement d'hydrogène sulfuré; effervescence.	
Tartrite antimonié.	Précipité jaune, orangé.	Couleur orangée sans précipité.	Précipité rouge orangé qui se redissout par un excès		
Oxide d'antimoine blanc.		Devient jaune après quelques instans	*D'Ammoniaque.* La liqueur perd sa couleur	La liqueur surnageante est précipitée en rouge orangé.	Ote la couleur orangée au précipité orangé.
Oxide d'antimoine sublimé.		Ne change presque pas de couleur			
Eau d'oxide d'arsenic.	Décomposition du sulfure comme par un acide	Devient un peu louche, couleur jaune.	Couleur jaune sans précipité.		
Sulfate de titanium.			Précipité vert foncé		
Acide molybdique		Précipité brun.	Précipité brun.	Non dissous.	

The new demand for hydrogen sulphide as a reagent required that the preparation might be started and stopped as necessary, and gave rise to a series of generating devices.[84] Since the familiar Kipp's apparatus did not come into general use until the late 1860's there was room for experiment by the earlier analysts into the most convenient ways of handling the gas. It is significant that both Heinrich Rose and Carl Remigius Fresenius (authors of the two most important analytical text-books of the nineteenth century) preferred to use solutions of the gas, calling it "liquid hydrogen sulphide".

The third mode of detecting metals, by the use of the blowpipe, merits an extended examination. Used by jewellers and enamellers in antiquity, the blowpipe began to be employed in quasi-analytical work during the seventeenth century. Robert Hooke described in Micrographia (1665) how he examined a stone (petrified wood) "in the flame of a Lamp, made very intense by the blast of a small Pipe, and a large Charcoal".[85] Johann Kunckel described the use of a blowpipe to reduce metal oxides in his book on glass. "Es kommt oft, dass man ein gar weniges metallischen Kalch oder dergleichen hat welches man gerne zusammen schmeltzen und was für ein Metall hällt sehen und probiren wolte: dieses kan auf keine Weise füglicher als auf diese geschehen umden man nur eine Kohle ein wenig ausholt, den Kalch oder was man schmeltzen will darein thut, und durch ein solch Röhrchen die Flamme eines starcken Lampenlichts darauf blaset es geht sehr geschwinden von Statten".[86] The phrase "es kommt oft" shows that this was not a rare operation.

It was in the middle of the eighteenth century however that the use of the blowpipe became systematized. J.A. Cramer gave a careful description of the instrument in 1741. "When small pieces of metal are to be melted, the best way to do it is to put them upon a piece of charcoal, with a small hollow made in it, and then direct the flame of a lamp having a large cotton, upon the small mass of metal to be melted, by blowing it thereon with a small crooked pipe; .... Let the pipe with which this is performed be made of copper, and let it have in its bending part, a hollow globe one inch in diameter through which the wind is to pass, that the moisture of the breath gathering into small drops may be collected within the cavity of this globe ..... Let the less aperture of this tube through the wind comes out, be so small as to admit hardly the smallest needle. This is called the cementing tube or blowpipe."[87] Cramer said that he was indebted to Ercker and Agricola and to "an indefatigable labour, the closest inspection, and hands that were not afraid of the blackness of charcoal." This reminds us of Hoover's preface to Agricola in which he says that the latter learned his trade at the lowest and wettest level, and serves to emphasize how deeply chemical analysis is rooted in metalliferous mining.

The extension of blowpipe analysis to general mineralogical situations is almost certainly due to Axel Friedrich Cronstedt who discovered nickel in 1751. Rival claims have been made for Anton von Swab[88], an assessor to the Mining Academy in Stockholm, but this seems to have stemmed from a mistake by Linnaeus. Cronstedt published anonymously a system of mineralogy in Stockholm in 1758, through which were scattered references to the blowpipe. In 1770 the work was translated into English by Gustav von Engeström who collected the blowpipe portions into a separate essay printed as an appendix. Linnaeus had believed that the original Swedish work was written by Von Swab, and so the legend grew up that von Swab was the founder of mineralogical analysis by the blowpipe.

Engeström, who had been Warden of the Mint in Stockholm, expressed his belief about Cronstedt's position thus: "The blowpipe is in common use among jewellers, goldsmiths, glassblowers etc., and has ever been used a little by the chemists and mineralogists: but, to the best of my knowledge, Mr. Cronstedt is the first, who made such an improvement in its use as to employ it in examining all mineral bodies. This gentleman invented some other apparatus, necessary in making the experiments, to go with the blowpipe, which all together make a neat little case that, for the facility of being carried in the pocket, might be called a Pocket Laboratory; and as neither the pocket laboratory, nor even the extensive use of the blowpipe is yet generally known, I think it will not be altogether useless to give a description of it".[89]

Anton von Swab had in fact described blowpipe techniques in his paper on native antimony in 1748,[90] and Rinman had similarly described its use in the examination of tin compounds in 1746, but neither of these accounts led to general systems of blowpipe analysis. Whatever doubt may exist about the relative contributions of these early workers, there is no doubt that the scope of blowpipe analysis was very considerably widened by the joint efforts of Torbern Bergman and Johann Gottlieb Gahn.

Bergman's essay De Tubo Ferruminatorio (1779) begins with a historical survey in which he gives credit to "Celebris noster metallurgus Andreas a Swab" and "Mineralogi nostri exercitatissimi Domini Cronstedt, Rinman, Engestrom, Quist, Gahn and Scheele".[91] A description of the instrument is followed by an account of the method of blowing (almost certainly inadequate for self-teaching), the structure of the candle flame, kinds of support (charcoal, or spoons of gold or silver), and the three fluxes (phosphate, alkali and borax). The metals treated in Bergman's essay are gold, silver, platinum, mercury, lead, copper, iron, tin bismuth, nickel, arsenic, cobalt, zinc, antimony and manganese.

Most of the experiments which Bergman describes in his blowpipe essay were by Gahn. Although Gahn was an almost fanatical devotee of the instrument, who never travelled without a blowpipe in his pocket and whose experience of its use enabled him "to determine in a few minutes the constituents of almost any mineral",[92] he was unwilling to put on record his observations and achievements. His work was edited and published by others, notably by Berzelius, by Thomson in his Annals of Philosophy, and by J.G. Children in his translation of Thenard's Traité de Chimie. There is some evidence that Gahn's reluctance to publish might have been connected with a partial colour-blindness; Berzelius refers to situations in which Gahn called certain shades yellow or dull yellow, which to Berzelius appeared red, and he goes on to recommend the collaboration of two people to avoid errors of that kind.[93]

Apart from the translations mentioned previously there was a considerable literature of the blowpipe in English. J.C. Children's translation of Berzelius is so copiously annoted and supplied with editorial comment that it almost ranks as an original work: the translator was conscious of this for he wrote in his preface "Some explanation, however, and to the author some apology perhaps is necessary, as to certain liberties I have taken with the original". In particular, Children rejected much of Berzelius's nomenclature and all his formulae (which he referred to as "perplexing ourselves with questions of atoms and half atoms, and by doubling this and halving that, endeavour to make nature bend to our preconceived opinions")[94], and also modified much that seemed to pertain more to Sweden than to England.

Faraday devoted sixteen pages of his Chemical Manipulation to the blowpipe, referring the student to the Children-Berzelius work for further information. As might be expected, Faraday's account is packed with detail, especially on the correct mode of blowing: there is no description of actual observations and their interpretation, for the work is not a text-book of chemistry.[95]

As a purveyor of scientific equipment J.J. Griffin was obviously well acquainted with all the details of construction of blowpipes and accessary apparatus, and as a translator of foreign chemical works he must have known the literature intimately. His essay on blowpipe analysis, incorporated into his Chemical Recreations, is therefore of particular value: perhaps more than any other account, this could be used by a student working without a teacher.[96]

One of the most enthusiastic protagonists for blowpipe analysis in England was Lt-Colonel W.A. Ross, an old student at the Freiberg School of Mines. His book on the blowpipe (1884; 2nd ed. 1888)[97] was written at white heat, and sprinkled with italics, heavy type, every kind of punctuation mark, together with condescending derivations from Greek and Latin. Many of these must have been baffling to the reader as the following examples show: "decomposing" (Latin de, out of, and compono, I put together), p.30: "extemporised" (Latin ex, for, and tempus, temporis, time), p. 59. Sometimes the Latin came first, to be followed by one of Ross's explanations: "sine qua non" (Latin, without which not), p. 41. In spite of this propensity for explaining words that were probably clear enough to begin with, Ross refused to call a flame a flame, preferring instead his own word "pyrocone". The work contained sharp attacks upon Cronstedt, Engestrom, the City and Guilds of London Institute, and the Royal School of Mines. The bitterest attack was reserved for Berzelius, against whom Ross had some kind of animus that remains unexplained. Because Gahn died in 1819, and Berzelius published on the blowpipe in 1820, this was held to prove that Berzelius had stolen Gahn's work; further, such specific charges were made as that Gahn had invented the oil lamp appropriated by Berzelius. Yet even a cursory inspection of the work of Berzelius is sufficient to show that he freely and regularly gave credit to Gahn for improvements in techniques and apparatus.

A clearer insight into the state of Ross's mind on Berzelius is afforded by the incident of the bellows-blown blowpipe. Berzelius was not at all kindly disposed to supplying the blowpipe with air by mechanical means which he thought deprived the user of fine personal control; he said that the practice was as inartistic as using a bellows to play upon a wind instrument. To this Ross retorted that it was well known that the most beautiful wind instrument that Europe possessed- the English concertina- was indeed played upon through a bellows.[98]

Apart from the polemical style, the pro-German and anti-South Kensington bias, and the generally sustained inference that everyone but the author is a fool or a rogue, the book is significant in that it was aimed at artisans and apprentices whose interest in the subject was non-vocational. Ross visualised crowds of factory workers carrying out analyses of rocks and minerals, at first in pure form and purchased for practice, and eventually as picked up on the roadsides. He predicted that an inevitable result would be the production of cheap apparatus, ("I am in hopes that when a million of my artisan-countrymen take to blowpipe analysis, all this apparatus will be manufactured in England still more cheaply, and a great trade thereby obtained."[99]) Of course a million artisans did not take up blowpipe analysis, and it is difficult to understand why the hope was ever entertained that the analysis of roadside stones would prove a powerful attraction: it is interesting to speculate on what might have happened if these same intelligent artisans had been encouraged to turn their blowpipes onto foods, drugs or coloured sweets.

The beginner in blowpipe analysis would find no shortage of equipment to help or bewilder him. A footnote in Children's translation of Berzelius says that "Mr. Newman, of Lisle Street, Leicester-square, makes complete sets of apparatus for the blowpipe, containing everything that the operator can require". Table VII shows how Griffin's blowpipe sets compared with the modest suggestions of Bergman and Engestrom. Minerals for practice, too, were sold as collections (Children says "from Mr. Sowerby, King Street, Covent Garden, and Mr. Mawe, near Somerset-house, in the Strand".) Griffin's collection of fifty minerals ranged from zinc blende and galena to lepidolite and feldspar, and would certainly lead an assiduous student by easy stages to a complete mastery of blowpipe analysis.

The instrument itself was available in many different forms (see Fig. i). The plain form (a) allowed moisture from the breath to contaminate the specimen, to avoid which Cronstedt (b) and Bergman (c) introduced moisture traps. Wollaston's blowpipe (d) could be dismantled to fit the pocket, the three tubes packing together like a set of cork-borers. Griffin brought out his flexible blowpipe to enable the volatile products of the combustion to be blown towards the operator, and Ross (g) introduced his telescopic instrument to accommodate different lengths of sight. In teaching laboratories, Black's (f) was probably the most popular kind on account of its robust simplicity.

Table VII.

Bergman's Blowpipe Apparatus

Hammer and anvil with steel ring
Silver spoon
Forceps
Blowpipe
Candle and candlestick (tubular form)

Engestrom's "Taschenlaboratorium"

Hammer, steel plate and steel ring
Forceps
Steel for testing hardness
Magnet File Magnifying glass
Blowpipe with wire for cleaning orifice

Washing trough
Testing flask
Bottles for borax, phosphate and soda
Wax candle and candlestick (pricket type)

Griffin's Blowpipe set, priced 42 shillings in 1838

Japanned tin blowpipe with brass nozzle
Blowpipe lamp with support
Gas burner Steel tongs Glass tubes
Charcoal, with borer and holder
Platinum tongs, platinum foil, and platinum wire
Brass wire Spatula and spoon Triangular file
Square bottles for borax, soda, and phosphate
Four books of litmus, turmeric, brazil wood and lead test papers
Tin foil for reductions
Hammer and anvil Agate mortar and pestle
Box of lucifer matches
Twelve wooden boxes for reagents
Two small porcelain capsules
Japanned tin box, divided to hold the preceding articles

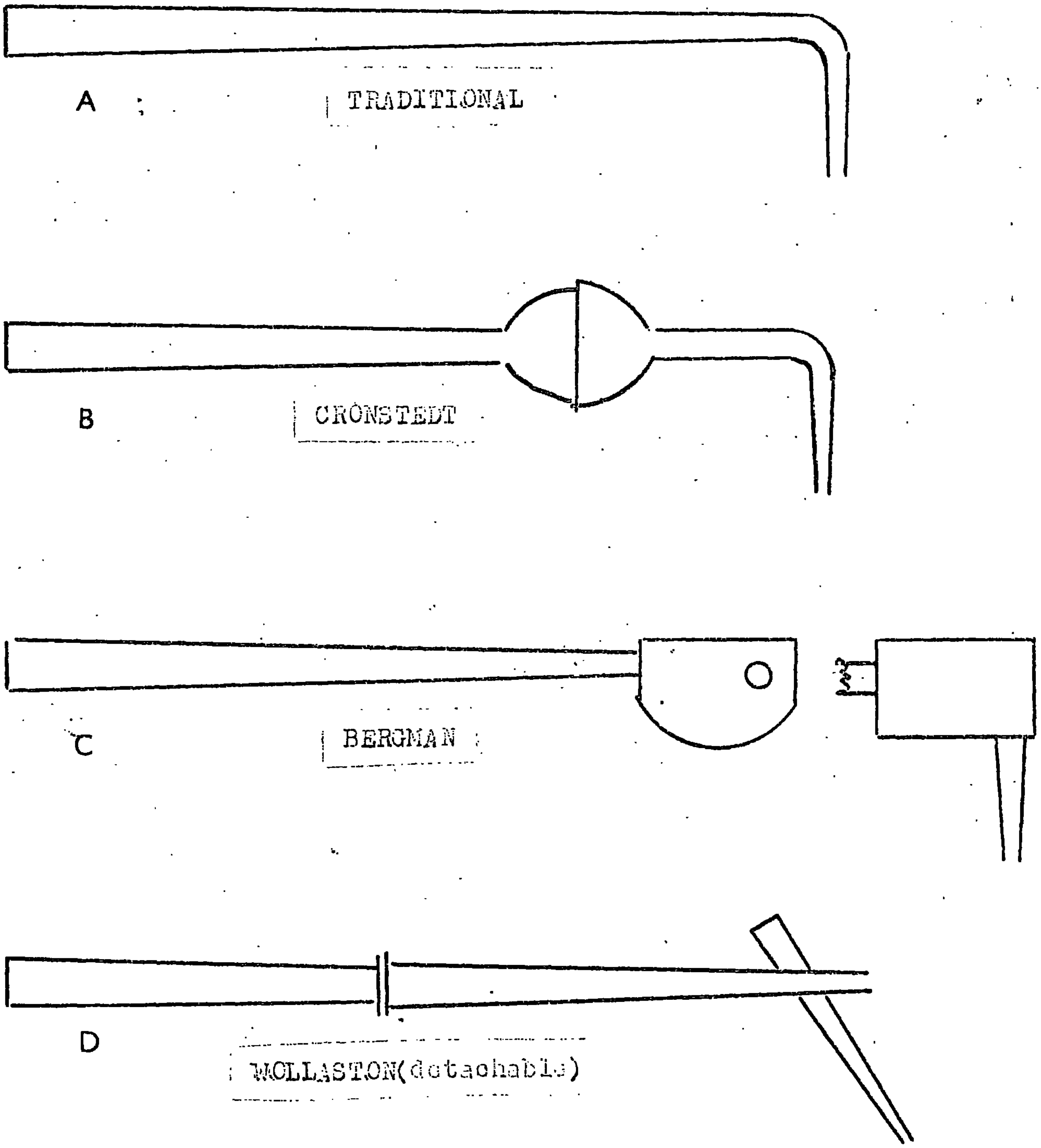
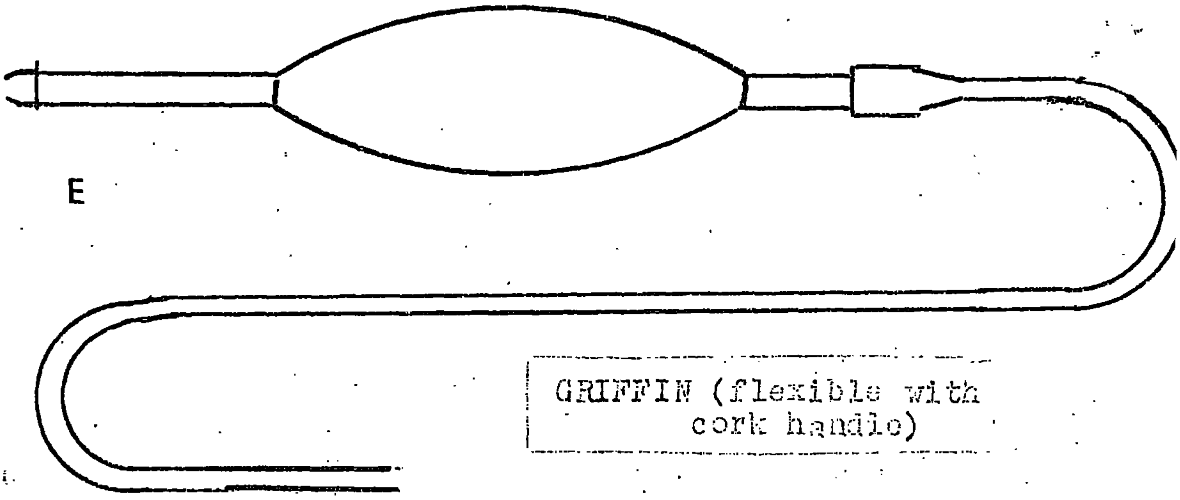
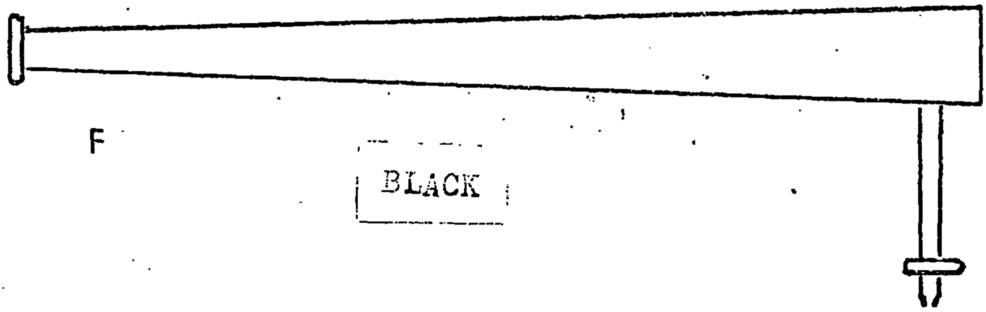

A
TRADITIONAL
B
CRONSTEDT
C
BERGMAN
D
WOLLASTON(detachable)

Fig i



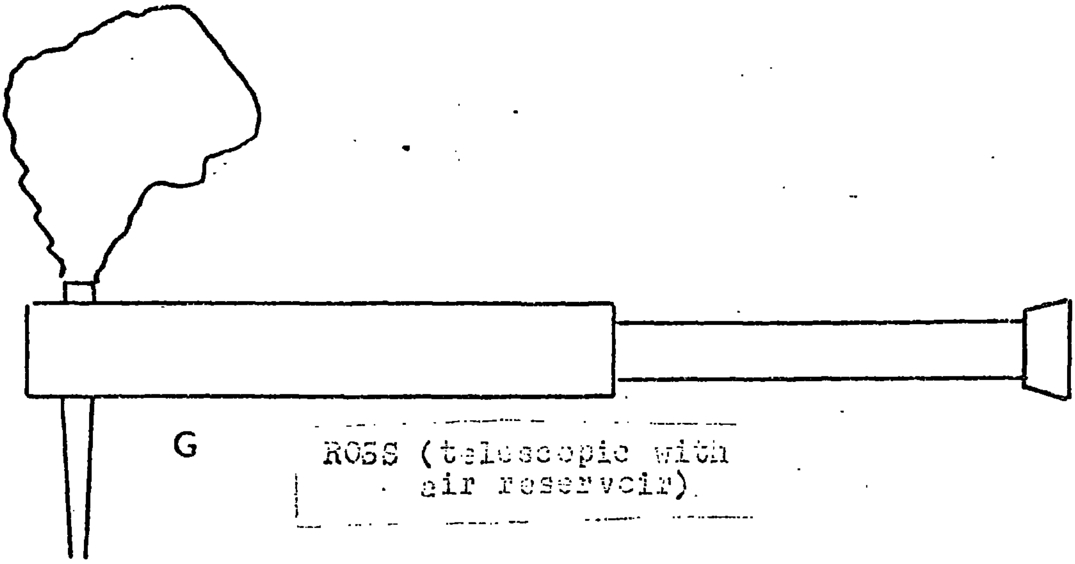
E

GRIFFIN (flexible with cork handle)



F

BLACK



G

ROSS (telescopic with air reservoir)

Fig. i continued.

The source of the flame occupied the attention of all who used the blowpipe in pre-Bunsen burner times. Bergman thought it immaterial if his candle was of tallow or wax, but considered the form and nature of the wick to be all-important. Gahn for a time used three small candles placed close together, but later substituted an oil lamp furnished with a large wick:[100] Berzelius recommended this lamp (burning olive oil) as the best flame for blowpipe work. Portable lamps, in which the wick was protected by a screw-down brass cover, made their appearance in the 1830's. Griffin suggested a mixed fuel for these lamps consisting of alcohol, turpentine, and a few drops of ether, but it is difficult to believe that this ever became popular.

The art of maintaining a steady blast of air for some minutes is easily acquired from a teacher but cannot well be expressed in writing. It is therefore not surprising that all the early writers devoted much space to this technique, nor that many mechanical devices were brought out to make the management of the blowpipe easier for beginners. Hassenfratz used a foot bellows after the manner of glassblowers, and Ross (Fig. i, g) suggested a wind reservoir on the blowpipe itself. Perhaps the most bizarre invention was that of Nasen who interposed between the mouth and the blowpipe a bladder held between the knees, compressing it in proportion to the strength of the blast required. Of this Berzelius said "By these pretended improvements, motions more or less troublesome have been substituted for a slight exertion of the muscles of the cheeks, and their inventors have demonstrated by their very contrivances that they did not know how to use the blowpipe."[101]

It is doubtful if anyone really acquired the art of blowing from books, but the description by Griffin probably comes nearer than any to being self-sufficient. To those who despaired of success he had this consolation to offer; "It is like the difficulty of turning round the right arm and right leg in contrary directions at the same time, which can be done after some practice".[102]

The references by Kunckel and Cramer to a hollowed out piece of charcoal (p.63,64)suggest that no fuller description was required. As the art of blowpipe analysis became more refined, it became necessary to consider the relative merits of different kinds of charcoal, and by 1777 Bergman was recommending especially the "carbo betulinus vel abietinus".[103] Berzelius credited Gahn with a preference for boxwood, but confessed that in Sweden there was not usually much choice beyond pinewood.[104] Hardwoods such as beech and oak were apt to contain iron, and in any case the more dense the charcoal the more easily it conducted heat away from the sample. Children added to Berzelius's account one of his translator's notes to say that in England the best charcoal obtainable was that from alderwood as used in the manufacture of gunpowder, and his choice was endorsed by Faraday.[105] Griffin thought that the wood was less important than the method of preparation.Living in towns, he took whatever came most readily to hand, provided that it was well burnt and free from bark. In industrial cities such as Glasgow a useful source was the residue from the manufacture of wood vinegar and particularly that from the Saturday distillation which had remained in the retort until Monday.[106]

Wood charcoal was inconvenient in form and the pieces were dirty to handle. Soon therefore Griffin turned to a prepared charcoal which could be moulded into blocks of required size and shape. The composition of the mixture was:[107]

Charcoal powder	9 parts by weight
Sodium carbonate	2 parts by weight
Borax	1 part by weight
Rice flour	$\frac{1}{2}$ part by weight
Water	8 parts by weight

The provision of these artificial charcoals in block form became of great importance in the last quarter of the nineteenth century when schools began to teach qualitative analysis under the Science and Art Department rules.

Where the reducing properties of charcoal were not required, metal supports of one sort or another had been tried. Bergman sometimes used a silver spoon, and even gold spoons were not unknown, but both were too easily fusible to be of real use. Wollaston's invention of the process for rendering platinum malleable led to the introduction of platinum foil as a support. Pieces measuring two inches by an inch and a half, "as thick as stout writing paper" were sold by Griffin for sixpence.[108] With a simple practical insight that would have done credit to Faraday Griffin suggested folding the foil into a hemicylinder and holding it in a pen-nib holder. The foil was not available in Sweden, so Gahn made use of platinum wire, thus making a tool which was to be closely associated with chemistry teaching up to the present day. Ross described this as the most beautiful perfect, and important invention ever contributed to blowpipe analysis: in this case his superlatives are justified. The wire was to be bent into a hook, moistened on the tongue, and dipped into the flux: when a bead of the latter had been formed by melting, it was to be touched lightly with the material under test. Gahn and Berzelius held the wire (it was about two inches long) between the fingers but Griffin recommended sealing it into a piece of thermometer tubing. The destructive shortening of the wire due to tin, lead, antimony and arsenic was recognised by Griffin: he also published a table of flame colourations[109] (Table VIII) (an analytical aid usually associated with the spectroscopic researches of Bunsen and Kirchoff twenty years later). In his later catalogues, Griffin took up the suggestion of Cartmell that the colours of lithium, sodium and potassium flames might be separated by the use of indigo solution or cobalt blue glass:[110] he thereupon offered for sale wedge-shaped bottles to hold the indigo solution.[111]

Plates of disthene, hard and infusible, were advocated by de Saussure, with apparently no other advantage than its ready availability to him. Smithson prepared thin sheets of white clay by beating it between pieces of paper (as goldleaf is made between skins): this, too, had no other merit than cheapness.[112] Slips of mica were often used in general laboratory practice in the way that microscope slides are used by a present-day chemistry student, and these, together with pieces of old porcelain were sometimes employed to support samples for blowpipe analysis. In 1871 Ross proposed the use of a thin aluminium plate: this was ten years before the introduction of the Hall-Herault process

Table VIII.

Griffin's Table of Flame Colourations, 1838.

Blue Flames	
Large intense blue	Chloride of copper
Pale clear blue	Lead
Light blue	Arsenic
Blue	Selenium
Greenish blue	Antimony
Blue mixed with green	Bromide of copper
Green Flames	
Very dark green, feeble	Ammonia
Dark green	Boracic acid
Dark green	Iron wire
Full green	Tellurium
Full green	Copper
Intense emerald green	Iodide of copper
Emerald mixed with blue	Bromide of copper
Pale green	Phosphoric acid
Very pale apple green	Barytes
Yellow Flames	
Intense greenish yellow	Soda
Feeble brownish yellow	Water
Red Flames	
Intense crimson	Strontium
Reddish purple	Lithia
Reddish purple	Lime
Violet	Potash

for making aluminium and the metal was still scarce and expensive. As usual, Ross conveyed the impression that his invention superseded every other kind of support, but in fact there were very few situations in blowpipe analysis to which charcoal and platinum wire were not adequate.

The virtue of the blowpipe (which justifies this extended treatment) was that it could be used on completely unknown samples without prior classification or separation. We now turn to the organic constituents of the proprietary medicines.

Until the last quarter of the eighteenth century the prime means of analysing organic bodies was destructive distillation. Lemery and Lefevre, among other members of the Academy of Sciences, had distilled animal and vegetable materials to yield phlegm, spirit, volatile oil, a caput mortuum.[113] There was a vast store of pharmaceutical and alchemi~~stic~~cal experience to draw upon in relation to the fractionation of the products and to the control of temperatures. Some of the fractionation devices are shown in Fig.ii, iii, iv. The simple alembic head could be mounted on a long-necked flask, or globular receivers could be fitted one into another to make a column. The contrivances of Glauber and Woulfe[114] could be extended to collect vapours of varying degrees of volatility, the compound distillation apparatus of Hassenfratz representing the ultimate complexity.[115]

The rate of heating, and the temperature attained, could be controlled by selecting from a rich diversity of furnaces. (Fig. v, vi)

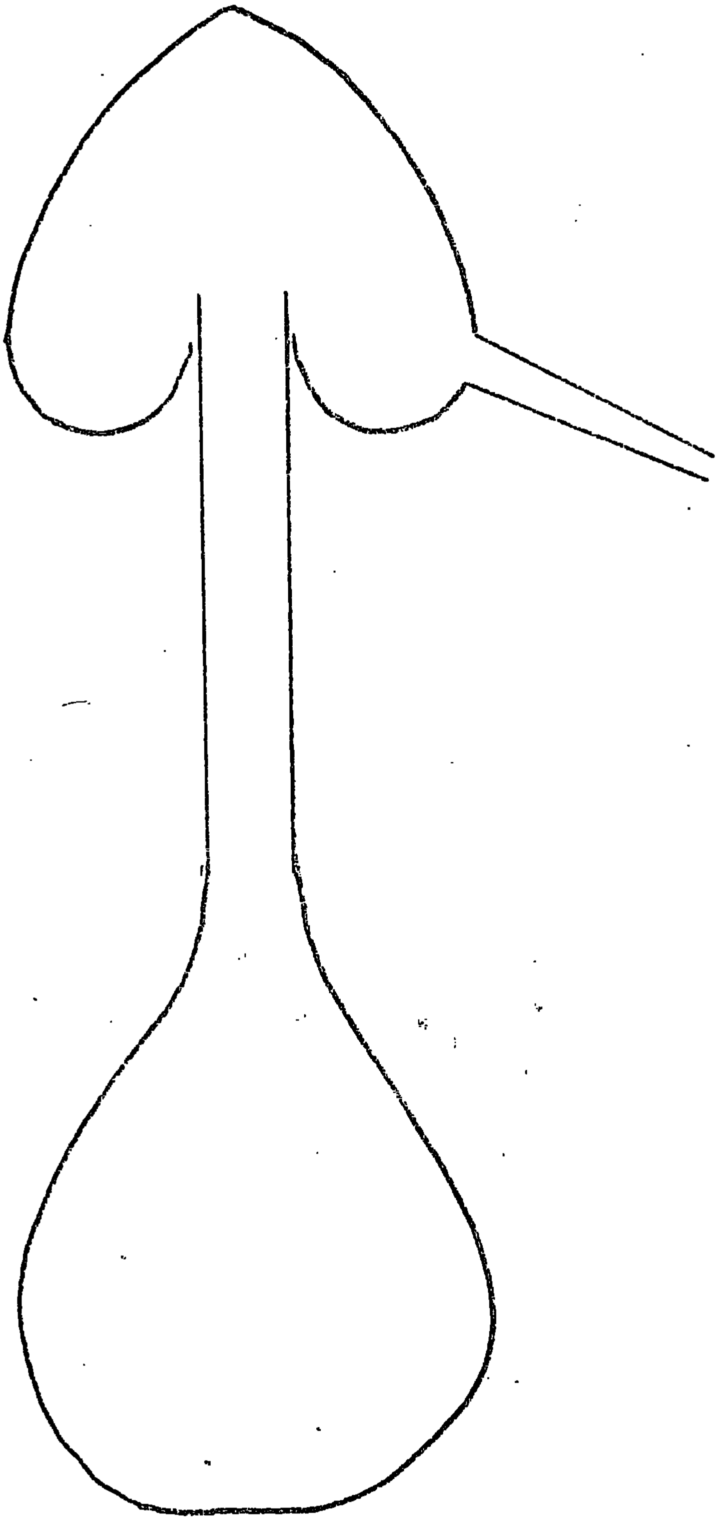


Fig. ii. Alembic head on Long-necked Flask.

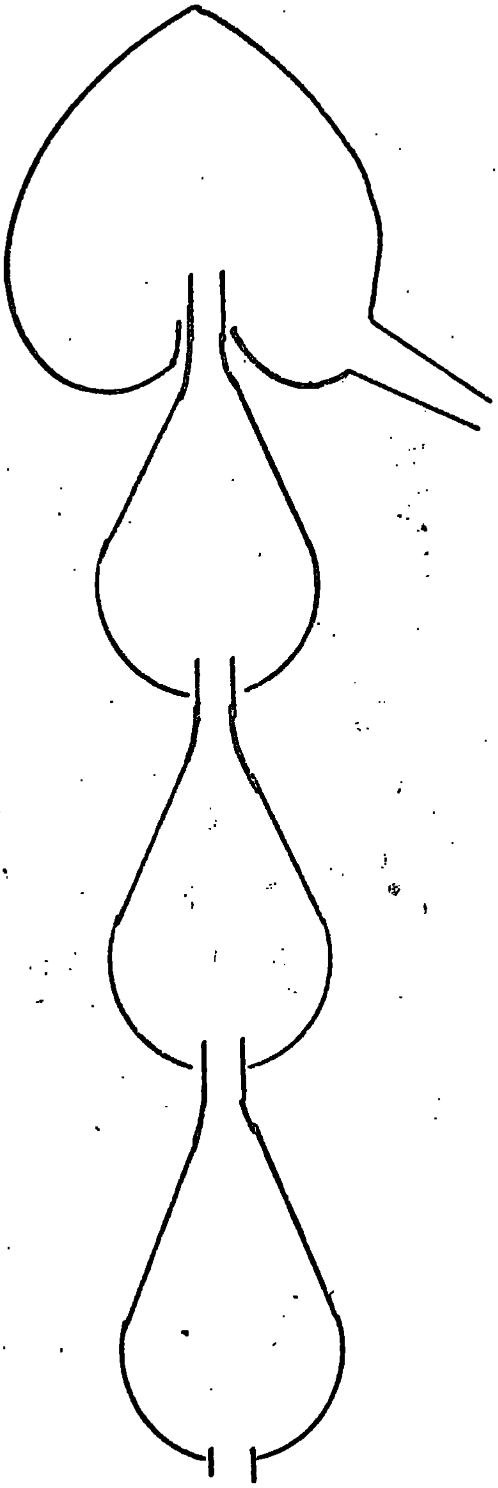


Fig.iii. Receivers built up into a column.

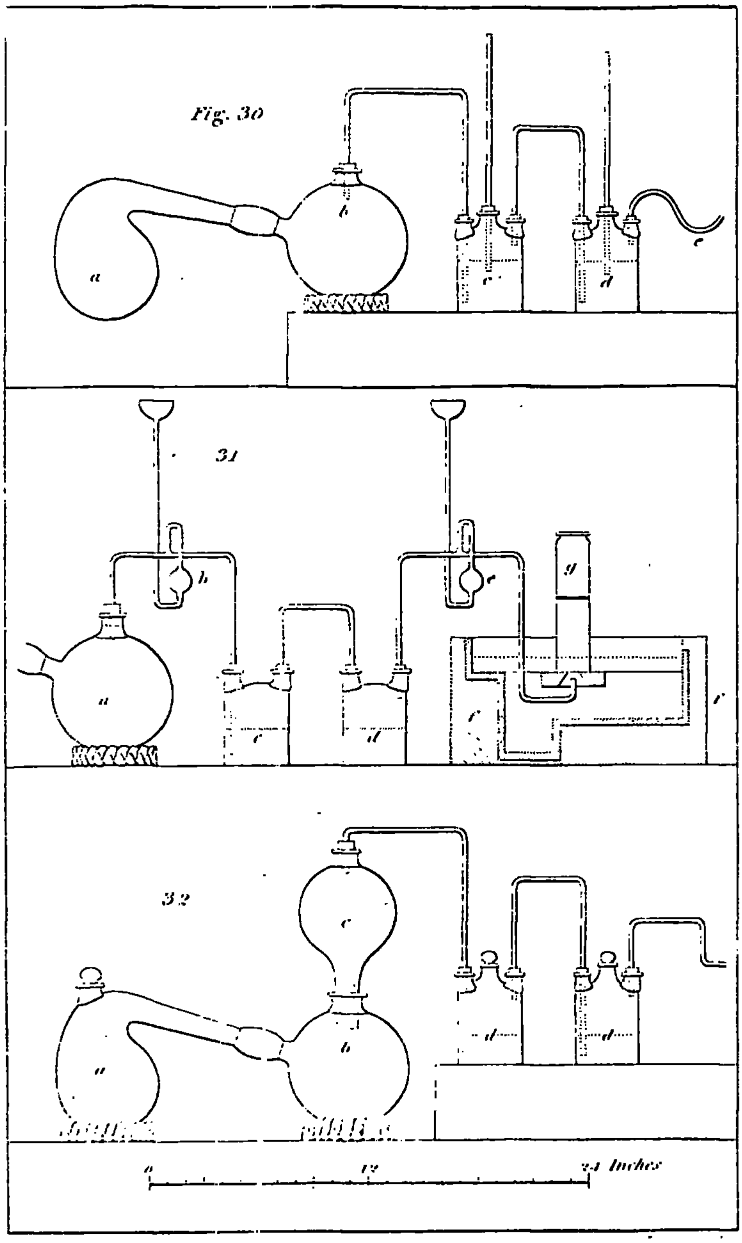


Fig. iv. Compound distillation apparatus of Hassenfratz.

The distilling furnace, the sand furnace, the reverberatory and wind furnaces gave a wide range of temperatures for sublimation, calcination or distillation, while the athanor (a slow combustion furnace of alchemistic origin otherwise known as the sluggard's furnace, the piger Henricus or slow Harry) was available for protracted experiments.[116] In general the temperatures would be lower than those to which we are accustomed, digestion taking place at about 40°C, distillation at 40 - 100°C, and sublimation at 100 - 300°C.[117]

Of course the main purpose of these furnaces was not analysis but preparative work. Thus Hopson describes the preparation of benzoic acid ("flowers of Benjamin") by the destructive sublimation of gum benzoin from a glazed vessel onto a paper cone.[118] On a larger scale, mineral acids were prepared in earthenware modifications of laboratory apparatus, and pyroligneous acid was made by the destructive distillation of wood.[119]

A second method of attack on vegetable substances was by way of water extraction. In the cold this was known as maceration, in the warm as infusion, and at boiling as decoction. These processes enabled Ure in 1824 to draw up a table of vegetable constituents: in addition to vegetable alkalis and acids these were

Sugar
Asparagin
Sarcocol
Gum
Ulmin
Starch
Resin
Bitter Principle
Extractive Principle
Tannin
Wood
Volatile Oil
Birdlime
Gluten
Cotton
Suber
Fixed Oil
Inulin
Camphor
Indigo
Guaiacum

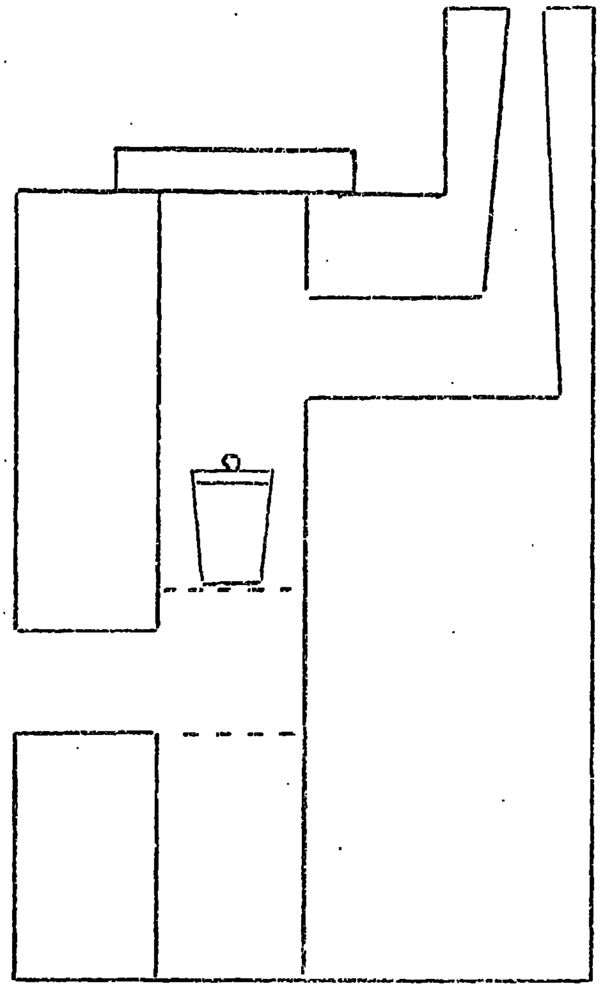


Fig. v. Calcination furnace.

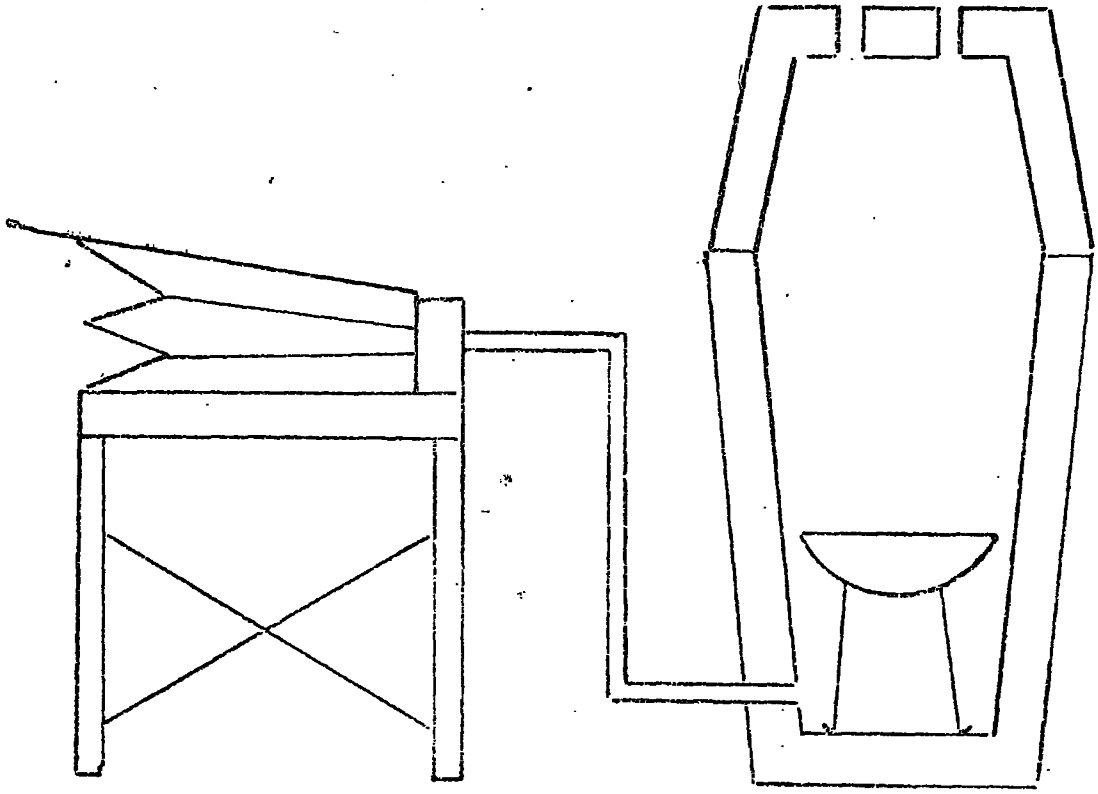


Fig. vi. Wind furnace.

Albumen
Caoutchouc
Balsam
Gelatin
Fibrin
Gum Resin

These were to be distinguished by appearance, taste and solubility in acid, alkali, water, and alcohol.[120]

The water or alcohol extracting process was used by Etienne Ossian Henry (Chief of Central Pharmacies of the Hospitals of Paris) in his examination of the several commercially available forms of jalap.[121] The jalap was extracted with warm alcohol for twenty-four hours and the resin obtained by distilling off the alcohol from the extract: the alcohol-insoluble residue was extracted with water. A combined attack by pyrolysis and water or alcohol extraction was used by J.W.F. Johnston of Durham in his analysis of resins. Mastic, Dragon's blood, gamboge, sandarach, common frankincense, olibanum, and guaiacum were examined. In the last case he noted the photosensitivity of the lead salt, and suggested a "photogenic paper" to be made by soaking in alcoholic extract of guaiacum, drying, and again soaking in lead acetate solution.[122]

Information about the ultimate composition of organic matter was obtained by Lavoisier, Berthollet, and de Saussure.[123, 124, 125] Their methods were based on the pneumatic techniques of Hales and Priestley,[126] and depended upon collecting volumes of carbon dioxide, and measuring the volumes of oxygen consumed. Important as this work was in other contexts, it is doubtful if it contributed to the identification of medicinal substances. The first major advance in this field was the publication by Gay-Lussac and Thenard in 1810 of their combustion method for determining carbon and hydrogen using potassium chlorate as oxidant. The apparatus (Fig.vii) was ingenious, the particular merit being the design of the half-bored stopcock by means of which a pellet of sample mixed with chlorate could be introduced without opening the system.[127] Gay-Lussac and Thenard analysed sugar, gum, starch, wood, resin, copal, wax, olive oil, (liquids were less convenient) fibrin, albumin, casein, gelatin, mucic acid, tartaric acid, citric acid, acetic acid and calcium oxalate. By these analyses they established the class of carbohydrates, containing hydrogen and oxygen in the same proportions as in water.

A limitation in their method lay in the difficulty of controlling the rate of heating. Two years later Berzelius overcame that difficulty by substituting a narrow horizontal combustion tube for the earlier vertical tube:[128] the oxidant was still chlorate and some of the reactions must have been violent. A gentler oxidant was introduced in 1816 by Gay-Lussac in the shape of copper oxide,[129] to this day a staple of the organic analyst. Berzelius collected the water in a receiver and weighed it directly, instead of deducing it from the volume of oxygen consumed.

The Berzelius method with Gay-Lussac's improvement was used by Ure to analyse thirty-four materials. Those likely to be found in medicines were sugar, gum arabic, resin, guaiacum, yellow wax, camphor, turpentine, castor oil, alcohol, ether, cantharides, benzoic acid, citric acid and tartaric acid.[130] We need not be concerned at this stage with the "correctness" of the results.

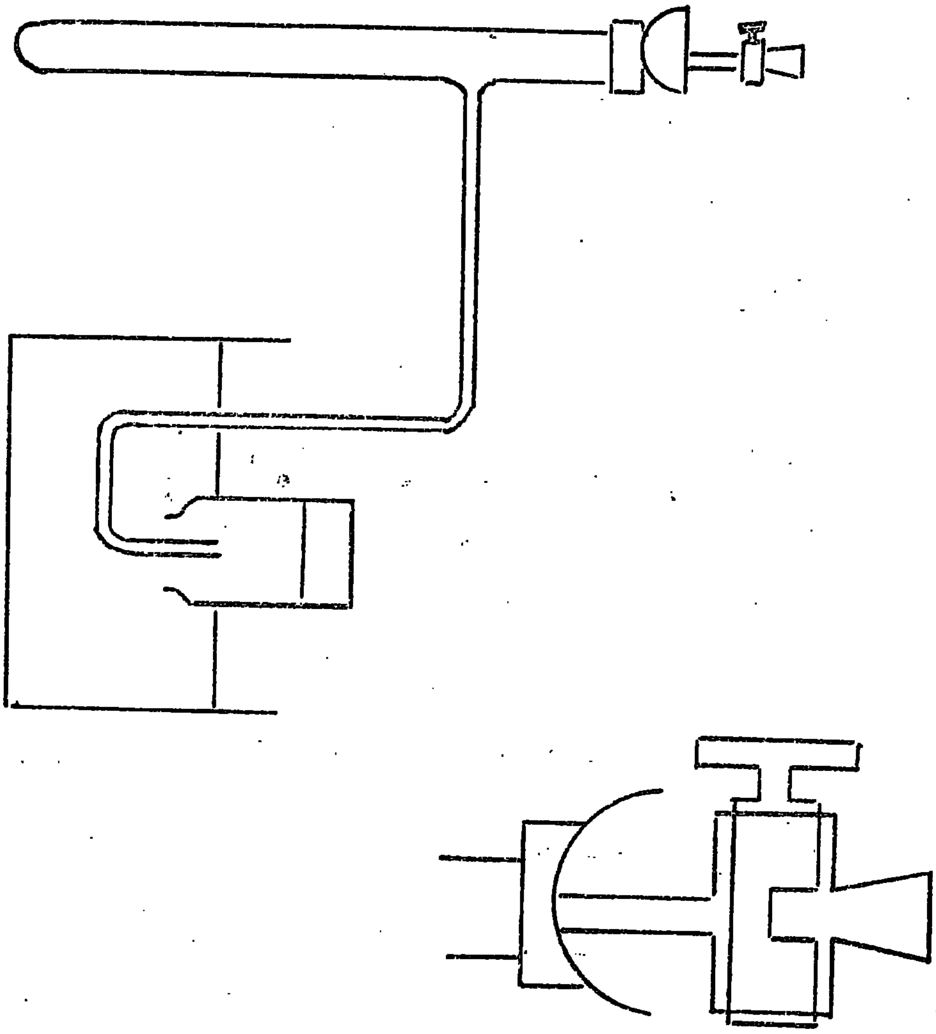


Fig.vii. Gay-Lussac and Thenard Apparatus, with detail of stopcock.

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Prout concerned himself with the moisture adsorbed in finely powdered copper oxide which caused high results when water was collected and weighed directly: he preferred to determine water by measuring the loss in weight of the combustion tube.[131] He analysed a wide range of sugars, starches and the common organic acids, but once more this work, although extremely precise, added nothing to the armoury of the commercial analyst.

By no means all organic compounds will oxidise completely when heated with copper oxide, intractable cokes being formed. For this reason Berzelius, between 1815 and 1827, reverted to the use of chlorate, diluted with common salt to moderate the reaction. A little unmixed chlorate was first heated to generate oxygen which swept out the apparatus: the sample was then combusted cautiously, and finally a further portion of chlorate provided oxygen to sweep out the products of combustion.[132] (Fig. viii). Water was collected in the bulb and in the straight calcium chloride tube. To absorb carbon dioxide, a small weighed vessel containing caustic potash solution was covered in chamois leather and pushed up through the mercury into the bell-jar. The main contribution was the technique of sweeping out with oxygen before and after the combustion, leading to the use of gaseous oxygen as the prime oxidant.

The definitive paper on organic analysis, laying down the methods which, with modifications, is in use to this day, was Liebig's "Über einen neuen Apparat zur Analyse organischer Korper, und über die Zusammensetzung einiger organischer Substanzen".[133] Liebig had been a pupil of Gay-Lussac so his paper was soon translated into French.[134]

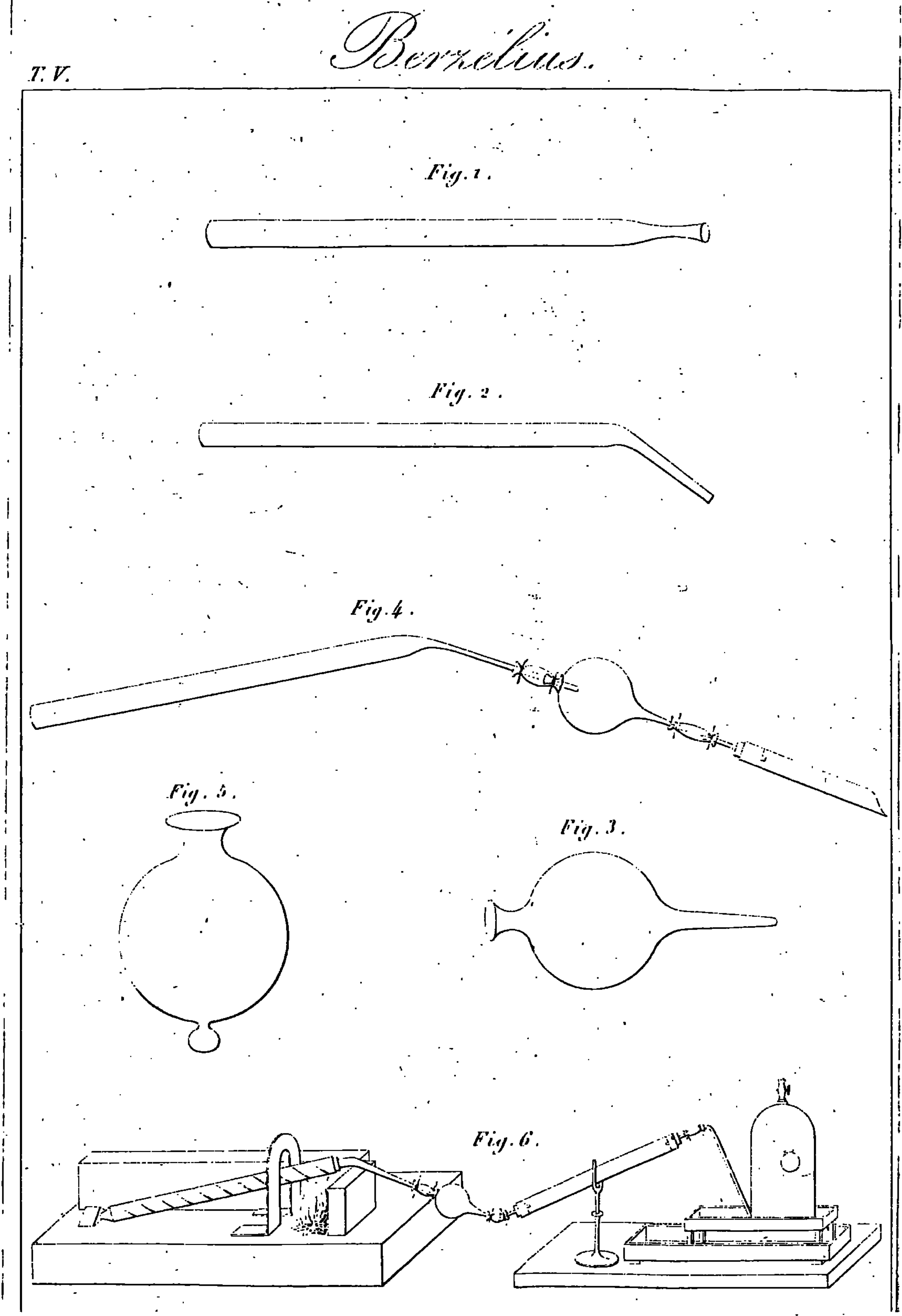

Fig.viii. Berzelius's apparatus for organic analysis.

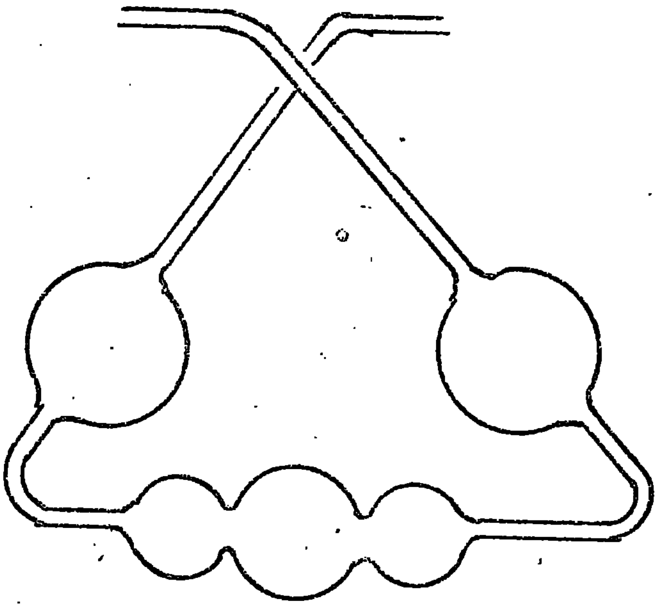

Fig.ix. Liebig's potash bulbs.

The heart of the apparatus was the potash bulb for absorbing carbon dioxide for the blowing of which Liebig gave complete instructions (Fig. ix).

The determination of carbon and hydrogen alone was not sufficient to characterise an organic compound. The other commonly encountered elements, nitrogen, sulphur and the halogens of ten reveal immediate differences between otherwise similar compounds. Thus benzoic acid and benzamide have very similar carbon and hydrogen percentages: the nitrogen figure would immediately bring out the difference. In 1834 the copper oxide combustion method of analysis was adapted to the determination of nitrogen by J.B. Dumas.[135] All the likely products of combustion of an organic compound except nitrogen will dissolve in caustic potash, so that any gas collected over this liquid will be nitrogen. [In practice, carbon monoxide and methane can sometimes be formed, leading to high results]. To avoid the inconvenience of mercury baths, the familiar nitrometer was invented by HugoSchiff in 1880.[136]

A second method of determining nitrogen was evolved by H. Will and F. Varrentrapp in 1841.[137] They made use of the fact that many nitrogenous organic compounds yield ammonia on heating with caustic potash: the ammonia was trapped in hydrochloric acid, converted to ammonium chloroplatinate and weighed in that form. Since the chloroplatinate weighs fifteen times as much as the contained ammonia, the precision is high. The annotated French translation of Will and Varrentrapp's paper suggests that the method was originally devised by Berzelius.[138] Not all compounds respond to this treatment, but a preliminary digestion with sulphuric acid before the potash distillation widens the range considerably. A further refinement is to raise the boiling point of the sulphuric acid by adding potassium sulphate, or to speed the digestion catalytically by means of copper, mercury or selenium compounds. This modified method was described by Kjeldahl in 1883, and is particularly useful with alkaloids and most naturally occurring compounds.[139]

The organic constituents of proprietary medicines, in so far as they came from plant sources, would not normally contain halogens, but the increased use of synthetics after 1860 brought these elements within the analyst's sphere of interest. It was therefore a happy circumstance that Carius published his method for determining halogens in 1860.[140] The material was mixed with silver nitrate and digested with fuming nitric acid in a sealed tube of thick glass: a heavily protected furnace was used to guard against frequent explosions. Five years later Carius extended his method to the determination of sulphur, phosphorus and arsenic.[141]

It must be recognised however that the determination of percentage composition is meaningful only when carried out on pure compounds. To break the formula for a secret remedy, the need was not so much for analysis as for identification, in which analysis might be one of the steps. This aspect of chemical history has received very little attention.

Where the gross structure of a plant survived in the mixture, as in dried leaves, flowers, stems, roots or seeds, the methods of pharmacognosy were applicable. The third London Pharmacopoeia of 1677 (*Pharmocopoeia Collegii Regalis Londini*) contained descriptions by Sir Hans Sloane of the botanical parts used: it was intended to help the apothecary select the correct drug rather than to help an analyst to identify it. The same motive inspired Pomet's *History of Drugs*. The title page of the fourth English edition (1748) mentions "the Methods of distinguishing the Genuine and Perfect from the Adulterated, Sophisticated and Decayed." There were drawings of the complete plant, together with descriptions and advice on selection; about liquorice for example "chuse your Liquorice fresh, smooth, of about two fingers thick, reddish without, and a Gold-colour within, easy to cut, and of a sweet agreeable Taste."[142] Only the taste would be of analytical use.

John Hill's *History of the Materia Medica* (1751) claims "Descriptions of all the Substances used in Medicine; their Origins, their Characters when in Perfection, the Signs of their Decay, their Chymical Analysis, and an Account of their Virtues, and of the several Preparations from them now used in the Shops."[143] The portion of the book devoted to inorganic ("fossil") bodies does contain much sound chemical information: copper salts are to be detected by the deposition of copper on the blade of a knife, and the alkaline nature of borax is shown by the displacement of ammonia ("an urinous smell") from sal-ammoniac.

As is to be expected, the plant sections of the book can offer only destructive distillation as a method of analysis, while for identification verbal descriptions have to suffice. Nevertheless Hill had the true analytical outlook, warning his readers against impositions upon their credulity: many toys and ornaments sold as jet are made of cannel coal, while the unicorn horns offered for sale are really only whales' teeth.

The 1836 London Pharmacopoeia was translated and annotated by Richard Phillips, and here some attempt was made to provide chemical tests, though the aim was still to guard against adulteration or substitution rather than to help in identification. Few vegetable matters are included in the notes on chemical tests, but the entry for benzoic acid will show that a real advance had been made: "Benzoic acid- when cautiously heated it totally evaporates with a peculiar odour. It is sparingly soluble in water, but plentifully in rectified spirit. It is entirely dissolved by solution of potash or by lime-water, and is precipitated by hydrochloric acid."[144]

When the plant was broken down by grinding only microscopic structure was preserved. About the middle of the nineteenth century the microscope began to be systematically applied to this kind of material. Arthur Hill Hassall, in his book on the adulteration of food (1855), provided camera lucida drawings of starch particles and of the common substitutes for tea leaves.[145] In 1864 Henry Deane and Henry B. Brady (both of Newcastle) published in the Pharmaceutical Journal a paper on the "Microscopical Research in Relation to Pharmacy", in which they examined the common preparations of opium. They showed camera lucida drawings of crystals such as morphine sulphate, meconic acid and papaverine. Two years later they examined meat extracts and showed the micro-crystalline shapes of creatine and potassium hydrogen phosphate. The two papers mark a transition from the pharmacognosy of the herbalists to micro-chemical examination, for both plant structures and their crystalline chemical derivatives are recognised.[146]

In the next decade there appeared a work in which the techniques of Hassall and of Deane and Brady were worked out completely. This was "Pharmacographia: a history of the principal drugs of vegetable origin" by Friedrich Fluckiger and Daniel Hanbury. It was a vegetable materia medica in which each drug was treated under the headings of botanic origin, history, description, microscopic structure, chemical composition, uses and substitutes.[147] Significantly, the [Royal] Institute of Chemistry, founded in 1877, required for its Fellowship examination the chemistry and microscopy of food and drugs: proof of competence in microscopy is still required of candidates for Public Analyst posts.

Identification of an organic compound by chemical means is nowadays held to depend upon the detection of the elements present, classification by reactions which define the functional groups and melting point determinations on the original sample and on one or two derivatives. It is now necessary to trace the development of these methods.

The eighteenth century exponents of the pyrolysis of organic bodies were aware of two distinct kinds of smell on burning: nitrogenous compounds gave a smell of burnt feathers, and non-nitrogenous compounds a smell of burnt sugar. Obviously the presence of a large proportion of carbon could mask the smell due to a small proportion of nitrogen, and furthermore the test required a sample of moderate size.

In 1843 Lassaigne published his "*Mémoire sur un procédé simple pour constater la presence de l'azote dans des quantités minimes de matière organique*", which was to become the standard method of testing for elements other than carbon and hydrogen.[148] He claimed success with quantities too small to be weighed, and used potassium instead of the more familiar sodium as the degrading agent. Compounds containing nitrogen yielded potassium cyanide which was detected as prussian blue. This was perhaps the greatest single step to be taken in organic qualitative analysis, for a negative Lassaigne test enabled the analyst to eliminate a wide range of likely constituents from a complex mixture. The solution from the sodium or potassium fusion could also be used to detect halogens by methods already familiar to inorganic analysts. After 1850, when Playfair discovered sodium nitroprusside by the action of dilute nitric acid on ferrocyanide solution,[149] the Lassaigne test could be extended to sulphur: under the conditions of the test, a sulphur-containing compound formed alkaline sulphides which gave a transient purple colour with nitroprusside.

The very convenient Beilstein test for halogens using copper wire did not come in until 1872,[150] though Griffin had used a brass wire to detect inorganic halides before the blowpipe in 1838.

The detection of characteristic groups depended on the attainment of a necessary level of preparative techniques, for most of the group reactions were essentially synthetic reactions. An obvious example is the diazotisation reaction used to synthesise azo-dyes, but equally applicable to testing for amines or phenols. This reaction was discovered by Peter Griess (whilst working as a brewery chemist at Burton-on-Trent); he described the diazonium compounds as "A new class of organic compounds in which hydrogen is replaced by nitrogen".[151] The first coloured compound founded on a phenol was prepared by Kekule.[152] Other preparative reactions which served to characterise unknown compounds were oxime formation due to Victor Meyer in 1822,[153] and the preparation of osazones from sugars by E. Fischer in 1887:[154] these yellow substances with well-defined crystal shapes and sharp melting points served to identify isomeric carbohydrates.

The melting point of such a derivative became one of the commonest features of organic qualitative analysis. The fact that an unknown body melted at a higher or lower temperature than one of known identity had been used to detect adulteration or substitution: in the analysis of Singleton's Eye Ointment (p. 102) the melting point of butter is compared with that of other fats. In a letter from David Brewster to Sir Joseph Banks, the statement is made that lead acetate melts at a temperature not much greater than that for beeswax.[155] The first person to make precise quantitative use of melting points was Chevreul in his great work on fatty acids. In the earlier papers he gave melting points in both Centigrade and Reaumur degrees, and to two decimal places.[156] As the work progressed (and no doubt as Chevreul began to appreciate the effect of traces of impurities on the melting points of low-melting solids) the figures are stated only to the nearest whole number.[157] The melting point is an analytical tool that has never lost its power.[158] The melting point of the original unknown, together with two derivatives of the kind previously mentioned, is sufficient to characterise a solid beyond reasonable doubt. Comprehensive tables of melting points were however late in coming onto the market, and only at the end of the nineteenth century could a student arm himself with this defence against his teacher's ingenuity.

There were tests that didnot result in crystalline derivatives, one of the earliest being the reaction between starch and iodine described in a fourteen-page paper by J.J. Colin and H.G. de Claubry in1814.[159] In 1866 Hugo Schiff contributed to the *Annalen* a paper forty-five pages long on the Schiff's bases (eine neue Reihe organischer Diamine).[160] In it he devoted a paragraph to rosaniline sulphate and aldehydes, describing what came to be known as Schiff's reagent. Some such colour reactions could be used for quantitative purposes. Thus in 1841 Trommer had described a method for identifying gum, dextrin, grape sugar and cane sugar. The materials were dissolved in potassium hydroxide solution and treated with copper sulphate: the colour of the liquid, and the precipitate formed on heating, were used to distinguish between the carbohydrates, but the method was not completely effective.[161] Eight years later Hermann Fehling at the Technische Hochschule in Stuttgart adapted Trommer's method to the quantitative determination of sugar and starch by means of a copper (Fehling's) solution. He said that his reason for embarking on this work was that he had no useable polarimeter at his command.[162]

The use of a polarimeter in sugar analysis was in fact the earliest example of analytical instrumentation. The birefringence of Iceland spar, and the strange quality of the light that had passed through such a crystal, had been observed by Huygens and studied by Newton. The application of the phenomenon to organic analysis is due to Biot who, between 1810 and 1818, studied the optical rotation due to turpentine, laurel oil, lemon oil, and camphor in alcohol (all likely to occur in medicines).[163] This list of materials was surpassed in number if not in usefulness by that of David Brewster in a letter to Banks (p. 94) describing "Experiments on the depolarisation of light as exhibited by various mineral, animal, and vegetable bodies".[164] His list included gum arabic, cherry tree gum, caoutchouc, white wax, rosin and white wax mixed, cells of honeycomb, manna, camphor, balsam of Tolu, fibres of flax and hemp, seaweed, adipocere ("from the burying ground of the Church of the Innocents in Paris"), benzoic and oxalic acids, spermaceti, soap, hair, silk, "the horny excrescence of the human foot", glue, isinglass, lead acetate, borax, amber, sulphur, ice, oil of mace, tallow. Reported as having no effect on polarised light was "the skin of a child two months before birth". This was largely a descriptive paper, though there was some attempt to establish a theory of optical acitivity.

In 1865 the polarimeter (in its specialised form of the saccharimeter, calibrated to give direct readings in terms of sugar) was used to detect lactose in a proprietary medicine purporting to be "saccharide of cod liver oil".[165] Comparisons were made with standard solutions of lactose. A major work in this field of the polarimetric examination of organic compounds was accomplished in 1879 by Hans Heinrich Landolt (better known for his part in compiling the Landolt-Bornstein Physico- Chemical Tables). His 'Optische Drehungs-vermogen Organischer Substanzen" describes the optical rotations of some 140 organic compounds, many of them - sugars, essential oils, alkaloids - being likely ingredients of medicines.

A useful property of essential oils is the refractive index. As early as 1814 Fraunhofer had devised an instrument by which the refractive index of liquids could be measured, but, depending as it did upon a hollow prism,, only large quantities could be examined. In 1871 Ernst Abbe invented his refractometer (made by Zeiss in Jena) in which a few drops of liquid could be investigated: a few years later his instrument was early taken up by the Public Analysts for such purposes as evaluating oil of sassafras. Adulteration of this, or several other oils, would quickly show in a changed refractive index.

Other optical aids to analysis had even longer histories, though their usefulness in commercial analysis was only later appreciated. In 1672 Isaac Newton had contributed to the Royal Society his "*Letter ....containing his New Theory about Light and Colors: where Light is declared to be not Similar and Homogeneal, but consisting of difform rays, some of which are more refrangible than others*"[166]. For two centuries after this demonstration of the compound nature of white light, discoveries continued to be made which promised to place new tools in the hands of the analyst.

It was well known to miners that the mineral horn silver (silver chloride) would turn black on exposure to light. Scheele examined the effect of different parts of the spectrum and showed that darkening occurred most rapidly in the violet. "In dieses farbichte Licht lege man ein Stuck Papier, welches mit Hornsilber bestreut ist: so wird man gewaht werden, dass dieses Hornsilber in der violetten Farbe weit eher schwarz wird, als in den andern Farben"[167] This he explained as a more rapid separation of phlogiston in the violet. In 1801 J.W. Ritter made the far reaching discovery that darkening occurred even more rapidly just beyond the violet end of the spectrum, and this was confirmed by Wollaston a year later.[168]

This was not the first of the extra-visible phenomena to be observed. William Herschel investigated the heating powers of different parts of the spectrum in 1800, using thermometers with blackened bulbs, and found the maximum heating effect just beyond the red end of the visible spectrum. He concluded "radiant heat will at least partly, if not chiefly, consist, if I may be permitted the expression, of invisible light"[169]

In spite of the early recognition of these powerful tools, infrared and ultraviolet radiation, they could not be applied to analytical practice until a great deal of theoretical insight had been obtained and a large reserve of instrumental resource built up. Interest must first centre upon emission spectra in the visible region.

A.S. Marggraf, about 1758, had prepared "cubic nitre" (sodium nitrate) by evaporating to dryness a solution of common salt in nitric acid. This nitre deflagrated with charcoal to give a yellow flame, whereas ordinary nitre (potassium nitrate) gave a bluish flame.[170] The first avowedly analytical use of the phenomenon of flame colouration was suggested by J.F.W. Herschel in a letter to the Edinburgh Royal Society. The title is significant: "On the Absorption of Light by Coloured Media, and on the Colours of the Prismatic Spectrum exhibited by Certain Flames; with an account of a ready Mode of determining the absolute dispersive power of any Medium, by direct experiment." Graphs of light intensities, looking remarkably like modern pen-recorder traces, described the spectra of spirit lamp flames when various salts were introduced. The elements discussed were calcium, strontium, barium, mercury, copper, and boron.[171]

The colour of a flame as perceived by the eye was not a precise enough property to distinguish between, say, the red of strontium, and lithium or the greens of barium and borate. When the emitted light is spread out into a spectrum, differences can readily be perceived; this was described by Fox Talbot who, as a pioneer of photography, was clearly alive to questions of chemistry and light.

In 1834 he set out the difference between the flames of lithium and strontium. "The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method."[172]

The "dark intervals" had already attracted attention. J. Fraunhofer in 1814 had mapped some 600 dark lines in the solar spectrum, believing them to be an inherent property of sunlight. The lines bear Fraunhofer's name though the first investigation of them was due to Wollaston whose narrow slit device for controlling the incident beam first made such observations possible.[173] The explanation of the dark lines as due to absorption by elements in the earth's atmosphere was advanced by David Brewster in 1833: he used iodine and sulphur vapours and nitrous oxide, thereby laying the foundations of absorption spectroscopy.[174] The method developed an instrumentation of its own when J.W.F. Herschel used photosensitive paper to make an "actinograph" which could measure the intensity of light.[175] J.W. Draper used a Daguerreotype plate for a similar purpose.[176] We may note in passing that at that early date (1845) all the essentials for infrared and ultraviolet absorption spectroscopy were known.

In the early experiments of Herschel and Fox Talbot, easily excited metals were examined, and the flame from a spirit lamp was sufficient. Bunsen saw that the method of spectral analysis could not be extended to recalcitrant metals without a better source of heat.[177] Piped gas was not available at Heidelberg when Bunsen took the chair in 1852, but was brought into the new laboratory in 1855. The burners were designed to provide light rather than heat and therefore burned pure gas. Returning after a vacation spent in England, Bunsen's pupil Roscoe brought back an Argand burner with a wire gauze at the top, in which - following on the experiments of Davy and Stephenson on miners' safety lamps - air and gas mixtures might be safely burnt.

The first Bunsen burner, about 1855, had four air holes in a square pedestal from which the chimney of the burner rose; if the air content of the mixture was too high, one or more of the holes could be stopped up. It seems certain that Peter Desaga, the University mechanic at Heidelberg, played a major part in the design of the burner.[178] Henry Watts says in his Dictionary of Chemistry that the rotating ring and the "rose" top were invented by Griffin: certainly burners showing both modifications are depicted in Griffin's 1877 catalogue under the title of "Griffin's Rose Gas Burners".[179]

The methods of mineral and metal analysis could be applied to mixtures, but those for organic analysis were applicable only to pure compounds. In order that such methods might be brought to bear on proprietary medicines, techniques of separation had to be worked out. The most useful of these, and a direct descendant from eighteenth century practice, was extraction with various solvents. Certain organic solvents had a long history of general or special use. Wine and vinegar were such well-known solvents for medicinals that they often made up the vehicle of liquid preparations. Turpentine was used as a solvent in the paint trade and also - since 1716 - as a dry-cleaning agent for "spotting"[180] garments, i.e. removing spots of illuminating oil or candle grease, two of the most commonly encountered hazards in an eighteenth century household. In general, though, the supply of organic solvents had to await the development of the chemical industries.

Faraday's work on the liquefaction of gases led him to compress illuminating gas from whale oil, from which source he isolated benzene in 1825.[181] In 1847 Hofmann set Charles B. Mansfield to examine the distillation products of coal tar, and in a lengthy paper entitled "Researches on Coal Tar" (1849) it was shown that benzene would dissolve "many resins, mastic, camphor, wax, fatty and essential oils, caoutchouc and gutta percha.[182]" Several factors contributed to the commercial production of benzene; the demand set up by W.H. Perkin, from 1856, for benzene to make aniline on the route to mauveine led to an offer of supplies from Miller and Co. of Glasgow at five shillings a gallon. Moreover, in 1866 Pullars of Perth set up a plant for drycleaning by means of benzene so that the supply would be further stimulated.[183]

The dangerous sweetness of lead acetate (sugar of lead) caused its frequent investigation in the later alchemistic period, and in 1610 Jean Beguin was able to describe a "burning spirit of lead" prepared from lead acetate: clearly this was acetone. In 1832 J.B. Dumas described the solvent in a short paper "Sur l' esprit pyro-acetique".[184] The eighteenth century industrial complex of wood - charcoal - pyroligneous acid - vinegar provided a possible source of acetone, as did the destructive distillation of metal acetates prepared from vinegar for the mordant trade.

In 1796 W.A. Lampadius, Professor at the Freiberg School of Mines, reported the preparation of "Sulphur alcohol" by distilling pyrites with moist charcoal.[185] Six years later the inseparable and sometimes indistinguishable N. Clement and C.B. Desormes prepared the liquid from sulphur and carbon, and showed that it contained no other element.[186] Berthollet, Thenard and Vauquelin analysed the "liquid sulphur of Lampadius" in 1812, and showed it to be carbon disulphide.[187] Its useful solvent properties were soon applied to the extraction of oils from seeds (previously effected by crushing in oil mills) and for the removal of fat from bones intended for the chemical manure trade. By 1829, C. Brunner of Berne was able to make the solvent on a manufacturing scale at twelve to fourteen ounces in an hour.

The chlorinated solvents appeared in close succession. Chloroform was discovered independently by Liebig and Soubeiran in 1831:[188] the bleaching powder needed to prepare it from alcohol or acetone had been known since 1799 and was freely available by the 1830s.

In 1834 Dumas analysed the compound and called it "chloroforme":[189] within the next decade the discovery of its anaesthetic properties ensured analysts of a constant supply. In 1840 Regnault examined the action of chlorine on chloroform and reported the preparation of carbon tetrachloride,[190] and in the same year Dumas carried out the preparation from chlorine and methane.[191] The modern method of manufacture from carbon disulphide and chlorine was introduced by Kolbe in 1843,[192] and the demands of the drycleaning trade ensured its success.

The alchemists were well acquainted with the process of "sweetening" oil of vitriol, and "Basil Valentine" describes the distilling together of sulphuric acid and alcohol to produce a sweet medicine.[193] The name "sweet oil of vitriol" was superseded by that of "sulphuric ether", partly on account of its mode of manufacture and partly because it was believed that sulphuric acid entered into its constitution. Valentine Rose showed in 1800 that ether contained no sulphur,[194] and in 1835 Dumas and Peligot described dimethyl and diethyl ethers in a lengthy paper on wood spirit and the various ethereal compounds derived from it.[195] The name ether however continued to be used indiscriminately to describe alkyl oxides and esters, until the latter term was introduced by Gmelin in 1848. Two years later A.W. Williamson reported to the British Association on the formation and constitution of ethers:[196] by that time, common ether was already in use as an anaesthetic and could be obtained by analysts.

The emergence of these organic solvents enabled the organic parts of a medicinal preparation to be separated from the mineral constituents, and perhaps to be further fractionated. It also made possible the separation of organic acids or bases from neutral organic bodies by fixing the acid or base with caustic soda or hydrochloric acid and extracting the free organic part with ether or other solvent immiscible with water. This was a direct outcome of the Stas-Otto techniques for extracting poisons (Chapter IV). In this way was satisfied Boyle's dictum of two centuries earlier, that one should "try what menstrua will dissolve the caput mortuum".

The use of solvent extraction implies the existence of apparatus in which layers of immiscible liquids can be separated. Such apparatus had evolved to meet the pharmaceutical need to separate oil from water in the preparation of essential oils from plant sources, and two main types existed. The first, known as the separatory vessel or the Florentine receiver (Fig. x) worked on the principle of decantation: there was no provision for shaking the mixture before separation. The second, known as the tritorium, was essentially a filter funnel with a very narrow orifice, so that the outflow of liquid was slow enough to allow the receiver to be changed when the lower layer had run off. Sometimes, as described by Robert Dossie, the funnel was bulbous in shape.[197] In 1818 William Henry described a separator furnished with a ground glass stopper and a stopcock.[198] This, apart from the long stem, was the modern separating funnel,

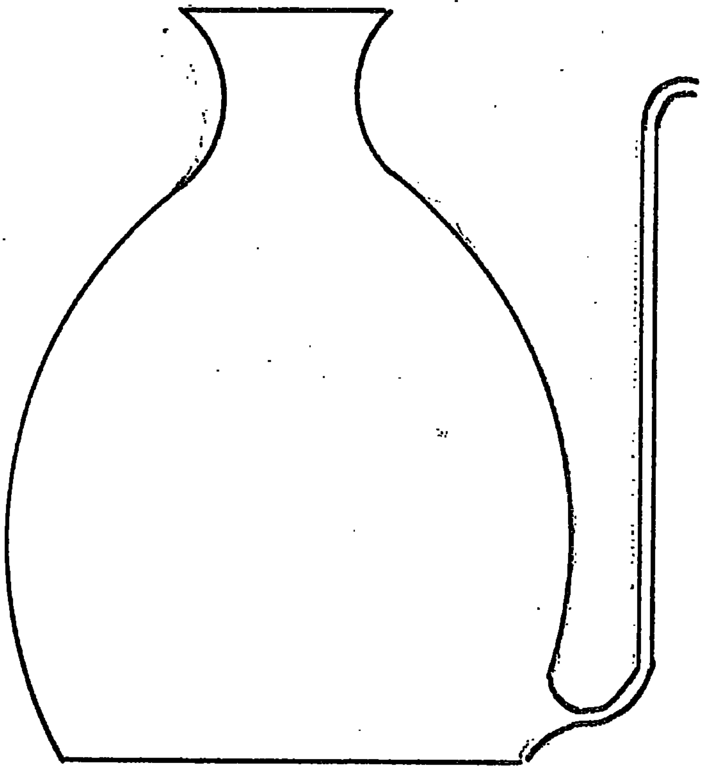

Fig.x. Florentine receiver in which oil and water in distillation products could be separated.

but as late as 1848 Carl Friedrich Mohr and Theophilus Redwood continued to advocate the use of vessels identical with those of Dossie.[199]

Solvent attack on organic materials could be a protracted business, and again pharmaceutical practice could be drawn upon for apparatus necessary for percolation or slow extraction. For extraction in the cold, some device such as Fig. xi could be used, whilst for hot liquids the percolator devised by Payen (Fig. xii), was available.[200] The well-known Soxhlet extractor was not invented until 1879, a product of the scientific examination of fats.

Separation of liquid extracts from solid residues could be accomplished only by decantation or by filtration. The earliest filtration device was the conical bag of flannel known from alchemistic times as the "sleeve of Hippocrates"; flannel and other cloths suspended on wooden frames continued to be used for rapid filtration until the end of our period. Fine particles would of course pass through a flannel filter, and for removal of these basins of porous stone (known as "percolating stones") were used in Dossie's time. The chief obstacles to their use were slowness of filtration and the difficulty of removing fine residues from the stone.

Unsized ("bibulous") paper was well-known in mid-eighteenth century practice, but its mechanical weakness when wet was a great disadvantage. For this reason it was often supported on a domestic colander. Many workers complained of the difficulty of getting good filter paper with both mechanical and chemical properties appropriate to accurate work, and instructions were sometimes given for chemical

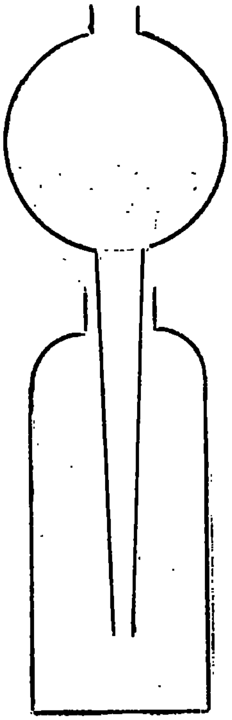

Fig.xi. For extraction in the cold, solid was placed in the bulb and solvent allowed to percolate through it.

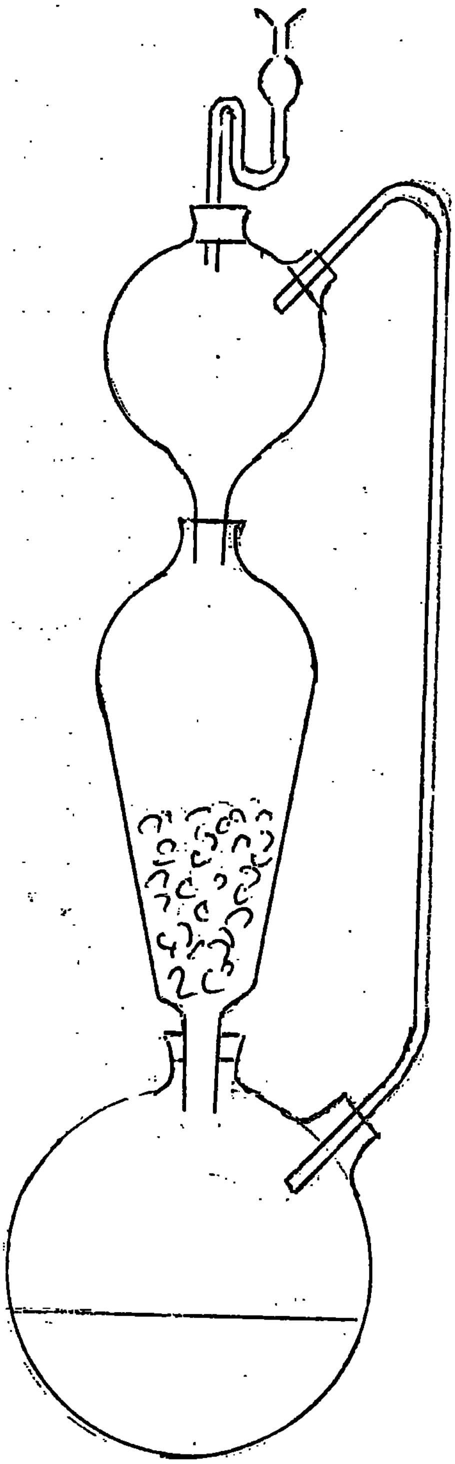

Fig. xii. Payen's hot percolator.

pre-treatment. The best kind of paper was generally held to be the Swedish with the watermark of J.H. Munktell, though J.J. Griffin began to make comparable papers about 1860. In his 1838 catalogue he had examined every available paper and listed the respective disadvantages.[201] This is another example of the tiresome and vexatious obstacles which the classical analytical chemists had to surmount before they could even begin to approach the complex analytical problems which confronted them.

At first, filter paper was supplied in squares and had to be cut into circles by the user. Mohr in 1837 devised a template of tin to make this operation easier,[202] and a year later Griffin installed machinery for this purpose in his Glasgow factory. Bunsen experimented with filtration under suction, using an aspirator bottle to provide reduced pressure, and strengthening the apex of the conical filter paper with a thin platinum cone.[203] The Gooch crucible, which allows filtration of corrosive liquids under reduced pressure, was invented in 1878.[204] The Buchner funnel, using a flat filter supported on a perforated porcelain disc, did not appear until the beginning of the present century, an outcome of Buchner's work on enzymes.

To summarise the available techniques, it can be seen that in 1800 the analyst could detect with certainty only the mineral constituents of a mixture, apart from such help as smell, taste, appearance, or physiological action might give him. A hundred years later he could detect the elements present in the organic parts, carry out laborious but effective separations, recognise many functional groups, and determine melting points. He might also make use of the beginnings of analytical instrumentation. In particular, he had descriptions of the microscopic appearance of plant parts and of many crystalline organic compounds. Most important of all, he had from 1874 a journal, The Analyst, devoted to exchange of information on the kinds of problems which an analyst might encounter in the service of the public.

It is instructive to see how an actual examination of a proprietary medicine was carried out with the minimum of theory to guide the operator. In 1830 T. Clark published a chemical examination of Singleton's Golden Eye Ointment,[205] the subject of several exposures in the medical press. Clark spent his youth in the service of Charles Macintosh, at that time making sal-ammoniac from soot and urine, and later in the chemical works of Charles Tennant at St. Rollox, Glasgow; he became apothecary to the Glasgow Infirmary, moving to Aberdeen as professor in 1836.[206] He is usually remembered as the originator of the soap test for hardness in water. The pots of ointment used in his analysis were brought from three different "respectable apothecaries in Glasgow". At the outset he stated his conclusion that the ointment consisted of a mixture of butter and the common red precipitate of mercury prepared by means of nitric acid (i.e. not the precipitate " per se", prepared by heating mercury alone).

The butter was recognised as follows: ten grains of the ointment were placed on a filter paper and warmed by the fire until the fat melted. As drops fell through the filter they were collected on a piece of window glass, and test drops of known butter, lard, and spermaceti were placed alongside them. The glass was set over a vessel of hot water and it was observed that the Singleton's fat melted at the same time as the butter, the others melting sooner or later than butter. "This observation on the melting point of the ointment, along with the former one on its smell, I consider quite sufficient for determining the nature of its soft constituent." [We should note, however, that no melting point is stated in degrees].

For the examination of the solid portion, the butter was dissolved out in oil of turpentine, and the residue collected on a filter, dried and weighed. Heating in a narrow tube resulted in the formation of a yellow deposit on the cooler part of the tube, with the liberation of fumes which turned litmus paper red; further heating yielded a mirror of mercury which could be rubbed into a globule with a feather. If the solid was boiled with potash and then heated in a narrow tube, no yellow deposit occurred but only the decomposition to mercury. This showed that traces of mercury nitrate were present in the original. Altogether this was a very careful and scientific approach.

Clark went on to say; "seven drachms of butter and one drachm of red precipitate cost one penny. They make an ounce of golden ointment which fills twelve pots. Not counting the duty, these sell at one guinea. A happier example of the transmutation of metals perhaps never occurred in alchemical times." Here we have a hint of the service that chemical analysis could render to a community.

This careful analysis may be compared with that of Hope's Hectic Pills published in the *Monthly Gazette of Health* for 1816.[207] The avowed aim of this journal was "to expose the nefarious practices of pretenders, who, for the sake of lucre, sport with the feelings and lives of their fellow creatures". The editor claimed superiority over every other journal in the analysis of secret preparations which "will enable the public to distinguish those which possess merit from such as are dangerous or inert". After such a preamble we are disappointed to find that the analysis invokes no chemistry. The steps are as follows:

a. A bitter taste is observed resembling that of foxglove.

b. The diseases for which the pill is recommended are treated with foxglove.

c. The directions state that the pill may be taken with any medicine except foxglove.

Therefore the active ingredient is foxglove.

This non-chemical approach may in turn be compared with Pearson's analysis of James's Powder in 1791, occupying fifty pages in the *Philosophical Transactions*.[208] Pearson investigated colour, feel and taste (" in about a minute there is a slight brassy taste") and determined by a method lacking in precision. The powder was examined under the blowpipe, and borax and phosphate beads prepared: on heating with pulverised tartar (potassium carbonate) silvery metallic grains were obtained. Finally the powder was extracted with water and tested with oxalic acid, barium chloride, lime water, litmus, silver nitrate, potassium cyanide, ammonium carbonate, nitric and hydrochloric acids. The results of these tests were compared with those from various attempts to copy James's Powder, and the conclusion was reached that the composition was bone ash and calx of antimony. There was never a specific and unequivocal test for any of the radicals present: indeed some of the tests suggest adulteration with zinc oxide. The decision was reached by a concensus of inferences. If the majority of experiments pointed to the presence of antimony, then antimony would be accepted in the face of a minority of negative results. This is in direct line with the mineral water tests of the seventeenth and eighteenth centuries. There were instructive analyses on poisonous compositions, but consideration of these is deferred until chapter four on toxicology.

CHAPTER IV

THE CHEMICAL DETECTION OF POISONS.

A considerable folklore has grown up round the subject of death by poisoning, involving such notions as the efficacy of the bezoar stone, the sweating of a unicorn's horn, the blanching of an emerald worn on the hand, the changing colour of brass dishes, and fatal encounters with the basilisk.[209, 210] Sixteenth century writers still debated if human beings might be nurtured on poisons, and the legend of the maiden fed on poison from infancy, whose kiss meant death to its recipient, has continued to inspire writers down to our own times. In "Rappaccini's Daughter" 1854 Nathaniel Hawthorne told of the beautiful Beatrice who drank the dew from poisonous flowers, but he forebore to name the species.[211] Richard Garnett was much more explicit. In "The Poison Maid" (1888) he described how her father "ever sedulous and affectionate, fed her with spoonsful of the honeyed froth that gathers under the tongues of asps. As she grew older and craved a more nutritious diet, she partook, at first in infinitesimal quantities, but in ever-increasing doses, of arsenic, strychnine, opium and prussic acid. ....She drank habitually from vessels of gold, for her favourite beverages were so corrosive that no other substance could resist their solvent properties".[212] This work (put into verse by Evelyn Sharpe) provided the libretto for Vaughan Williams' Opera "The Poisoned Kiss".[213]

The climate of opinion about poisoning and the official views of those concerned to uphold the law are clearly expressed in the accounts of the trials in connection with the death of Sir Thomas Overbury in 1606.

The Lord Chief Justice (Coke) reminded the jury "that of all Felonies, murder is the most horrible; of all murders poisoning the most detestable". Poisoning was rare in England, although " the devil had taught divers to be cunning in it, so that they might poison in what distance of space they please ..... in one month, two, three or more, as they list; which they four manner of ways do execute, 1. gustu, 2. haustu, 3. odore, 4. contactu".[214] [The reference to poisoning by contact reminds us that in the trial of Sir John Hollis it was said that the life of Queen Elizabeth was threatened by means of a poisoned saddle][215] The charge against Richard Weston in the Overbury case was that he "did obtain and get into his hand certain poison of green and yellow colour, called Rosalgar, (knowing the same to be deadly poison) and the same did maliciously and feloniously mingle and compound in a kind of broth poured out into a certain dish; and the same broth so infected and poisoned, did give and deliver to the said Sir Thomas Overbury". As to what might be expected in proof of the indictment, the jury were warned "That albeit the poisoning in the indictment be said to be with Rosalgar, White Arsenick, and Mercury Sublimate, yet the jury were not to expect precise proof on that point, shewing how impossible it were to convict a poisoner who useth not to take any witnesses to the composing of his sibber sauces".[216] In other words, if precise proof of the nature of the poison were required, every poisoner would escape justice - a clear statement of conditions before the rise of the science of toxicology.

There were still occult overtones to the idea of poisoning. Among those tried in the Overbury case was Anne Turner, and evidence was admitted about her dealings in magic. She had inherited from Simon Forman (the original of Ben Johnson's "Alchemist") some documents of witchcraft - a parchment bearing all the names of Holy Trinity" and upon the parchment was fastened a little piece of the skin of a man".[217] Such was the effect of her testimony that when some timber in the court emitted a cracking noise it was thought that the devil was intervening to prevent his secrets being made public, and it took a quarter of an hour to calm the people again. Consternation of a different kind was caused by the production of a note signifying " what ladies of the Court loved what lords: but the Lord Chief Justice would not suffer it to be read openly in the Court".

Even to the mind of learned and enquiring men, the subject of poisoning was surrounded by mystery and approached with credulous acceptance. The questions put by members of the Royal Society to Sir Philberto Vernatti, Resident in Batavia in Java Major, included the following.[218] "Whether the Indians can so prepare that stupefying Herb Datura, that they make it lye several Days, Months, Years, according as they will have it, in a Man's Body, without doing him any hurt, and at the end kill him, without missing half an Hours Time ? ..... What Poison is it that the King of Macanar in Colebees is said to have particular to himself, which not only kills a Man immediately, that hath received the slightest Wound with a Dart dipped therein, but also within half an Hour's time, makes the Flesh, touched with it, so rotten that it will fall like a Snivel from the Bones.[219] ..... Whether in Pegu and other Places in the East-Indies, they use a Poison that kills by smelling, and yet the Poison-Smell is hardly perceived".[220]

The mood of helplessness in the face of threats and suspicion of death by poisoning seems to have lifted to a certain degree in the middle of the eighteenth century. At the trial of Mary Blandy in 1752, some attempt was made to find and identify the poison. The prisoner had formed an attachment for an army officer, who persuaded her to do away with her father in order to obtain his money, and who provided her with a white powder. The family doctor, Anthony Addington, performed certain tests on the suspected food: these tests which included sublimation, smell of vapour, acid reaction and certain precipitation tests were also performed on a known sample of arsenic.[221] C.A. Mitchell has pointed out that one of the tests, precipitation with potassium carbonate, would only work if the arsenic was adulterated with salts of calcium.[222] The important consideration here was not the imprecise nature of the chemistry, but the fact that chemistry was invoked and its evidence regarded as admissible.

A comparison between known and suspected poison was made in 1765 at the trial of Naim and Ogilvie.[223] Dr. James Scott, an Edinburgh physician, testified that his experiments on authentic white arsenic showed that if it were stirred into a bowl of tea with milk and sugar, it would stay suspended long enough for a person to drink it: if honey were used as a sweetening agent, the suspension would persist for a longer time. In this case there was no attempt to identify the poison - indeed one medical witness said that he could not identify arsenic - but merely to show that there was no chemical obstacle to its having been used.

France and Germany began to pay attention to the science of toxicology as part of forensic medicine in the 1780's, but the subject was neglected in England until the early years of the nineteenth century. John Gordon Smith, whose book on the principle of forensic medicine appeared in 1821, said that the subject at that date remained in comparative obscurity in Great Britain, a view that was confirmed by Christison. "The principles and practice of toxicology, founded in 1814 by Orfila, had scarcely begun to be appreciated, or even known, in the British Isles in 1822.[224] Smith commended his book to magistrates, barristers and medical practitioners, and he bases his account of poisoning on the premise that " in Great Britain, we shall generally have to do with cases in which the administration of deleterious substances is suspected; and for the most part, I presume it will be matter of no great difficulty to surmise what particular article has been employed."[225] Table IX shows Smith's classification of poisons (based on that of Orfila). Since he expected to be able to deduce the agent of poisoning without much difficulty, his chemical reagents are not particularly sophisticated and all his tests seem to have been made with the following resources:-

Lime water
Silver Nitrate
Copper Sulphate
Ammonia
Potassium Bicarbonate
Copper
Iron
Charcoal
Hydrogen Sulphide
Sulphuric Acid

Table IX.

Classification of Poisons in 1821 (J.G. Smith)

Corrosive:-	Mineral Acids Oxalic Acid Corrosive Sublimate Copper Arsenic Barium Salts
Astringent:-	Lead
Acrid or Rubefacient:-	Helleborus Niger Aconite Veratrum Album Euphorbia Colocynth and Gamboge in excess
Narcotic:-	Opium Henbane Laurel
Natcotico-acrid:-	Foxglove Hemlock Deadly Nightshade
Septic:-	Animal and Gaseous poisons - not usually administered criminally

As might have been predicted from the general analytical chemistry of the period, Smith was able to give convincing tests for most metallic salts, and these we have collated into Table X. For the vegetable poisons, on the other hand, he can offer only symptoms, taste, and uses which throw light on the kinds of circumstance in which a particular poison is likely to be encountered.

The Table X reveals certain interesting features in social and chemical conditions prevailing in 1821. Mercury was particularly to be sought in the form of vermilion used in colouring cheese; sugar of lead (lead acetate) was used in sweetening wines that had gone sour, and verdigris (basic copper carbonate and acetate) was usually present in copper cooking utensils. These last might both be detected by means of the vinegar smell produced on treatment with sulphuric acid. The tests ~~of~~ for antimony suggest that in its commonest form, tartar emetic, it was considerably adulterated: pure antimony sulphide is bright orange, not brownish-red, and the sulphuric acid test is not unequivocal. Lastly one is surprised to note that the blowpipe is ignored in the tests for metals, for at that time and for many years afterwards it was the analysts most versatile tool.

Two years after the publication of Smith's book there appeared a formidable work in three volumes by Paris (whose knowledge of medical literature was encyclopaedic) and Fonblanque who was a barrister. From the combination of medical and legal minds we can expect this work to reflect informed opinion as to what the courts might require, and what they might be given in evidence. At first it seems that Paris was more than sanguine in his claims for chemistry.

Table X.

Summary of Tests for Mineral Poisons (J.G. Smith 1821)

Arsenic:-	Alliaceous smell on heating with charcoal
	White precipitate with lime water
	Yellow precipitate with silver nitrate
	Green precipitate with copper sulphate and potash or ammonia
	Yellow precipitate with hydrogen sulphide
Mercury:-	Brick red precipitate with potash
	Yellow precipitate with lime water
	White precipitate with ammonia
	Silvery deposit on copper
	Quick silver formed on heating with charcoal
Copper:-	Black precipitate with hydrogen sulphide
	Red coating on iron
	Pale blue precipitate with potassium carbonate
	Dark blue colour with ammonia
Silver:-	Metal formed on heating with charcoal
Antimony:-	White precipitate with sulphuric acid
	Brownish red precipitate with hydrogen sulphide
Lead:-	Metallic lead on calcination
	Black precipitate with hydrogen sulphide
	White precipitate with potassium carbonate
Oxalic Acid:-	White precipitate with lime water
Sulphuric Acid:-	"So well known .... that they require no particular description here".
Nitric Acid:-	Addition of copper gives orange vapour, peculiar smell, and blue solution.

"The labours of the modern chemist, indeed, have enabled us to recognise and identify each particular substance by its properties and habitudes with an infallible delicacy, which the Physician of a former age could scarcely have anticipated, and much less practised."[226] No other evidence, says Paris, can weigh against the discovery of the poisonous substance in the stomach or stomach contents. It was sometimes pleaded that putrefaction had gone too far for the detection of poison to be possible: putrefaction was indeed a course for disgust and revulsion, but was no chemical barrier to the performance of the required tests, and the law could expect that every experiment directed to that end should have been scrupulously performed. Nevertheless, Paris appeared inclined to the view that even mineral poisons underwent chemical changes, after the death of the victim, which prevented their detection by chemical means. Orfila showed that the cause of this kind of failure lay in looking only at the stomach and not at other organs and tissues.

Robert Christison, one of the founders of British Toxicology and a former student of Thenard Robiquet, Gay-Lussac and Orfila, graded the value of chemical evidence in a clever way. Of first importance was poison found in the stomach or intestines, followed by that found in vomited matter: less weight was attached to poison in food, drink or medicine taken by the patient (because it might have been added later), and least of all to poison in the possession of a suspect and for which he cannot satisfactorily account.[227] At a time when several toxic substances could be bought without formality for the alleged purpose of killing cats, it was not difficult for anyone found in possession of poison to produce some plausible explanation, and Christison was right to put possession at the end of his list. The list is important because it shows a rudimentary attempt to do a book-keeping exercise on the total poison involved, although the concept was premature: even in the case of the most readily detectable poison, arsenic, such accounting was not possible for several decades.

It should be noted that Christison placed evidence from chemical analysis third in order in which it should be taken. His scheme was:

I. Symptoms, especially suddenness of onset and rapidity of progress
II. Morbid appearances
III. Chemical analysis
IV. Experiments on animals, such as feeding suspected food to a dog.

This low position was not undeserved. More than ten years later Taylor was to write in his treatise in Medical Jurisprudence: "In the present state of our knowledge, chemistry, with few exceptions, furnishes us with the means of identifying with certainty a mineral poison only. The greater number of vegetable poisons are beyond the reach of chemical analysis. Botanical characteristics may sometimes serve to point out the nature of the substance, but only in those instances where the plant has been swallowed with its leaves or other parts entire. If the extract or inspissated juice have been administered, or if the poison were in the form of infusion, tincture or decoction, a chemical analysis will commonly be of no avail .... It is true that there are tests for morphia, strychnia, and a few others; but these are on the whole unsatisfactory, as a basis for chemical evidence of poisoning."[228]

If chemistry was acknowledged to be less than adequate what could be hoped for in the courts ? Taylor referred to cases within his own knowledge where arsenic was at first identified and later shown to be laurel water (prussic acid), arsenic claimed for sulphuric acid and arsenic for oxalic acid. The effect of these hasty statements was disastrous. "It is obvious that if a man can be compelled to admit in cross-examination at a trial for poisoning, that he has been once mistaken on a question so important and requiring so decided an answer, a jury may easily be induced to believe that the witness may have made a second mistake.[229]

In fact, professional chemists were uneasy about the whole state of forensic analysis. C.R. Fresenius, probably the greatest authority on pure analytical chemistry in the middle years of the nineteenth century, examined the position of the chemist appearing as an expert witness and asked the very pertinent questions: "What is chemistry able to perform with regard to the detection of poisons, and what may properly be demanded of the chemist?" The warning that chemical evidence might be misinterpreted by laymen was followed by some plaintive remarks on the situations in which a chemist might find himself. "If he chooses one of the older methods and finds no arsenic thereby it will be said 'How can a chemist apply such a method ?'

Are we not in possession of improved and far more correct methods ? Had he used the apparatus of Marsh he would have found arsenic.' Well, suppose he uses the apparatus of Marsh and detects arsenic, the advocate of the accused will undoubtedly object. 'In what estimation are we to hold these results, obtained by means of a method liable to every possible deception and error ?'[230] Fresenius concluded with the hope that some standardisation of methods could be agreed upon, with the object of protecting chemists - and the art of analysis - from the contumely to which they were often exposed.

It was usually an easy matter for opposing counsel to throw doubt upon the value of chemical evidence, particularly in the days when scientific witnesses were called on a partisan basis and not, as now, to be expert witnesses to serve the court. As it happened, a number of important cases provided platforms for the humiliation of chemical witnesses (although most of them were medical men). In 1856, for example, the trial of William Palmer the Rugeley poisoner, afforded an opportunity for Sergeant Shee to bait A.S. Taylor: on the detection of strychnine Taylor was forced to admit that when he had poisoned four animals with that substance he had been able to recover the poison in only one case. Later he stated that he preferred to use rabbits rather than dogs for experimentation and Shee said " I will take your answer [to mean] that you are afraid of dogs."[231] The great toxicologist was also manoeuvered into a partial agreement that the course of his analysis might be influenced by a statement of the symptoms.

It is possible that Taylor in common with other analysts was over confident in the sensitivity of his tests: he claimed for instance to be able to detect one thousandth of a grain of tartar emetic (that is 0.06 mg or about 0.02 mg antimony) almost certainly far too low a figure for the complex organic environment of stomach contents.[232] A year later, Taylor (who was given to public discussion of his evidence and methods) re-examined the question of the detection of strychnine. The article stated "The discrepancy in the views of the chemical witnesses at the trial of Palmer, regarding the answers to these questions was a subject of public remark, and certainly for a time reflected discredit on professional evidence".[233]

W. Herapath of Bristol (described as "probably the most eminent chemical analyst in this country") was a witness at the trial of a man charged at Bodmin Assizes in July 1857 with murdering his grandchild by means of phosphorus paste spread on bread. No phosphorus could be detected in the body. "In fact Mr. Herapath found it necessary at this trial to lay aside chemistry as altogether inadequate to solve the question, and to base his opinion on the symptoms and appearances of the body". The unsatisfactory nature of the chemical evidence in the Smethurst trial (1859) is mentioned on p.[234] 141.

These examples relate to the first half of the nineteenth century, and it might have been assumed that as the century progressed the courts might have come to place more confidence in the scientific witness in general. However as late as 1889 when the trial of Mrs. Maybrick took place, Mr. Justice Stephen used harsh words in his summing up. "There was such a thing in forensic medicine as a kind of subtle partisanship which very much diminished the value of the evidence given. Any person who had been in the habit of attending committees at the Houses of Parliament, and hearing evidence there given by engineers and persons connected with the mechanical arts, must have learned that the mere fact that a man went into the box and said this, that, or the other, did not by any means qualify them to receive unhesitating belief. One had to take a great deal of the scum from the testimony of skilled witnesses."[235]

Now this trial was about arsenic, and in 1889 the detection and estimation of arsenic were very secure. It might be thought that there could be no argument about facts. Nevertheless, the quantities of arsenic discovered by analysts for the two sides did not correspond: this was probably due to the lapse of time between the two analyses, water having been lost from the organs in the intervening weeks. There is however a further obstacle to the automatic acceptance of chemical evidence, to be found in the nature of the evidence itself. Thus when a chemist says that he has found an acid, he has probably observed a change in colour in an indicator; when he says he has found strychnine, he has found a violet colour when acid and dichromate have been added. The forensic question will always be whether or not such changes in colour, appearance of precipitates, or other phenomena bear the interpretation which the chemist puts upon them. [This applies with equal force today when colour changes may be replaced by meter readings or traces from the automatic pen of a recorder.]

There could be no scientific toxicology, that is a system whereby different investigators working on the same material would get the same results, until the chemistry of the vegetable poisons was thoroughly worked out. At the beginning of the nineteenth century the class of substances now known as alkaloids were called vegetable alkalis, but because this term was applied also to potash from plant sources Dumas in 1835 changed the name of its present form.[236] The first alkaloid to be isolated in a pure form was morphine (along with its attendant acid, meconic acid) by F.W.A. Setumer.[237] This discovery led to further investigations of medicinally active plants along the same lines, and by 1820 Pelletier and Caventou had isolated strychnine, brucine, quinine, cinchonine and veratrine. Of the alkaloids that were toxicologically significant, atropine, hyoscyamine and aconitine were known by the end of 1833. A valuable test for the class in general consisted in the liberation of ammonia, or a smell of burnt feathers, on heating with lime. In 1843 Lassaigne published his fusion method for detecting nitrogen: he fused with potassium (sodium is more commonly used today), boiled the extract with ferrous sulphate, acidified and added ferric chloride to yield prussian blue.[238]

The first clue to the general structure of alkaloids was obtained by Gerhardt in 1842 when he obtained an oil (quinoline) by distilling quinine, strychnine and cinchonine with solid caustic potash.[239]

In 1834 Runge had obtained some nitrogenous bases from coal tar,[240] and these were shown by Hofmann to be identical with those obtained from alkaloids.[241] The general chemistry of the pyridine and quinoline bases was therefore applicable to alkaloids, and such reagents as picnic acid, tannic acid, phosphomolybdic acid and potassium mercuric iodide could be used to separate the class from other classes of organic compounds. Work on the equivalent weights of organic bases led to the use of platinum chloride (chloroplatinic acid) and gold chloride as precipitating agents. Some of these precipitates, especially the picrates, could be used for identification by way of characteristic melting point, particularly when taken with the melting point of the original alkaloid. Blyth in 1878 also gave a list of sublimation temperatures for alkaloids.[242] Three years earlier he had published a table of colour tests with sulphuric and nitric acids: this was not likely to be specific and indeed it recalls Brande's table of ferrocyanide colours for metals (p. 61)[243]

Alkaloid	Sulphuric Acid			Nitric Acid
	cold	warm	hot	
Strychnine			Yellow	Pink
Brucine			Yellow	Red
Morphine			Brown	Orange
Atropine			Brown	
Aconitine		Brown	Black	
Veratrine	Orange	Scarlet	Claret	
Solanine	Yellow	Brown	Brown	

For these tests he used one tenth milligram. He also used Wanklyn's ammonia method (boiling with permanganate and testing distillate with Nessler's reagent) to classify alkaloids according to their nitrogen content. A curious feature is that he used one milligram samples and quoted results to two decimal places: one is bound to wonder what sort of balance would give this precision. In fact such precision was not necessary for the poisons were classified into four groups possessing (1) less than 1% (2) about 2.5% (3) about 4% (4) over 10%. This is a clever and useful separation in groups.

Other colour tests were obtained with ammonium molybdate and with sodium nitroprusside.[244] Altogether we may say that although few really specific tests were known, comparison of various classifications by solubility in organic solvents, colour tests, precipitations and melting points, supplemented by appeals to taste and such physiological tests as that for mydriatic effect, would enable a patient and painstaking analyst to establish the identity of a pure alkaloid.

First, however, the material had to be separated from its other organic contaminants. J.R. Stas in 1852 had examined the means of separating nicotine from other organic compounds,[245] and his method, refined by F.J. Otto became standard. The principle of the Stas-Otto separation was that saltsof alkaloids would dissolve in aqueous alcohol, but would not be extracted by ether: fatty substance could thus be separated and, after adding alkali, the free alkaloid would be dissolved in a second ether extraction. Most toxicologists had their own variants on the fundamental method, some preferring chloroform to ether.

The solutions and residues from the above tests could then be boiled with hydrochloric acid and potassium chlorate to obtain a solution on which tests for the metallic poisons might be carried out. In this way, suspected organs or food could be subjected to a complete analysis for poison. The procedures and methods in vogue at the end of the century were neatly summarised in the *Chemical News* for 1890.

So far we have considered only the traditional poisons, metals and plant products. In the last quarter of the century two domestic poisons began to be toxicologically important: these were carbolic acid and its derivatives, and ammonia. In the last decade of the 19th century carbolic acid was responsible for as many deaths as opium, and ammonia for as many as strychnine.[246] In both cases, and in distinction to other poisons, females appeared as often as males in the lists, revealing the hazard of household poisons about which concern continues to this day. Whereas the other poisons were usually *dispensed* in error to the consumers, these were *taken* in error, apart from their very widespread use in suicide.

Both substances could most easily be recognised by smell, which pervades through other odours (yet the smell did not prevent their being taken accidentally). The discovery of diazonium compounds by P. Griess provided a colour test for carbolic acid and other phenols:[247] and Nessler's solution furnished an extremely sensitive test for ammonia.[248]

At the close of our period, Blyth could write: "If poison is the very last form of death feared by eminent political persons, it is not so much owing to a different state of society as ..... to an ever advancing chemistry which is able in many instances to separate and detect the hurtful and noxious thing, although hid for months deep in the ground."[249] We may contrast this with Taylor's statement of fifty years earlier that he could provide a list of poisons which might infallibly produce death without leaving a physical or chemical trace of their presence in the body, but he forbore to do so as it would place dangerous knowledge in the hands of the public.[250]

The present writer would wish to dispel the notion that improved chemical techniques had - or have now - made analysis into a mechanical routine. Fresh combinations of interfering agents impose fresh problems and every complete analysis of an unknown mixture is, in a sense, a research. This explanation is necessary to account for the existence of numbers of tests for the same element or compound. The layman will always ask why there is not one agreed test for each entity, and the answer must always be that changing circumstances call for changing approaches: often an analyst is forced to forego his favourite test and choose one that is intrinsically less satisfactory, on account of the condition of the sample presented to him. We pass now to a consideration of some poisons that call for special mention.

Table XI.

Reagents and Apparatus for Poison Analysis 1844.

Acids:- Sulphuric, Nitric, Hydrochloric, Oxalic, Tartaric, Acetic.

Alkalies:- Potash, Soda, Ammonia and their carbonates. Lime.

Salts:- Barium Chloride and Nitrate, Calcium Chloride and Sulphate, Silver Nitrate, Iron Sulphate, Potassium Ferrocyanide, Sodium Phosphate, Copper Sulphate, Potassium Iodide, Lead Acetate, Mercuric Chloride, Manganese Dioxide, Barium Carbonate, Ammonium Oxalate.

Ammonium Sulphide, Hydrogen Sulphide, Iron Sulphide, Strontium Sulphate, Stannous Chloride, Gold Chloride, Platinum Chloride, Iodic Acid, Ferric Chloride, Black Flux, Soda Flux.

Litmus paper and Rose paper.

Copper filings, foil and wire, Tin filings and foil, Zinc foil, Gold leaf and foil, Silver, Platinum foil and wire.

Platinum crucible with lid. Platinum cup. Thin glass tubing, Watch glasses, Test-tubes, Glassplate. Florence flasks; Large and small retort with receiver. Filter paper. Spirit lamp.

Table XII.

Reagents in Griffin's Toxicological Cabinet (1877)

Ammonium Carbonate	
Ammonium Oxalate	
Ammonium Sulphide	
Barium Chloride	
Barium Nitrate	
Charcoal Powder	
Copper pure foil	
Copper Sulphate	
Ferric Chloride	X
Ferrous Sulphate	
Ferrous Sulphide	
Galls (Tincture)	
Gdd Chloride	X
Flux (black)	
Indigo Sulphate	
Lead Acetate	
Mercuric Chloride	X
Platinic Chloride	X
Potassium Dichromate	X
Potassium Carbonate	
Potassium Cyanide	
Potassium Ferricyanide	
Potassium Ferrocyanide	
Potassium Hydroxide	
Potassium Iodide	X
Potassium Nitrate	
Silver Nitrate	
Sodium Carbonate	
Sodium Phosphate	
Tartaric Acid	
Tin Chloride	
Zinc (free from Arsenic)	

(those marked X would be of particular use in alkaloid testing)

Table XIII.

Schedule of Poisons in Pharmacy Bill 1868 (31-32 Vict 121)

Part I	Arsenic and is Preparations
	Prussic Acid
	Cyanide of Potassium and all Metallic Cyanides
	Strychnine and all poisonous vegetable Alkaloids and their Salts
	Aconite and its Preparations
	Tartar Emetic
	Corrosive Sublimate
	Cantharides
	Savin and its Oil
	Ergol of Rye and its Preparations
Part II	Oxalic Acid
	Chloroform
	Belladonna and its Preparations
	Essential Oil of Almonds unless deprived of its Prussic Acid
	Opium and all Preparations of Opium and of Poppies.

The Toxicology of Arsenic.

The statistics quoted in Table XIV show arsenic to have been one of the most frequently encountered poisons. This is not surprising, for the most usual form, white arsenic or arsenious oxide, is odourless and almost tasteless and easily mixed with food. Moreover it had widespread uses in commerce and the useful arts, and so was easy to obtain without exciting suspicion. It was in fact so easy to obtain that it was often mistaken for some harmless substance, and accidental poisoning - sometimes on a large scale - was of fairly regular occurrence.

Accidental poisoning due to eating coloured confectionary is dealt with in a separate section (p. 161), but in 1854 A.S. Taylor (himself a toxicologist) was nearly the victim of a different kind of hazard.[257] His story, under the heading "How Families are Poisoned", opens dramatically. "On the 17th of the present month, when about to cut the loaf placed on my table for breakfast, I observed some green patches and streaks over the partially burnt lower crust." Taylor scraped off the green patches, and on testing the material found it to be Scheele's Green. Further investigations at the bakery showed that the newly baked bread was cooled on shelves that had recently been painted a bright grass-green colour. The baker was quite ignorant of the fact that the paint contained arsenic; the painter however was well aware of what he was doing, saying that without arsenic it was impossible to get a good green, and that he had never heard of any deaths resulting from its use.

Table XIV.

Poisoning Statistics for 1837 - 38

From Med. Gaz. November 1839

541 deaths, comprising 282 males and 259 females

Opium:-		
Laudanum	133	
Opium	42	
Other opium preparations	21	196
Arsenic		185
Sulphuric Acid		32
Prussic Acid		27
Oxalic Acid		19
Mercury and Corrosive Sublimate		15
Mixed or Compound Poisoning		14
Oil of Bitter Almonds		4
Poisonous Mushrooms		4
Colchicum; Nux Vomica, of each 3		6
Nitric acid, caustic alkali, tartar emetic, acet. morphia, strychnia deadly nightshade, aconite, of each 2		14
Bichromate, silver nitrate, Goulard's extract*, iron sulphate, tin chloride, hellebore, castor oil seeds, savin, hemlock, cantharides, cayenne pepper, of each 1		11
		527
Unknown	14	
		541

*Often called Lead Triacetate in contemporary literature (e.g. Taylor: Medical Jurisprudence, London 1844, 186) but would now be considered a basic lead acetate in dilute acetic acid.

Deaths certainly did result, as described by Dr. Edward Lankester in 1860.[252] At a public dinner held in that year a green blanc mange had been served, after eating which three people died; the colouring matter was copper arsenite. A more common source of danger from this compound lay in the practice of colouring wallpaper with the pigment: and from a combination of unsound science and misapplied aesthetics, such wallpaper was often hung in damp unheated bedrooms where a fungus could develop, causing the liberation of gaseous arsenic hydride.[253] In his evidence before the Parliamentary Committee on the Sale of Poisons, Dr. A.S. Taylor stated that the largest quantity of arsenic used in this country was employed by the makers of wallpaper.[254] This drew a sharp rejoinder from Mr. A.E. Fletcher who manufactured arsenical pigments. "Let blame be laid at the right door, and let the public be assured that it is not the looking at cheerful walls, the fingering of brightly ornamented books, nor the weaving of tastefully coloured clothing that will hurt them, but the dwelling in ill-ventilated rooms, and a continual dread of pure water, will."[255]

While the Parliamentary Committee was actually taking evidence the walls of the Excise Office were hung with arsenical wallpaper. George Phillips the chemist to the department ("Phillips of the Excise") was asked to examine the atmosphere of the rooms for volatile arsenic products. This he did by hanging in the rooms sheets of paper inpregnated with silver nitrate:[256] of course no arsenic was detected. F.A. Abel, the chemist to the War Department at Woolwich Arsenal refined the tests by aspirating air through a solution of silver nitrate, and again found no arsenic: he concluded that the possibility of ill effects from inhabiting rooms hung with arsenical wallpaper had been disproved.[257] However in 1863 a coroner's jury at Plumstead returned a verdict to the effect that a child of five years had died from arsenic poisoning, the result of sleeping near to a green painted wall.[258]

The confusion of results arose through failure to perceive the essential conditions for a poison hazard to occur. If the rooms were dry, no decomposition of the starch paste would take place, and arsenite would not be reduced to arsine. Many of the cases of poisoning were not due to arsine however but to dust from the walls. Taylor (who played a heroic part in the whole story) collected dust from dwelling houses and shops where the suspected wallpaper was in use, and in all cases found it to contain arsenic.[259] As was almost inevitable when a new hazard was recognised, all manner of complaints began to be associated with arsenical wallpaper. A certain Mr. E.H. Corbould was summoned to Osborne House to execute a piece of work for the Queen, and while thus engaged was given a room at the Victoria Cottage. "The bed was everything a gentleman could desire. It was well covered with Witney blankets of the newest and the best kind; and I was informed by the servant that, in the event of my requiring more, I should find a couple of thicker blankets folded at the foot of the bed. When, however, I felt the quality of those on the bed, and which were like so many good sheepskins, I said it was not very likely that I should require the extra ones. The room, too, felt deliciously warm in every part". In spite of this care, as soon as Mr. Corbould got into bed he felt cold, and neither the extra blankets nor a well-lined Spanish cloak could stop his teeth chattering:

pain and nausea were followed by deep sleep. In the morning, when the servant brought his tea, Mr. Corbould exclaimed "Why, its arsenic" when his glance took in the brilliant green wallpaper. When he related his experience to the Queen, she ordered the paper to be stripped off, not only from that room but from all others in the Palace. Mr. Corbould attributed his survival to the fact that he had taken a small glass of brandy and water.[260] Mention must also be made of the case of "a fine parrot, which was hung in one of the rooms [which] all at once drooped and refused food". The room, predictably, was papered in a green flock paper.[261]

The most common source of accidental arsenical poisoning was of course white arsenic. This material, which seemed to be stored in the most unlikely places, was often mistaken for icing sugar and dusting powder. The early volumes of The Analyst contain frequent references to this last, the years 1878 and 1879 being particularly noteworthy for "Violet Powder" cases.[262] As an example of purely domestic danger of arsenic poisoning we may note the case admitted to Bristol Royal Infirmary, also in 1879. A woman was making a meal pudding, watched by her small son and daughter: the boy found a paper parcel in the cupboard and saw that it contained a white powder which he thought was flour. The boy tipped the powder into the pudding mixture, with the result that five of the family became seriously ill: no one knew how the arsenic came to be in the cupboard.[263]

One of the most famous cases of white arsenic poisoning on a large scale occurred in 1858. "A serious misfortunate has occurred, and a great crime has been committed, of which the law will take no cognizance. A hecatomb of victims has fallen beneath the careless error of an inconsiderate lad. A sacrifice so vast has rarely fallen to the shame of any one shop-boy before this time. Many a druggist's lad has slain his one, two, or three victims; this boy counts the dead by dozens'. The lad, of course, was not the real criminal. A person named Hardaker was in the habit of selling peppermint lozenges in the market place at a price of sixpence per pound, at a time when good quality lozenges cost about twice this price. By a common practice, the lozenges were adulterated with plaster of paris, known to the trade as "Daff". The purpose of this pseudonym was probably to ensure that underlings in both buying and selling firms should not know what was being used. In this case, Hardaker asked for twelve pounds of Daff, and the druggist informed his boy that it was kept in a cask in the corner; there were two casks, and one contained white arsenic, which was supplied, used and distributed to the public. [There are variants on this story: the <u>Annual Register</u> says that Hardaker was the vendor but that a third person, Joseph Neal, was the maker].[264] After four deaths had occurred, an alarm was raised and some of the poisoned sweets were recovered: but at least fifteen people died and upwards of two hundred were ill. The druggist, Hodgson of Shipley, was indicted at York Assizes on a charge of manslaughter but the trial was stopped on the ground that there was no case to answer.[265]

Scheele's Green, so often the culprit in cases of accidental poisoning, provided one of the earliest of the purely chemical tests for arsenic. Others were the formation of a yellow precipitate with ammoniacal silver nitrate, known as Hume's test, and the precipitation of yellow arsenic sulphide.[266]

It was generally agreed that these precipitation reactions were influenced too much by the initial chemical state of the arsenic to provide unmistakable proof. More reliance was therefore placed upon a reduction test devised by Berzelius. The suspected matter, or one of the precipitates mentioned above, was mixed with black flux (potassium carbonate and charcoal) and heated in a drawn out glass tube: if arsenic was present a metallic stain or mirror appeared on the cooler parts of the tube. Some toxicologists, led by Christison of Edinburgh, objected that small traces of the metal might be lost through solution in the flux, and indeed the test was not very sensitive. Nevertheless Berzelius was the first to suggest a way of overcoming the ambiguities of the precipitation tests.

This, then, was the state of chemical analysis when Marsh's test was launched into the world in 1836. Marsh's own account says that he was anxious to find a way to avoid the uncertainty associated with the use of black flux. The apparatus was the embodiment of simplicity.(Fig.xiii) It was made from three-quarter inch diameter glass tubing bent into the form of a syphon with limbs about five and eight inches long. The stopcock, mounted in cork, was secured with a little "common turpentine lute", and the whole apparatus was fixed to a wooden stand by means of elastic bands, described as "two elastic slips cut from the neck of a common bottle of India rubber". A small zinc rod was placed

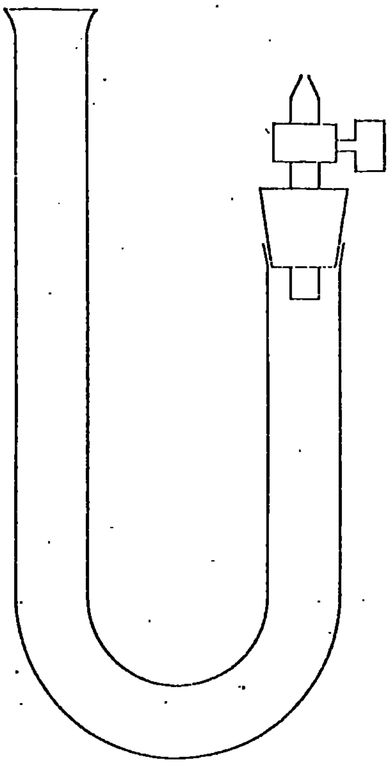

Fig. xiii Original form of Marsh's apparatus, 1836

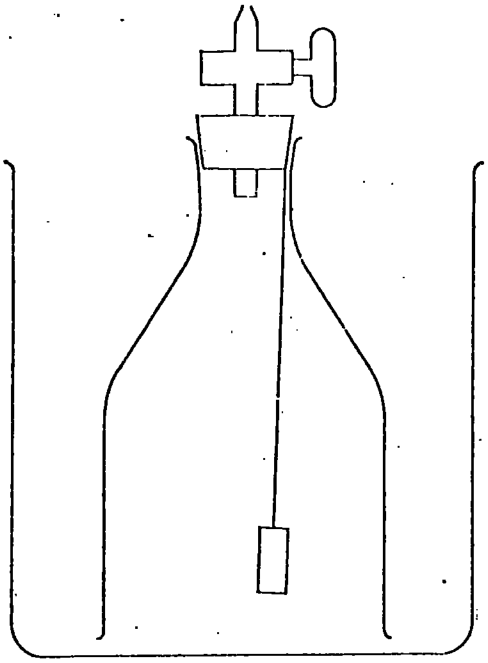

Fig. xiv Marsh's apparatus modified for large volumes, 1836

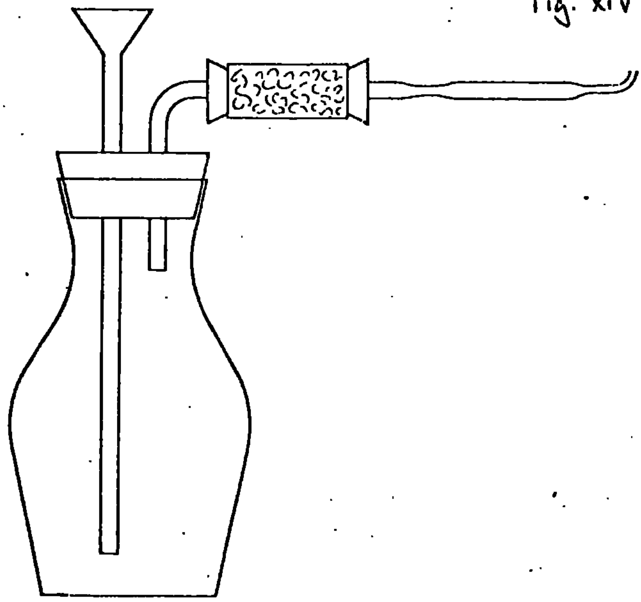

Fig. xv Marsh–Berzelius apparatus, 1837

in the short limb and kept from slipping into the other limb by the insertion of a short glass rod: dilute sulphuric acid was poured in, the air displaced, and a suitable volume of hydrogen collected for testing. The preliminary blank test was applied by burning the hydrogen at the jet and allowing the flame to play onto a piece of crown glass (with a warning that the glass might sometimes fly to pieces). If no stain appeared on the glass, the material under test - either in solution or suspended in water - was added through the open limb, and a further volume of hydrogen collected and burnt. Serious losses owing to frothing sometimes occurred when materials such as stomach contents were examined and directions are given for breaking the froth with "sweet oil" (glycerol).

With the spirit of the true experimenter Marsh was sure that the apparatus could yet be improved, and in a fine burst of do-it-yourself prose he declared:- "Indeed I say unequivocally that there is no town or village in which sulphuric acid and zinc can be obtained, but every house would furnish to the ingenious experimentalist ample means for his purpose; for, a two ounce phial with a cork and piece of tobacco pipe, or a bladder with the same arrangement fixed to its mouth, might in cases of extreme necessity, be employed with success, as I have repeatedly done for the purpose".[267]

The chemical reactions upon which Marsh's test depend were well known in 1836. Scheele had mentioned the thermal decomposition of arsine in 1775; Proust, in his researches on tin (1798) had shown that a foul-smelling gas was generated when arsenic-bearing tin dissolved in hydrochloric acid.[268] Tromsdorf in 1803 had described similar results with arsenical zinc, and in 1815 Gehlen had made a thorough study of arsine, dying from the results of inhaling it.[269] In 1821 Serullas suggested the generation of arsenic hydride as a forensic test for arsenic.[270] Marsh was however the first to describe a simple apparatus and to state clearly the conditions for its effective use.

The circumstances of James Marsh's life do not reflect the importance of his place in the history of chemical analysis. He was known as the "practical chemist" at Woolwich Arsenal and was assistant to Michael Faraday at the Military Academy there. At the time of his death in 1846 at the age of 52, his weekly wage was thirty shillings, and his wife and family were quite unprovided for. The anonymous author of the account in the "Biographie Universelle" suggests a reason; "Mais la passion des liqueurs fortes s'empara graduellement de lui, elle hata sa fin".[271] Though financial reward seems to have evaded him, Marsh received a number of scientific honours, not merely for the arsenic test but for his researches into electricity and for his invention of the quill fuse for use with explosives. Among these honours were the gold and silver medals of the Society of Arts, a silver medal from the Board of Ordinance and another from the Crown Prince of Sweden.[272] Many features in Marsh's writing seem to reflect the influence of Faraday, particularly the delight in evolving practical manipulative tricks, (Wöhler's "Kleine Handgriffe") and the utilisation of commonplace objects for scientific purposes.

Marsh's test achieved notoriety in 1840 for its part in altering the course of French justice at the trial of Marie Lafarge. This case, of which it was said "it tended not a little to divert their thoughts from the fancied insult they had received from England, and to diminish the changes of a war", involved a number of leading toxicologists, doctors and chemists. M. Lafarge, a supposedly wealthy iron founder, had married the twenty-three year old Marie Capelle, whose family was well connected in army and banking circles. Less than a year later he died in suspicious circumstances and the young widow was charged with murder by arsenic poisoning. Orfila, the lion among toxicologists, could find no arsenic in any of the samples submitted to him, but the court called for a fresh examination of the body. The report in the Annual Register - usually so restrained in tone - made the most of the sensational aspects of the situation. "The coffin was little more than three feet below the surface; and when opened, the body presented a hideous spectacle, and so much decomposed that instead of the usual instruments, it was necessary, in order to take from it what was wanted, to use a spoon, which was sent for from the village".[273]

This time Orfila and his assistants found arsenic in every place in which it was sought, and Marie Lafarge was sentenced to life imprisonment. Orfila listed some of the factors which had contributed to the contradictory results; "La cause a ete ici un tube casse, la une portion trop minime de matiere soumise a l'analyse, ailleurs une flamme un peu trop forte, enfin un certain mahque d'experience pour se servir de l'appareil de Marsh, qui demande une grande pratique".[274] Raspail claimed to have found arsenic in the zinc used by Orfila in his tests, but this evidence was brought forward too late to influence the court. The laymen's view was justifiably expressed in a newspaper report. "Within two days the accused was declared innocent by the verdict of science, and now she is judged guilty by the verdict of the same science."

From 1836 to 1841, Marsh continued to modify his apparatus and method (Fig. xiv), particularly in the twin directions of achieving a partially quantitative result, and of distinguishing arsenic from antimony; this distinction was particularly important because antimony was sometimes administered as an emetic in poisoning cases. Except for filtering off the larger particles, Marsh did not attempt to separate organic matter prior to carrying out the test, although the experiments of a number of workers showed such a separation to be necessary for success. William Odling (third President of the Royal Institute of Chemistry), for example, described the case of a soil containing 0.07% As_2O_3 which gave negative results in Marsh's apparatus until the organic matter had been destroyed by boiling with sulphuric acid. 275 Schneider had suggested digestion with sulphuric acid and common salt, the arsenic being distilled off as $AsCl_3$ and absorbed in water, Marsh's test being applied to the aqueous solution. As early as 1839, Orfila had destroyed organic matter by dry combustion with potassium nitrate, later replacing this treatment by wet oxidation with concentrated nitric acid; this was twenty years before Carius proposed his sealed tube method for quantitatively oxidizing organic compounds.

The stain produced on a cold glass or porcelain surface in Marsh's original process gave only qualitative results. A step towards quantitative evaluation of the arsenic was made by Berzelius in 1837, when he passed the mixture of arsine and hydrogen through a glass tube, heated in the middle, before ignition at the jet; the mirrors of arsenic so formed were capable of quantitative interpretation. This device (Fig. xv) became standard under the name of the Marsh-Berzelius apparatus.[276]

The Marsh test, with its various modifications, was examined critically by Liebig and Mohr,[277] Thenard, Dumas and Regnault,[278] Chevallier,[279] and Lewis Thompson.[280] The latter decided:-

"All circumstances considered, I fear we can only regard Mr. Marsh's very ingenious test for arsenic as furnishing good collateral evidence, capable indeed, in scientific hands of giving very correct indications, but wholly unfit to be entrusted to those unaccustomed to careful chemical manipulation. I say this with a thorough conviction of the great utility of Mr. Marsh's test, and am only sorry that its evidence is not unequivocal".

The publication in 1841 of Hugo Reinsch's test, in which arsenic was deposited on copper foil from hydrochloric acid solutions, gave to chemists a much needed alternative to the Marsh test.[281] Reinsch's test was first used for medico-legal purposes by Christison at Edinburgh in 1844, at the trial of a Mrs. Gilmour who was accused of murdering her husband. The new test arose out of an observation by Fuchs that the presence of ferric iron caused copper to dissolve in hydrochloric acid.[282] Reinsch, preparing to study this reaction, noticed that strips of copper placed in commercial hydrochloric acid developed black stains, and traced the cause to arsenic in the acid.

The method was eagerly taken up in America, where D.P. Gardner (1842) published a lengthy examination under the title "*On the Application of M. Reinsch's test for the detection of Arsenic to Medico-Legal Enquiries*".[283] In the same year Christison proposed a refinement in the following way: the arsenic coated copper was to be cut into strips and heated in a flask until octahedral crystals of arsenious oxide formed in the neck, and these were to be dissolved in water for testing with silver nitrate, copper sulphate and hydrogen sulphide.[284]

Because the Reinsch test required so little manipulative skill, it was looked upon as a safer method than that of Marsh, and was put to use before the necessary safeguards had been adequately studied. The trial of Smethurst in 1859 caused a sensation because once again contradictory conclusions were reached. Odling and Taylor showed that the copper used in the test had itself contained arsenic, and a further uncertainty was caused by the presence of chlorate which sometimes inhibited the test. Herapath dismissed the affair in scathing words:- "The fact is, the whole set of operations were a bungle. Reinsch's process is not applicable where nitrates and chlorates are present.[285] There being no Court of Criminal Appeal at that time, the Home Secretary placed all the scientific evidence in the hands of Sir Benjamin Brodie for reconsideration. This example of the intervention of a chemical ombudsman resulted in Smethurst's acquittal.

A few years later, though, he wrote in Ure's Dictionary of Chemistry:- "I prefer the principle first proposed by Reinsch and have always acted upon it".

Many attempts were made to improve the means of distinguishing antimony from arsenic, the most successful being that of Fleitmann.[286] This paper showed that when an alkaline solution containing arsenic and antimony is heated with aluminium, only the arsenic is reduced to its hydride. When applied to arsenic alone, the additional merit was claimed that aluminium and alkali were more easily obtained free from arsenic than were zinc and sulphuric acid. This test however never became really popular, and many standard works on chemical analysis do not mention Fleitmann.

From time to time Hume's silver nitrate test was revived as a finish to the Marsh test, the gases being led through cotton wool or over filter paper soaked in the reagent. In 1874 Mayerçon and Bergeret suggested the use of mercuric chloride as a reagent for arsine, and a convenient form of apparatus for holding the filter paper in the gas stream was devised by Gutzeit in 1879.[287]

When Marsh's test was first published, the long reign of Queen Victoria was just about to begin. As that reign drew to its close, the subject of arsenic testing again assumed importance in the eyes of the general public. In 1900, the beer drinkers of Lancashire began to fall sick in their thousands, due to what was eventually diagnosed as chronic arsenic poisoning, traced to the use of contaminated sugar in brewing, and ultimately to arsenical sulphuric acid used in the sugar refinery. To allay popular anxiety and criticism, the Society of Public Analysts and the Society of Chemical Industry set up a joint committee to examine and report on methods for detecting arsenic with particular reference to beer.[288] For easy manipulation and quick results the committee recognised the merits of the Reinsch test. For accurate work in skilled hands however, they recommended the Marsh-Berzelius test as the most certain chemical method for the detection of arsenic. The special Analytical Commission set up by "The Lancet" in 1892 to examine arsenical wallpapers also used the Marsh-Berzelius method. Yet as we have seen, even so precise and elegant a method did not ensure that forensic struggles over the presence and quantity of arsenic were to cease.[289]

Opium.

We have alluded in Chapter II to the abnormally high death rate in England due to opium and morphine poisoning. In the last decade of the nineteenth century there were 1,655 such deaths in England and Wales, and of these 984 were accidental, and 660 suicidal. These figures indicate the ease with which opium preparations could be obtained.[290] There are hints that organisations for the shelter of unwanted children were the largest purchasers of these nostrums. Thomas Mackern, in "Lucian Playfair" (1857), tells the story of the ominously named "Child's Peace", speaking of " a plethoric green bottle containing the landed laudanum in disguise; forth it came, glorified by an emblematical label, addressing society in general, mothers and nurses in particular, to the effect that the invaluable compound it contained was the result of a life-long, laborious research into the vegetable kingdom of nature; its discoverer, one of the unrecognised benefactors of mankind had terminated his labours only with his life; and the prescription was the sole legacy remaining to his large orphaned family, for whose sole benefit and support it was now vended, retail and wholesale at the "Peace" warehouse, and by all respectable chemists and druggists throughout the United Kingdom of Great Britain and Ireland; that it sold for 2s. 9d., 4s.6d., 11s. and 32s. the bottle, the largest the cheapest: foundling hospitals and orphan asylums allowed twenty-five percent".[291]

This is no figment of a novelist's imagination as an editorial in the Medical Circular shows. After a warning to the "Mothers of enlightened England" to pause ere they administered the soothing dose, it goes on to suggest two unsavoury explanations for the prevalence of the practice. "While the helpless infant is kept in a state of narcotism or unnatural stupor, 'dosing' away its time in its wretched bed or filthy cradle, its unfeeling parent or nurse is too often engaged elsewhere, in scenes of riot and debauchery.[292] It was not only the children of the poor who suffered in this way: "the practice is also common in the families of the middle classes, and covertly, and with impunity, in the mansions of the nobility ...... The motives which induce the practice are of varied culpability, but always censurable". The second alleged motive was indeed censurable, and we would hesitate to accept the editor's unsupported judgment: but similar charges have been made about the Sandgate district of Newcastle in the days of its occupation by the Irish labourers. The editor held that the soporifics were "a common instrument of murder in the hands of the wretched parent ..... the unholy desire of robbing the death club of its burial fee [is] the common cause of this misery and crime".

Godfrey's Cordial was selected for special condemnation on account of the manner of its sale. Like other proprietary medicines it was put up in labelled bottles, but unlike most of the others it was also sent out in bulk: the retailer could obtain a carboy or a cask containing many gallons. This enabled him not only to bottle the medicine cheaply, but also to sell it 'loose' in pennyworths, to his poorer customers (without a stamp of course). Not surprisingly the article concluded "the sale of Godfrey's Cordial, as well as that of "Syrup of Poppies" and other baby poisons, has continued for some years steadily to increase".

All the well-known opium preparations were responsible for deaths at some time. The ethical paregoric was after sold for quietening children. On March 3rd 1845 an inquest was held at Bolton on a child of seven months. The child was illegitimate and was put out to nurse with Rachel Turner at 4s. a week, and was regularly given "sleeping stuff" because it cried at night. The dose was usually a teaspoonful of paregoric, bought from a man who stated that he was a mechanic, but sold drugs and kept a baker's shop. He often made his own paregoric of camphor 30 gr. benzoic acid and opium each 36 gr. oil of aniseed 30 drops and proof spirit a pint: he also sold opium, laudanum, corrosive sublimate, arsenic and various other drugs. Perhaps the most revealing feature of the case was the mother's observation that she had had two illegitimate children previously, had given both paregoric, and both had died.

A witness said that she had had three illegitimate children, all dead before the age of six months, all having had paregoric regularly. At another inquest in Bolton, "sleeping stuff" was prepared by a spinner who also sold cakes: she took a pennyworth of opium, a pennyworth of treacle and a gill of water and boiled them all together. This mixture she was in the habit of selling for children "but not to any great extent".[293]

Two cases of child poisoning were reported at Huntingdon, syrup of poppies having been administered to quieten the children. "Many of these persons who keep small chandler's shops, and sell drugs, are daily labourers, and leave their wives to conduct the business".[294]

The medicine known as 'chlorodyne' excited a great deal of interest, both medical and chemical, and occasional claims and counter-claims concerning its composition. It was invented by Dr. Collis Browne in 1846, and was first used in India: when the inventor returned to this country in 1855 we begin to hear of its use in hospitals, in regular practice and in druggists' counter practice. None of the users could agree about the identity of the original, particularly as to the number of morphine alkaloids present and as to the inclusion of dilute hydrocyanic acid.

The name itself came under fire in 1869 when Dr. Charles Kidd suggested that it meant "green pain".*[295] In November of that year Dr. T.S. Dowse of Charing Cross Hospital attacked the inventor for lending his name to a secret preparation while a registered medical

* The name was coined from chloroform anodyne.

practitioner. Also questionable was the manufacture of the medicine by Mr. Davenport, ex-President, examiner, and member of Council of the Pharmaceutical Society. Dowse guessed the ingredients to be opium, belladonna, chloroform, prussic acid, capsicine, peppermint oil, treacle and perhaps Indian hemp, on the grounds of physiological action (though one of the physiological actions must have been taste).[296]

Published formulae, some based on alleged analysis and others on information about the original, differed in the nature of the ingredients, and differed enormously in the proportions of chloroform and morphia. In an attempt to sort out a confused situation Edward Smith, a Fellow of the Chemical Society, set out first to prove the presence of morphia: the scale of his examination widened until he believed that he had made a complete analysis.[297] The sample showed an acid reaction to litmus, and steam distillation yielded (a) an ethereal solution of oil of peppermint recognised by inflammability and taste; (b) an aqueous layer which reduced acidified dichromate and was therefore identified as containing alcohol, probably from a tincture; this layer also gave silver nitrate tests for cyanides, which taken with the acid reaction pointed to prussic acid; (c) a layer of chloroform; identified by blackening with silver nitrate after boiling. The residue from the distillation had a pungent taste of capsicum, gave the alcohol precipitate characteristic of a gum, and showed a positive test for sugar with potassium copper tartrate. A fresh sample was extracted with alcohol and acetic acid, and the alkaloids precipitated by addition of potash: ferric chloride and nitric acid gave the colour tests for morphine. Scarcely any of the above tests would be accepted nowadays, but the whole represents a masterly attack on a very difficult problem. The chemical evidence did not however resolve the problem, for eight further communications appeared in that volume of the *Pharmaceutical Journal* alone: and indeed the controversy continued to the end of the century. The book of pharmaceutical formulas published by the "*Chemist and Druggist*" in 1902 and based on an edition of 1898 listed no fewer than fifteen rival formulas for chlorodyne.

The product was introduced into more complex preparations, as cough-drops, cough-mixture and lozenges. The warming sweets on sale today under the name of "Victory Lozenges" were originally known as "Chlorodyne Lozenges".

Apart from adding to the general total of opium, or morphine products on the market, the chlorodynes qualify for a place in this chapter on account of poisoning cases which have been recorded from time to time.[248] Sometimes chlorodyne was given by mistake for other medicines: in 1863 a case was reported in which a black draught was prescribed but chlorodyne given instead.

The detection of opium presented great difficulties on account of the complex nature of the substance.[249] It is a brownish-black material, resembling bitumen in appearance, but possessing a heavy spicy odour. If it were simply a matter of identifying a lump of opium, then the smell was sufficiently characteristic, and any doctor or druggist could have given an unqualified verdict. On solution, or recovered from the stomach, the smell was usually masked by others and chemical tests were required. There is, of course, no test for opium with its twenty or more constituents: but it was usually held that a test for morphine and for meconic acid would adequately characterise the drug. Indeed meconic acid itself was probably sufficient, as it was contained in no other natural product but opium, but here a forensic obstacle intervened. If a man died and the analyst found only meconic acid in the stomach the counsel for the defence might ask "Is meconic acid a poison ?".

Three chemical tests for morphine have been accepted, none of them specific when taken in isolation: nitric acid gives a red colour; ferric chloride in neutral solution a blue colour, and iodine is liberated from iodic acid and detected by its blue colour with starch. It can readily be seen that large numbers of organic impurities would interfere with these tests. The last reaction clearly depends upon the reducing property of morphine, and suggests many other sensitive tests. For example, hexacyanoferrate(III) can be reduced to hexacyanoferrate(II) (old style ferricyanide to ferrocyanide) and prussian blue developed with ferric chloride. That the position was never completely satisfactory until the various spectrophotometers became available is shown by the appearance of a paper - as late as 1937 - listing 21 methods of identifying morphine.[300] The general remarks about alkaloids (p. 121) are obviously applicable to morphine.

The test for meconic acid was no more satisfactory, consisting in the development of a red colouration with ferric chloride: it is well known that red to violet colours are given by most hydroxylated compounds, and particularly by those which are also carboxylic acids. There were supplementary tests to distinguish the meconic acid colour from these others, but the skill and experience called for was of a high order.

C.M. Tidy, a doctor by training and a chemist by profession, listed a number of cases in which the chemical tests had failed to detect opium. He concluded that by far the most important consideration was the length of time between taking the poison and death: the delay after death in carrying out the analysis was far less important.[361]

Prussic Acid.

Prussic acid and its salts, the cyanides, are in a class by themselves: the speed with which the poison acts, the high volatility and ease of hydrolysis of any poison left over constitute special problems for the medical attendant and the chemist. On the other hand, the characteristic smell and the existence of two very sensitive tests mean that if the poison is suspected quickly enough, detection is certain. Scheele isolated the free acid in 1782 but for long before that, laurel leaves, bitter almonds and peach kernels had been a source of danger. A communication to the Royal Society in 1731 had this to say: "A most dangerous Poison which was never before known to be so, though it has been in frequent Use among us ....
It has the smell of the bitter Almond, or Peach-kernel, and has been for many Years in frequent Use among our Housewifes and Cooks, to

give that agreeable Flavour to their Creams and Puddings. It has also been in much Use among our Drinkers of Drams (one part of Laurel Water to four of Brandy)".[302]

The occasion of the article was the death of two women. A servant, Martha Boyse, lived with a person who sold this liquid, and obtained some to give to her mother as a very rich cordial. The mother gave some to her sister who kept a shop, and the sister sold some to a customer. The latter died within a few hours. The shopkeeper ran in alarm to old Mrs. Boyse and told her the story. The old lady was so confident of the virtues of the cordial that she drank three teaspoonfuls to demonstrate its harmlessness, sat down in a chair and died immediately.

Scheele's prussic acid contained five percent but there was a wide range of strengths available in the shops: this dilute acid was commonly prescribed by doctors in suitable admixture, and was therefore stocked by druggists. There is much evidence that it was frequently handled without much care. In July 1860 a case was tried before Lord Chief Justice Cockburn in which a young medical student was alleged to have given an overdose to his mother.[303] The chemist from whom the acid was bought deposed that a drachm had been requested: the drachm would contain sixty minims; he did not measure it, but gave what he considered to be one-fourth part of the bottle. The counsel's questions and the chemist's answers ran thus:

Q. "As you say you did not measure it, can you tell us how much prussic acid you really did give to this gentleman ?

A. I cannot say to a drop. I am sure he had fifty drops .....

Q. If you were told to give a patient so many minims, should you give him so many drops ?

A. Certainly not.

Q. Can you tell us the strength of the acid you sold ?

A. I don't know what strength it was. I should think about four percent".

That such a discussion could take place about one of the two most deadly poisons known, indicates that prussic acid poisoning would be far from rare.

On Christmas Eve 1857 an ex-convict was charged with murdering a young woman with prussic acid, which he had obtained from a druggist through the intermediary of a carrier's porter. When questioned as to why he had sold so dangerous a substance through a third party, the chemist replied that it was a regular practice for carriers and their employees to purchase drugs for customers.[304]

The rapidity of death meant that there was not much time to dispose of containers, so that usually a bottle labelled with the name of the poison would be found: this evidence, coupled with the smell about the lips of the deceased was usually acceptable. There were occasions, though, in which the container was labelled with some other name, as yet another example of the hazard of mistaken dispensing. In 1856 a chemist dispensed prussic acid for castor oil: here the evidence was strengthened by the entries in the prescription book which showed that prussic acid and castor oil had been requested on the same morning.[305]

The best test for prussic acid was the formation of prussian blue: the suspected matter was boiled with ferrous sulphate, acidified and treated with ferric chloride. This test was proposed by Lassaigne and reported upon by Thenard, Magendie and Vauquelin.[306] Unfortunately this paper contained a misprint in which ferrous sulphate was described as ferric. Edward Turner called attention to the error in 1828, and said that many British journals had perpetuated it: medical men with slender chemical attainments might attempt the test and fail.[307]

Another useful test was to evaporate some of the suspected material with a little yellow ammonium sulphide with consequent formation of thiocyanate: on addition of a ferric salt a blood red colour was produced. Both these colour tests were extremely sensitive.

Strychnine.

Strychnine, discovered in 1818 by Pelletier and Caventou in the seeds of strychnos nuxvomica and the S. Ignatius bean, shares with prussic acid the reputation of being the deadliest common poison. It is a white powder with a very bitter taste. As with so many other poisons, strychnine was easily available as a vermin killer: "Butler's Vermin Killer" contained five percent strychnine mixed with flour and soot, "Battle's Vermin Killer" (which survived well into the twentieth century) contained twenty-three percent, mixed with flour, sugar and prussian blue, and "Gibson's Vermin Killer" contained half a grain of the alkaloid in each powder.[308] As late as 1889 A.H. Allen reported on two dozen powders sold as vermin killers. The average strychnine content was twelve percent, or two grains in a three-penny packet. "Rough on Rats" was an exception, since it contained only arsenic.[309]

The admixture with soot or prussian blue would in most cases preclude the use of these powders for the purpose of murder: but it is easy to imagine that children would taste them and that suicides would swallow them. In fact the literature of such occurrences is vast, and we can only select a few illustrative cases. In 1857 a surgeon at Seaham Harbour treated a young woman who, after a matrimonial tiff, swallowed a packet of Battle's, two drachms of laudanum and half a drachm of red precipitate: prompt attention with the stomach pump saved her life.[310] Servant girls were prone to the temptation to end their unhappy lives with vermin killer. Thus, an eighteen year old servant in the house of a grocer was detected in pilfering money, forgiven (sic) but discharged: she bought a six-penny packet of vermin killer (this was a double size) at a druggist's and successfully poisoned herself. The ease with which the poison was obtained is further illustrated by the case of the maid of all work aged fourteen, made miserable by her mistress's cruelty, who took a ginger beer bottle to a local shop and obtained threepennyworth of vermin killer.[311]

The visiting medical officer to Stamford Gaol records a case of a woman committed to the prison who took in a packet of Battle's powder under her petticoat and successfully ended her life.[312] Also successful was a packet of "Barber's Magic Vermin Killer".[313]

Such cases do not usually present the analyst with any problem, for the packet or bottle is almost always left. In the range of sample sizes usually available after a poisoning case, three tests for strychnine were applicable. First the exceedingly bitter taste, which obviously was not specific, but was nevertheless extremely sensitive. Also extremely sensitive, and not requiring any elaborate separation was the physiological test on a frog (known as Marshall Hall's test), tetanic convulsions being produced on the presence of strychnine. For the chemist, though, the colour test with sulphuric acid and an oxidising agent proved the most satisfactory. In 1846 Otto had suggested the use of potassium dichromate with sulphuric acid, giving a colour range of blue to violet to red and then to almost colourlessness:[314] an objection to this was the coloured nature of the reagent. Other oxygen producers were the oxides of lead, manganese and chromium, of which manganese was the most effective. Letheby suggested a completely colourless environment for the test by producing the oxygen by way of electrolysis of sulphuric acid. It is clear that so transient a colour range would require complete and thorough separation of the alkaloid from other organic matter. On that score, probably more than any other, failure of the test in forensic investigations would turn.

Failures did occur, and the particular case that attracted most notice was that of William Palmer, the Rugeley doctor who poisoned a betting acquaintance with strychnine, having previously made him ill with antimony. This, like the case of Smethurst, was an unfortunate one for the public image of the analytical chemist. Jacob Bell of the Pharmaceutical Society said of this case the "dignitaries of church and state, senators, learned professors, the notaries of fashion, and the slaves of commerce, took a respite from their ordinary pursuits". Organs and other matter (in a condition which was far from satisfactory, the arrangements having been interfered with by Palmer) were sent for analysis to A.S. Taylor. The analysis involved a search for arsenic, antimony, mercury or other metals, prussic acid, oxalic acid, opium, strychnine, veratrine, nicotine and coniine. Only a small quantity of antimony was found, all other tests being negative. It was known however that the accused had bought quantities of strychnine which could not be accounted for, and that the symptoms of the deceased had been those of strychnine poisoning.[315]

Taylor came in for a great deal of criticism because he appeared to change his mind as the trial progressed. He justified his change of opinion in a lengthy paper in Guy's Hospital Reports, quoting earlier cases in which no poison had been detected in the body but in which the clinical, pathological and moral considerations outweighed the negative evidence: but even Taylor, the principal contender in this forensic struggle, could only say what others had said and were to say again "that the conflict of scientific testimony elicited on this and other points at the trial of this great criminal, has thrown disgrace upon the medical profession, and has created in the public mind a feeling of insecurity in relying upon scientific opinions under any circumstances". It must also be stated that Taylor's first report, in which he mentioned the small quantities of antimony, did not contain any conclusion about the cause of death.[31b]

The important question is why the strychnine test failed, in this and other cases. The usual answer was that the poison was decomposed by the degenerative processes at work in a dead body. However, at the time of the Palmer trial (1856) Letheby put half a grain of strychnine into a dog's stomach and sealed it in a jar: thirteen years later, Tidy was able to recover all the strychnine from the remains. The true explanation is almost certainly that the matter for testing was not sufficiently purified: very many organic compounds (reducing agents) would take up the oxygen upon which the colour test depended. Thus in Taylor's notesof the examination he says that the acidified dichromate turned green, a common reaction with easily oxydised organic matter and perhaps in this case occasioned by the alcohol used in the extraction.

Oxalic Acid.

The risk of accidental poisoning by oxalic acid was high in England for three reasons. First the material was in widespread domestic use for removing stains from linen, for dressing leather and for whitening wood benches, for which purposes it was sold as 'salts of lemon' or 'salts of sorrel'. The second reason was the external similarity between oxalic acid and Epsom salt, the latter being consumed in enormous quantities. The third reason concerned the sale of chemicals by unqualified persons, often in conditions in which errors were almost inevitable. The juryman-chemist in "Pickwick Papers" who asked to be excused attendance in court pleaded: "I've left nobody but an errand-boy in my shop. He is a very nice boy, my Lord, but he is not acquainted with drugs: and I know that the prevailing impression on his mind is, that Epsom salts means oxalic acid: and syrup of senna, laudanum".[317] It will be remembered that the plea failed.

In the section on opium, we have alluded to the sale of narcotic preparations by general dealers: and Taylor, in his report on the sale of poisons in 1864, refers to the sale of poisons by oilmen, grocers and village shopkeepers.[318] Thus it was only to be expected that customers who asked for Epsom salt would often be supplied with oxalic acid. On March 23rd 1849 the rector of Weldon in Bedfordshire was found dead: near the body was a tumbler and a paper marked "Purified Epsom Salts". Analysis proved the packet to have contained oxalic acid, and it could only be concluded that an unknown druggist had supplied the wrong material.[319]

A case which attracted greater attention on account of the coincidence of two unfortunate circumstances occurred in August 1863. A fifty year old labourer was in the habit of taking salts and senna, and one Saturday night on returning from market he and his wife entered a druggist's shop in Holborn and requested a pennyworth of each substance.

Two labelled packets were supplied, but when the couple reached home and opened the packets it was found that neither contained senna: appearance suggested that both packets contained salts. The wife went back to the shop, but finding it closed returned home and gave the salts to her husband, who became ill and died in about ten minutes. When the doctor was called he found that the packets were clearly labelled 'Epsom Salt' and 'Oxalic Acid - Poison', but neither the man nor wife could read. The widow brought an action against the druggist for loss of her husband's earnings, and was awarded one hundred pounds: for although the packets were correctly labelled, oxalic acid had been supplied in place of senna when no confusion of appearance could occur.[320] This case was parallelled by another reported by Christison. An apothecary's lad sold clearly marked oxalic acid for Epsom salt, and the apothecary pleaded that the lad could not read.[321] Publicity and warning did not prevent this kind of accident persisting over many decades. In 1872 two sailors returned from a voyage and asked their landlady to procure two black draughts for them: both became very ill and one died, the draughts having contained oxalic acid in place of Epsom salt.

Because of the ease with which it could be acquired, oxalic acid was a favourite means of suicide. The coroner's returns of 1837-8 show that out of nineteen cases of this kind of poisoning fourteen were suicidal: perhaps because of the proximity to the London market, most of these occurred in Middlesex.[322]

It is surprising that the poisonous properties of the acid were still uncertain in 1814. For some time there was actually a doubt as to whether oxalic acid could reasonably be classified with the other common acids as corrosive poisons.[323] Two exhaustive papers by Christison and Coindet in 1823, fifty pages in all dealt with the mode of action, pathological changes, postmortem indications and chemical tests.[324] A similar, but more restricted, enquiry by Taylor appeared in 1838.[325]

Solid oxalic acid could be distinguished by its crystalline form: for although magnesium sulphate and zinc sulphate were similar, these both left a residue on heating whereas oxalic acid volatilised completely. However the usual spot tests in cases of suspected confusion with Epsom salt were the sour taste and the acid reaction: although not exclusive, in the particular circumstances which usually prevailed these tests were adequate.[326] Calcium oxalate is insoluble in water, so tests with lime water or calcium chloride were soon employed. If these tests were applied by the inexperienced, sulphuric or phosphoric acids might be confused with oxalic. A saturated solution of calcium sulphate gave an almost specific test for oxalate, provided barium and strontium were absent. In general it was not necessary to be very precise about the identification of oxalic acid or its salts: on account of the easily detectable taste, the substances were not commonly used homicidally and therefore the great forensic battles about the interpretation of tests (such as raged over arsenic and strychnine) did not take place.

Poisonous Colours in Confectionary.

In May 1831 The Lancet published a six page paper by Dr. W.B. O'Shaughnessy on the detection of gamboge, lead, copper, mercury and chromate in sugar confectionary. The declared aim of the paper was to lay before the public and the medical profession a calm dispassionate statement of the existence of these poisons in articles designed especially to appeal to children. "I am fully aware of the hazardous task that individual undertakes who ventures in this country to signalise such abuses. The wrath of the particular trade is, of course, especially excited".[327] Accompanied by a medical colleague, O'Shaughnessy had bought as many examples of coloured sweets and cake decorations as he could find: some were expressly sold for eating, others for decoration only. In the tables that follow, only those sold for eating are considered.

Red colours:- 10 samples
2 Cochineal
2 Vermilion
2 Vegetable lakes on alumina or lime bases
1 Red Lead
1 Red Lead + Vermilion
1 Lead Chromate + Vegetable dye
1 Cochineal + Vermilion
6 samples contained poisonous colours

Yellow colours:- 7 samples
4 Gamboge
1 Lead Oxide
1 Naples Yellow (Sb_2S_3)
1 Vegetable Lake

6 samples contained poison

The greens were all prussian blue mixed with vegetable lakes; this was alluded to as "containing no hurtful compound".

The methods of analysis are instructive. First the sample was broken to see if the colour was external or throughout. In the former case, the sweet was washed in a wineglass of water and the liquid separated by decantation: vegetable colours are soluble. If the colour is of mineral origin, the sugar of the sample must be dissolved out in boiling water, leaving the pigment behind. The pigment was to be heated over a small flame, using a piece of mica as a support: in this way mercury could be detected by its alternate blackening and reddening, and by its final volatilisation. Lead salts were recognised by blowpipe tests and by dissolving in nitric acid and reprecipitating with hydrochloric acid: antimony was tested for by means of the orange precipitate with hydrogen sulphide. Most curious was the mode of decomposing prussian blue. This was boiled with a suspension of mercuric oxide until the blue colour disappeared: red specks of ferric oxide were formed and were to be filtered off (though what happened to the excess of mercuric oxide - also red and insoluble - is not clear), redissolved and tested with ferrocyanide.

Clearly these tests were not unequivocal, especially the last, but they certainly served to show up mineral colouring matters which were more likely to be poisonous than not. No copper arsenate was found, and O'Shaughnessy's explanation is revealing. "That description of pigment, as well as Scheele's green, are seldom or never sold pure in the paint shops, but are usually imitated by the carbonate of copper and lime. Thus, fortunately for public health, the dishonesty of one trade affords it some protection against the reckless negligence of the other".

Two years later The Lancet had still to report that "parents, indeed, are but little aware of the fact that the illnesses which they so often notice in their children after eating these articles of confectionary, frequently depend on the action of a mineral or vegetable poison, and not on the indigestion to which it is vaguely attributed".[328] Sometimes the source of the poisoning was difficult to trace, depending as shown above on the adulteration of an adulterant. Indeed it may be that O'Shaughnessy's test for prussian blue depended on the adulteration of his mercuric oxide with lime. The careful and honest dealer was of course at the mercy of his suppliers, as is shown by an account of sweetmeats coloured with apparently harmless sap green dissolved in brandy : unfortunately the sap green (ostensibly prepared from buckthorn berries) was improved with the addition of copper by the manufacturer.[329]

The reports of the Analytical Sanitary Commission[330] did not go much further than the previous reports of O'Shaughnessy in precision of analysis or in the lists of colours encountered, except in the important matter of arsenical colours. They did however name the tradesman from whom the articles were bought, in itself an index of confidence in the analyses. The reports almost dull the reader's imagination with their reiteration of examples of lead, arsenic, mercury and chromate. Two cases will show what was encountered:-

Dog and Hare. 88th sample purchased of A.C. Bowler, 13 Commercial Road.

The nose and ears of the dog, and the tongue of the hare, are coloured bright-red with vermilion. The body is spotted with large patches of gamboge and burnt umber, as also was the figure of the hare which lay as its feet; while the green pigment of the base, of which there was a very large quantity, contained chromate of lead, and consisted of the pale variety of Brunswick Green.

94th sample purchased of Mr. Dunsmore, 17 Middle-row Holborn.

The confectionary of this parcel is made up into a variety of forms and devices, as hats, jugs, baskets, and dishes of fruit and vegetables. One of the hats is coloured yellow with chromate of lead, and has a green hat-band around it coloured with arsenite of copper: a second hat is white with a blue hatband, the pigment being prussian blue. The baskets are coloured yellow with chromate of lead; into the colouring of the pears and peaches, the usual non-metallic red pigment, chromate of lead and middle Brunswick green enter largely: while the carrots represented in a dish are coloured throughout with red oxide of lead, and the tops with the same green. This is one of the worst of all the samples of coloured sugar confectionary submitted to analysis, as it contains no less than four deadly poisons".

It should be noted that the Committee did not consider prussian blue as more than "more or less injurious", while the others were classed as "deadly". Prussian blue was a regular ingredient of green china tea, and large cargoes to the value of £2000 were sent from the Tyne to Canton for this express purpose.[331]

In 1858 another series of reports was published in The Lancet. The summing up at the end of the second report suggested that the effect of the earlier publications had been to lessen the incidence of the worst poisons: red lead, vermilion and copper arsenite were - at least in London - much less frequently encountered.[332] This was probably due to the policy of publishing names and addresses rather than to the raising of standards of public opinion, for the improvement did not extend to other kinds of adulteration. The notorious Bradford case (discussed in our arsenic section) occurred in the same year as the Analytical Sanitary Committee was congratulating itself on the improvement in colouring matters.

When the enlarged edition of Hassall's "Food and its Adulteration" appeared in 1876, a number of simplifications to the methods of analysis were recommended. As a preliminary to the detection of mineral pigments, the sweets were to be ashed, and the organic-free residue tested. This was implicit indication that mercury and arsenic sulphide were not to be expected. For vegetable colours, the changes in tint as the solution was made more or less acid were to be noted, as was also the effect of bleaching agents such as chlorine.

Already however a problem of much greater complexity to the chemical analyst was beginning to appear, though Hassall did not regard it as a problem. "A great variety of colours are now prepared from coal tar, nearly every tint being imitated. Against the employment of these dyes, including the aniline dyes, there is little to be urged, provided they are pure".[333] The control of synthetic organic food colours remains a problem - with many non-chemical overtones - to the present day.

CHAPTER V

THE EMERGENCE OF THE PROFESSIONAL ANALYST.

The techniques and apparatus of chemical analysis could make no impact upon the social scene without a body of men who, on the one hand were trained and qualified, and on the other recognised by public opinion and by legislation. The steps toward the establishment of this position constitute the last part of our study.

The reader of textbook chemistry is likely to know the names of only three British chemists of the eighteenth century, Black, Priestley and Cavendish. He is likely also to know that the first had qualified ~~w~~as a physician, the second was a minister of religion and the third a wealthy amateur, and thus to conclude that there was almost no professional chemistry in this country at the time. This however is to overlook the long practical tradition in English chemistry. In his "Essay on the Importance and Utility of Chemistry", Samuel Parkes wrote "Is your son born to opulence - is he the heir to an extensive domain; make him an analytical chemist, and you enable him to appreciate the real value of his estate, and to turn every acre of it to the best account".[334] Here he was giving expression to a belief held implicitly for nearly two centuries, that chemistry was the key to national and personal prosperity. As long ago as 1663 Robert Boyle showed in his "Usefulness of Experimental Natural Philosophy" the mutual advantages that could accrue to both artisans and philosophers from a scientific study of trades. This view was so readily accepted that Thomas Sprat had found it necessary to tilt at those chemists who sought "to gain the Indies from every crucible".[335]

Since the days of Queen Elizabeth I there had flowed into this country a stream of German metallurgists and assayers, chiefly from the Harz Mountains and the district round Freiberg in Saxony: a German colony was engaged in smelting copper at Keswick in the sixteenth century.[336] Later, the aftermath of the Thirty Years War in Germany, with the consequent need to rebuild a damaged economy, led to the evolution of the chemist-economist of which J.R. Glauber was typical. His six-part book "*Teutschlands Wohlfahrt*" (1656-61) in particular illustrates the attitude of a chemist to the utilisation of natural resources. Such men were known as 'projectors', and a number of them came to England by Royal invitation to investigate the possibilities of metalliferous mining, especially in Cornwall and the Pennines.[337]

Probably the best known of these economic consultants was J.J. Becher whose name is usually associated with the phlogiston theory. He came to England in 1680 to report on the Cornish tin mines on behalf of Prince Rupert, but he also turned his attention to coal tar and the use of water power.[338] Becher and Glauber were both pilloried by J.C. Adelung in his seven volume "*Geschichte der menschlichen Narrheit*": Adelung lumped these pioneers of chemical technology with "Schwarzkünstler, Goldmacher, Teufelsbanner, Zeichen - und Liniendeuter, Schwärmer, Wahrsager, und anderer philosophische Unholden".[339] Nevertheless, their influence was to be seen in eighteenth century England, where a trade in sulphuric acid, copperas, sal-ammoniac and inorganic pigments was firmly established.

A British school of useful chemistry formed itself around William Lewis ("Commercium Philosophico-Technicum" 1763), Robert Dossie ("The Elaboratory laid open, or, the Secrets of Modern Chemistry and Pharmacy Revealed" 1758), Joshua Ward, Peter Shaw, George Fordyce and Peter Woulfe. These, in different ways, occupied themselves with the production of chemicals in commercial quantities and in describing the operations of commercial chemistry. Peter Shaw[340] indeed saw chemistry as "an Art whose Essence is in Action", and joined with Hawksbee in proposing a course of chemical lectures to improve arts, trades and business: among the arts explored were preserving vegetables, making wines and spirits, distillation, extraction of oils, pharmacy, mineralogy, mining, metallurgy and pyrotechny.[341] Similarly Bishop Watson, who entered upon his professorship at Cambridge when he "knew nothing at all of chymistry, had never read a syllable on the subject nor seen a single experiment on it", prefaced the first volume of his "Chemical Essays" with a plea for the improvement of such arts as dyeing, painting, brewing, distilling, tanning, glass making, and the preparation of enamels, porcelain, artificial stone, common salt, sal-ammoniac, salt petre, potash and sugar.[342]

Chemistry thus became firmly established as the handmaid of the useful arts, so that books and popular magazine articles on the subject brought a ready response. The "Lexicon Technicum" (J. Harris, 1710) found a long list of subscribers and such publications as the "Universal Magazine" (1747) carried informative accounts of chemical processes.

A picture from that magazine (Pl. IV) which has become the standard view of an eighteenth century laboratory, shows not the private laboratory of a philosopher but a place devoted to preparation on a commercial scale. It is no surprise therefore that one of the six committees of the Society for the Encouragement of Arts, Manufactures and Commerce (now the Royal Society of Arts, founded 1745) dealt with the place of chemistry in the useful arts. Nor that one of the last events of the century was the creation by Count Rumford and Sir Joseph Banks of the Royal Institution in Albemarle Street "for diffusing the knowledge and facilitating the general introduction of useful mechanical inventions and improvements and for teaching by courses of philosophical lectures and experiments the application of science to the common purposes of life."[343]

This then was the legacy which the nineteenth century inherited from the eighteenth: the aim of chemistry was to make things rather than find out what was in things. It is noteworthy that the first "exposures" of proprietary medicines were in the form of directions for copying the originals, rather than analyses: synthesis was well understood by English chemists. There were many "Operative Chemists" in practice who were familiar with the use of common reagents and apparatus, quite outside the domain of the medical schools, and some of these carried out analyses on behalf of clients.

A typical case is that of F.C. Accum (1769 - 1838), originally trained as a pharmacist and for a year Assistant Chemical Operator at the Royal Institution under Humphry Davy. He later (1803) became Lecturer in Chemistry at the Surrey Institution, Blackfriars Bridge. At his home in Old Compton Street, Soho, he conducted classes in chemistry,

Printed for J. Hinton at ye Kings Arms *in St Pauls Church Yard London. 1747.*

39. A First View of Practical Chymistry, in 1747.

Pl. IV

including the art of analysis and also sold reagents and apparatus.[344] In 1816 he published a book about analytical reagents, "*A Practical Essay on Chemical Reagents or Tests*", and three years later we meet with an example of his analytical practice. A poor charwoman had bought an ounce of green tea, and having infused it she added a teaspoonful of spirit of hartshorn as was her custom. The liquid turned deep blue, and when she complained to her grocer he "took a sample of the suspected tea leaves to Mr. Accum the chemist, who analysed it and pronounced it to contain copper."[345] The demand for equipment and chemicals suggests a volume of analytical work for which it is not easy to find explicit proof. Thus the end paper to the 1811 edition of Samuel Parkes "*Chemical Catechism*" carries an announcement to the effect that Parkes's other engagements would now preclude his attending to the preparation of those chemical tests or reagents advertised for sale in earlier editions, but that they could be obtained from Mr. Phillips in Poultry.[346]

Later this same Mr. Phillips was engaged in providing an analytical service to the public. When Henry de la Beche founded the Mining Record Office at No. 5 Craig's Court, Charing Cross, he sought permission from the Chief Commissioner of Woods and Forests to attach a laboratory for an analytical chemist, where the public might obtain analyses of soils, rocks and minerals at a fixed charge - Richard Phillips being the analyst.[347]

That the public did require analyses and were prepared to patronize analytical chemists is shown by an account of such a laboratory which existed in Newcastle, owned by Dr. Thomas Richardson, pupil of Playfair and Liebig, lecturer at the town's Medical School and founder of the Blaydon Chemical Manure Works. "Thomas Richardson, Assayer and Professional Chemist, Begs respectfully to inform the Manufacturers, Mining Proprietors, Agriculturists etc., of this District, that he has Opened an Extensive and Complete Laboratory where he is prepared to execute Analyses and Examinations of Ores, Soils, Waters, and other Products and to give instruction in every Branch of Chemical Research, on the following Terms:-

Ores, Alloys etc.	10s 6d per Metal
Soils, Manures etc.	10s 6d per Sample upwards
Coals, Clays, Limestones and other Minerals	from £1/1s to £4/4s
Examination of Saline Substances including Alkalimetry and Chlorimetry	from 5s upwards
Qualitative Examination of Water	10s 6d to 21s
Quantitative Examination of Water	£2/2s to £5/5s
Gaseous Compounds and Mixtures	from 21s upwards" 348

These are high prices, particularly in a provincial town, and they suggest that the demand was ~~urgent~~ great.

There were also the specialized demands of the alkali and bleach makers who had to be able to compare their products with those from other regions, and of the assay masters whose offices were concerned with hall-marking precious metals. Apart from the technical developments associated with these requirements (Chapter III) we cannot say that either class of men greatly influenced the public view of the chemist.

From time to time chemists were officially consulted, as when Davy and Faraday were called to report on mining explosions and fires. Of a less spectacular nature, but perhaps of deeper significance to the standing of chemistry, was the employment of Lyon Playfair to test for hydrogen sulphide in the atmosphere of Buckingham Palace, on account of untrapped sewers beneath the building. "I painted a small room on the basement floor with white lead and showed that it was blackened next morning. The kitchens were furnished with batteries of charcoal fires, without flues, and the fumes went up to the royal nurseries. To prove this, I mixed pounded pastilles with gunpowder, and exploded the mixture in the kitchens; the smell of the pastilles pervaded the whole house, and brought down, as I wished, the high court officials to see what was the matter".[349]

The later 1830's saw the presence of chemists in London in numbers sufficient to warrant the idea of a chemical society being discussed. The objects of the projected society were of far-reaching significance to the profession of chemistry and to the status of the chemist. They were "the promotion of chemistry and those branches of science immediately connected with it by the reading, discussion and subsequent publication of original communications".[350] It might have been hoped that the body of chemists, supported on one side by a growing industry and on the other by research into the fundamentals of the science, would have used the new society to establish their position, to make a move both provocative and definitive to which the profession could have looked back as the origin of its being. However the word 'chemist' was not used and the Chemical Society was therefore different from the Royal College of Surgeons or the

Society of Apothecaries. The emphasis was on the activity and not on the composition of the Society. Candidates were to be proposed by three members, personally known to one, and elected by a ballot in which three-quarters of those present should be in favour: but there was no suggestion of qualification in chemistry, or even of elementary knowledge of the subject. In this respect the Chemical Society was not materially different from the various Literary and Philosophical Societies in the country.

Also founded in 1841, and receiving its Charter in 1843, the Pharmaceutical Society seized for its members the opportunity which the Chemical Society had missed: the aims of the Pharmaceutical Society as described in their Charter were " for the purpose of advancing chemistry and pharmacy, and providing an uniform system of education of those who should practise the same, and also for the protection of those who carry on the business of Chemists and Druggists".[351] Here then were three aims, the advancement of the subject, the education of its practitioners, and the protection of the profession, only the first of which was shared by the Chemical Society. A corollary to this situation was that the right to enjoy the title of 'chemist' passed to registered members of the Pharmaceutical Society. The heart of the matter was expressed in the "*Medical Circular*" for 1853: "There is not a word in the English language so frequently misapplied as chemist. A chemist is a man who understands and practises chemistry. To him belongs the investigation of the composition of all material bodies, and their relation with each other".[352]

Even within the chemical industry there was no general agreement about what constituted a chemist, his training or his function. This was largely due to the nature of the nineteenth century chemical industry. For most of the century, the term "chemical works" meant an establishment where salt was converted into soda by the Leblanc Process, the mineral acids and bleaching powder being collateral products. When we consider that a small compact area such as Tyneside could support twenty-four such factories in the 1850's and also that the total United Kingdom production of soda at that time was 133,200 tons per annum, together with 13,100 tons of bleach, (accounting for an annual salt consumption of 137,500 tons)[353] it is ~~obvious~~ likely that ~~most~~ many of the country's industrial chemists were employed in this trade. But what kind of chemists were they ? Table XIV shows the background and training of a number of leading figures in the Leblanc trade, and it is immediately clear that success in this industry does not correlate with formal education in chemistry. What is revealed in the whole is further confirmed in detail. Thus, sulphuric acid for the soda trade was made by the chamber process, a salient feature of which was the twin towers in which the acid was concentrated and denitrified. One of these towers was invented by Gay-Lussac, successively professor at the Ecole Polytechnique, the Sorbonne and the Jardin des Plantes: the other was invented by John Glover who had entered the industry as a plumber engaged in joining up the lead chambers.[354] The difference in their background did not materially affect their contribution to the chemical industry

By contrast Table XV shows that the pioneers of the dyestuff trade were chemists with a formal training, usually with a pronounced German bias, and orientated towards research. The synthesis of new dyestuffs

Table XIV.

Leading Figures in the Alkali Trade

J. Muspratt	(1793 - 1885)	Apprentice pharmacist. Naval Officer
W. Gossage	(1799 - 1877)	Pharmacist
W. Losh	(1770 - 1861)	Studied chemistry at Cambridge: also in Sweden, Germany and France.
J.C. Gamble	(1776 - 1848)	Presbyterian Minister
H. Deacon	(1822 - 1876)	Works trained - encouraged by Faraday
H.L. Pattinson	(1796 - 1858)	Works trained
W. Weldon	(1832 - 1885)	Journalist
G. Lunge	(1839 - 1923)	Ph.D. Breslau
L. Mond	(1839 - 1909)	Student of Kolbe and Bunsen
C. Allhusen	(1806 - 1890)	Merchant : commercial training

Table XV.

Leading Figures in the Dyestuff Trade

H. Caro	(1834 - 1910)	studied chemistry in Berlin
W.H. Perkin	(1838 - 1907)	pupil of Hofmann
P. Griess	(1829 - 1888)	pupil of Hofmann
K.A. Martius	(1838 - 1920)	pupil of Hofmann
I. Levinstein	(1845 - 1916)	studied chemistry in Berlin
Greville Williams	(1829 - 1910)	pupil of Hofmann, Anderson and Playfair
R. Meldola	(1849 - 1915)	pupil of E. Frankland
O.N. Witt	(1853 - 1932)	studied chemistry at Zurich

called for the selected use of known techniques - nitration, sulphonation, reduction and diazotisation - such as could be assimilated from a formal course. Also the growing points of chemical theory, particularly the ideas of valency and structure, belonged to organic chemistry and so theory, experiment, and industrial production could go hand in hand.

The Leblanc process had no theory and very little research: even today it would take a brave man to attempt a mechanism for the production of blackash in a revolving furnace. Such semisolid mixtures as are involved in the equation

$$Na_2SO_4 + CaCO_3 + 4C \rightarrow Na_2CO_3 + CaS + 4CO$$

called for empirical control: the foreman would inspect the surface of the melt and on the basis of colour, the appearance of 'soda candles', and his experience of the past, would judge the right moment to stop heating.[353] The analytical chemist (if the works had one) was confined to the laboratory where his burette and hydrometer assessed the value of the product, but the control of the plant was in the hands of the foreman or senior workman. Many of these rose to positions of high responsibility in the industry, which was only proper according to the prevailing way of thinking in Victorian England. For this was the ~~end~~ era of the self-made man. Samuel Smiles (whose "Self Help" appeared in 1859) was the spokesman for the aspirations of all who intended to "get on": his method was to show, by examples from the lives of notable men, how industry and thrift could conquer every obstacle.

So, in this individualistic, free-for-all alkali trade, where owner and workman were often picking up their knowledge side by side, the great Victorian virtues seemed to be given concrete form. Such descriptions as "works trained" or"came up the hard way" became canons of excellence in themselves without any attempt to compare the results with those of other kinds of training and background. Yet because of its size and its prosperity, it was experience in this trade rather than in the more esoteric dyestuff trade which shaped public opinion about the nature and function of a chemist.

This climate of public opinion had a cumulative effect, in that formal training in chemistry seemed to many to be a waste of time. Roscoe reported that fathers would bring their sons to Owen's College with the request that they might be taught just sufficient chemistry for the trade of a dyer or a brewer or a calico printer. On being told that the boy must study general chemistry for two or three years before beginning upon its applications, the parent would often reply that if that were the system, then he could not afford to have his son waste time in this way.[356] The wider effects of this mood of anti-intellectualism have been examined by Ashby,[357] and further discussed by Houghton.[358]

There was an additional reason for the unhappy public image of the chemist. While industrialists were demonstrating that money could be made in chemicals without formal instruction in the science, and while the pharmacists were establishing their right to the title of chemist, chemistry was being assailed in educational circles as a subject not fitted for serious study.

So far as school chemistry was concerned, the legacy of Liebig had been debased into a mechanical routine of tests performed in a room whick reeked of hydrogen sulphide: the popular name of "stinks" for school chemistry, and the taunt of "test-tubing" at the British Association meetings, showed how low in esteem the subject stood.

At many of the Institutes where chemistry was taught as well as at the Universities, sensationalism was the order of the day, and since the late eighteenth century chemistry had been treated as an amusing subject for dilettantist audiences. Of Dr. Johnson's time it was said that the love of dabbling in experiments infected "parson and prelate, lawyer and scholar, author and schoolmaster, burgess and aristocrat".[359] Isaac Milner's lectures in connection with his Jacksonian Chair at Cambridge were hilarious affairs. "What with him, and what with his German assistant Hoffmann, the audience was always in a high state of interest and excitement. He did not treat the subjects under discussion very profoundly, but he contrived to amuse us and we generally returned laughing heartily at something that had occurred during the lecture."[360]

The Pneumatic Institute in Bristol was the scene of unedifying chemical parties. A distinguished company including Samuel Taylor Coleridge, Robert Southey and Thomas Wedgewood gathered there to breathe nitrous oxide from green bags made of oiled silk.[361] Joseph Cottle, a Bristol bookseller who became publisher to Southey and Coleridge, described the extraordinary behaviour of a Miss M- who, after breathing nitrous oxide from the bag, rushed out into the street, leaping over a great dog which stood in her way. "Dr. Beddoes now expressed a wish to record my testimony also and presented me with his green bag; but being satisfied with the effects produced on others, I begged to decline the honour. The Pneumatic Institute, at this time, from the laughable and diversified effects produced by this new gas on different individuals, quite exorcised philosophical gravity, and converted the laboratory into the region of hilarity and relaxation. The young lady's feats, in particular, produced great merriment and so intimidated the ladies, that not one after this time could be prevailed to look upon the green bag, or hear of nitrous oxide, without horror".[362]

Southey was enraptured with the effect of the gas as an intoxicant and wrote to his brother in 1799 "Davy has actually invented a new pleasure for which language has no name. Oh excellent air-bag ! Tom, I am sure that the air in heaven must be this wonder-working gas of delight".[363] It was not only the Lakeland Poets (the Laureate among them) who took part in such scenes: William Froude conveyed some of the gas from Professor Daubeney's lectures to the austere common room of Oriel College Oxford in the days when the Fellows included John Henry Newman, although there is no record that the future cardinal actually breathed the gas.[364]

Cartoonists frequently lampooned this aspect of chemistry. George Cruckshank's drawing of a laughing gas frolic (Pl. V) appeared as a book illustration: the cartoons of Gilbray (Pl. VI) and Rowlandson (Pl. VII) are well-known, but their contemporary impact cannot have helped the chemist to appear as a responsible professional man. The scene of the Gilbray

Laughing Gas.

Pl. V

One of two illustrations by George Cruickshank for J. Scoffern's <u>Chemistry No Mystery</u>, 1839.

Pl. VI

LECTURE BY DR. GARNETT AT THE ROYAL INSTITUTION.
Davy acting as Assistant. Count Rumford standing by the door.

Pl. VII

Caricatures of popular chemical lecturers and their audiences by James Gillray and Thomas Rowlandson.

picture is the Royal Institution, and in actual fact this Institution (where the staging of children's lectures is still a most important function) did much to foster the idea of chemistry as popular entertainment. Thomas Graham, for instance, recommended to a lecturer that "a small piece of potassium thrown into a glass of water, or upon a piece of ice, never fails to excite a gentle murmer of applause".

The treatment of chemistry in books, too, often tended to obscure the intellectual rigour of the subject. In "Chemistry No Mystery" (1839) J. Scoffern masked a sound approach to the facts by an air of flippancy: a series of lectures was supposed to have been delivered by an Old Philosopher to a village audience in South Devon, and the hearers were promised "I am going to teach you many new games". Chemistry was made to appear as a series of practical jokes (although the maximum of instruction was extracted from each). Such episodes as the strong man act at a fair which had to be abandoned due to a carefully placed stink-bomb, or the lady who used bismuth white as a cosmetic and turned black when she bathed in the water at Harrogate may have been good teaching material but they can have done little to acquire for the chemist a position alongside the doctor or the lawyer.

There were of course official chemists outside the university and teaching systems but these seem to have achieved their positions almost by accident. The 1863 Alkali Act provided for inspection and control of gaseous effluent from registered alkali works. However the Board of Trade was not required to appoint a chemist, but only "any fit and proper person".[366] He in turn could apply "any Test or make any Experiments he may think proper for the purpose of ascertaining the Efficiency of the Condensing Apparatus, or the Quantity of Gas condensed". It was good fortune that led to the appointment of Dr. R. Angus Smith, a consulting sanitary chemist from Manchester, to this responsible post: the impact of Smith has recently been examined by R. McLeod,[367] but the significant fact for our study is that the provisions of the Act did not call for a man of such calibre.

The occasion which first brought the analytical chemist into public view was the passing of the Adulteration of Food Act in 1860. The bare facts are as follows. In 1850 Mr. Thomas Wakley, M.P. for Finsbury, coroner for Middlesex and editor of The Lancet, a man who generated passion and controversy in every sphere in which he was active, set up on behalf of The Lancet an Analytical Sanitary Committee to investigate food additives and substitutes. The work of analysis was done by Dr. Arthur Hill Hassall, who examined all manner of eatables under the microscope and made camera lucida drawings of their structures, and Dr. Henry Letheby who performed the purely chemical tests, particularly on mineral fillers and colouring matters. Reports of the Committee were published in The Lancet[368] and collected in book form in 1855. The result of this enquiry showed that detection was possible, and led to the setting up of a Select Committee of the House of Commons from the finding of which the 1860 Act sprang. The terms of the Act were that Courts of Quarter Sessions were permitted (though not compelled) to appoint analysts: Vestries and District Boards within the Metropolitan area were allowed the same privilege. In 1872 the right to appoint analysts was extended to Boroughs which were separate Police Authorities. The person appointed was to possess "competent medical, chemical and microscopical knowledge".[369] Here then was official admission that the person and function of an analyst existed, but the fact that he was to be a paid servant of the Vestries and Boards lowered his status if he was a chemist: in fact the post was often held in plurality by the Medical Officer of the district. Complaints that the Vestries would see to it that only incompetent or corrupt analysts were appointed were made during the first fifteen years of operation of the Acts. Even before the first Bill became law The Lancet wrote "Doubt is increased by the fact that the parties authorized to appoint the analysts are vestries, district boards and town councils. Now these bodies consist in a great measure of shopkeepers, of whom it can hardly be expected that they should carry out Mr. Scholefield's Bill with vigour and effect".[370] The editorial went on to say that analysts should have been appointed under the Privy Council.

The same allegation was made (presumably by W. Crookes) in Chemical News. "Vestrymen are, for the most part, Tradesmen. Even when the Vestry contains members who are not traders, but men of independent fortune, inspired by a laudable desire to save their fellow-parishioners in their local Parliament, by regulating the number of their gas-lamps, examining the state of their roads, and watching over the salubrity of their domestic arrangements these, being mostly dependent on the minor class of tradesman for their re-election are, naturally, reluctant to give offence to their constituents".[371] Dr. C. Alder Wright, lecturer in chemistry at St. Mary's Hospital described a typical interview between members of a semi-illiterate board and an experienced chemist, in which the board asked questions that were foolish and irrelevant, and sometimes unjust in their implications. "In your experience of cases under the Act did you usually succeed in getting your Clients off ? We always consider that that is more creditable to a man than merely obtaining convictions".[372] He further suggested that the salary paid to the analyst was left wholly to the discretion of those who appointed him, so that by offering a poor salary the authority could ensure that the best man did not apply. This is borne out by a list of salaries published in 1874[373] (Table XVI) in which the figures range from £350 per year at St. Georges Hanover Square Vestry to 2/6 per sample at Wandsworth and Rotherhithe. Wright summed this up accurately. "The low average rate of remuneration is one great cause why the highest class of chemists have, as a rule, not come forward as candidates for such appointments".

The question of the relationship between the fee offered and the quality of the work done was raised again by the same author, this time in Chemical News. "It does not require demonstration that if anyone professes to do analytical work for fees which cannot possibly remunerate a properly qualified man for the expense of his education, he must slur over the work in some way: accurate methods requiring time, labour, and above all skill, are discarded in favour of rough and rapid tests: the work is done at race-horse speed and without due care and attention:

Table XVI.

Remuneration for Food Analysis in the Metropolitan Area.

Fulham:	5s. to 21s. per sample
Greenwich:	£100 per year
Lewisham:	£50 per year + 10s. per sample
Limehouse:	£150 per year
Plumstead:	£50 per year
Rotherhithe:	2s. 6d. to 10s. per sample
Strand:	£100 per year
Southwark:	
(S. John, S. Thomas, S. Olave):	£50 per year
Southwark (St. Saviour):	£105 per year
Wandsworth:	2s.6d. to 10s. 6d. per sample
Westminster:	£100 per year
Whitechapel:	10s.6d. to 21s. per sample.

it is even alleged that occasionally the work is not done at all, the results being simply the offspring of the analyst's imagination". 374 Whether or not this was so the important fact was that some people believed it to be so: the inevitable result was "a rapidly growing distrust of chemists generally and their analyses in the eyes of the public, and a consequent diminution in the state of the professional chemist". Even chemists themselves began to be concerned about the low standard of work. John Pattinson, a consulting chemist in Newcastle addressed the Newcastle Chemical Society on the subject. After discussing the outcry about differing results from different food analysts he said that many of the simple chemical products of Tyneside - soda, sulphur, manganese - were in the same situation. "Large profits have been made by buying soda ash by one chemist's test in one district and selling by that of another chemist in another district". 375

High and low analysts were referred to in the chemical press. An editorial in Chemical News for 1876 spoke in terms of extreme bluntness about the diversity of analysts. "To accuse any professional chemist of incompetence is an exceedingly delicate matter. Yet the fact that "high" and "low" analysts exist, and that they are known and sought after when occasion serves, cannot be overlooked ..... we have heard of a chemist ..... who in alkalimetry used to determine the point of saturation by placing a drop of the liquid upon his tongue, and who generally made every sample from 1.0% to 1.5% better than reality". 376 The account closed with an advertisement for a young man capable of making a thorough chemical analysis of water, competent to direct workmen, must know London well, and have some knowledge of accounts - for a salary of £2 per week. What sort of chemist, it was asked, would combine the posts of analyst, messenger, foreman and clerk for less than the wages of a collier.

The circle was, in fact, becoming progressively more vicious, and the discredited analyst was thus offered lower rewards until " the Public Analyst is paid at a lower rate than a Nuisance Inspector, Surveyor of Roads, or even the Parish Beadle". The British Association was so concerned about the unreliability of analytical work that its 1874 meeting voted £10 to a committee for investigating analytical methods in the chemical manure trade.[377] The committee did not get much support from firms of consulting chemists, for many of those whose results were most notorious refused to divulge their methods.[378]

There was a widespread feeling that only a scheme for organising chemists into a professional body could save the situation. In fact two organisations were formed, one concerned with analysts in particular and the other with the general body of chemists. Before we examine these we must look at the relationship that existed between the Chemical Society and working analytical chemists. An unsigned article in Nature suggested that the Chemical Society was in the best position to supply evidence of fitness to practise chemistry, and that its charter would prove an obstacle to the establishment of any new body:[379] this view was challenged by W.N. Hartley in the same journal, on the ground that examination and training schemes had never been part of the Society's programme. Whatever the intentions of the founders however, the designation F.C.S. was indeed used to hint at professional competence. [Early calendars of this University add F.C.S. to the names of members of the chemical staff].

It was argued that the Royal Astronomical Society with its F.R.A.S. and the Geological Society with its F.G.S. were both known to consist largely of enthusiastic amateurs: but the parallel was not complete because chemistry was an occupation as well as a science. An anomymous writer to Chemical News suggested that Fellows of the Chemical Society should be given one of two further lettered distinctions - C.F. (Competent Fellow) and I.F. (Incompetent Fellow).[380] In general, the right of the Society to admit all who professed an interest in the science was upheld, David Howard pointing out that the Society had honoured itself by admitting "John Dalton, teacher of mathematics and William Herschel, organist". The Chemical Society in fact stood then where it stands now, content with the excellence of its publications, and relying on a large membership to finance them.

The Public Analysts made their own reply to criticisms of their competence. A meeting was held on August 7th 1874 at the City Terminus Hotel, Cannon Street, at which Theophilus Redwood took the Chair. At this meeting there was much criticism of the framing of the 1872 Act and of some of the recommendations of the Parliamentary Committee. Two of these particularly outraged the Public Analysts. The first was that only one teaching institution in the country ("South Kensington" - later the Imperial College of Science and Technology) should be competent to assess the skill of candidates for admission to the ranks of the Public Analysts. But all agreed that certification must come.[381]

On the second vexatious recommendation, that the ultimate referees in cases of disputed analyses should be the chemists at the Inland Revenue Laboratory, some explanation is necessary. The Laboratory was founded in 1842 in connection with the Tobacco Act of that year. Under its Chief, George Phillips (referred to in disdainful terms by Hassall as "Phillips of the Excise") the work was extended to cover other dutiable commodities, particularly ales, wines, and spirits through a subsidiary establishment at the Customs House. The chemical testers were largely drawn from the ranks of excisemen who showed some aptitude for laboratory work and, within the narrow scope of the Laboratory's requirements were efficient enough. But they were in no sense analytical chemists - though the Parliamentary enquiry before the 1860 Act made repeated reference to the 4000 inspectors and 70 chemists; Hassall made great play with these figures when he revealed the adulterations, even to dutiable commodities, which had escaped their notice. In 1874 Phillips was succeeded by James Bell, a former student of A.W. Williamson at University College London, who had worked in the Laboratory since 1846. Bernard Dyer in his account of the early years of the Society of Public Analysts speaks slightingly of Bell, but there appears to be little justification for this. Certainly Bell took a leading part in standardising methods of food analysis (he published "The Analysis and Adulteration of Foods" in

1881 - 83) and also occupied a prominent place in the professional organisation of chemists as President of the Institute of Chemistry.[382] The main criticism should be against the system whereby the analytical methods used by the Excise Laboratory were not published and discussed at meetings of scientific men, and against the impossible mantle of infallibility which the Act required the Principal of the Laboratory to meet.

The outcome of the 1874 meeting was the founding in December of that year of the Society of Public Analysts. Redwood from the Pharmaceutical Society, Hassall the veteran food analyst, Wanklyn the authority on water analysis and Allen the author of "*Commercial Organic Analysis*" were office bearers, and it can be safely said that - outside of the heavy chemical field - all the best analysts of the country were members. Their main object was to exchange information about methods of analysis, legal notes, and the pitfalls to which the work exposed them. Information about authorities paying low fees, or in other ways failing to support their analysts was also to be shared. At first the vehicle of publication was the *Chemical News*, by a personal arrangement with Crookes, but a quarrel over the inclusion of a particular paper ended this arrangement in 1876. The Society then used its own organ *The Analyst*, originally registered in the names of two members as the Society was not at first a corporate body.

Analysts now had a professional body and a journal, but the question of a recognised qualification had still to be settled. It was clear that no University course was directed to the particular ends that the profession required and that the public was entitled to expect.[383]

The Chemical News continued to carry pleas for a tighter organisation within the chemical profession, including the provision of certificates of proficiency and the regulation of professional practice. In March 1876 the paper drew attention to a new kind of danger to the professional chemist unless an organisation was formed quickly: the Board of Trade needed a consultant on water purity and sewage treatment, and although the work involved was largely chemical, they had appointed an engineer to the post. If this was an indication of a trend then control of the profession was urgent. At first it seemed that the Society of Public Analysts might extend its ranks to become a body for general chemists, but the spate of letters that followed the water engineer episode showed that official recognition and certification must be treated as one issue.

In the closing months of 1876 the formation of an Association of Professional Chemists (or an Institute) was talked of at Chemical Society meetings, and early in 1877 the Board of Trade was approached about registration of one of these titles. Officials at the Board of Trade expressed the opinion that the Pharmaceutical Society was already an Institute of Professional Chemists, and its diplomas were a sufficient guarantee of competence. In this the officials showed ignorance of the existence of more than one kind of chemist: on the other hand, the pharmacists had indeed the Pharmacy Act of 1868 to prove their title to the designation of chemist. This Act said that it should be unlawful for any person to "sell or keep open shop for retailing, dispensing, or compounding Poisons, or to assume or use the Title "chemist and druggist" or Chemist or Druggist, or Pharmacist or Dispensing Chemist or Druggist" unless he were registered under the Act.[384] [It should be noted that the name Analytical Chemist was outside the terms of this Act.] To meet this objection, the name of the new body was changed to the Institute of Chemistry, and for the second time a society of chemists had failed to include the word chemist in its title. As it happened, the first subscribers to the new Institute were representative of all branches of chemistry, including pharmacy. Teaching was represented by Professor E. Frankland of the Royal School of Mines, R. Galloway of Dublin and Crum Brown of Edinburgh; pharmacy by John Attfield, professor at the Pharmaceutical Society's school, and M. Cartleighe, examiner in chemistry to the same society; analysts by F.H. Manning, E. Nevill and C.T. Kingzett; and Government bodies by R. Angus Smith, Chief Alkali Inspector, F.A. Abel, Chemist to the War Department, and James Bell, Principal of the Government Laboratory. The President (J.H. Gladstone) and Vice-President (W. Crookes) of the Chemical Society were also among those listed.

Still concerned that there should be no infringement of the Pharmaceutical Society's right to certify competence, the Board of Trade would not allow the Institute to issue certificates of membership or registration, though this was remedied by the terms of the Royal Charter in 1885. In the first volume of <u>The Analyst,</u> the proposed Institute had been welcome as an organisation for conferring status upon the qualified and exposing the impostor, in the face of "the absurd blunders of a number of empirics who have usurped the name of chemist".[385]

In later issues however the tone became critical and hostile: there were suggestions that for purely mercenary reasons the Institute would like to see the Society dissolved, and there appeared such phrases as "the famous self-styled Institute of Chemistry".[386]

From time to time representations were made to the Local Government Board to obtain specific recognition of the Institute's certificates of membership after training and examination, so that only those qualified in this way might receive appointments as Public Analysts. Although the Institute was the only body to conduct examinations covering the whole field of chemical analysis, mineral, metallurgical, organic, toxicological, food and drugs, this concession was not made: it was probably inevitable that it should not be made at that time. However, at the end of the century of our study, the Local Government Board issued to authorities concerned in appointing Public Analysts a circular in which the diplomas of the Institute were specifically, though not exclusively, mentioned. "It will be observed that the regulation requires that every person appointed on or after the First day of January 1900 to the Office of Public Analyst shall furnish such proof as the Board may deem sufficient of his competent skill in and knowledge of (a) analytical chemistry, (b) therapeutics, (c) microscopy .... The Board may state that it would accord with their existing practice to accept as sufficient doumentary evidence of the required qualifications under the Acts, the Diploma of Fellowship or Associateship of the Institute of Chemistry of Great Britain and Ireland".[387] Although the regulation applied only to Public Analysts, always a minority of the total number of chemists engaged in analysis, its supreme importance lay in the fact that for the first time, in a Government document, a qualification in analytical chemistry obtained after training and examination was held to be in the public interest.

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JAMES CROSSLEY ENO
and the Rise of the Health Salt Trade

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JAMES CROSSLEY ENO AND THE RISE OF THE HEALTH SALT TRADE

W. A. CAMPBELL

FOLLOWING an innocent custom which used to prevail, Ward 11 in the Royal Victoria Infirmary was known for many years as the J.C. Eno Ward. It is doutbful, though, if many of those who read the name had any idea of the profound scientific and social changes which lay behind it.

James Crossley Eno was born in 1820 in the Barrack Square, a site now covered by the Leazes Dwellings: here, in a district largely inhabited by carters and cowmen, his mother kept a small general dealer's shop. The commercial hub of Newcastle in those days was in Sandhill and The Side, and young Eno was fortunate enough to serve an apprenticeship to a druggist there; he must have had many opportunities to listen to the talk and observe the habits of the merchants, coal-owners and shipping agents who thronged the neighbourhood. Moreover, physicians and surgeons were beginning to take a more active share in the government of the town, and such men as Thomas Headlam and Sir John Fife would be seen visiting their business friends at the Guildhall, the Exchange and the Mansion House. That such collaboration between doctors and traders did take place—and not always to the pleasure of other interested parties—is borne out by the scurrillous account of one such meeting: "Doctor Headlam and his hat were there, Mr. Fife and his stays, Tom Doubleday, sonnet writer and soap boiler was there, Reid the auctioneer and pawnbroker was there, and the Green-eyed monster was there. . . . . Let the quacks of Newcastle, medical and political, stick to their own business."[1]

Perhaps this introduction to the leading medical society of the town may have influenced Eno in his choice of a post, for when his apprenticeship was completed he joined the staff of the old Infirmary in the Forth as dispenser: this was a reasonably well paid office, bringing him sixty pounds a year as compared with forty-two for the Matron and one hundred for the surgeon. In addition to dispensing prescriptions, he pulled teeth and also did some conservation work; it was said that some prominent citizens carried "Jimmy" Eno's gold fillings for half a century.[2]

The shape of his subsequent career, however, depended on his meeting with Dr. Dennis Embleton, that formidable physician, author, antiquary and naturalist. Embleton was in the habit of prescribing a refreshing, effervescent drink made by stirring into water a mixture of sodium bicarbonate and citric acid, and this preparation would of course have been made up by the dispenser. No doubt Eno heard appreciative comments from the patients, for in 1852 he set up as a druggist at No. 5 Groat Market and commenced the manufacture of the effervescent mixture in the back premises of that address. Such at least is the story as told by Embleton and recounted by Page.[3] It seems clear, however, that Eno started his business a year before Embleton became a visiting physician at the Infirmary, and it is probable that similar prescriptions were in use in a number of places. The site of the old pharmacy in the Groat Market is now covered by the newspaper office, Thompson House.

Eno's experience during his apprenticeship on the Quayside came to his aid, for he pushed the sale of his product by distributing free samples lavishly to the ship captains who traded from the Tyne, and in this way the fame of Eno's Fruit Salt was carried round the world. The business prospered, and its owner was able to buy a large house in Rye Hill, moving in 1865 to No. 5 Summerhill Terrace: his near neighbour at this new address was John Mawson who had joined Michael Faraday's nephew in founding the pharmaceutical firm of Mawson and Proctor, and who met his death in the nitroglycerine explosion on the Town Moor in 1867. Although described in the directories as "chemist", Eno never qualified by examination but proceeded M.P.S. in 1868 under a regulation which covered men who had been in business before that date.[4] Eventually the demand outstripped the capacity of the little premises in the Groat Market and in 1876 Eno moved to London, acquiring a large house and grounds at Dulwich and a factory site at New Cross. He never forgot the debt that he owed to Newcastle, and when in 1899 Sir Riley Lord, as Lord Mayor, put out an appeal for £10,000 to complete the fund for building the new Infirmary, Eno responded with a cheque for £8,500; this, with a number of earlier donations, brought his total contribution to well over £9,000.[5] He died in May 1915, aged ninety-five.

To understand the extraordinary success of the fruit salt, or health salt, trade we have to go back to the seventeenth century. Until the early years of that century only a handful of substances could qualify for the title of "salt" (choosing an unsophisticated definition as mineral substances crystallisable from water). These would include common salt, soda, potash, nitre, alum, copperas, sal-ammoniac, argol and borax, and upon these ancient and mediaeval technology had to depend.[6] About 1624, however, the German chemist J. R. Glauber experienced the curative properties of a mineral spring near Vienna, and isolated from the water, which was bitter and laxative, a new salt which he called sal mirabile; he later (1648) found the same salt in the residues from his process for making hydrochloric acid by acting upon common salt with oil of vitriol, and the salt is now known as Glauber's salt or sodium sulphate. At about the same time, cowherds on Epsom Downs noticed that their cows would not drink the water from a certain spring, and on trying the water for themselves found it, too, to be bitter and laxative. In the 1640's Epsom water became renowned as a medicine, but the active ingredient was not isolated until 1695 when Nehemiah Grew, a physician from Coventry and a pioneer of plant physiology, prepared sal anglice or Epsom salt. In 1698 he took out a patent for its manufacture, and thus Epsom salt is the first true patent medicine: a company was formed in 1700 and a factory opened at Shooter's Hill to exploit Grew's patent.

The fact that both Epsom salt and Glauber's salt were physiologically active and were obtained from mineral springs was to have important social and scientific consequences. The immediate social consequence was that the watering places increased in popularity. The effect was felt not only in such famous spas as Bath, Cheltenham, Tunbridge and Harrogate, whose story has been told elsewhere,[7] but hundreds of small village springs began to be endowed with powers verging on the miraculous. An eighteenth century treatise on the use of mineral waters internally and externally claimed the following list of cures:—"Leprous eruptions, Elephantiasis, Convulsions, St. Vitus's Dance, Histeric complaints, Giddiness, Headache, Toothache, Ruptures, Insanity, Melancholy, Epilepsy, Apoplexy, Rheumatism, Deafness, Gout, Cholera morbus, Jaundice, Stone and Gravel, Thirst, Dropsy, Fever, Lethargy, Universal Debility without any particular disease, Hydrophobia, Hiccough, Hoarseness, Profuse Spittings, Plague, Varicose swelling of the Legs, Diabetes, Violent Fits of Intoxication."[8] The author felt that the reference to curing intoxication needed some justification, and pointed out that sailors restore their drunken shipmates by throwing them into the sea. There were some, however, who recognised that the exercise and strict diet associated with "taking the waters" might be at least as valuable as the actual salts. Dr. Clanny of Sunderland (a surgeon in Nelson's navy, and inventor of a miner's safety lamp) went so far as to suggest that here might be a means of sorting out malingerers from genuine sufferers. "There are many people who apply for admission to hospitals for the sole purpose of living for a few weeks at free quarters—and many who are admitted for real complaints acquire habits of idleness which are soon followed by laziness and a total want of principle; these evil consequences might in a great measure be prevented were mineral waters more generally employed among the diseased poor. In chronic cases the employment of going to the water would keep them in proper exercise, if it was within two or three miles."[9]

The northern countries were by no means behind in this kind of enterprise. Mackenzie, in his "View of Northumberland" mentions saline, sulphureous and chalybate springs with accounts of their healing properties. Longwitton Hall in Hartburn parish, for instance, was "said to have been used with the best effects in cases of scurvy, agues, and sore eyes." The Holy Well at Warksburn was good for "agues, gravel and other obstructions", while Wingates in Longhorsley parish "performed many remarkable cures in scrofulas, external inflammations, stomach complaints, debility, hæmorrhages, etc." At Bingfield near Hexham the curious and doubtful virtue was claimed that "fish or worms put into it instantly expire".

The forlorn hope that such isolated places could be made into attractive spas was not often fulfilled, and the natural disadvantages of the situations were often exacerbated by blunders in planning. Thus at Debdon Wells between Alnwick and Rothbury, a Dr. Thomas Sharp had gone to considerable expense in laying out a bath, but found visitors reluctant to bathe in the waters, "the situation being so much exposed to passengers on the road."[10] Problems of accommodation and recreation were successfully solved at Gilsland: "At the Shaws Hotel there is a good library, which, for a small acknowledgment, is open to the visitors. It contains a selection of very appropriate and amusing books. Drinking the waters, walking, riding, conversation, reading, music, billiards and dancing leave no room for ennui . . . . The amusing studies of Mineralogy, of Botany, and Antiquities may be advantageously pursued at Gilsland."[11]

The best-exploited local spa was that of Shotley Bridge, startlingly declared to cure "a tendency to decomposition". The spring had been known for centuries as the Hally Well, and an old rhyme gave assurance that

> "No scurvy in your skin can dwell
> If you only drink the Hally Well".

In 1837 a Quaker named Jonathan Richardson paved the ground surrounding the well, making three circular steps to lead down to the water, and built a thatched cover supported on rustic poles. (Fig. 1). Next the ancillary services were provided; "The shaded rural seats, the rustic thatched well, the adjoining saloon and reading room where the daily papers are accessible, the convenient bathroom, the carriage drives, the promenades and all the arrangements amid the most charming scenes, prove the proprietor's liberality and are extremely inviting to the visitor". It only remained to furnish a list of cures and these were soon forthcoming. An old man alleged to have been discharged from the Infirmary as incurable and then to have taken the waters for three weeks "completely recovered his strength: . . . A lady from an adjoining town who had been afflicted for years with a stomach complaint which rendered her life miserable, and for which she had spent a great deal of money in vain, visited Shotley to drink the waters, and after a few weeks returned home and continues in excellent health: . . Dr. A. B. Granville, author of 'The Spas of England', bathed in the water at 98°F. and experienced a sensation of clearness in the head (but said this might be due to the purity of the air in that place)."[12]

Fig. 1. The Well at Shotley Spa. circa 1840.

All this was too much for Robert Surtees who had witnessed the inflation of Shotley Spa from his nearby home at Hamsterley Hall, and he parodied the proceedings in his novel "Handley Cross". There he described the enterprise of Roger Swizzle, a penniless apothecary: "Hearing of a mineral spring at Handley Cross which, according to usual country tradition, was capable of curing everything, he tried it on himself, and either the water or the exercise in walking to and fro had a very beneficial effect on his somewhat deranged digestive powers. He analysed its contents, and finding the ingredients he expected, he set himself to work to turn it to his own advantage. . . . . Half the complaints of the upper classes he knew to arise from over-eating and indolence, so he thought if he could originate a doctrine that, with the use of Handley Cross waters, people might eat and drink what they pleased, his fortune would be as good as made."[13]

We have seen that not every spa prospered, and even to those that did came only that small section of the population who could afford a holiday in the country. To spread the trade on a wider front, attempts were made to sell bottled waters in the towns, and some temporary success was achieved particularly during the cholera epidemics: but no British product had the wide sale of, for example, Vichy or Spa waters on the continent. The next step was to evaporate the mineral water to dryness and send the residual salts into the towns so that the purchaser might redissolve them in water in his own home: however, such an evaporation process was slow and costly in fuel.

It is at this point that scientific and social change meet, for while the demand for mineral waters was being fostered by the proprietors of the wells, doctors and chemists were learning how to analyse the waters. The qualitative tests that had been evolved in the eighteenth century (associated particularly with the names of Bergman and Kirwan)[14][15] were supplemented in the early nineteenth century by quantitative methods (due especially to Gay-Lussac and Mohr acting under the impulse of the growing chemical industry).[16][17]. By the mid-century it was possible to state with certainty the identity and proportion of the common metals and acids present in a mineral water. Instead of evaporating the water to recover its salts, it was now necessary only to analyse the water and to mix the appropriate salts from the shelves of the dispensary: the stage was set for the founding of the health salt trade.

In 1857, a druggist named Alfred Bishop had the idea of incorporating unpalatable medicines into effervescing granules: a typical formula contained citric acid, sodium bicarbonate and Epsom salt.[18] These preparations became very popular and were used for administering iron and quinine, but soon people began to ask for the effervescent vehicle without the active drug: in fact, a new craze in pleasant summer drinks grew up, and the medicinal salt was replaced by sugar and flavouring. The lemon-flavoured variety swept the country under the names of Lemon Kali, Al Kali or Sherbert, the advertisement often suggesting an oriental origin. Since the material was often sold in farthing lots by grocers, cheaper substitutes for citric acid were sought. The more reputable makers used tartaric acid, but inferior preparations contained potassium hydrogen sulphate, under a trade euphemism of "Tartraline".

The sale of fruit salts, in common with most other proprietary medicines, was promoted by means of the new technique of newspaper and magazine advertising invented by the soapmakers, and particularly by the firm of Pears. In this respect it is pleasant to record that Eno never resorted to the worst excesses of the pill and potion vendors. In fact his advertisements (written by himself) were so lofty and rarified in tone as to be almost incomprehensible. Where others used short eye-catching slogans Eno set free an avalanche of words, usually culled from writers who made little concession to the reader. On one occasion Lord Lytton was plundered for the following gem:—"This Life is a great Schoolmaster, and Experience the Mighty Volume. It is only through woe that we are taught to reflect, and gather the Honey of Wisdom not from Flowers but Thorns". Cautionary words such as these were often accompanied by some picture such as Figs. II and III, not calculated to turn the mind towards the virtues of fruit salts. Best of all, however, were the unsolicited testimonials contributed by a retired general living at Ascot. "Here stands the cherished bottle on the chimney-piece of my sanctum, at home my household god, abroad my vade-mecum..... I give the following advice to those wise persons who have learned to appreciate its inestimable benefits:—

"When Eno's salt betimes you take
No waste of this Elixir make,
But drain the dregs and lick the cup
Of this, the perfect pick-me-up." [19]

Although we cannot now determine who first thought of making therapeutic use of the reaction between an organic acid and a carbonate, we can be sure that many comfortable

Figs. II & III. Illustrations to Eno's Advertisements fortunes have been built upon it. The current edition of Martindale's Extra Pharmacopoeia contains the names of twenty-two products based on this simple formula.

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Bladders, balloons and gas-bags

Some early techniques in manipulating gases

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The word 'gas' was first used by J. B. van Helmont in about the year 1648 to distinguish a class of aeriform substances which were not condensable vapours. Historians of chemistry have speculated on the etymology of the word, some deriving it from the Dutch 'geest' or the German 'geist' (= a spirit) and others from the Greek 'chaos', a term which Paracelsus had used to denote an air. There is really little need for speculation as van Helmont himself has indicated that the term 'chaos' was in his mind when he invented the name of gas. 'Halitum illum Gas vocavi non longe a chao veterum secreto' [1]. The connexion between the two words becomes more apparent when one reflects that the letter 'G' in Flemish (van Helmont's native tongue) has roughly the same sound as 'Ch' in Greek. Nevertheless this derivation was evidently not known to Walter Skeats when he compiled his famous *Etymological Dictionary*.

Most of van Helmont's preparations were carried out in closed systems, resulting in explosions, a fact which led him to believe that a gas could not be contained in a vessel. Progress in the experimental chemistry of gases depended upon the provision of an apparatus in which a gas might be generated and collected without bursting the vessel; two centuries of evolution from Boyle to Kipp were required before this ideal could be realized [2]. An interim solution was found in the use of bladders which, of course, would expand according to the volume of gas generated. For a period of about a hundred and fifty years, bladders (together with their descendants, balloons and gas-bags) served as receivers, pressure gauges, safety valves and even as gas generators.

A number of forces combined to encourage the emergence of such a technique for handling gases: the work of Robert Hooke and Robert Boyle, itself founded upon that of Evangelista Torricelli and Otto van Guericke, in which air was shown to be a material substance; the inexorable demand for a theory of respiration, due in part to the experiments of Jean Rey, John Mayow and Stephen Hales, and in part to the impasse into which chemical thinking had been brought by the doctrine of phlogistonism; and the discovery (that is the description and characterization) of individual gases, associated particularly with the names of Torbern Bergman, Joseph Black, Henry Cavendish, Daniel Rutherford and Carl Wilhelm Scheele.

Of all the workers in this field, however, Scheele made more consistent use f bladders than anyone else. This may have been due to the extreme poverty f his circumstances which made it impossible for him to supply his laboraory with expensive glass-ware. The familiar picture of Scheele's method for reparing oxygen ('fire air') shows a bladder used as a receiver (Fig. 1). The rrangement was not entirely satisfactory, for the pressure required to distend he bladder sometimes caused a blowhole to appear in the soft glass of the etort. Some purification of the gas was attempted by introducing into the ladder a little milk of lime to absorb acidic impurities.

The bladders were tested before use by blowing up, tying tightly and hangng them up for several days. When Scheele wished to use a bladder in an xperiment he selected one that had remained hard and fully blown up: for ome reason he preferred the animal of origin to be an ox, whereas most orkers prescribed pig bladders. Johann Joachim Becher, for instance, in the ixty-four part diagram of essential chemical equipment appearing in his *aboratorium Portatile* (Part I of the *Tripus Hermeticus*, 1689) depicted a ladder and string, labelling it 'vesica suilla cum volumine chordae sive lamenta'. A century later, William Brownrigg in his work on the comosition of Pouhon Water specified 'a strong swine's bladder' [3].

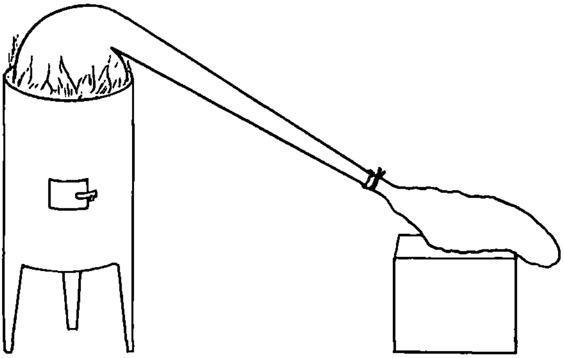

Fig. 1

To prepare a gas by the action of a solid on a liquid (e.g. nitric oxide by the ction of iron on nitric acid) the following procedure was adopted. Some lings of the metal were placed in a bladder previously smeared inside with il, the bladder was squeezed to expel all the air and then tied over the neck f a bottle filled to the brim with acid. The bladder was partially unfolded to llow some filings to drop into the acid and when sufficient gas had been berated the bladder was tied off and quickly removed from the neck of the ottle.

Sometimes Scheele collected gases (he called it 'catching air') in bladders ithout the use of bottles. In these cases some filings were dropped into a ladder as before, but a tight ligature was made immediately above the place where the filings were: acid was then introduced into the second compartment and the neck tied off. When the preparation was to commence, the ligature separating the solid from the liquid was loosened and the two reactants allowed to mix. Carbon dioxide ('aerial acid') was prepared in this way from acid and chalk.

If a gas contained a water-soluble impurity, it could be washed by tying the bladder containing the gas over the neck of a bottle filled with water and passing the water backwards and forwards from the bladder to the bottle. This operation was made more complex than the others by reason of the bottle being corked: it was therefore necessary to remove the cork inside the bladder. The reason for this is not clear, though the practice may have arisen out of the technique of mixing gases in known proportions, when the original gases were contained in separate bladders. This elegant process is best described in Scheele's own words: 'Will ich zweyerley Arten Luft in einem Kolben oder Glas zusammen mischen, lass ich erstlich eben so viel Wasser aus dem mit Wasser gefulletem Glase in die Blase laufen, als ich Luft dem Maasse nach haben will, darauf binde ich das Glas uber eine mit einer andern Art Luft gefülleten Blase, und lasse das übrige Wasser in diese Blase laufen da ich dann, sobald als das letzte Wasser ausgelaufen, sogleich den Kork wieder ins Glas setze [4].' [1]

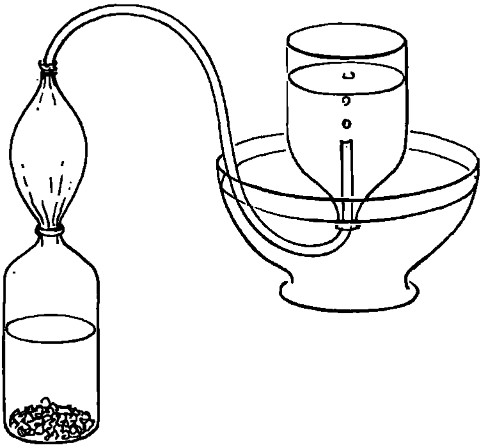

Fig. 2

The use of bladders as a safety valve or as a means of regulating pressure in a system has continued to this day in the form of the balloon on an anaes-

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[1] 'To mix two kinds of air in a flask or glass, I first allow to run from the water-filled flask into the bladder a quantity of water equal in volume to the air that I wish to collect. Then I tie over the flask a bladder filled with another kind of air and allow the remainder of the water to run into this bladder, putting back the cork into the flask as soon as all the water has run out.'

thetic machine. An exactly similar use was described by Priestley in his work on artificial mineral water for the Navy, undertaken as a result of a dinner-table conversation with the Duke of Northumberland when the talk turned to the preservation of fresh water at sea. Priestley's apparatus (Fig. 2) designed for impregnating water with carbon dioxide, was attacked by Dr. Mervyn Nooth. 'In some Trials which I made with Dr. Priestley's apparatus it always happened that the water acquired an urinous flavour.' To this argument Priestley brought powers of controversy sharpened by contests in other fields, asserting with dark inference: 'That Dr. Nooth did produce an impregnated water which he could not swallow without reluctance I am far from doubting, because that might happen from a variety of causes. But that the urinous flavour came from the bladder as such, I will venture to say is not possible [5].'

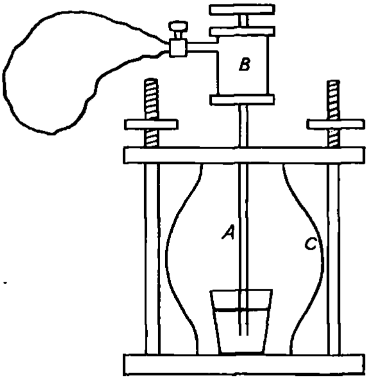

Fig. 3

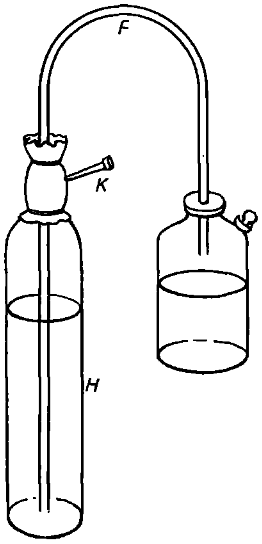

Fig. 4

The first attempt to pass carbon dioxide from a bladder into water under pressure was made in 1803 by William Hazeldine Pepys (Fig. 3). *B* is a 'condenser' (i.e. a pump) through which gas is drawn from the previously filled bladder and forced into the water contained in the drinking glass, by way of the silver tube *A*.

A different kind of pressure regulating device, in fact a rudimentary form of Bunsen valve, was described by Bergman in his essay on artificial mineral waters. The moist bladder joining the tall bottle *H* to the bent tube *F* in Fig. 4 was pierced with a needle *K*. 'Praeterea collo tuboque alligatur vesica madida, ut vi quasi retineatur erumpens aura, cavendum tamen est, ut nimium intendatur resistentia, quum in hoc casu nullum provocatur acidum aereum, ideoque foramine acu *K* facile claudendo, pro re nata temperetur oportet exitus [6].'

Before the introduction of vulcanized rubber tubing, bladders were cut into small pieces and used for joining glass tubes. The practice was in vogue for more than a century; Stephen Hales had used slips of bladder in his botanical experiments, and Robert Dossie, Charles Rivington Hopson and Michael Faraday all testified to the value of the material for this purpose. Faraday, with characteristic thoroughness, explained its use in detail: 'Moistened bladder is in constant requisition in the laboratory for closing joints; when soaked for some time in water, till it becomes clammy, it is very adhesive, and adheres well to glass. It should be cut into strips of the proper size, and then applied as a bandage to the place. It does not always require the application of twine to keep it in its situation, so that occasionally, when inconvenient, tying may be dispensed with. If after being soaked it be wiped dry with a cloth and then moistened with white of egg, its adhesion is increased, and the use of twine rendered quite unnecessary [7]. That the tying of joints could be a chore to be avoided is indicated by the space devoted to 'chemical knots' in several practical books of the early nineteenth century. Karl Friedrich Mohr gives several pages of illustrations of appropriate knots in his *Practical Pharmacy*. They are not original, having been taken from a manual of seamanship: the 'pyrotechnical knot', for instance, was merely the common clove hitch [8].

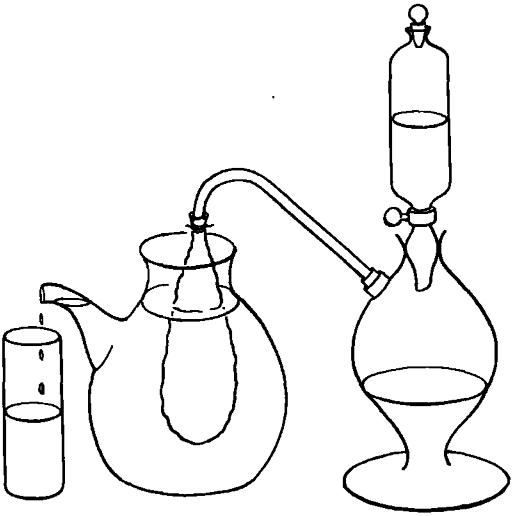

Fig. 5

An unusual use of bladder as a measuring device is to be found in Sir Humphry Davy's apparatus for soil analysis (Fig. 5). Calcium carbonate was estimated by releasing carbon dioxide from the soil by addition of hydrochloric acid. The gas distended a bladder immersed in water and the amount of water displaced was measured in a cylinder. Davy estimated two grains of calcium carbonate for every ounce of water displaced. If the quantity of gas were ever sufficient to stretch the walls of the bladder, the pressure would increase and Davy's simple relationship would no longer obtain.

The claim that gases prepared or collected in bladders acquired an unpleasant taste took on a wider significance as the practice of inhaling 'factitious airs' in the course of medical experiments became widespread. The famous Pneumatic Institute at Bristol, in which the young Davy did his work on nitrous oxide, was founded by Thomas Beddoes to foster investigation into the medical properties of gases. Matthew Boulton and James Watt, partners in the great Birmingham engineering works, constructed the equipment required by the Institute, including bags of oiled silk 'commonly made to contain from twenty to twenty-four ale quarts of air'. It was claimed that these were more convenient than bladders and free from the objectionable taste, a claim which was rejected by Cavallo: 'The principal imperfection of these bags consists in the smell of the oiled silk, which proves nauseous and almost intolerable to delicate persons [9].' Later, Watt invented a process for ridding the bags of their smell, making use of the absorptive power of charcoal which was sifted through the material. There is no record of the use of charcoal to decontaminate bladders; these were usually treated with salt solutions, and finished off with spirit of wine.

Other pieces of equipment made by Boulton and Watt included brass connecting pieces and stopcocks to be tied into the neck of a bladder or gas-bag. As late as 1877, the London firm of Griffin offered such connecting pieces for a shilling each; at the same period a bullock's bladder cost sixpence and a sheep's twopence, a caution being added that these ought to be washed periodically in glycerine and water to prevent cracking. In this respect, oiled silk bags were not noticeably superior to bladders, as Watt had to warn his customers: 'When the silk bags are not in use they should be hung up by a string tied to the neck of the faucet; folding or creasing them is hurtful [10].'

In spite of smell or taste, a distinguished company, including Samuel Taylor Coleridge, Robert Southey and Thomas Wedgwood, gathered at the Pneumatic Institute to breathe from the green bags. Joseph Cottle, a Bristol bookseller who became publisher to Southey and Coleridge, described the extraordinary behaviour of a certain Miss M—— who, after breathing nitrous oxide from the bag, rushed out into the street, leaping over a great dog which stood in her way. 'Dr. Beddoes now expressed a wish to record my testimony also and presented me with his green bag; but being satisfied with the effects produced on others, I begged to decline the honour. The Pneumatic Institute, at this time, from the laughable and diversified effects produced by this new gas on different individuals, quite exorcised philosophical gravity, and converted the laboratory into the region of hilarity and relaxation. The young lady's feats, in particular, produced great merriment and so intimidated the ladies, that not one after this time could be prevailed upon to look at the green bag, or hear of nitrous oxide, without horror [11].'

Southey, however, was enraptured with the effects of the gas. He wrote to his brother in July 1799: 'Oh Tom! Such a gas has Davy discovered, the gaseous oxyde! Oh Tom! I have had some; it made me laugh and tingle in every toe and finger tip. Davy has actually invented a new pleasure for which language has no name. —Oh excellent air-bag! Tom, I am sure the air in heaven must be this wonder-working gas of delight [12].' It was while working with the 'green bag' that Davy discovered the anaesthetic properties of nitrous oxide, though the discovery was overlooked for nearly forty years until Horace Wells, an American dentist, demonstrated its usefulness in dental surgery.

A typical scene at a lecture on nitrous oxide was depicted by George Cruickshank in one of the illustrations which he contributed to Scoffern's *Chemistry No Mystery* (Fig. 6). If it is difficult to imagine the Lakeland Poets taking part in such a frolic (the Laureate among them) it is even harder to believe that similar frolics took place in the austere common room of Oriel College, Oxford, in the days when the Fellows included theologians as eminent as John Henry Newman. Nevertheless, the gas was brought from one of Professor Daubeney's lectures by William Froude, and introduced to the senior members. There is, however, no record that the future cardinal and founder of the Oratory actually partook of the gas [13].

The invention by Macintosh and Hancock of methods for waterproofing cloth made available a new material for gas-bags, though neither this material nor oiled silk possessed the elasticity of bladder. Bags made from waterproof cloth were employed less for medical and philosophical experiments than as containers for air or oxygen for use with the blowpipe. For this purpose they could be purchased fitted with pressure boards to maintain a steady wind supply. They were also used to supply oxygen for limelights in connexion with public lectures and theatrical performances, bags for this purpose having a capacity of up to eighteen cubic feet.

Balloons were offered for sale in the middle of the nineteenth century, but these seem to have been toys inspired by the recent aeronautical experiments rather than substitutes for bladders in scientific work. Thus a spherical balloon, said to rise with hydrogen but not with coal gas, cost one shilling; for thirty-five shillings one could be purchased in the shape of an elephant and for sixty-three shillings in the shape of Mr. Punch, six feet high and nine feet in circumference [14]. These balloons were made of goldbeater's skin, usually coloured and pleated in gores, and were therefore practically non-elastic.

Some of the traditional applications of bladders persist to this day, with the substitution of rubber balloons for earlier materials. For instance, the popular lecture demonstration of the density of hydrogen was first made by Joseph Black, using an amnion [15]. In the course of some physiological experiments,

Fig. 6

carried out on behalf of the Medical Research Council in 1953, members of the British team which climbed Everest were required to blow up balloons after great physical exertion in order to furnish evidence about the efficiency of oxygen–carbon dioxide exchange in the lungs. Lastly, workers who handle radioactive materials are sometimes asked to provide samples for breath analysis in a similar fashion, and in some countries the motorist charged with drunken driving is encouraged to pay his silent tribute to the pioneers of pneumatic chemistry.

Acknowledgment

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THE DEVELOPMENT OF QUALITATIVE ANALYSIS FROM 1750 TO 1850 PART 1

BY

W. A. CAMPBELL AND C. E. MALLEN

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THE DEVELOPMENT OF QUALITATIVE ANALYSIS FROM 1750 TO 1850 PART 1

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W. A. CAMPBELL AND C. E. MALLEN

When Wurtz coined his epigram "La chimie est une science francaise; elle fut constituee par Lavoisier d'immortelle memoire" he considerably overstated his case. It might be said with a good deal more truth that qualitative analysis is a Swedish science, founded by Torbern Bergman. For although due honour must be given to the pioneer work of Libavius, Tachenius, Kunckel, Boyle, du Clos, Pott, and Marggraf, who described tests for particular substances, it was Bergman who first organised the tests into a systematic procedure. The first texts of qualitative analysis, as the term would be understood by a present day analyst, are Bergman's two essays (1779, 1780) "De analysi Aquarum" and "De Terra Gemmarum".

In the eighteenth century, analytical chemistry was mainly practised by mineralogists and metallurgists, and flourished in those places where there were progressive mining industries. A. E. Nordenskjold (1880) writing on the history of Swedish natural sciences said "It was natural that a certain practical skill in distinguishing minerals and ores should speedily be developed in a country so rich in mines as Sweden". Similarly, analysis lagged behind in countries where mineralogical enquiry was looked down upon. We find Thomson (1836) p.353, lamenting that "the department of analytical chemistry, and even mineralogical investigations in general, have been sneered at by several chemists in this country, as a branch of chemistry below the notice of men of true science".

The object of the present study is to trace the development of qualitative analysis up to Fresenius, later editions of whose "Chemical Analysis" are still in use. In this preliminary survey. we outline the scope of the field, show some typical systems in modern tabular form, and draw certain conclusions about the factors which seem to have determined the lines of development. For while there is no lack of excellent biographical material concerning Bergman, Klaproth, Vauquelin and Stromeyer (*see* Weeks, M. E. ,1939 ; Bugge, 1929, and Ferguson, E. G., 1941) little space has been devoted in the standard literature of the history of chemistry to the analytical methods introduced or employed by these workers.

The qualities that are nowadays considered desirable in an analytical procedure are :

(i) it should be specific for the substance sought or at least highly exclusive.
(ii) the chemical changes involved should be easy to discern.
(iii) it should be economical in time.
(iv) the procedure should give practically quantitative separation.

In practice, the analyst's skill and judgment are shown more by his choice of a suitable qualitative test than by its mere execution. The vast amount of work on spot tests carried out in recent years has brought us nearer to the ideal of having a reagent for each ion, sensitive to minute quantities of the required ion and insensitive to all others.

Few analytical methods available in the eighteenth and early nineteenth centuries had the properties mentioned above. Separations were rarely sharp, and the operator was usually content if he could precipitate the greater part of the desired element. To achieve even this often called for the skill of a tight-rope walker as the following quotation from Thomson (1836) p.370 shows, "Unless we add ammonia in excess, the precipitate which falls is apt to contain muriatic acid, and is in part redissolved again while we are washing it on the filter. But we should avoid a great excess of ammonia, because it might dissolve a portion of some of the substances at first precipitated". On a neighbouring page there are references to magnesia being " partially precipitated " and " a portion of the magnesium " remaining in solution. There is also described the separation of iron from manganese by a method due to Herschel " which is apt to fail, unless we are very careful of the quantity of ammonia added ; a very little too much throws down manganese along with the iron ".

The analyst's time was not the costly factor that it has since become : it is not surprising therefore to find tests prescribed that require the setting aside for several hours of the solution under examination. Such a test is that described by Vauquelin (1799) p.81, for distinguishing aluminium from beryllium by the formation of crystals of alum. "La combinaison de l'alumine avec l'acide sulfurique donne, par l'addition de quelques gouttes de sulphate de potasse, des cristeaux octaèdres d'alun. La glucine . . . . . ne fournit point d'alun avec l'acide sulfurique et la potasse". We have repeated this test, and find that even normal solutions require 2-3 hours, whereas 0.5 normal solutions require about 18 hours. It would seem that a full 24 hours would have to elapse before the result of such a test could be pronounced negative.

Because most of the specimens submitted for analysis were of mineral origin, one of the greater difficulties encountered by the early workers was that of bringing the substance into solution. Cronstedt, whose " Mineralogy " appeared in 1758, avoided this difficulty by working upon the mineral in the solid state. He, with von Swarb in Stockholm and Engestrom in London, drawing largely upon methods described by Cramer of Leyden, initiated systematic blowpipe analysis. This mode of examining metallic and earthy bodies was further perfected by Berzelius, who in turn borrowed copiously from the benevolent but indolent Assessor Gahn. Even when wet methods of analysis had reached a high state of development, the blowpipe often remained the only satisfactory way of deciding between several metals precipitated by the same group reagent. Thus, Thomson (1836) p.371, having precipitated nickel, cobalt, manganese and zinc as sulphides says " The easiest way of determining the nature of the metal in these precipitates is to test them before the blowpipe ". Berzelius (1840) also, having tested his solution with hydrogen sulphide, would submit any precipitate which might be formed to the blowpipe " which provides the best and most certain signs by which inorganic bodies are recognised ". It might be remarked in passing that Berzelius in this context gave a definition of qualitative analysis that is the quintessence of understatement. " In carrying out a qualitative analysis, it is necessary to look for all those substances that one suspects may be present in the mineral, and then to prove that it does not contain any others ". This, surely, is on a level with Percy Scholes' definition of organ playing as " the art of putting down the right notes and holding them for the right length of time ". That Berzelius held the blowpipe to be one of the most important pieces of equipment in the laboratory is shown by Wohler's (1875) account of the apparatus that he was required to provide when he joined the famous Stockholm laboratory in 1823 ; "Ich bekam für meinen alleinigen Gebrauch einen Platintiegel, eine Waage mit Gewichten, eine Spritzflasche, und musste mir vor allem eine Löthrohr anschaffen, auf dessen Anwendung Berzelius grossen Werth legte ".

But while blowpipe analysis was being brought to such a high degree of perfection, Bergman (1780) pp.72-117 was approaching the problem of rendering minerals soluble. He powdered his mineral finely, mixed it with sodium carbonate and ignited it strongly in an iron crucible for 3 or 4 hours. After extraction with hydrochloric acid, the insoluble portion might be silica or might be undecomposed mineral. It was Klaproth who showed that the analysis is invalid if any of the mineral remains undissolved. He achieved complete solution by using, where necessary, more powerful fusion agents such as caustic potash, and by repeated evaporation of the hydrochloric acid extract with small quantities of acidified water. More and more however, it came to be realized that the most important factor in obtaining complete solution was particle size.Thomson (1836) p.36 tells a cautionary tale of two students to whom was given a Brazilian chrysoberyl for analysis. One was at great pains to powder his portion as finely as possible, and achieved complete solution, finishing the analysis in a few days : the other, less attentive to detail, did not spend long enough over his pulverisation and found that fusion and extraction were of no avail, so that "after spending a great many days in these disagreeable repetitions he was unable to render the mineral soluble in muriatic acid, and gave up the analysis in despair". Vauquelin (1799) p.71, in his essay on the analysis of stones says " La pulvérisation est donc le premier travail qui doit occuper l'artiste, et quoique mécanique, il éxige des précautions assez grandes ".

During the period when mineralogists and assayers were busily investigating the composition of the earth's crust, another influence was at work upon analytical chemistry, namely the recrudescence of interest in the spas and watering places. With the revival of the practice of taking the waters, marked in England by the increased popularity of Bath under Nash, came an awareness of the need for accurate chemical knowledge of the mineral contents. Even the celebrated Dr. Black (*see* Ramsay, 1915) was prevailed upon, in 1770, to examine the water from a spring at Coxlodge, to the immediate north of Newcastle upon Tyne, and reported that it should " draw strong and deep coloured infusions from tea, malt and other vegetables ". This kind of analytical problem focussed attention on to the wet methods of testing for acid radicles, such as had been described by Bergman, but which had been overshadowed by the dry tests carried out upon minerals. The dry test for a nitrate, for instance, consisted in throwing the substance on to glowing charcoal and observing if any local increase in the rate of combustion occurred : this test had been used by John Mayow (1674) and continued to be described by Rose and Fresenius. The latter also heated his solid nitrates with powdered potassium cyanide, a test which we have found to result in a most gratifying explosion. Bergman (1779,) p.127, on the other hand, tested for nitrates in solution by the appearance of brown fumes on adding sulphuric acid ; " Adfusione acidi vitriolici concentrati nitrosum, ubi adest, expellitur, particulari odore et fumo rubro dignoscendum". Wet tests for sulphates and chlorides had of course been known since the time of Boyle. The reagent, as a chemical tool, was now coming into its own. Wiegleb had shown how to distinguish between iron, copper and zinc by means of Prussian alkali (*see* Hopson, 1789), and Brande (1821) gave a long list of coloured precipitates obtainable with potassium ferrocyanide, hydrogen sulphide and ammonium sulphide.

All chemical literature during this period suffered from the lack of a standardised nomenclature, but perhaps analytical literature with its need to impart precise directions, suffered more than most. As examples of misleading names we may quote the following from Bergman ; Sal ammoniacus fixus (Calcium chloride), Tartratus vitriolatus (Potassium sulphate), Sal acetosellae (Potassium hydrogen oxalate). Even when not actually deceptive, the names were often unwieldly, the more so when there were no formulae or equations to summarise the wordy explanations. Examples are Terra ponderosa salita (Barium chloride), Alkali minerale vitriolatum (Sodium sulphate) and Alkali volatile aeratum (Ammonium carbonate). It is all the more surprising to find occasional alleviations of the general turgidity of style that this kind of nomenclature engenders, as when Bergman (1779,) p.99, describes the " most beautiful blue " of a cuprammine ; " Cuprum omne dejectum, si alkali volatile abundat, iterum solvitur cum colore cyaneo pulcherrimo ". Nearly forty years after Lavoisier's noble crusade to clean up chemical terminology Griffin (the founder of the scientific instrument firm) could write in the preface to his translation of Rose's textbook (*see* Rose, 1831) " it is by no means a common opinion among chemical students in England, that Chloride of Ammonium is synonymous with Muriate of Ammonia ", Rose's work incidentally is unrelieved by formulae, while Fresenius uses them only in paragraph headings. There was of course confusion about atomic and equivalent weights so that different formulae were used by different chemists.

Another strange feature of early analytical procedures is the frequent appeal to the sense of taste. A residue of silica on a filter paper was judged to be washed clean when it no longer tasted of hydrochloric acid. Beryllium salts were distinguished from those of aluminium, in Vauquelin's essay, by their sweet taste, and Klaproth (1789) recognised alumina in chrysoprase by the fact " qu'elle avoit bien la saveur doucereuse et en memetems styptique de l'alun ". On the subject of recognising the constitutents of mineral waters by taste Berzelius observes slyly that the fact that a substance has a peculiar taste early in the morning depends on the state of the tongue and proves nothing.

We append tables to show the usual procedures adopted by Bergman, Klaproth, Thomson, Berzelius, Rose and Fresenius, but it should be remembered that the methods were varied according to the kind of substance under examination. Both Rose and Fresenius in their prefaces, reminded readers that any scheme of analysis must be regarded as a suggestion for dealing with simple problems, and that the experienced analyst should draw on his store of knowledge for an appropriate mode of investigating complex substances. Neither of these great pioneers, in fact, would have given any credit to a student who " worked through the groups " in an unimaginative way.

The table showing teacher-pupil relationships is merely a guide, for there were many cases similar to those of Berzelius and Gahn, or Scheele and Bergman where, as Retzius remarked, it was difficult to know " who was docens and who discens ".

Subsequent communications will deal with blowpipe analysis, water analysis, the national contributions, and with nomenclature.

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Table I. Principal Workers in the Field of Qualitative Analysis

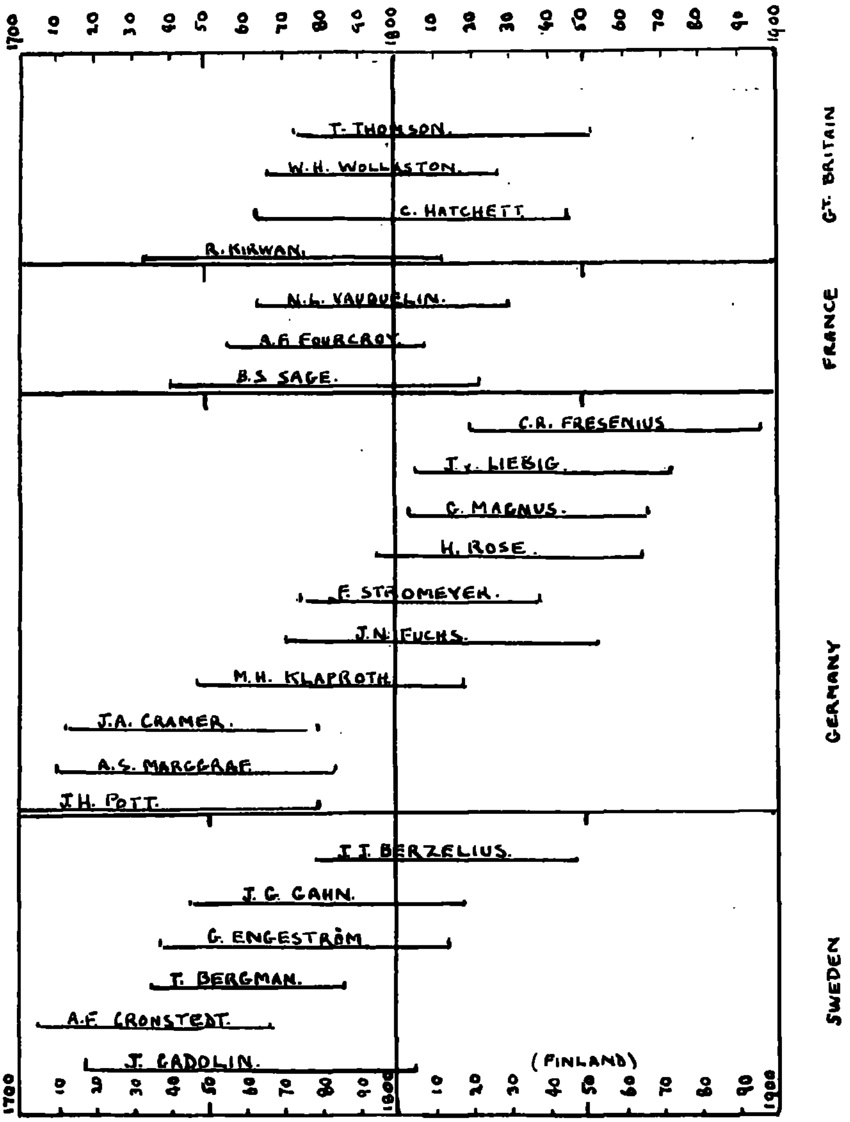


Table II. Teacher-Pupil Relationships in the Swedish, German and French Analytical Schools

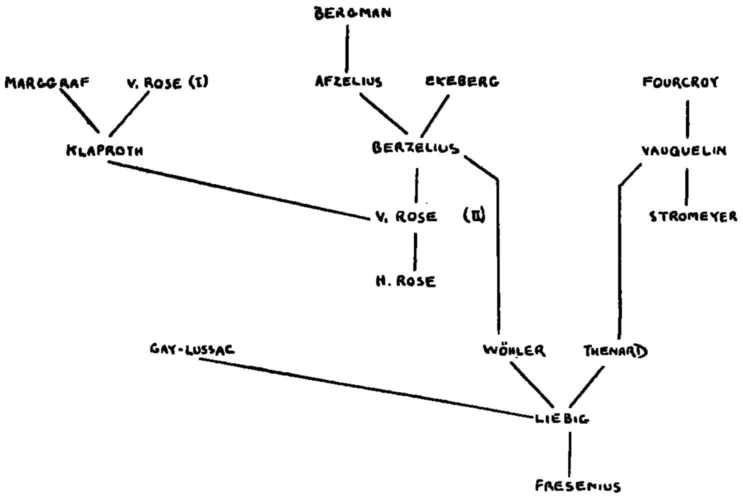
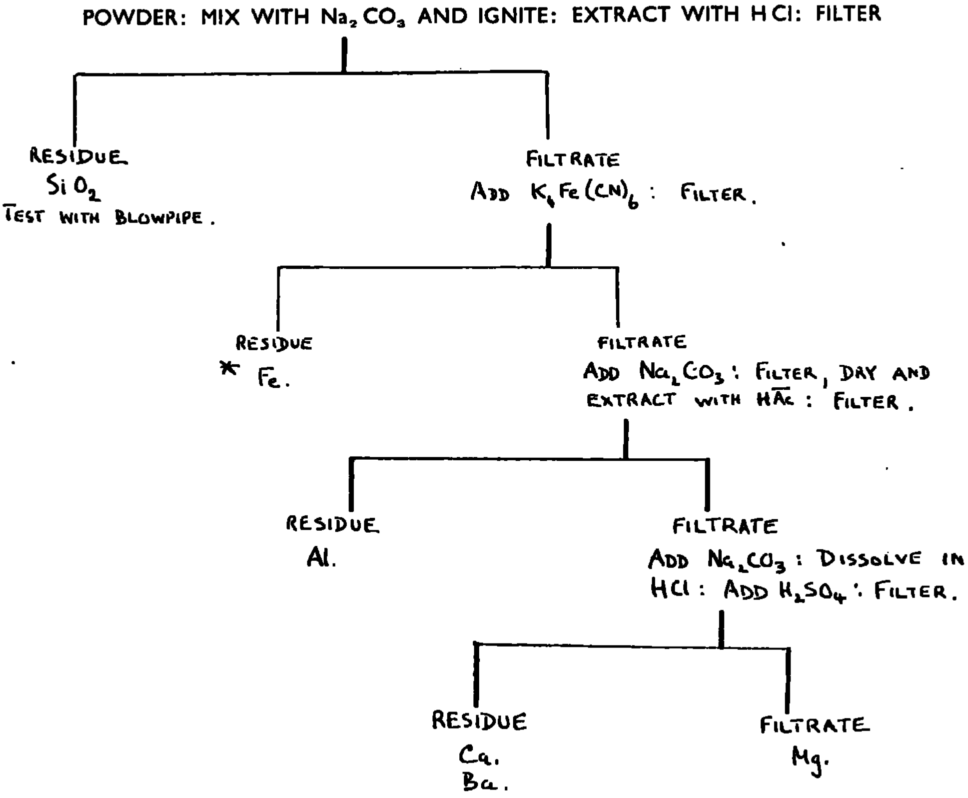


Table III. Bergman's System for Analysis of Stones



*Note Poor Separation of Iron by Precipitation as Prussian Blue

Table IV. Klaproth's System for Analysis of Stones

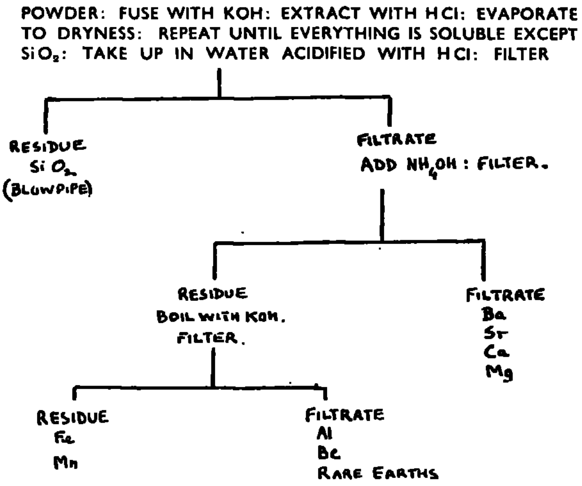
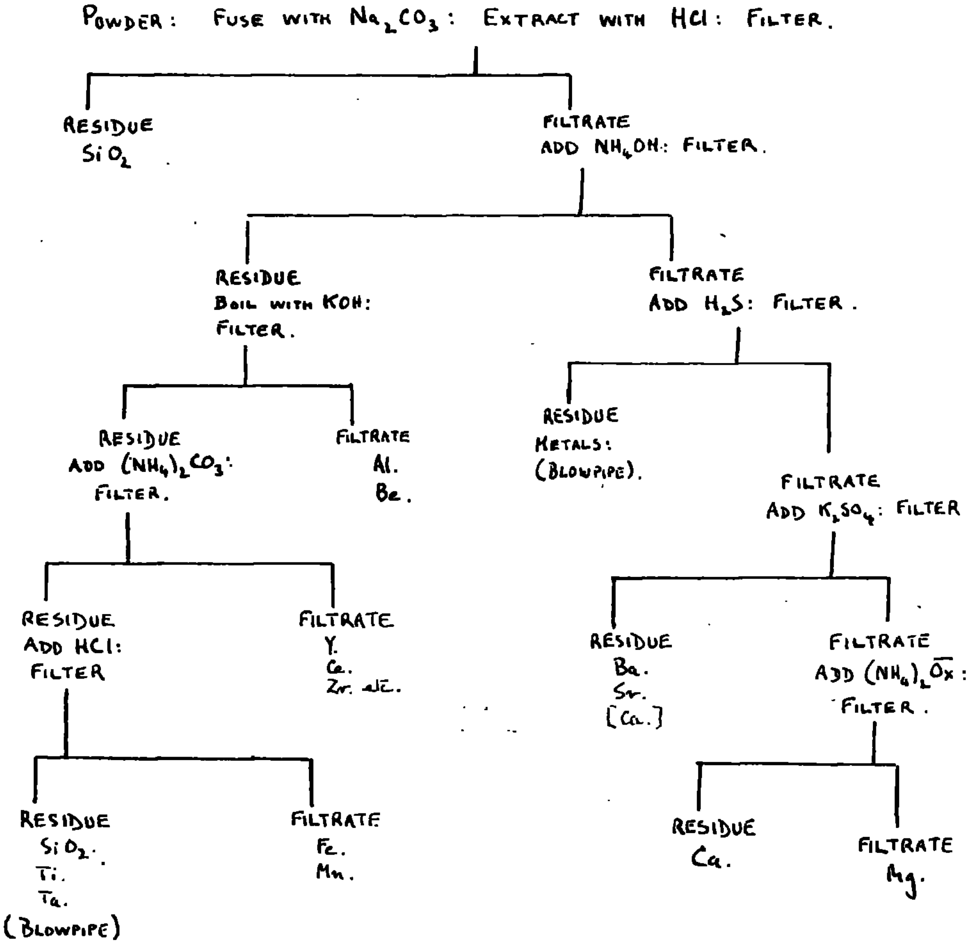


Table V. Thomson's System for Mineral Analysis



[*Note Incomplete Separation of Manganese. Table VI]

Table VI. Berzelius's System for Mineral Analysis

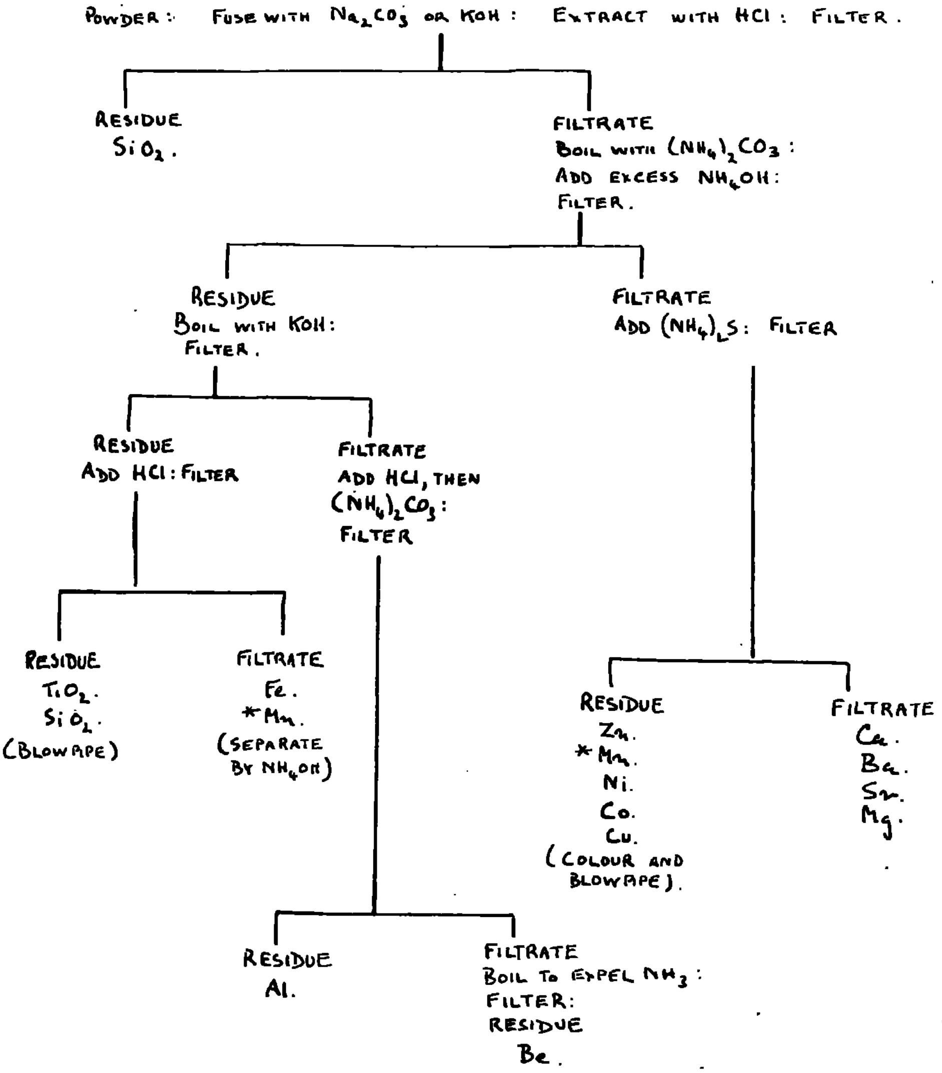


Table VII. H. Rose's General System for Qualitative Analysis

1	K	9	Mn.	17	Bi.	25	Sb.
2	Na.	10	Zn.	18	Cu.		
3	NH_4	11	Co.	19	Ag.		
4	Ba.	12	Ni.	20	Hg.$^{+}$		
5	Sr.	13	Fe^{++}	21	Hg^{++}		
6	Ca.	14	Fe^{+++}	22	Au.		
7	Mg.	15	Cd.	23	Sn^{++}		
8	Al.	16	Pb.	24	Sn^{++++}		

Note that As is not included among the metals, nor the possibility of its being precipitated in Group I mentioned below.

Dissolve the substance, and make the solution acid :

I add H_2S.

Black	Precipitate	Indicates	16-22
White	„	„	14
Yellow	„	„	15, 23, 24
Red	„	„	25

II Add $(NH_4)_2S$.

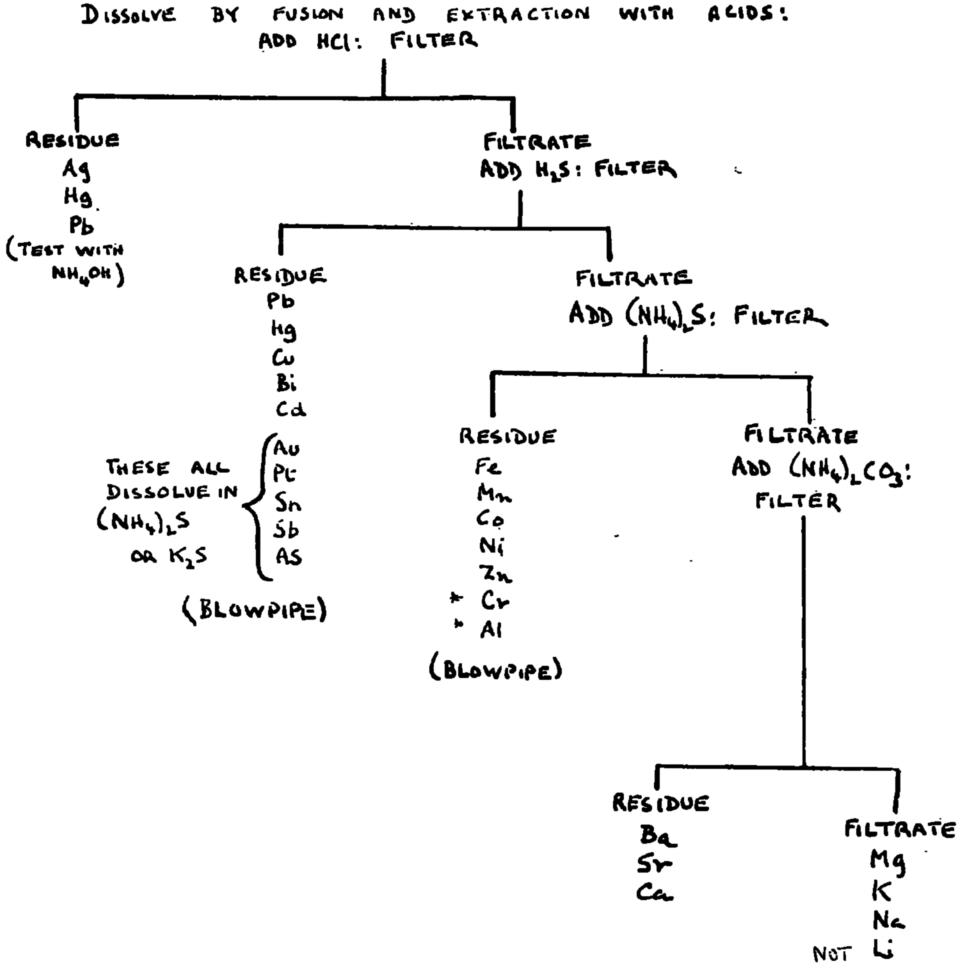
White	Precipitate	Indicates	8, 10
Pink	„	„	9
Black	„	„	11 — 13

III Neutralize and Add K_2CO_3

Precipitate	Indicates	4 — 7
Precipitate with NH_4OH	„	7

105 pages are devoted to tests for individual elements.

Table VIII. Fresenius's General System for Qualitative Analysis



*Chromium and Aluminium are, of course, precipitated as hydroxides and as sulphides

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PART II. MINERAL WATER ANALYSIS

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One of the most distinctive features of 18th century social life in England was the gaiety of the watering places. For while London remained the centre of the worlds of politics and fashion, the centre of entertainment had moved to places such as Bath. Although Epsom and Tunbridge Wells had enjoyed an earlier popularity, Bath under Nash outstripped them all. "The story of how the fashionable life of Bath, the establishment of a routine and a whole code of etiquette, were created by a penniless adventurer makes one of the curious romances of the 18th century" (1). Not that the idea of a fashionable spa originated at Bath, for in the 16th and 17th centuries there were many on the continent that already enjoyed fame and drew distinguished visitors to take the waters. Thus Blaise de Montluc, maréchal de France, after revising his Commentaires in 1571 sought the waters at Bagnères de Bigorre in the Pyrenees "pour soigner ses douleurs et ses blessures".

With the social interest in the spas there grew a gathering curiosity about the medical and scientific attributes of the waters themselves. It is significant that up to 1780 there had appeared thirty-four papers on mineral waters in the Philosophical Transactions of the Royal Society: and when it is remembered that the whole range of science, liberally interpreted, had to find space in this journal, and that such popular topics as comets and monstrous births were competing for room, some idea is gained of the interest that the chemical and medical qualities of mineral waters held. Further, there sprang up a vast literature in book form until it seemed that every country doctor had written a pamphlet setting out the virtues of his local spring. One such work published in 1787 listed sixty-eight diseases known to be remedied by bathing: these included epilepsy, melancholy, diabetes and dropsy.

It is not surprising therefore that chemists should have turned their attention to the problems of mineral water analysis, in other words to the problems of detecting small quantities of dissolved material by means of "tests" or reagents. By the middle of the 18th century, when our period opens, a considerable amount of knowledge had accumulated. During the previous century, Boyle had prescribed a number of tests based on change of colour or on precipitation: this latter kind he called tests by inspissation. Boyle's reagents are listed in Table I. It is worth noting that Boyle re-introduced the technique of using papers impregnated with coloured reagents, a technique described by Pliny in his Natural History as a refinement of the gall test for iron appearing as an adulterant in verdigris: "Deprehenditur et papyro galla prius macerato, nigrescit enim statim aerugine inlita" (2).

These tests were to be applied in a hit-or-miss manner, there being no notion of the successive narrowing of the field of possibility that is implicit in group analysis. Boyle posed a number of questions which helped to classify a mineral water, but this classification was not claimed as a chemical analysis of the contents of the water, a conception for which chemistry was not yet theoretically prepared. Boyle's questions were, however, very pertinent: "Will they lather with Soap, or if not, what quantity of curdiness produced? How much Caput Mortuum (residue) is formed? What dissolves the Caput Mortum, and what colour does the earthy part impart to Venetian glass if mixed with the powder before fluxion?" (3). This last is a significant forerunner of the bead tests to be introduced nearly a century later. We have selected the work of Boyle as a landmark in the development of mineral water analysis on account of the penetrating nature of his intellect, most clearly seen when we compare his questions with those of his contemporary Sir

William Petty (1684): "How it quenches thirst with Meat or otherwise; . . . . whether it purges; whether it promote Urine, Sweat or Sleep; . . . . whether a sprig of mint will grow in it equally as in other water; in what time it will putrify or stink" (4).

However, this is not to dismiss summarily the work of other pioneers in this field. Samuel Duclos (not Domenic, with whom he is often confused), for instance, used most of the reagents described by Boyle, with the addition of iron sulphate and extract of irises. He examined with the aid of the microscope the residues obtained by evaporating the waters, as did Johann Juncker who, following Becher, was able to recognise Glauber's salt by its "parallelogrammatical rhomboids" (5). Instead of evaporating to dryness, Nehemiah Grew (1695) concentrated to a small bulk some water from a popular spring at Epsom, and so obtained crystals of Epsom salts.

The second half of the 18th Century saw the establishment of a mental climate in which a truly scientific approach to the problems of mineral water analysis could flourish. The publication in1779 of Bergman's "De Analysi Aquarum" marked the beginning of this new approach, though it is only fair to add that some of the techniques described were refinements of those used by Cavendish and by Brownrigg twenty years earlier. Bergman's treatment was thorough and critical: his chapter headings included the observation of physical qualities, precipitation with reagents, methods of collecting volatile constituents, examination of residues, and—most telling of all—the confirmation of the analysis by synthesis (6). The list of reagents used by Bergman (Table II) is surprisingly revelant to modern analysis, though several points require further explanation.

The large group of vegetable tinctures for acid-alkali detection is, in fact, only a small selection of those which have been made to serve at some time: Faraday, for instance, experimented with extract of rhubarb. One reason for the prolonged seach for new reagents in this class was that freshly prepared extracts were necessary on account of bacterial fermentation, and the coloured part of a particular plant would be available only during a short season. It was this consideration which led Watt to suggest red cabbage as most suitable for winter use. Not until 1864 did the solid colouring matter of litmus appear in a stable form from which solutions could be prepared as required.

A second noteworthy point about Bergman's list is that tincture of galls appears side by side with potassium ferrocyanide as a test for iron. The non-specific nature of the galls test had been noted by Tachenius and by Boyle, though some of Boyle's objections had little to do with mineral water analysis. Nevertheless, if the reasonable assumption is made that iron is the only metal likely to be found in a mineral water apart from the alkali and alkaline earth metals, tincture of galls remained a useful test. Klaproth increased its sensitivity by suspending in the freshly drawn water a slice of gall-nut on a silk thread: even minute quantities of iron formed a blue cloud round the reagent. An interesting corollary to this test was the belief of certain 18th and 19th century wine merchants that they could identify wine matured in the cask by its giving a blue colouration with a secret liquid provided for the purpose: the liquid was ferric chloride solution which gave a dark colour with most extracts of wood.

Potassium ferrocyanide became available in 1752 when Macquer showed how to prepare it by digesting prussian blue with potassium carbonate solution. Prepared in this way it usually contained some ferric ions and on acidification regenerated prussian blue: it was thus held in suspicion as a test for iron. However, after Scheele (1782) had described the pure salt and Klaproth had shown how to prepare a solution for analytical use, potassium ferrocyancide increased in repute. Indeed, in 1821 Brande published a table of coloured precipitates for thirteen metals (Table III). (7) Potassium ferricyanide ("red prussiate of potash") was first described by Gmelin in 1822: the use of this reagent removed the necessity for allowing the mineral water to stand until aerial oxidation had converted the iron to the ferric state.

Another test for iron, proposed by Gehlen and improved by Klaproth enjoyed popularity for a period. This was the formation of a precipitate with ammonium succinate or ammonium benzoate. Used by Dr. Marcet in his analysis of Brighton waters, it was more in the nature of a separation than an identification and was used by Thomson to separate iron from manganese (8).

In 1799 there appeared a book which, in its influence upon subsequent work, was no less important than that of Bergman. This was the Essay on the Analysis of Mineral Waters by Richard Kirwan. This book was characterized by a careful and critical examination of all that was known at the time about mineral water analysis. Each reagent was discussed with respect to the circumstances of its use and the interpretation of the results obtained. Nevertheless, Kirwan was not completely convinced of the usefulness of tests by reagents as opposed to the examination of the residue after evaporation. "Tests as commonly applied are generally allowed to afford only conjectural not demonstrative inference even of the species of salts contained in mineral water, at least in the cases that most frequently occur" (9). He quotes Gioene (who analyzed volcanic lava as well as mineral waters) as saying that he will not pursue his enquiry by tests any further "for though tests are not without their use, yet no certain conclusion can be drawn from them".

Two factors contributed to this reluctance to rely upon the evidence furnished by reagents alone. The first was the lack of any standard of purity and concentration of the reagent solutions. Duclos, for example, believed that common salt consisted of two parts, a first part which would crystallize out in the cold and a second, "succulent" part which would only crystallize after evaporation of the solution (10). The idea of chemical identity was as yet imperfectly understood. Boyle saw the need for controlling the concentration of a reagent, but in this he was ahead of his time. "In trying of Mineral Waters, it is usual to make use of a Tincture of Galls, without considering the Alterations which may be made in the Tryal, by an Uncertain Proportion of Galls: Wherefore I usually make use of a settled Proportion, as 5 grains to an ounce" (11).

Reagents were commonly made up in rain water, which Marggraf held to be the purest form of water obtainable (12). Hoffmann, however, in a short essay on the examination of mineral waters which was published in 1736 stated clearly that all reagents must be made up with distilled water (13). Kirwan and later workers emphasized the twin necessities of purity and concentration. Here we see the influence of quantitative upon qualitive analysis. The rising chemical industry brought into being the new art of alkalimetry, and this in turn required solutions of standard strength. Henry (1829) reconized the value of such solutions in qualitative work. "It will be found extremely useful to keep the three mineral acids, the alkalis and the alkaline carbonates in a liquid form, and of such strength that one measure of the one will neutralize either one measure, or some simple multiple of one, of the other" (14).

The second factor which seemed to limit the value of the results obtained by tests was of a theoretical nature. Briefly, the problem may be stated thus: if sodium, magnesium, chloride and sulphate are found, are the salts present soldium sulphate and magnesium chloride or sodium chloride and magnesium sulphate? Only the work of the late 19th century physical chemists, Raoult, Ostwald, van't Hoff and Arrhenius, and the theory of dilute solution which they established, could show how irrelevent the question was. Meanwhile, the only guide available to chemists was the table of affinities arranged by Geoffroy, modified by Bergman and greatly expanded by Lavoisier (15). Now since these tables were based on empirical data, they usually gave the "right" answer, that is the salts which crystallized out on evaporation were those which had been predicted. There were, however, complications caused by changes in temperature and concentration. This was stated by Andrew Fyfe: "The salts obtained by evaporation are not the same as exist in solution, new affinities having been brought into play during the performance of the analysis, by which decompositions are effected and new salts are formed" (16). He goes on to quote Murray as saying that in a water showing tests for calcium, magnesium, sodium, sulphate and chloride, the salts present would be calcium chloride, magnesium chloride, sodium chloride and sodium sulphate, but that on evaporation calcium sulphate would be formed. This work was not completely wasted, as it helped to prepare the ground for the work of Berthollet, Wilhelmy and Gladstone which culminated in the enunciation by Guldberg and Waage of their Law of Mass Action. The practice of calculating quanties of ions as specific salts is still adhered to in industrial water analysis, solely as a convenience.

As the 19th century advanced, the main centre of interest in water analysis shifted from the medicinal properties of mineral springs to the potability and industrial fitness of town water supplies. In 1847 the Waterworks Clauses Act appeared, collecting into one act the numerous separate agreements of local water companies, and charging the suppliers with the duty of providing "pure and wholesome water". Special penalties were reserved for those who allowed gas-works effluents to pollute the water supply. In the same year Thomas Clark published his paper "On the examination of water for towns", (17) in which he described his soap solution method for determining hardness and his process for softening water, patented in 1841.

As the population of London grew, the water in the Thames contained more and more sewage, and this water provided the drinking supply for most of the surrounding area. It was not, however, until 1854 that the connection between impure water and cholera outbreaks was demonstrated beyond all doubt, and even then the truth was accepted only with reluctance. The importance to chemistry of this awakened interest in the presence of organic matter in water supplies was that new methods of detecting ammonia were sought. Our period may be considered to close with the discovery, in 1856, of Nessler's famous reagent for detecting and estimating ammonia (18). It is interesting to record that from 1860, portable sets of equipment for the analysis of water, complete with all the necessary reagents and an instruction manual, could be had in London for about three pounds.

We end on the note on which we began. A century of mineral water analysis had not shaken the popular belief in the efficacy of the spas. Dickens' portrayal of Bath in "Pickwick Papers" (1837) still showed the rigid code of behaviour and the pump-room ceremonial of Nash's day. While in "Handley Cross" (1854) Surtees gave a vivid picture of the rise of a flourishing town about its mineral spring, with no other claim to fame than a water that could cure all complaints, and a Dr. Swizzle to see that none went without its benefits.

TABLE I

Regents used by Boyle in examing mineral waters.

Tincture of Galls

Decoction of Logwood

Infusion of Lignum Nephriticum*

Spirit of Urine (ammonia)

Dantzick or English Vitriol (Sulphuric Acid)

Soap

Syrup of Violets

Solution of Sublimate (mercuric chloride)

Aqua Fortis (Nitric Acid)

Tincture of Brazil wood

"Succedaneum" (From its method of preparation, by distilling sal-ammoniac with sulphur and potassium carbonate, this was evidently ammonium polysulphide).

*This curious reagent, fluorescent and sensitive to light, has been examined by Partington, Annals of Science, 11, 1955, p. 1-26.

TABLE II

Reagents used by Bergman in mineral water analysis (1779). (Modern names are used).

Tincture of Heliotrope	vegetable colours used as Acid-Alkali indicators
„ „ Brazil Wood	
„ „ Turmeric	
Syrup of Violets	
Tincture of Galls:	Iron
Potassium Ferrocyanide:	Iron, Copper, Manganese*
Sulphuric Acid	Barium
Oxalic Acid	Lime
Sodium Ammonium Phosphate	
Potassium Carbonate	All Earths
Ammonium Carbonate	
Lime Water	Carbon Dioxide
Barium Chloride	Sulphates
Calcium Chloride	(Ambiguous results)
Silver Nitrate	Chlorides
Mercury (I) Nitrate	Occasional use only
Mercury (II) Nitrate	
Mercuric Chloride	See below†
Arsenious Oxide	Sulphides
Lead Acetate	
Calcium Polysulphide	Not to be used
Ferrous Sulphate	
Alum	
Alcohol	Precipitates all salts if sufficient is added

*Called "Magnesia" by Bergman.

†The red precipitate sometimes formed was not recognised: iodine was not discovered until 1811.

TABLE III

Brande's Scheme for identifying metals in solution by means of potassium ferrocyanide.

Metal	*Colour*
Manganese	White
Iron (Fe^{++})	Pale Blue
„ (Fe^{+++})	Prussian Blue
Zinc	Yellowish white
Tin (Sn^{++}(	White then yellow then blue
„ (Sn^{++++})	Pale yellow
Copper (Cu^{+})	Lilac
„ (Cu^{++})	Deep brown
Lead (Pb^{++})	White
Cobalt	Pale green
Uranium	Deep brown
Nickel	Grey
Titanium	Deep blue
Mercury	Greenish white
Silver	Cream
Platinum	Yellow

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Portrait of a Quack:
Joshua Ward (1685-1761)

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"*Of late, without the least pretence to skill*
Ward's grown a famed physician by a pill."[1]

* * * *

"*Before you take his Drop or Pill,*
Take leave of friends and make your Will."[2]

These lampooning couplets bear testimony to the impact upon the contemporary scene of the fame and notoriety of Joshua Ward, "restorer of health and father to the poor", pioneer of chemical industry, quack doctor and royal protégé.

The details of Ward's early life are obscure: it has been suggested that he was descended from the lords of the manor of Wolverstone in Suffolk, and that he worked as a drysalter in Thames Street, London, but these statements lack adequate documentary confirmation.(3)

The first authenticated fact of Ward's career is his entry into Parliament in 1717 as member for Marlborough. At the election a certain Mr. Roberts had been returned, but Ward seized the indenture of election, erased the name of Roberts and substituted his own, the operation being effected with the help of a bogus mayor of Marlborough. The committee of privileges, to whom the case was referred, reported that "twenty-one had voted for Mr. Roberts but none for Mr. Ward", and ordered the erasure of Ward's name from the list of members.(4) Before the act of erasure was carried out, however, Ward had removed himself to France. The episode is tactfully dismissed in the Annual Register, "on account of a particular affair (he) was obliged to go abroad".

Although Ward remained in France for about eighteen years, very little is known about this period of his life. Indeed, the wildest and most contradictory reports have appeared in the literature. J. T. Smith, who was keeper of prints and drawings at the British Museum in the early part of the nineteenth century, held that Ward had been a friar and the inventor of Friar's Balsam.(5) Dr. Paris, on the other hand, claimed that Ward had been a footman and had picked up the recipes for his nostrums while attending his master on the continent.(6) Needless to say, there is no evidence to support these rumours. We have, however, the testimony of John Page, afterwards secretary to the Treasury, that Ward lived by selling patent medicines in Paris and at Dunkirk: and it is clear from the pattern of his subsequent career that he had gained some acquaintance with chemical enterprises during his stay in France.

Not until Ward's forty-ninth year, in 1733, did he achieve fame. Pardoned by George II and returned to England, he began under royal patronage to push the sale and use of his medicines. Three houses in Pimlico, near St. James' Park, were bought with the King's help and used as a clinic and dispensary; over the door was carved in large letters "MISERIS SUCCURRERE DISCO".(7) The hospital became so popular that Ward found it worth while to take a house in Threadneedle Street to serve as a subsidiary clinic, and in addition he had rooms in the almonry office at Whitehall. From these three centres the medicines were sold at prices which varied according to Ward's estimate of the patient's means.

The stock in trade consisted of a sweating powder, a sweating draught, a fistula paste, a purging powder for dropsy, an essence for headache and an emetic drop and pill. Only the last two, however, caught the popular imagination, and Ward was accused of attempting to cure every human ailment by means of the drop or the pill. The composition of the medicines remained secret until two years after Ward's death when the formulæ were disclosed by John Page in a booklet entitled "Receipts for preparing and compounding the Principal Medicines of the late Mr. Ward". These formulæ are shown in appendix I. During Ward's lifetime the art of analysis had not progressed far enough to enable a complex mixture to be identified completely, Several famous physicians, including Sir Hans Sloane and Dr. Meade, claimed to have found out the secret, but they relied not upon chemical examination but upon deduction from the observed effects on the patient.

From the outset, the popularity of the drop and pill was anonymously and virulently attacked in the pages of the Grub Street Journal. The campaign opened in the last week of November 1734 with an article by "Misoquackus". Here, the testimony of Lord Chief Baron Reynolds that his servant girl had recovered from a palsy "when all that the regular practice of physick could suggest had been tried in vain", was set against twelve cases in which the pill had been taken with fatal results. This article was nevertheless moderate and judicial in tone, suggesting that while good might sometimes come from taking Ward's medicines, the element of danger was too great to be ignored. It was also suggested that the symptoms in those cases where poisoning had occurred were similar to those caused by compounds of antimony.(8)

In December, the same journal made much of a pamphlet by Dr. Daniel Turner setting out the official medical objections to Ward's remedies, and in the last issue of the year published a defence of Ward so disingenuous as to be certainly of editorial inspiration, over the name of "Obadiah Anticlysterpipus".(9) The character of the campaign changed in 1735 after Ward had contributed a reply in his own defence. Typical of the style is this extract from No. 263, January 1735. "The learned Mr. Ward, whose abilities and great success are too well known among the undertakers, coffin makers and sextons to be blasted by your slanderous pen! If he can kill by one Drop only, whilst others must fill phials and quart bottles to do it, it shows him the greater artist! I say a Quack is a very useful person in a commonwealth, especially if it is too populous as ours is".(10)

Ward was not without his genuine defenders. Henry Fielding for instance expressed his obligation to Ward: "for I am convinced that he omitted no care in endeavouring to serve me, without any expectation or desire of fee or reward". (11) In a letter to Sir Horace Mann, Horace Walpole expressed approval of the headache lotion. "He (Ward) rubs his hand with some preparation and holds it upon your forehead from which several have found instant relief."(12) Even John Wesley spoke of a way "that would as compendiously save the soul as Dr. Ward's pill and drop heal the body".(13)

The crusade against Ward evidently did little damage to his reputation and may indeed have provided him with free advertisement: at all events he continued to make and sell the preparations until his death in 1761. There

was nothing new in the use of antimony as a cure, nor in the claim that nearly all diseases could be vanquished by its aid. The writer of the "Triumphal Chariot" (1604) held that "Lupus and cancer yield to it, so does caries and the most malignant and neglected of ulcers, even those that are alive with worms cannot withstand it".(14) By the early eighteenth century it was well known that glass of antimony possessed emetic and purging properties, and this had been testified to by Hoffmann,(15) Geoffroy (16) and Lemery. The latter could not resist endowing it with all the virtues of a panacea, adding that it was good for "Hypochondriack Melancholy, the Itch, the Small Pox, Malignant Fevers, and the Scurvy".(17) We must recognise, however, that in an age when overeating and heavy drinking were common pursuits, and gross obesity a prevalent condition, relief might have been found in a medicine which was both purgative and emetic.

The actual preparation of the medicines was in the hands of two assistants named White and D'Osterman. In some cases these two altered Ward's formulæ for practical reasons, when considerations of solubility or incompatibility made changes necessary. After Ward's death the book of recipes passed to John Page who continued the business for a time. Page published the formulæ, together with the modifications of White and D'Osterman, adding a revised price list. (18) He charitably ascribed the lower prices to the fact that he, unlike Ward, was not solely dependent upon the sale of medicines for his livelihood. Any profits in excess of a certain amount were to be devoted to two institutions, "the Asylum for the Support of Female Orphans, and the Magdalen for the Protection of Penitent Prostitutes". Page's preface suggests that White and D'Osterman were kept on as technical staff by means of a direct grant from the King.

In 1736, Ward commenced the manufacture of sulphuric acid at Twickenham, moving to Richmond in 1740. This venture also seems to have depended upon the technical skill of White, described as "John White, the Ingenious Chymist who carried on the Great Vitriol Works at Twickenham".(19) The apparatus consisted of two rows of round-bottomed flasks of about fifty gallons capacity, partly buried in sand and so placed that the necks were horizontal. A charge of nitre and sulphur, contained in an iron dish and standing on a small earthenware pot, was introduced into the neck of each flask and ignited by touching it with a red hot iron. Each flask contained a small quantity of water, and the neck was closed with a wooden plug. When the combustion was complete, a fresh charge of sulphur and nitre was introduced and the process continued until the acid was judged to be of sufficient strength to justify concentration by distillation.(20)

At first Ward relied upon secrecy to guard his process, but in 1749 he took out a patent with White: by this time, however, Roebuck at Birmingham had already patented a superior process carried out in lead chambers. The chemistry of the process used by Ward had been described by a number of authors, including the pseudonymous Basil Valentine (1604) and Nicholas Lemery (1675). Nevertheless three small but important adjustments to the mode of operation seem to have originated with Ward and his co-workers. The form of the apparatus allowed the charge of sulphur and nitre to be renewed without disturbing the dilute acid inside; the arrangement of the flasks made it possible for a man to be gainfully employed for the whole of his time, for when the last charge had been ignited the first flask was ready for a new charge; and lastly the scale on which the work was carried out represented a definite transition from laboratory to industrial conditions. The success of the venture can be gauged from the fact that the price of sulphuric acid fell to something between 1/6d. and 2/6d. per pound, or one sixteenth of its former cost. It will be remembered that when Dr. Johnson bought oil of vitriol from a chemist's shop at Temple Bar in 1772, he paid one penny for an ounce.(21)

Ward was a heavily built man with a claret stain on his right cheek, on account of which he was known as "Spot" Ward. He was sensitive about this mark which "drew upon him the blessing of every gin-drinking, furmity woman or shoe-black", (22) and it is interesting to note that Loving's portrait (Fig. I) shows the disfigurement while Bardwell's (Fig. II) does not. The view is commonly held that Ward is depicted in Plate V of Hogarth's "Harlot's Progress", in which two physicians argue while their patient dies. (23) It is difficult to reconcile this with the fact that the series was completed in 1731 and engraved in 1732, when Ward had not yet returned to England or found fame as a quack-doctor. Another Hogarth picture said to contain a caricature of Ward, together with Taylor the oculist and Mrs. Mapp the bonesetter, is the "Consultation of Physicians" or "Company of Undertakers". Since this print appeared in 1736, in which year the Grub Street Journal was engaged in vilifying all three unorthodox practitioners, it is possible that Ward is represented although no noticeable likeness can be discerned.

Ward died at Whitehall on November 21st, 1761. His will (Appendix II) shows considerable generosity of character, and in fact his concern for the poor seems to have been genuine enough: on two occasions he contributed handsomely to funds to help the victims of disastrous fires. The record of his life is one of sustained indifference to organised opposition, and is best summed up in the words:

> "Dr. Joshua Ward, the Celebrated Quack, who first began to practise Physic about 1733, and combatted for some time the united efforts of Wit, Learning, Argument, Ridicule, Malice and Jealousy, by all of which he was opposed in every shape that can be suggested."(24)

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APPENDIX I

Composition of Ward's Medicines as disclosed by Page

Emetic Pill :

Glass of Antimony	4 ozs.
Dragon's Blood	1 oz.

Mix with Sack or Mountain Wine to make pills of 1½ grains.

Emetic Drops :

Glass of Antimony	½ oz.
Malaga Wine	1 quart

White Drops :

Aqua Fortis	16 ozs.
Sal Ammoniac	7 ozs.
Mercury	4 ozs.

Warm till all the mercury has dissolved.

Sweating Powder No. I:

Ipecacuanha	1 oz.
Liquorice	1 oz.
Opium	1 oz.
Nitre	4 ozs.
Vitriolated Tartar	4 ozs.

Sweating Powder No. II :

White Hellebore	6 ozs.
Liquorice	6 ozs.
Opium	5 ozs.
Common Tartar	1 lb.
Refined Nitre	1 lb.

Fistula Paste :

Alicampane Root	1 lb.
Fennil Seeds	3 lb.
Black Pepper	1 lb.
Honey	2 lb.
Powdered Sugar	2 lb.

Liquid Sweat :

Spirits of Wine	1 gallon
White Wine	½ gallon
Saffron	8 ozs.
Cinnamon	4 ozs.
Salt of Tartar	2 ozs.
Opium	1 oz.

Dropsy Purging Powder :

Jalap	1 lb.
Cream of Tartar	1 lb.
Bole Armenic	1 oz.

Essence for the Head-Ache :

French Spirits of Wine	2 lb.
Rock Alum	2 ozs.
Camphor	4 ozs.
Essence of Lemon	½ oz.
Volatile Spirit of Sal Ammoniac	4 ozs.

APPENDIX II

Joshua Ward's Will

(*Made March 1st*, 1760 ; *proved January 8th*, 1762)

Margaret Gansel (sister)	£500
Ann Manley (sister)	£500
Rebecca Ward (niece)	£2000
Alexander Moreton (servant)	£150
William Wood (coachman)	£100
Thomas Lane (groom)	£50
Charles Tyler (postillion)	£50
Mary Bright (servant)	£50
Col. William Gansel (nephew)	£1000 with three pictures of his own choice

A further £500 to be distributed at the discretion of William Gansel.

Executors : Ralph and Thomas Ward, sons of nephew Knox Ward.

(*Gentleman's Magazine*, 1762, *p.* 208).

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W. A. Campbell

Some Landmarks in the History of Arsenic Testing

The court's decision in a trial for murder may depend solely on the result of a chemical analysis. No satisfactory foolproof method for detecting arsenic, one of the most commonly used poisons, was available before 1836, when Marsh's test was first launched. With modifications by Berzelius, who made the test quantitative, it has been recognized as the most certain chemical method for the detection of arsenic. In 1841 Reinsch devised an alternative test, useful for its easy manipulation and quick results. The author describes the development of these and other methods, and gives an account of some of the important trials in which their outcome influenced the final decision.

A POISONER in search of a material with no striking colour, no readily discernible taste or odour, and with physiological effects similar to the symptoms of some innocent complaint, would not need to look beyond arsenious oxide. It is easy, therefore, to understand why this substance has long been the mainstay of those who have sought to remove the more inconvenient of their fellow men, from the *cantarella* of the Borgias to the notorious examples of the last hundred years.

Before the nineteenth century, however, the means of detecting the poison were presumptive and inadequate. The symptoms of the illness and the post-mortem appearance of the body were usually considered, but these observations were clearly not precise enough to distinguish between different mineral poisons. The aim, in fact, was to secure evidence of poisoning rather than to identify the poison. To this end, food that had been prepared for the deceased was sometimes fed to a dog, on the precarious premise that what will kill a man will kill a dog. The only test for arsenic to receive universal recognition was the odour of garlic produced when suspected food or stomach-contents were thrown on to red-hot coals; and even this was sometimes frustrated by the plea that the dead man had lately eaten onions.

EARLY CASES

The rise of chemical technology which took place about the end of the 18th century, and the widespread application of chemistry to the arts and trades, led to an unforeseen increase in the number of cases of accidental poisoning due to arsenic. The pages of *The Lancet*, *The Times* and *Chemical News* tell their own grisly tales. An Analytical Sanitary Commission set up by *The Lancet* collected samples of food from a wide range of sources and found, among other things, that nearly all the pigments used in making highly coloured confectionery were poisonous. One example from the 1855 report[1] will indicate the scope of the problem:—

James Marsh (1794-1846). Reproduced by courtesy of the Borough Librarian, Woolwich

> 'Mixed Sugar Ornaments
> 95th sample:—purchased from J. Robinson,
> Maiden Lane, Covent Garden.
>
> These mixed sweets are cast in different forms representing birds, fish, rabbits, etc. The colours used consist of the usual red organic pigments, Prussian Blue, and Gamboge, while the bases or stands of all the ornaments are thickly painted with Emerald Green or Arsenite of Copper.'

A year earlier Dr A. S. Taylor, the professor of forensic medicine at St Mary's Hospital, had published an account of a different kind of hazard involving copper arsenite in paint, under the heading 'How Families are Poisoned.'[2] His story opens with authentic biographical drama: 'On the 17th of the present month, when about to cut the loaf placed on my table for breakfast, I observed some green patches and streaks over the partially burnt lower crust.' Taylor scraped off the green patches and discovered the material to be Scheele's Green. Further investigations at the bakery showed that the newly baked bread was cooled on shelves that had recently been painted a bright grass-green colour. The baker was quite ignorant of the fact that the paint contained arsenic; the painter, however, was well aware of what he was doing, saying that without arsenic it was impossible to get a good green, and that he had never heard of any deaths resulting from its use.

Deaths certainly did result, as described by Dr Edward Lankester in 1860. At a public dinner held in that year a green blancmange had been served, after eating which three people died; the colouring matter was copper arsenite. Even more disturbing in its overtones was the report in *The Times* for the same year of the sale of yellow Bath buns dyed with arsenic sulphide; the chemist who had supplied the pigment expressed deep regret and said that he had intended to supply lead chromate!

This same Scheele's Green, so often the culprit in cases of accidental poisoning, provided one of the earliest of the purely chemical tests for arsenic. Others were the formation of a yellow precipitate with ammoniacal silver nitrate, known as Hume's test,[3] and the precipitation of yellow arsenic sulphide.

It was generally agreed that these precipitation reactions were influenced too much by the initial chemical state of the arsenic to provide unmistakable proof. More reliance was therefore placed upon a reduction test devised by Berzelius. The suspected matter, or one of the precipitates mentioned above, was mixed with black flux (potassium carbonate and charcoal) and heated in a drawn-out glass tube: if arsenic was present a metallic stain or mirror appeared on the cooler parts of the tube. Some toxicologists, led by Christison of Edinburgh, objected that small traces of the metal might be lost through solution in the flux, and indeed the test was not very sensitive. Nevertheless Berzelius was the first to suggest a way of overcoming the ambiguities of the precipitation tests.

MARSH'S TEST

This, then, was the state of chemical analysis when Marsh's test was launched into the world in 1836. Marsh's own account says that he was anxious to find a way to avoid the uncertainty associated with the use of black flux. The apparatus was the embodiment of simplicity (*see* Fig. 1). It was made from $\frac{3}{4}$-inch diameter glass tubing bent into the form of a syphon with limbs about 5 and 8 inches long. The stopcock, mounted in cork, was secured with a little 'common turpentine lute,' and the whole apparatus was fixed to a wooden stand by means of elastic bands, described as 'two elastic slips cut from the neck of a common bottle of India rubber.' A small zinc rod was placed in the short limb and kept from slipping into the other limb by the insertion of a short glass rod: dilute sulphuric acid was poured in, the air displaced, and a suitable volume of hydrogen collected for testing. The preliminary blank test was applied by burning the hydrogen at the jet and allowing the flame to play on to a piece of crown glass (with a warning that the glass might sometimes fly to pieces). If no stain appeared on the glass, the material under test—either in solution or suspended in water—was added through the open limb, and a further volume of hydrogen collected and burnt. Serious losses owing to frothing sometimes occurred when materials such as stomach contents were examined and directions are given for breaking the froth with 'sweet oil' (glycerol).

With the spirit of the true experimenter Marsh was sure that the apparatus could yet be improved, and in a fine burst of do-it-yourself prose he declared: 'Indeed I say unequivocally that there is no town or village in which sulphuric acid and zinc can be obtained, but every house would furnish to the ingenious experimentalist ample means for his purpose; for, a two ounce phial with a cork and piece of tobacco pipe, or a bladder with the same arrangement fixed to its mouth, might in cases of extreme necessity, be employed with success, as I have repeatedly done for the purpose.'[4]

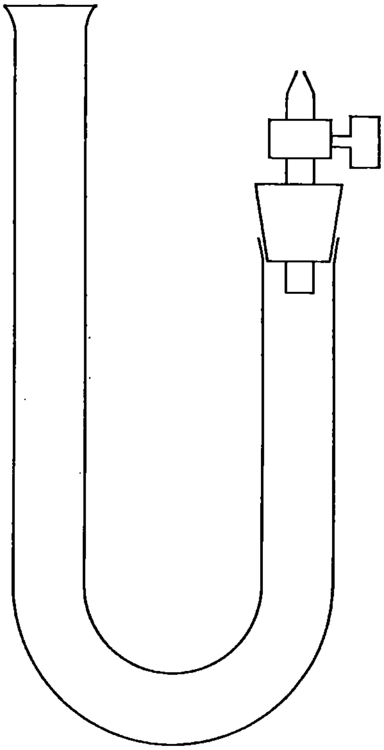

FIG. 1. Original form of Marsh's apparatus, 1836

The chemical reactions upon which Marsh's test depend were well known in 1836. Scheele had mentioned the thermal decomposition of arsine in 1775; Proust, in his researches on tin (1798) had shown that a foul-smelling gas was generated when arsenic-bearing tin dissolved in hydrochloric acid.[5] Trommsdorff in 1803 had described similar results with arsenical zinc,[6] and in 1815 Gehlen had made a thorough study of arsine, dying from the results of inhaling it.[7] In 1821 Serullas suggested the generation of arsenic hydride as a forensic test for arsenic.[8] Marsh was however the first to describe a simple apparatus and to state clearly the conditions for its effective use.

The circumstances of James Marsh's life do not reflect the importance of his place in the history of chemical analysis. He was known as the 'practical chemist' at Woolwich Arsenal and was assistant to Michael Faraday at the Military Academy there. At the time of his death in 1846 at the age of 52, his weekly wage was 30*s*., and his wife and family were quite unprovided for. The anonymous author of the account in the *Biographie Universelle* suggests a reason: 'Mais la passion des liqueurs fortes s'empara graduellement de lui, elle hâta sa fin.'[9] Though financial reward seems to have evaded him, Marsh received a number of scientific honours, not merely for the arsenic test but for his researches into electricity and for his invention of the quill fuse for use with explosives. Among these honours were the gold and silver medals of the Society of Arts, a silver medal from the Board of Ordinance and another from the Crown Prince of Sweden.[10] Many features in Marsh's writing seem to reflect the influence of Faraday, particularly the delight in evolving practical manipulative tricks (Wöhler's *kleine Handgriffe*) and the utilization of commonplace objects for scientific purposes.

MARIE LAFARGE

Marsh's test achieved notoriety in 1840 for its part in altering the course of French justice at the trial of Marie Lafarge. This case, of which it was said 'it tended not a little to divert their thoughts from the fancied insult they had received from England, and to diminish the chances of a war,' involved a number of leading toxicologists, doctors and chemists. M. Lafarge, a supposedly wealthy iron founder, had married the 23-year-old Marie Capelle, whose family was well connected in army and banking circles. Less than a year later he died in suspicious circumstances and the young widow was charged with murder by arsenic poisoning. Orfila, the lion among toxicologists, could find no arsenic in any of the samples submitted to him, but the court called for a fresh examination of the body. The report in the *Annual Register*—usually so restrained in tone—made the most of the sensational aspects of the situation. 'The coffin was little more than three feet below the surface; and when opened, the body presented a hideous spectacle, and so much decomposed that instead of the usual instruments, it was necessary, in order to take from it what was wanted, to use a spoon, which was sent for from the village.'[11]

This time Orfila and his assistants found arsenic in every place in which it was sought, and Marie Lafarge was sentenced to life imprisonment. Orfila listed some of the factors which had contributed to the contradictory results: 'La cause a été ici un tube cassé, là une portion trop minime de matière soumise à l'analyse, ailleurs une flamme un peu trop forte, enfin un certain manque d'expérience pour se servir de l'appareil de Marsh, qui demande une grande pratique.'[12] Raspail claimed to have found arsenic in the zinc used by Orfila in his tests, but this evidence was brought forward too late to influence the court. The layman's view was justifiably expressed in a newspaper report. 'Within two days the accused was declared innocent by the verdict of science, and now she is judged guilty by the verdict of that same science.'

MODIFICATIONS OF TEST

From 1836 to 1841, Marsh continued to modify his apparatus and method (*see* Fig. 2), particularly in the twin directions of achieving a partially quantitative result, and of distinguishing arsenic from antimony; this distinction was particularly important because antimony was sometimes administered as an emetic in poisoning cases. Except for filtering off the larger particles, Marsh did not attempt to separate organic matter prior to carrying out the test, although the experiments of a number of workers showed such a separation to be necessary for success. William Odling (third President of the Royal Institute of Chemistry), for example, described the case of a soil containing 0·07 per cent As_2O_3 which gave negative results in Marsh's apparatus until the organic matter had been destroyed by boiling with sulphuric acid.[13] Schneider had suggested digestion with sulphuric acid and common salt; the arsenic was distilled off as $AsCl_3$ and absorbed in water, and Marsh's test was applied to the aqueous solution. As early as 1839, Orfila had destroyed organic matter by dry combustion with potassium nitrate, later replacing this treatment by wet oxidation with concentrated nitric acid; this was twenty years before Carius proposed his sealed-tube method for quantitatively oxidizing organic compounds.

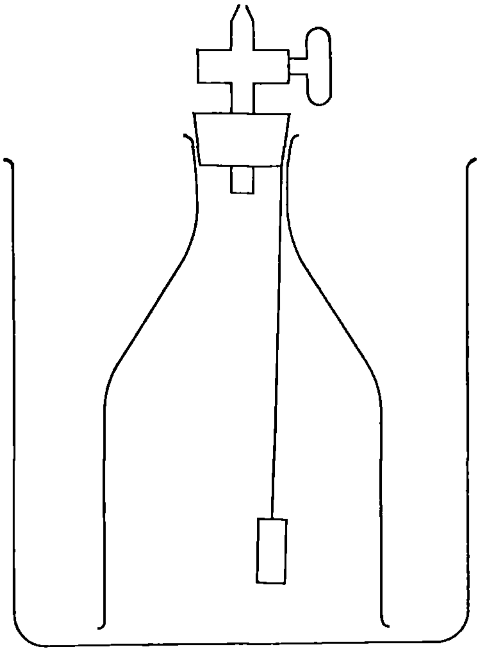

FIG. 2. Marsh's apparatus modified for large volumes, 1836

The stain produced on a cold glass or porcelain surface in Marsh's original process gave only qualitative results.

A step towards quantitative evaluation of the arsenic was made by Berzelius in 1837, when he passed the mixture of arsine and hydrogen through a glass tube, heated in the middle, before ignition at the jet; the mirrors of arsenic so formed were capable of quantitative interpretation. This device (*see* Fig. 3) became standard under the name of the Marsh–Berzelius apparatus.[14]

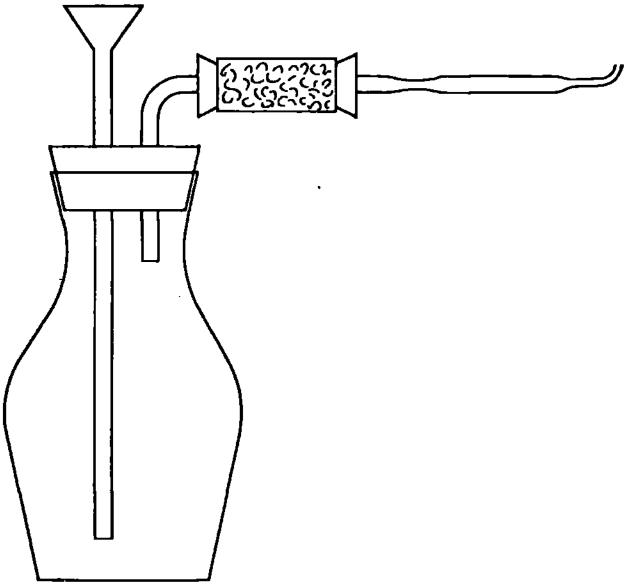

Fig. 3. Marsh–Berzelius apparatus, 1837

The Marsh test, with its various modifications, was examined critically by Liebig and Mohr,[15] Thenard, Dumas and Regnault,[16] Chevallier,[17] and Lewis Thompson.[18] The latter decided: 'All circumstances considered, I fear we can only regard Mr Marsh's very ingenious test for arsenic as furnishing good collateral evidence, capable indeed, in scientific hands of giving very correct indications, but wholly unfit to be entrusted to those unaccustomed to careful chemical manipulation. I say this with a thorough conviction of the great utility of Mr Marsh's test, and am only sorry that its evidence is not unequivocal.'

REINSCH'S TEST

The publication in 1841 of Hugo Reinsch's test, in which arsenic was deposited on copper foil from hydrochloric acid solutions, gave to chemists a much-needed alternative to the Marsh test.[19] Reinsch's test was first used for medico-legal purposes by Christison at Edinburgh in 1814, at the trial of a Mrs Gilmour who was accused of murdering her husband. The new test arose out of an observation by Fuchs that the presence of ferric iron caused copper to dissolve in hydrochloric acid.[20] Reinsch, preparing to study this reaction, noticed that strips of copper placed in commercial hydrochloric acid developed black stains, and traced the cause to arsenic in the acid.

The method was eagerly taken up in America, where in 1842 D. P. Gardner published a lengthy examination under the title 'On the Application of M. Reinsch's test for the detection of Arsenic to Medico-Legal Enquiries.'[21] In the same year Christison proposed a refinement in the following way: the arsenic-coated copper was to be cut into strips and heated in a flask until octahedral crystals of arsenious oxide formed in the neck, and these were to be dissolved in water for testing with silver nitrate, copper sulphate and hydrogen sulphide.[22]

Because the Reinsch test required so little manipulative skill, it was looked upon as a safer method than that of Marsh, and was put to use before the necessary safeguards had been adequately studied. The trial of Smethurst in 1859 caused a sensation because once again contradictory conclusions were reached. Odling and Taylor showed that the copper used in the test had itself contained arsenic, and a further uncertainty was caused by the presence of chlorate, which sometimes inhibited the test. Herapath dismissed the affair in scathing words: 'The fact is, the whole set of operations were a bungle. Reinsch's process is not applicable where nitrates and chlorates are present.'[23] A few years later, though, he wrote in Ure's *Dictionary of Chemistry*: 'I prefer the principle first proposed by Reinsch and have always acted upon it.'

FORENSIC ANALYSIS

In fact, professional chemists were uneasy about the whole state of forensic analysis. C. R. Fresenius, probably the greatest authority on pure analytical chemistry in the middle years of the 19th century, examined the position of the chemist appearing as an expert witness and asked the very pertinent questions: 'What is chemistry able to perform with regard to the detection of poisons, and what may properly be demanded of the chemist?' The warning that chemical evidence might be misinterpreted by laymen was followed by some plaintive remarks on the situations in which a chemist might find himself. 'If he chooses one of the older methods and finds no arsenic thereby it will be said "How can a chemist apply such a method? Are we not in possession of improved and far more correct methods? Had he used the apparatus of Marsh he would have found arsenic." Well, suppose he uses the apparatus of Marsh and detects arsenic, the advocate of the accused will undoubtedly object. "In what estimation are we to hold these results, obtained by means of a method liable to every possible deception and error?" '[24] Fresenius concluded with the hope that some standardization of methods could be agreed upon, with the object of protecting chemists—and the art of analysis—from the contumely to which they were often exposed.

Many attempts were made to improve the means of distinguishing antimony from arsenic, the most successful being that of Fleitmann.[25] This paper showed that when an alkaline solution containing arsenic and antimony is heated with aluminium, only the arsenic is reduced to its hydride. When applied to arsenic alone, the additional merit was claimed that aluminium and alkali were more easily obtained free from arsenic than were zinc and sulphuric acid. This test, however, never became really popular, and many standard works on chemical analysis do not mention Fleitmann.

From time to time Hume's silver nitrate test was revived as a culmination of the Marsh test, the gases being led through cotton-wool or over filter-paper soaked in the reagent. In 1874 Mayerçon and Bergeret suggested the use of mercuric chloride as a reagent for arsine, and a convenient form of apparatus for holding the filter-paper in the gas stream was devised by Gutzeit in 1879.[26]

When Marsh's test was first published, the long reign of Queen Victoria was just about to begin. As that reign drew to its close, the subject of arsenic testing again assumed importance in the eyes of the general public. In 1900, the beer-drinkers of Lancashire began to fall sick in their thousands, because of what was eventually diagnosed as chronic arsenic poisoning, traced to the use of contaminated sugar in brewing, and ultimately to arsenical sulphuric acid used in the sugar refinery. To allay popular anxiety and criticism, the Society of Public Analysts and the Society of Chemical Industry set up a joint committee to examine and report on methods for detecting arsenic with particular reference to beer.[27] For easy manipulation and quick results the committee recognized the merits of the Reinsch test. For accurate work in skilled hands, however, they recommended the Marsh–Berzelius test as the most certain chemical method for the detection of arsenic.

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PETER WOULFE AND HIS BOTTLE

By W. A. Campbell

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Few pieces of laboratory equipment are better known or have been put to more varied use than Woulfe's bottle; it has long served as gas generator, wash bottle, receiver, and more recently as the body of a home-made cloud chamber. About Woulfe himself most of us know a great deal less, and the curious place that he occupies in the history of chemistry may be worth recording.

Peter Woulfe was born in 1727, probably in Ireland, but just where is not known;[1] no portrait of him is known to exist. He certainly lived for some time in Clerkenwell, moving in 1771 to Barnard's Inn, a subsidiary of Gray's Inn. He was presumably esteemed by his contemporaries, for the Royal Society elected him to its fellowship in 1767, and in the following year awarded him the Copley Medal.[2] Woulfe had his share of that eccentricity in the grand manner which was so characteristic of the eighteenth century. His rooms, though spacious, were so crowded with furnaces and the scientific paraphernalia of the day, that it was only with difficulty that visitors could reach the fireside. Indeed, they could only gain access to the rooms at all by using a secret code of knocks, a signal often heard at four o'clock in the morning, at which hour he would entertain his friends to breakfast. He died in 1803 from an inflammation of the lungs which developed from a chill caught during a stage-coach journey from Edinburgh to London.[3]

To the end, Woulfe remained an unconverted alchemist, expressing a hope that his method of distillation might "discover the mercurial and colouring earths of Beccher." This method was announced in 1767, in a paper entitled "Experiments on the distillation of acids, volatile alkalis, etc., showing how they may be condensed without loss, and how thereby we may avoid disagreeable and noxious fumes."[4] The apparatus described was not, however, the three-necked, square-shouldered bottle with which we are familiar.

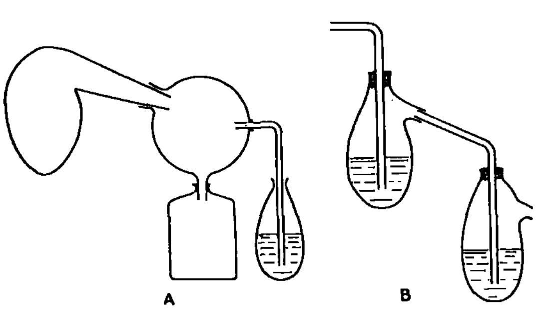

FIG. 1.—*Apparatus used by Woulfe in 1767*

In one experiment he used a globular vessel with two outlets, one connected to a dry flask and the other to a flask containing water (Fig. 1A). By this means, any vapour which did not condense in the dry flask was made to pass through the water, and was there absorbed. In another experiment he used three double-necked, round-bottomed flasks in series, each containing water (Fig. 1B). In this way he was able to distil a mixture of 30 lb. of nitre with 60 lb. of green vitriol without there escaping into the room any of those fumes "which have such an effect on the lungs of the operator as frequently to make him spit blood."

Neither the apparatus nor the use to which it was put originated with Woulfe; both had been described by Glauber in 1648.[5] Actually, Woulfe acknowledged that he had obtained the idea from "the common apparatus for reviving mercury from cinnabar." However, Samuel Parkes in 1824 said bluntly "It is also remarkable that this able chemist (Glauber) employed a series of receivers for the process similar to those now in use: and adapted them to each other exactly in the manner directed by Mr. Woulfe. This inestimable apparatus, which Woulfe has given to the public as his own, was actually drawn and described by John Rudolph Glauber more than a hundred years before Mr. Woulfe was born."[6] Here Parkes' indignation has upset his arithmetic.

Jean Joseph Welter, about 1820,[7] improved the bottle by furnishing the middle neck with a safety tube of the sort usually fitted to the top of Kipp's apparatus. Even Welter, according to Kopp,[8] was anticipated by Glauber. He was certainly anticipated in part by Lavoisier, whose textbook of 1789 contains a drawing of three triple-necked bottles connected in series, the middle neck of each holding a long straight tube.[9] This safety tube Lavoisier ascribed to his colleague, Hassenfratz.

It is clear that many hands have moulded the apparatus into its present form. Let the last word come from Michael Faraday, moderate in language but, as always, faultless in precision. Writing in 1827 he refers to "an arrangement of vessels, first discovered by Glauber, but which with some modifications, has since received the name of Woulfe's apparatus."[10]

I wish to thank Prof. P. L. Robinson who encouraged my interest in the history of chemical manipulation.

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