

## PHYSICIANS, CHEMISTS AND THE ANALYSIS OF MINERAL WATERS: “THE MOST DIFFICULT PART OF CHEMISTRY”

Noel G. Coley

In the first volume of his *Physical and chemical essays* (1779), Torbern Bergman, professor of chemistry and pharmacy at Uppsala in Sweden, discussed the chemical analysis of natural waters, including mineral waters. He remarked that when a weighed quantity of a mineral water was evaporated to dryness the weight of the residues usually amounted to no more than a minute fraction of the original weight of water, yet it might contain six or eight ingredients including salts and earths, which had first to be identified and then separated to determine their proportions. Bergman remarked that, “An accurate analysis of waters is justly considered as one of the most difficult problems in chymistry.”<sup>1</sup> Most eighteenth-century mineral water analysts were inclined to agree. Quite apart from the problems of identifying small quantities of salts and earths with very similar chemical properties, there was no guarantee that the residue left after evaporation contained the *same* ingredients as the mineral water itself. J. A. Chaptal, professor of chemistry and a practising physician at Montpellier, observed that new compounds were sometimes formed during evaporation whilst others present in the mineral water were decomposed.<sup>2</sup> In either case the results of analysis would be misleading. Thomas Garnett, writing about Harrogate waters in 1794, put the blame for the unreliability of mineral water analysis on the “very low state of chemical knowledge, together with the many difficulties which attended the examination of mineral waters . . .”<sup>3</sup>

To analyse a mineral water it was first necessary to know the chemical identity of the dissolved substances. This in itself was difficult since the quantities held in solution were usually very small and many of the compounds dissolved in mineral waters were so similar in their chemical properties that it was hard to distinguish between them. Yet for a reliable chemical analysis these closely related salts and earths had to be identified either in the mineral water itself or in the residues which remained after evaporation. In the latter case, the analyst also had to be aware of any chemical changes which might have occurred during the evaporation. It is clear

Noel G. Coley, M.Sc., Ph.D., C. Chem. FRSC, Staff Tutor in History of Science, The Open University (SE Region), St James's House, 150 London Road, East Grinstead, W. Sussex RH19 1ES.

<sup>1</sup> T. Bergman, *Opuscula physica et chemica*, 3 vols., Uppsala, 1779–83; English transl. by Edmund Cullen, *Physical and chemical essays*, 2 vols., London 1784–8, vol. 3, Edinburgh, 1791, vol. 1, p. 109. For biographical information on Bergman see W. A. Smeaton in C. C. Gillispie (ed.), *Dictionary of scientific biography*, vol. 2, New York, Scribner, 1970, pp. 4–8; and *idem*, ‘Torbern Olof Bergman: from natural history to quantitative chemistry’, *Endeavour*, n.s., 1984, 8: 71–4.

<sup>2</sup> J. A. Chaptal, *Éléments de chimie*, 3 vols., Paris, 1790; English transl. by W. Nicholson, *Elements of chemistry*, 3 vols., London, 1791; 2nd ed., 1795, vol. 1 (1795), pp. 293–4.

<sup>3</sup> T. Garnett, *A treatise on the mineral waters of Harrogate*, Bradforth [sic], 1792; 2nd ed., 1794, p. 5.

### *The analysis of mineral waters*

therefore that the practical difficulties of mineral water analysis were indeed considerable. For success the analyst needed to be astute, competent, and highly experienced.

The chief aims of mineral water analysis were to promote and improve their use in medicine, to identify impurities which ought to be removed from the waters before they were used in medical treatment, and, most important, to be able to prepare mixtures as nearly identical as possible to those mineral waters best known for their curative properties. Most of those who wrote on the subject in the eighteenth and early nineteenth centuries were physicians practising medicine at one of the spas. Most owed a substantial debt to seventeenth-century workers like Robert Boyle or the German medical systematist, Friedrich Hoffmann (1660–1742), who became provincial physician for Halberstadt in Saxony, famous for its mineral springs. Hoffmann made a study of mineral water analysis, basing his chemical tests on those described by Boyle.<sup>4</sup> Hoffmann's first book on mineral waters was published in 1703.<sup>5</sup> Among the constituents of mineral waters he recognized common salt, fixed alkalies (sodium and potassium carbonates), and several sulphates. He distinguished magnesia from lime using sulphuric acid which formed crystals of a bitter-tasting salt (Epsom salt) with magnesia and a tasteless, sparingly soluble compound (gypsum), with lime. Hoffmann recognized that the *spiritus mineralis* of mineral waters was an "air" which turned litmus pink. He found that it could be removed by boiling the mineral water, placing it under a vacuum or adding sugar after which the water produced an ochry deposit and no longer turned blue with tincture of oak galls, the usual test for iron. Thus it seemed that one function of the *spiritus mineralis* was to hold iron salts in solution. Hoffmann's work is recognized as a significant contribution to the chemical examination of mineral waters, but the collection of chemical tests he introduced cannot be described as a systematic method of mineral water analysis. This was an important objective of later eighteenth-century writers on the subject.

The first attempt to systematize mineral water analysis in England was made by Thomas Short, a Sheffield physician who wrote on certain English mineral waters in the 1730s.<sup>6</sup> Short criticized all the earlier writers on mineral waters including Boyle and Hoffmann and tried, though without much success, to work out a method of testing mineral waters using such well-tried reagents as the vegetable colours, silver nitrate, mercury salts, sugar of lead, oil of tartar, common acids, sal ammoniac, and tincture of galls. While he was often able to identify some of the commoner constituents of mineral waters, the volatile components, long recognized as important for their medicinal properties, seem to have completely baffled Short:

<sup>4</sup> R. Boyle, *Short memoirs for the natural experimental history of mineral waters*, London, 1684–5. Boyle's methods are discussed and summarized in N. G. Coley, "'Cures without care': chymical physicians and mineral waters in seventeenth-century England", *Med. Hist.*, 1979, 23: 191–214, on pp. 207–10.

<sup>5</sup> F. Hoffmann, *Methodus examinandi aquas salubres*, Halle, 1703; extracts transl. into English by P. Shaw, *New experiments and observations upon mineral waters . . . extracted from his [F. Hoffmann's] several essays on the subject and illustrated with notes*, London, 1731, 2nd ed., 1743.

<sup>6</sup> T. Short, *The natural experimental and medicinal history of the mineral waters of Derbyshire, Lincolnshire and Yorkshire . . . particularly those of Scarborough . . . together with the natural history of the earths, minerals and fossils through which the chief of them pass*, London and Sheffield, 1734.

they fly off in the Air, and seem lost to our senses; no vessel or matter we have, can collect or retain them after they are taken out of the Spring . . . they seem as small as particles of light or fire, or even electrical fire . . . [they] seem to be either an acid, alkali, iron, sulphur or the inflammable matter . . .<sup>7</sup>

Such confusion, which was common to many eighteenth-century physicians who dabbled in mineral water analysis, made the achievement of reliable analytical methods extremely difficult. Nevertheless, he continued to develop methods of mineral water analysis during the next 30 years until in 1766 he published his *Institutes: or an introduction to the examination of mineral waters, proposing methods for discovering their impregnating principles with greater certainty and exactness than has hitherto been done*. But despite its title, this book still offered no more than a random collection of qualitative tests; it was neither an organized method of analysis, nor was it exhaustive.

Short's contemporary Peter Shaw,<sup>8</sup> in translating part of Hoffmann's work in 1731, pointed out that Hoffmann had doubted the possibility of finding a perfect method of determining the precise contents of mineral waters and had been content just to discover the main ones. Shaw thought he could do better than that and in 1734 in a book on Scarborough Spa he classified the substances commonly found in mineral waters into salts, earths, sulphurs, and fumes or spirits.<sup>9</sup> He argued that there was nothing supernatural about mineral waters as had sometimes been imagined. They were not formed under the agency of a vital spirit in the earth but were just ordinary water containing dissolved mineral matter and he aimed to show that an "exact and satisfactory enquiry" (chemical analysis) could be made. For this purpose he described one or two tests which would be sufficient to identify each substance dissolved in the water. The most difficult problem was to identify one salt in the presence of another. For instance, nitre and common salt were often found together in the residues from mineral waters after evaporation and Shaw knew that both gave off fumes when heated with oil of vitriol. When nitre was present its red fumes masked the white fumes from common salt so he proposed to condense them. Pure nitre would then give *aqua fortis* (i.e., nitric acid) while the mixed salts would give *aqua regia* (a mixture of nitric and hydrochloric acids).

The term "sulphur" had often been used loosely to describe any inflammable residue from a mineral water, but Shaw restricted his discussion to brimstone alone. He mentioned the blue flame of burning sulphur, its acid fumes and choking smell. He also described the reactions of brimstone when ignited with powdered charcoal and nitre and its combination with alkalis to give a reddish mass of "liver of sulphur" (alkali polysulphides) which gave a precipitate and a smell of bad eggs when mixed with water. Lastly, he noted the vigorous exothermic reaction of brimstone when heated with iron and other metals. It is perhaps significant for the slow development of mineral water analysis to observe that this chemical identification of sulphur

<sup>7</sup> *Ibid.*, p. 13.

<sup>8</sup> For a discussion of Shaw's chemical work see Jan V. Golinski, 'Peter Shaw: chemistry and communication in Augustan England', *Ambix*, 1983, 30: 19–29.

<sup>9</sup> P. Shaw, *An enquiry into the contents, virtues and uses of the Scarborough Spaw waters, with the method of examining any other mineral water*, London, 1734.

### *The analysis of mineral waters*

remained largely unrecognized in medical circles. About 30 years later, when bitter arguments arose over claims that sulphur was one of the active constituents of Bath waters, the famous “sulphur controversy”, the true nature of sulphur was misunderstood by all the protagonists.<sup>10</sup>

Shaw’s analytical scheme always began by describing the topography of the spring, the physical characters of the water, and any spontaneous changes which occurred on standing. One sample of the water was allowed to evaporate slowly by exposure to the air; another was evaporated by heating over the fire and the two residues were compared. A third sample was distilled and the “spirits”, pure water, and residue were collected separately. Lastly, the residue after distillation was boiled with pure water and the solution was filtered and crystallized to separate the earths and salts from it. Each fraction was then carefully tested. Shaw claimed that by this method, a “tolerably exact and instructive analysis may be made and an useful . . . account given of the contents and virtues of any mineral water.”<sup>11</sup> Certainly this scheme was the nearest thing to a systematic analysis available in English in the 1730s; it was quite widely used and could be made to yield superior results. For example, Alexander Sutherland, a Bristol physician, used Shaw’s methods to analyse the Hotwell water in 1758.<sup>12</sup> He found a calcareous earth, vitriolic and marine acids, and the mineral spirit, but *no* nitre, alum, iron, or sulphur, a considerable improvement on most earlier analyses, which were generally confused and claimed the presence of all of these things with others besides.

Shaw also tried, though without much success, to deal with the volatile “spirits” of mineral waters. He tested them by smell and taste, also observing whether the water made the drinker feel intoxicated! He collected them in bladders and tried to weigh them, but in line with contemporary beliefs he regarded them all as forms of common air. It was only as the distinct chemical identities of different gases were recognized by eighteenth-century chemists that this aspect of mineral water analysis could be improved.

In the 1740s William Brownrigg, a physician of Whitehaven in Cumberland, made some experiments on the waters of Spa in Belgium which led him to suggest that the volatile spirits of mineral waters were the same as the “damps” of coal-mines. He noted that as the gases were expelled from the water a turbidity developed and this led him to conclude that “this aerial fluid is closely united to [i.e., chemically combined with] the other principles.”<sup>13</sup> Brownrigg’s paper appeared in 1765 and two years later Henry Cavendish published a paper on the water from a pump in Rathbone Place, London, in which he had found fixed air.<sup>14</sup> As a result of his experiments Cavendish

<sup>10</sup> N. G. Coley, ‘Physicians and the chemical analysis of mineral waters’, *Med. Hist.*, 1982, **26**: 123–44, on pp. 133–7.

<sup>11</sup> Shaw, *op. cit.*, note 9 above, p. 86.

<sup>12</sup> A. Sutherland, *The nature and qualities of Bristol Water, illustrated by experiments and observations with practical reflections on Bath Waters occasionally interspersed*, London, 1758.

<sup>13</sup> W. Brownrigg, ‘An experimental enquiry into the mineral elastic, spirit, or air, contained in Spa water; as well as into the mephitic qualities of this spirit’, *Phil. Trans. R. Soc. Lond.*, 1765, **55**: 218–35, on p. 227. A first version of this paper was read at meetings of the Royal Society in 1741–42; *Journal Book R. Soc. Lond.*, vol. 17 (1739–42), pp. 375, 394, 404.

<sup>14</sup> H. Cavendish, *Phil. Trans. R. Soc. Lond.*, 1767, **57**: 91–108.

observed that, while lime itself was only slightly soluble in water, when the water was saturated with fixed air the lime first became totally insoluble, but with twice the quantity of fixed air it dissolved completely. These curious observations were followed up by the London apothecary Timothy Lane, who showed that fixed air also held iron in solution and in fact he thought it “highly probable, that fixed air is generally necessary to the impregnation of mineral springs.”<sup>15</sup> By the time Brownrigg returned to his experiments in the 1770s, Joseph Priestley and others had become interested in using fixed air to prepare *artificial* mineral waters, mainly for their supposed lithontriptic properties, but also as a proposed cure for sea-scurvy.<sup>16</sup>

It was from the late 1770s that the problems of mineral water analysis were investigated by Bergman, who also recognized the importance of fixed air, which he called the aerial acid and regarded as the true *spiritus mineralis* of the ancients.<sup>17</sup> In addition Bergman identified hepatic air (hydrogen sulphide), nitrogen, and common air in various mineral waters. In qualitative tests he used barium chloride for sulphates, silver nitrate for chlorides, concentrated nitric acid for sulphides in the so-called “hepatic waters”, oxalic acid for lime, and tincture of galls or potassium ferrocyanide for iron, but he doubted whether other chemical reagents in common use were reliable. For example, calcium gave a precipitate with sodium and potassium carbonates, but if magnesium sulphate were present the result would be ambiguous because gypsum (calcium sulphate) might also be formed. Similarly, alum was not reliable and mercury nitrate gave variable results. Lead acetate was not a safe test for chlorides as lead chloride was likely to dissolve in the very dilute conditions found in mineral waters. Bergman therefore dispensed with all of these reagents.

Moreover, though he knew that precipitation did not always result in the complete separation of salts dissolved in mineral waters, he tried to make his analyses quantitative as well as qualitative. Unfortunately a problem arose when precipitates were heated to dryness before weighing. As different salts retain different amounts of water of crystallization when heated, Bergman’s analysis figures were always imprecise about the weight of water in each salt residue. This problem was to be overcome by the Irish chemist Richard Kirwan at the end of the eighteenth century, but in the meantime Bergman’s methods were employed by physicians like Thomas Garnett, George Pearson at St George’s Hospital, and John Elliott, physician to the Prince of Wales, who described the medicinal properties and chemical composition of a large number of mineral waters in 1784.<sup>18</sup>

The French have long appreciated the curative properties of natural mineral waters, and in the eighteenth century they were recognized as national assets. In 1780

<sup>15</sup> ‘A letter from Mr. Lane, Apothecary of Aldersgate Street, to the Hon. Henry Cavendish, FRS, on the solubility of iron in simple water, by the intervention of fixed air’, *ibid.*, 1769, 59: 216–27, on p. 225.

<sup>16</sup> J. Priestley, *Directions for impregnating water with fixed air in order to communicate to it the peculiar spirit and virtues of Pymont Water*, [etc.], London, 1772. Priestley’s method is illustrated in his *Experiments and observations on different kinds of air*, 3 vols., London, 1774–77; vol. 2 (1775), p. 263. His carbonated water was offered to the Navy as a cure for scurvy: D. McKie, ‘Joseph Priestley and the Copley Medal’, *Ambix*, 1961, 9: 2–12.

<sup>17</sup> Bergman, *op. cit.*, note 1 above, vol. 1, p. 151.

<sup>18</sup> J. Elliott, *An account of the nature and medicinal virtues of the principal mineral waters of Great Britain and Ireland: and others most in repute on the Continent. To which are prefixed directions for impregnating water with fixed air . . .*, London, 1769.

### *The analysis of mineral waters*

provincial doctors throughout France were asked by the Paris Société de Médecine to investigate the chemical composition of their local mineral waters. A. F. de Fourcroy too became interested in the problems of mineral water analysis,<sup>19</sup> turning first to Bergman's work, with which he quickly became dissatisfied on at least two counts. Firstly, he thought some of Bergman's reagents were unnecessary and reduced the number by half. Secondly, he pointed out that Bergman's procedures were not systematic and outlined a method by which the analysis could be built up step by step. Precipitating agents which yielded the lightest residues were used with the first samples of the mineral water, while those producing heavier precipitates were used later in the process. Each test was made using a large excess of the reagent and several pounds of the water to ensure a sufficient quantity of precipitate for a reliable result—a technique adopted by other eighteenth-century mineral water analysts. In each test a fresh sample of the water was used; it was not a matter of removing one salt after another from the same sample. Beginning with limewater, Fourcroy used dilute sulphuric acid, ammonia, sodium hydroxide, silver nitrate, and mercurous nitrate in succession, but his methods were still open to the objection that one salt in the water might interfere with another. Furthermore, each test indicated the presence of more than one substance, a drawback recognized by Thomas Garnett in 1790, who wrote,

However exact we may be in our investigations, and whatever degree of purity is possessed by different substances which we mix with the mineral waters in order to discover their principles; if it be granted that each test is capable of indicating two or three different matters, dissolved in the waters a doubt will always remain.<sup>20</sup>

Something better was needed and at the end of the century Richard Kirwan proposed a system of mineral water analysis based on the works of Bergman and Fourcroy, as well as German analysts like M. H. Klaproth and the Italian V. A. Gioanetti.<sup>21</sup>

Klaproth was an extremely accurate chemical analyst who was concerned mainly with the composition of minerals; he discovered or rediscovered several new elements including uranium, strontium, and titanium.<sup>22</sup> In 1790 Klaproth analysed the mineral water of Carlsbad and introduced the method of drying his precipitates to constant weight, igniting them at red heat where possible. This procedure was later adopted by Kirwan. Gioanetti published a brief account of his analyses of mineral waters at St Vincent and Courmayeur in 1779.<sup>23</sup> He used Bergman's methods with great care, but made his own contribution to mineral water analysis with a method involving the neutralization of carbonates with precisely measured quantities of an acid. This was

<sup>19</sup> W. A. Smeaton, *Fourcroy, chemist and revolutionary, 1755–1809*, Cambridge, 1962, pp. 20ff., 112–18.

<sup>20</sup> T. Garnett, *Experiments and observations on the Horley Green Spaw, near Halifax . . .*, Bradford, 1790, p. 4.

<sup>21</sup> R. Kirwan, *An essay on the analysis of mineral waters*, London, 1799.

<sup>22</sup> Klaproth's analytical work is discussed in comparison with that of Kirwan in F. Szabavary, *History of analytical chemistry*, Oxford, Pergamon Press, 1966, pp. 114–24.

<sup>23</sup> V. A. Gioanetti, *Analyse des eaux minérales de S. Vincent et de Courmayeur dans le Duché d'Aoste avec une appendice sur les eaux de la Saxe, de Pré S. Didier et de Fontane-More*, Turin, 1779. Gioanetti's work is compared with Bergman's in E. Rancke Madsen, *The development of titrimetric analysis till 1806*, Copenhagen, 1958, pp. 71–82.

in effect a simple titration procedure, although the quantities involved were stated in gravimetric rather than volumetric terms. Gioanetti remarked that he was uncertain whether he had found the exact point of saturation and as he did not use an indicator this remained in doubt. Volumetric methods were not used successfully in mineral water analysis before the nineteenth century.

Kirwan tried to determine the limits of sensitivity of precipitation tests. He used gravimetric methods and followed Klaproth in working wherever possible with ignited residues, to ensure that all the water had been driven off. He also tried to identify one substance in the presence of others and to estimate the proportions of each, giving details of methods for various mixtures of sulphates, chlorides, and residues containing nitre. Kirwan agreed with Fourcroy that Bergman had used qualitative tests haphazardly and argued that the results were incomplete. By this he meant that while the presence of individual acids and bases could be detected using precipitation reactions, it was impossible to say which acid was combined with which base. Thus Kirwan thought that Bergman's tests did not reveal the true chemical composition of the mineral waters and the analyst had to guess what earths and salts were actually present using the theory of elective affinities.

Kirwan was aware of the relative solubilities of salts and gave a list of what he called incompatible (i.e., insoluble) salts, though he realized that at the dilutions common in mineral waters such incompatible salts may exist in the solution together. His explanation foreshadowed later ionic and molecular solution mechanisms. He suggested that the acidic and basic parts of incompatible salts were held in solution due to the "resistance of the particles of water to that motion and separation from each other, which the action of the divellent powers of the saline particles would necessarily induce."<sup>24</sup>

In other words, the stronger the attraction of the constituent particles of the salt to each other (i.e., the less soluble the salt), the greater the dilution must be before this attraction is counterbalanced by the resistance of the water particles (molecules) keeping them apart. For example, the attractions between vitriolic acid and barytes, marine acid and silver, or fixed air and lime, Kirwan said, are so great that they act on each other when present at dilutions of only 1 part in 80,000 to 100,000 of water. He suggested that a table of relative solubilities could be drawn up and remarked that as precipitation reactions can never be complete they are unsuitable for quantitative experiments.

It has been said that Kirwan's chief aim was to make Bergman's methods quicker and simpler, but the impact of his work on analytical chemistry was more profound than that. He identified some of the pitfalls of solution analysis, drew attention to its theoretical basis and to the need to understand more clearly the dynamics of the chemical reactions involved, as well as improving the practical techniques themselves. He showed that evaporation followed by heating and weighing was a questionable procedure and argued that to obtain reliable results the salt residues should always be in the same state of hydration. Like Klaproth, he preferred to use anhydrous salts which had been heated to redness and avoided the partially hydrated forms used by

<sup>24</sup> Kirwan, *op. cit.*, note 21 above, p. 140.

### *The analysis of mineral waters*

Bergman and others. Kirwan became famous for his analytical work and his results were widely cited. He was among the leading European analytical chemists of his day, along with Klaproth in Germany and L. N. Vauquelin in France.

While a knowledge of the composition of mineral waters facilitated classification and enabled physicians to advise patients more reliably about their properties and uses, it also improved the prospects of preparing them artificially by dissolving the correct proportions of salts, earths, and gases in pure distilled water. Since minute amounts, even traces, of dissolved matter were considered essential to the medicinal properties of these waters, careful analysis was essential before there could be any hope of preparing artificial mixtures with curative properties approaching, let alone identical to, those of the natural waters. Indeed, Bergman asserted that no mineral water analysis should be considered complete until such a mixture could be prepared using the results: "if then the water thus treated, exactly and perfectly resembles the water which has been examined, it must afford an irrefutable argument that the analysis has been properly conducted."<sup>25</sup> Since this resemblance principally concerned the medicinal properties of the water, it followed that in mineral water analysis the physician would be the final arbiter of the chemist's work.

The preparation of artificial mineral waters had been actively studied in England, France, and Germany from the 1680s onwards and in the eighteenth and nineteenth centuries successful mineral water companies were established in France and other European countries. The best known is undoubtedly that of Jacob Schweppe, founded in Geneva about 1780.<sup>26</sup> Another interesting commercial venture supplying manufactured mineral waters for medicinal purposes originated with Friedrich Struve, a physician of Dresden, who in the 1820s claimed to be able to prepare numerous artificial mineral waters with,

all the qualities and properties, *in the most minute degree*, of their corresponding natural springs, as well in the effect produced on the human body in its most refined distinctions, as in their chemical analysis . . .<sup>27</sup>

Struve opened centres supplying manufactured mineral waters, resembling those of Carlsbad, Ems, Marienbad, Pyrmont, Spa, Seidschutz, Pullna, and Vichy, among others, in a number of European towns and cities including Berlin, Dresden, Leipzig, Königsberg, Moscow, Warsaw, and Brighton, where he arrived in 1825.

The German Spa at Brighton was highly regarded by some well-known physicians. A. B. Granville, who had met Struve in Dresden, was impressed with his work and

<sup>25</sup> Bergman, *op. cit.*, note 1 above, vol. 1, p. 213. Fourcroy made the same point in his *Leçons élémentaires d'histoire naturelle et de chimie etc.*, 2 vols., Paris, 1782, vol. 2, p. 406. Others followed this advice (e.g., Elliott, *op. cit.*, note 18 above).

<sup>26</sup> Douglas A. Simmons, *Schwepptes. The first 200 years*, London, 1983; N. G. Coley, 'The preparation and uses of artificial mineral waters (ca. 1680–1825)', *Ambix*, 1984, 31: 32–48, on p. 40.

<sup>27</sup> F. L. Kreysig, *A treatise on the internal use of the natural and factitious waters of Carlsbad, Marienbad, Ems, etc.*, transl. Gorden Thompson (pt. 1) and W. F. Bekenn (pt. 2), London, 1824, p. 10. Kreysig's description of Struve's work was based on F. A. Struve, *Remarks on an institution for the preparation and use of artificial mineral waters . . . to which are added testimonials by Dr Kreysig . . . and Dr Clarus . . .*, London, 1823.



recommended the waters available at the German Spa to patients in his fashionable London practice from 1826.<sup>28</sup> Ten years later Charles Daubeny, professor of chemistry at Oxford, commented on Struve's claim to omit none of the ingredients no matter how small the quantity and, like Granville, he agreed that Struve's artificial mineral waters resembled the natural waters very closely.<sup>29</sup> William Prout, who recommended Vichy water as a solvent for urinary stones, thought that carefully produced artificial mineral waters were as efficient as the natural products. The chief difference arose, he said, not from the composition of the waters, but from the absence of concomitant factors such as a fresh environment, diet, exercise, and new friendships which accompany a visit to a spa in its season.<sup>30</sup> Golding Bird, another fashionable nineteenth-century physician, also prescribed Vichy water for uric acid gravel. He said that for those not able to travel to the spa itself,

The artificial Vichy water prepared at the German Spa at Brighton . . . possesses all the value of the natural water. Indeed I think, it is preferable from its purity, and from its being more highly charged with carbonic acid . . .<sup>31</sup>

But the main significance of Struve's work lay in his careful, detailed analyses of the various mineral waters. His results were as accurate as they could be so long as chemical analysis was restricted to traditional quantitative methods. Struve might claim to include traces of dissolved matter, but some of these were exceedingly minute and until far more sensitive methods of analysis were available the most minute traces of dissolved matter would remain undetected. This brings us to the most important innovation for precision in mineral water analysis of the nineteenth century, the discovery of spectrographic analysis by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff. In 1857 Bunsen developed a method of identifying volatile metals by means of the flame test using a platinum wire dipped in the test solution and held in the colourless flame of his gas burner. Three years later, working with Kirchhoff, he devised an important refinement of this method by passing the coloured light through a prism and focusing the resulting spectrum on a white screen. Almost at once, two new alkali metals, caesium and rubidium, were discovered in the mineral waters of Durkheim and in the mineral petalite.<sup>32</sup> Only a minute amount of material was needed to detect these elements with the spectroscope, whereas in a traditional chemical investigation it would have been necessary to evaporate 40 *tons* of the water or work up 150kg of the mineral to obtain measurable amounts of caesium and rubidium. Thus spectrographic analysis proved very much more delicate than

<sup>28</sup> A. B. Granville, *Spas of England*, London, 1841, repr. London, Adams and Dart, 1971, pp. 571–7. He also wrote on German spas and on the waters at Vichy; *idem*, *The spas of Germany*, 2 vols., London, 1837, (2nd ed., 1838); *idem*, *The mineral springs of Vichy*, London, 1859.

<sup>29</sup> C. Daubeny, 'Report on the present state of our knowledge with respect to mineral and thermal waters,' *Rep. Br. Ass. Advmt Sci.*, 1836, 5: 3–93, on pp. 53–6.

<sup>30</sup> W. Prout, *On the nature and treatment of stomach and renal diseases*, 5th ed., London, 1848, pp. 439–43.

<sup>31</sup> Golding Bird, *Urinary deposits*, 4th ed., London, 1853, p. 162.

<sup>32</sup> R. Bunsen, *Ann. Phys.*, 1860, 110: 161–89; G. Kirchhoff and R. Bunsen, *ibid.*, 1861, 112: 337–81; R. Bunsen, *ibid.*, 119: 1–11.

### *The analysis of mineral waters*

precipitation reactions could ever be and from the 1860s spectroscopic methods were to become important in mineral water analysis.

Using the new method, the analysis of a mineral spring in the Wheal Clifford copper mine near Redruth, Cornwall was reported to the British Association meeting at Bath in 1864. The spring, 1,320 feet below the surface, yielded 150 gallons of water per minute at 122–3°. It was analysed by W. A. Miller, professor of chemistry at King's College, London, at the request of Charles Lyell. Miller found 8–10 times more lithium salts in this spring than in any other then known and he suggested that, as the use of lithium in medicine was limited by its price and no less than 800 pounds of lithium salts per day could be obtained from this spring by simple precipitation methods, it offered a good commercial prospect.<sup>33</sup> Also by a chemical method introduced by Bunsen and Kirchhoff using  $\text{PtCl}_4$  to separate potassium, caesium could be extracted in much smaller amounts. Miller wrote,

It was by following this method and examining the washed platinum salt [ $2\text{KCl.PtCl}_4$ ] in the spectroscope that Caesium was ascertained to exist in this water. No evidence of the presence of Rubidium was thus procured, though possibly had I been able to operate on a still larger quantity of water, I might have been able to detect it.<sup>34</sup>

At the same meeting Henry Roscoe, also at the request of Lyell, reported on his spectroscopic analysis of the Bath water, which revealed the presence of lithium and copper but no caesium or rubidium.

Spectroscopic methods became very popular due to their reliability, sensitivity, and convenience. Many chemists who had been interested in the composition of mineral waters turned their attention to spectroscopic methods as a means of improving their results. For example R. H. Davies, a pharmaceutical chemist, made a spectroscopic examination of various mineral springs at Harrogate in 1866 that revealed the presence of minute quantities of alkali and alkaline earth metals previously unsuspected.

I have submitted the residues of above thirty of the medicinal springs of Harrogate to spectrum analysis, and the results of this investigation are more important than were first anticipated; they all without exception show the presence of lithium in the waters, strontium is present in the majority and barium exists in a great many.<sup>35</sup>

Davies followed up his qualitative spectrographic observations with gravimetric methods to determine the quantities of barium and strontium salts in the principal springs of Harrogate.

Thus mineral water analysis, which had seemed simple to chemical physicians in the late seventeenth century, proved so difficult in practice that by the 1860s it had

<sup>33</sup> W. A. Miller, 'Chemical examination of a hot spring containing caesium and lithium in Wheal Clifford, Cornwall', *Chem. News*, 1864, 10: 181–2.

<sup>34</sup> *Ibid.*, p. 182.

<sup>35</sup> R. H. Davies, 'Note on the existence of lithium, barium and strontium in the Medicinal Springs of Harrogate', *ibid.*, 1866, 13: 302–3.

become the province of highly trained chemists using the latest physical and chemical techniques of analysis. Considering the nature of the problems involved, it is easy to understand why those who tried to discover the chemical contents of mineral waters in the eighteenth century met with such difficulties. Even the simple technique of evaporating off the water to obtain the dissolved solid constituents posed problems for the chemical analyst, although from the late seventeenth century onwards, salts extracted from some mineral waters by this method were on sale in apothecaries' shops. This was especially useful for all those mineral waters which could not be kept sweet in wooden casks during transportation. It was easy to reconstitute mineral waters in the home by dissolving their dry salts in fresh water and after 1775, with the invention of Nooth's apparatus and the recognition of the important role played by fixed air, even effervescent waters could easily be prepared. Epsom salt (magnesium sulphate), first extracted on a commercial scale by Nehemiah Grew in the 1680s, was sold in very large quantities. These developments stemmed from efforts to analyse mineral waters and as analytical methods were improved chemists and physicians made useful contributions to the means of identifying closely related salts and earths in very small quantities and also to gravimetric techniques. The persistent belief that even minute traces of salts were essential to the medicinal properties of the waters promoted the search for greater sophistication and accuracy. This could sometimes be used to commercial advantage as Struve, Schweppe, and others found, yet the introduction of spectrum analysis showed that, no matter how careful the analysis, there would always remain traces of minerals too minute to be detected by chemical methods.

The analysis of mineral waters provided a rationale for their use in medicine which supported the enthusiastic recommendations of physicians. Even where there seemed to be no obvious connection between the chemical constituents of the water and the medicinal virtues claimed for it, the very existence of a chemical analysis gave the water added appeal as a curative agent and many physicians were able to turn this to good advantage in attracting patients to the spas in Britain, France, Germany, and throughout Europe. Thus while mineral water analysis certainly proved to be most difficult, the efforts of physicians and chemists to perfect it in the eighteenth and nineteenth centuries yielded benefits of various kinds for the improvement of inorganic chemical analysis in general and for some medical practitioners.