MINERALOGICAL MAGAZINE, MARCH 1973, VOL. 39, PP. 4–24

A. F. HALLIMOND LECTURE 1972

Mineral analysis and analysts

M. H. HEY

British Museum (Natural History), Cromwell Road, London, S.W. 7

SUMMARY. The history of the chemical analysis of minerals is shortly reviewed. Following rapid developments between 1770 and 1810, few important changes took place for close on 130 years; new procedures led to simpler and more convenient separations but not, on the whole, to greater accuracy. The older analyses are, in general, neither worse nor better than modern ones, and analyses can only be assessed on internal evidence, if available, or on the reputation of the analyst.

The development of microchemical and colorimetric techniques in the last 40 years has resulted in a great reduction in the amount of material required for a mineral analysis; 5 to 20 mg is usually sufficient, and in favourable cases a complete analysis may be possible on less than 1 mg. Some modern instrumental methods are considered, and it is concluded that they cannot wholly replace the classical wet-chemical methods in their modern developments.

W. F. Hillebrand (1894) deplored the tendency of some petrologists to demand large numbers of very incomplete rock analyses, and his remarks are considered apposite today.

THE beginnings of mineral analysis are lost in the mists of pre-history: we know from Biblical and Egyptian records that a form of fire-assay for gold and silver was in use some 3000 years ago, and there can be little doubt that metallurgists evaluated any new source of ore by smelting a sample. The fire-assay of gold and silver had approached modern standards of accuracy some 600 years ago if not earlier, and *ad hoc* methods for the assay of many metallic ores have certainly been known for a comparable time.

Between 1757 and 1781 Marggraf made many advances of analytical significance, including the distinction between soda and potash, the use of ferrocyanide as a reagent for iron, the use of the microscope as an aid in the identification of salts (largely ignored for the next century!), and a notable economy in the amount of material used for analysis. However, he does not appear to have attempted the complete quantitative analysis of any mineral. The earliest attempts at a complete analysis I have been able to trace[1] are by Torbern Bergman: in 1774, an ankerite from Vester Silfberg 'dedit ferri calcinati 22, magnesii calcinati albi 28, calcis aëratæ 50', and in 1777 he attempted, with little success, complete analyses of emerald, ruby, sapphire, topaz, and hyacinth (probably idocrase). It therefore seems appropriate to celebrate the bicentenary of complete mineral analysis today with a short review of progress.

In the short space of 17 years, and despite ill-health, Bergman achieved a great deal, and though many of his results were of no great accuracy, his methods provided the foundation on which later workers have built. They may be illustrated by his analysis

---

[1] I have not been able to check whether the 'Analyse du gypse' by Lavoisier (1768) is a complete analysis. Black appears to have made a complete analysis of limestone, but the date of this is not known.

(1782) of an asbestos from La Tarentaise, Savoy: complete decomposition was only attained, after several methods had been tried, by fusion with twice its weight of a mixture of equal parts of potassium carbonate and charcoal. The fused mass being then treated with aqua regia, the gelatinous silica was separated, washed, and dried; it amounted to 64 %. The filtrate gave a precipitate with sulphuric acid, 6 % of the weight of the mineral, 'quæ spathum ponderosum erant' [i.e. barium sulphate; but this was probably gypsum], and on evaporation a further 'calcis vitriolatæ 12 libræ' separated; in the remaining solution, potassium ferrocyanide precipitated 7 % of prussian blue, corresponding to 1·2 % 'ferro calcinato' or ferric oxide, and finally 'Residuus liquor ope alkali fixi aërati dedit 18,6 magnesiæ aëratæ'; but this precipitate contained some alumina, as was shown by dissolving it in sulphuric acid, igniting gently, and leaching, when 3·3 % alumina remained. Apart from the supposed baryta and a low magnesia, this is a surprisingly good analysis of tremolite (cf. analyses of asbestos from La Tarentaise in Lacroix, *Min. de France*, 1895, **1**, 647); evidently adsorption of alumina by the gelatinous silica balanced the incomplete precipitation of silica by simple extraction of the melt with acid. This source of error was soon corrected: in 1787 Klaproth wrote 'Dieser bey ähnlichen Arbeiten mir öfter vorgekommene Umstand, unter denen durch Säuren ausgelösten Erden noch Kieselerde zu finden, beweiset abermals, wie äusserst vorsichtig der Schiedekünstler vornehmlich bey Untersuchungen von Stein und Erdarten zu verfahren habe'.[1]

Once started, progress was rapid: in the first edition of his *Elements of Mineralogy*, 1784, Richard Kirwan was able to tabulate 74 analyses of rocks and minerals by Achard, Bergman, Bindheim, Gerhard, Scheele, Withering, and others, including many of his own. By 1800, 14 more elements had been added to the 28 recognized[2] in 1770: Be and Cr by Vauquelin, W, Mo, and Ba by Scheele, Zr and U by Klaproth, Yt by Gadolin, Ti by Gregor, Sr by Crawford, and Te by Müller von Reichenstein, and many more analyses, of varying quality, had been published.

Many important advances in analytical chemistry in this period were due to M. H. Klaproth, a particularly careful and accurate analyst. In the six volumes of his *Beiträge zur chemischen Kenntniss der Mineralkörper*, published from 1795 to 1815, he gives full details of his methods[3] 'Bei dem, mir selbst nur zu sehr bewussten, Mangel der Unfehlbarkeit, empfehle ich diese Prüfung um soviel dringender, weil mehrere meiner Erfahrungen . . . mit den, von Andern angegebenen, zum Theil in einem auffallenden Widerspruche stehen'.[4]

---

[1] 'I have several times observed siliceous earth along with other earths dissolved in acids; this should suggest how cautious a chemist ought to be, particularly in analyzing different kinds of stones and earths.'

[2] Na, K, Ag, Au, Cu, Mg, Ca, Zn, Hg, B. Al, C, Si, Sn, Pb, P, As, Sb, Bi, S, Mn, Fe, Co, Ni, F, Cl, and Pt; that Mn is distinct from Mg was recognized as early as 1740 by J. H. Pott, but it continued to be known as magnesia nigra even after Gahn had isolated the metal (Bergman, *Opuscula*, **2**, 201); the name manganese, which had been used for the black oxide, was formally transferred to the metal by L. B. Guyton de Morveau in his French translation (1780) of Bergman's *Opuscula*.

[3] It is, perhaps, worthy of note that no analysis of menaccanite other than Klaproth's of 1797 (*Beitr. chem. Kennt. Min.* **2**, 226) appears to have been published.

[4] 'Being only too well convinced of my own fallibility I recommend this examination [i.e. the repetition of his work] with the greater eagerness, since the results of several of my experiments . . . are in striking contrast to those given by others' (*Beitr. chem. Kennt. Min.* **1**, vii–viii).

One important technique introduced by Klaproth was the use of caustic alkali fusions to attack acid-resistant silicates; he employed silver crucibles (*Beitr. chem. Kennt. Min.* **1,** xi–xii), and noted that for this purpose they are such superior to platinum.[1] After long neglect, occasioned by the fact that commercial caustic alkali was for long relatively impure compared with the carbonate, caustic alkali fusion has recently come into favour again; but few analysts outside France[2] seem to have recognized the superiority of silver crucibles over those of iron or nickel for this purpose.

It is, perhaps, worth noting that the electrochemical series of metals was recognized as early as 1780 by Bergman (*de praecipitatis metallicis*), and was employed quantitatively by Klaproth (e.g. copper was precipitated from solution by a cylinder of metallic tin, and tin by one of zinc; *Beitr. chem. Kennt. Min.* **2,** 260).

Bergman had brought a degree of order into qualitative analysis by his recognition of more or less specific reagents for certain acids and metals; by 1800 quantitative mineral analysis had become recognized as an important branch of chemistry and textbooks soon began to appear. F. Szabadváry (1966) cites Lampadius' *Handbuch zur chemischen Analyse der Mineralkörper* (1801) as the first of these; I have not been able to see it, but Accum's *Practical Essay on the Analysis of Minerals* (1804) covers much the same ground, dealing with apparatus and with the preparation, purification, and testing of reagents, and giving procedures for the analysis of a considerable number of minerals. The available techniques were still very imperfect, and in particular the balances were not sensitive enough: Klaproth's balance appears to have weighed to ½ grain (about 30 mg) so that although he normally took 5 to 10 grammes of a mineral for analysis, his results were only accurate to ½ % at best, as he clearly recognized. Many later workers have been less cautious.

The modern period

Gravimetric analysis. Most eighteenth-century analysts had tacitly assumed that minerals are constant in composition, but Berthollet doubted this (see, e.g. Berthollet, 1803), and, to quote Szabadváry (1966): 'The good analysts did not provide theories to explain their work, while the good theoretical chemists did not assist the spread of their views owing to their poor results.' The basic laws of chemistry—the Law of Constant Proportions (Proust, 1799), the Law of Equivalent Proportions (Richter, 1792), and the Law of Multiple Proportions (Dalton, 1805, 1808; Thomson, 1807, 1808; Wollaston, 1808) could not be established without better analyses than their proponents could muster initially; and when these laws were generally accepted,[3] the determination of reasonably accurate equivalent weights again called for improvements

---

[1] I have not been able to trace the author of the delightful mnemonic for the substances that must not be handled in platinum: *In dem Tiegel von Platin / Schmilz nicht Arsen, Wismut, Zinn, / Kupfer, Antimon und Blei / Oder Ätzendalkali.*

[2] See, e.g. Carnot, 1898.

[3] Some doubts persisted for many years; as late as 1860 Marignac thought that slight differences might occur in the composition of various compounds; and, of course, both sides in the controversy were right: most compounds are strictly stoichiometric in composition, but some are not—e.g. pyrrhotine.

in analysis.[1] Not only better techniques, but better balances were needed, and these were steadily developed. Accum (1808) mentions weights of 1/100 grain (**1**, 14) but in practice appears to have weighed to 1/10 grain (~ 7 mg; **1**, 25 ff.); Pfaff's balance (1821) would weigh to 1 mg, and the balance described by Berzelius in 1841 used a 5 mg rider, so that he was able to insist on a summation not more than 1·5 % out, working on a 1 g sample. Even with the improved balance, this could not have been attained without the many improvements in technique supplied by Berzelius or under his stimulus. Except where he had to deal with a certain range of very difficult separations, some of which were troubling analysts a century later, for example the separation of aluminium and beryllium, or of titanium from niobium and tantalum, most of Berzelius' analyses will stand comparison with modern work. Indeed, there is never any justification for rejecting an analysis merely because it is old.[2]

With the work of Berzelius, then, we enter on the modern period of gravimetric analysis, though many detailed improvements were still to come; a number of separations still gave trouble, and there were no satisfactory weighing forms for a few elements. As an example of the gradual development of methods for a difficult separation, we may consider the analysis of wavellite, which presented the double problem of separating alumina and phosphate and of determining the latter.

In 1818 Fuchs made two analyses of wavellite from Devon and one of a wavellite from the St. Jacob mine, Amberg, which he had described in 1816 as a new phosphate of alumina under the name lasionite, believing wavellite to contain only alumina and water. His lasionite analysis was made by precipitating the phosphate by the addition of calcium chloride to a solution of the mineral in the minimum of caustic potash; the alumina was then precipitated by adding ammonium chloride to the filtrate from the calcium phosphate; the summation of 99·28 % was reasonable, and he accepted the analysis (it is, in fact, in excellent agreement with the accepted formula of wavellite). But when he tried the method with his sample of Devon wavellite he got a grossly high summation, which he traced to incomplete precipitation of the calcium phosphate, the solution having been too strongly alkaline (the 'alumina' then contained not only the missing phosphate, but calcium also); clearly this method was not reliable. He then tried another method: the alumina was precipitated as a sodium aluminium silicate ('kunstlicher Natrolith') by adding an excess of a sodium silicate solution to an acid solution of the mineral; the phosphate was precipitated as calcium phosphate in ammoniacal solution after removal of the silica. Fuchs was aware that the composition of the calcium phosphate was liable to vary with the conditions of

---

[1] While the work directed to the determination of equivalent or atomic weights led to many advances in ordinary gravimetric techniques in the early nineteenth century, most atomic weights were fairly well known by 1830; atomic weight determinations have for a century now been highly specialized operations with relatively little bearing on the bulk of analytical work.

[2] It is, however, always important to read the text, whether the analysis be new or old, and not to merely extract the tabulated analysis. A classical example is the alleged occurrence of scolecite in the Auvergne, reported in most textbooks as late as 1922 if not later; this originates in a misprint in Guillemin's analysis (1826) of mesotype (which could be scolecite or natrolite or mesolite) from the Auvergne: in the tabulated analysis, 'chaux' is printed, but a glance at the analytical procedure two lines lower down will show that the oxide in question was in fact soda! The slip was pointed out by several authors, including Lacroix (1896), but still persisted.

precipitation, and endeavoured to meet this difficulty by precipitating a known amount of calcium as phosphate, to obtain an empirical conversion factor; but although his results were good the weighing form was clearly unreliable.

Berzelius (1819) varied Fuchs' separation by fusing the wavellite with sodium carbonate and silica, leaching the mass, and removing the small amount of silica leached out with ammonium carbonate. And he dealt with the uncertain composition of the calcium phosphate[1] by dissolving it in sulphuric acid and separating the lime as sulphate by addition of alcohol (a method still useful for the separation of small amounts of calcium from much magnesium; see, e.g. Hillebrand and Lundell, 1929, p. 488). But he had a further problem, in that he had shown that the Devon wavellite contains fluorine, so that the calcium phosphate precipitate would contain fluoride; he attempted an indirect method, removing the sulphate from the filtrate from the gypsum with barium chloride, and then adding a large excess of ammonia to precipitate barium phosphate; the fluoride was then arrived at by subtracting the CaO and P_2O_5 from the weight of calcium phosphate plus fluoride first obtained. Unfortunately, barium phosphate is appreciably soluble in presence of ammonium salts (Rose, 1829, p. 398), and in consequence Berzelius' figures for P_2O_5 and HF are only approximate.[2]

It is not surprising that Rose (1829, pp. 398 and 404) wrote: 'Die Trennung der Phosphorsäure von andern Substanzen ist manchmal mit den grössten Schwierigkeiten verbunden. . . . Ganz besonders schwierig ist es, die Phosphorsäure von der Thonerde zu trennen.'[3] When a separation of phosphoric acid from most other metals had been achieved, he advocated precipitating it as the calcium or barium salt, and then determining lime or baryta in the ignited and weighed precipitate (p. 407).

In 1833 Otto showed that phosphate could be determined accurately as magnesium pyrophosphate after precipitation as magnesium ammonium phosphate; and he found that if tartrate was added this precipitation could be carried out in the presence of, inter alia, alumina. But recovery of the alumina was difficult, and the magnesium pyrophosphate from such a separation was often impure (Rose, 1851).

In 1851, Sonnenschein described the now standard method of precipitation as ammonium phosphomolybdate[4] and conversion of this to magnesium ammonium phosphate; but while this is an excellent method for determining the phosphate, the problem of determining the bases it was combined with remains, since the filtrate from the ammonium phosphomolybdate contains a large excess of molybdate that must be removed with H_2S. In the same year Reynoso described a method that became very popular for the removal of phosphate from solutions—the treatment of a nitric acid solution with a large excess of metallic tin—but the removal of the phosphate is often

---

[1] Ignited calcium phosphate precipitates vary between hydroxy-apatite with 55·82 % CaO and 42·39 % P_2O_5 and $Ca_3(PO_4)_2$ with 54·23 % CaO and 45·77 % P_2O_5; both Fuchs and Berzelius appear to have obtained precipitates near $Ca_3(PO_4)_2$.

[2] An attempt to recalculate the analysis using modern atomic weights (Berzelius' 1819 values for Ca and P are high) showed that the weight of barium phosphate reported is impossible; it is probable that 245·8 cg is a slip for 295·8.

[3] The separation of phosphoric acid from other substances is often very difficult. . . . It is particularly difficult to separate phosphoric acid from alumina.

[4] L. Svanberg had recommended ammonium molybdate as a sensitive qualitative reagent for phosphate in 1848.

imperfect. Not until 1927 did a satisfactory method for the determination of aluminium in the presence of phosphate become available, when Berg described their separation with 8-hydroxyquinoline—but it is still necessary to destroy the excess 8-hydroxyquinoline before proceeding to the determination of the phosphate. This was a particularly troublesome separation, and efficient methods were available for most separations by the time of Rose's textbook (1829).

Though H_2S had been introduced as a reagent by Gay-Lussac in 1811 and was soon widely used for appropriate quantitative determinations, the classical scheme of cation groups for qualitative tests and quantitative determinations first appears in Rose's textbook of 1829; but the wealth of techniques already available, combined with a somewhat unsystematic and typographically poor layout, made this a difficult book for the beginner. Recognizing this, Fresenius set out to produce a textbook that would serve the elementary student as well as the more experienced analyst. His *Anleitung zur qualitativen chemischen Analyse* of 1841 and its quantitative companion of 1846 gave very full experimental details, and an orderly, systematic procedure well adapted to most mineral analyses; these texts laid down the pattern of analytical teaching for over a century, with remarkably little modification. In some ways this has been unfortunate, for Fresenius deliberately omitted a considerable number of elements, some because of their rarity, and some because their reactions were not well enough known for them to be incorporated satisfactorily in the scheme:[1] and this limited selection has formed the basis of most university courses of analytical chemistry ever since (indeed the difference between the 3rd (1853) edition of Fresenius and a standard textbook of the 1920s is remarkably slight; the Fresenius scheme, with an appendix of *Reactions of some less Common Elements*, which includes Ti as well as V, Mo, W, etc., was still used by Fenton (1943)). Hardly ever will a chemistry graduate have any notion of the analytical behaviour of titanium, zirconium, tantalum, niobium, vanadium, selenium, the rare earths, the platinum metals, or some dozen other elements—if, indeed, he is fortunate enough to have learnt any wet-chemical analysis at all.

Some remarks by W. F. Hillebrand and G. E. F. Lundell (1929, p. 2) are perhaps appropriate here: 'The determination of an element in its pure compounds by volumetric or gravimetric procedures is a mechanical operation which bears the same relation to the analysis of mixtures that finger exercises do to the playing of a piano. Training along such lines is necessary. It should be understood, however, that it is only a beginning. Too often, the training of the student stops at this point. If he pursues the subject no further, he carries away an entirely erroneous conception of the analyst's task and of the accuracy that he should obtain. The test of an analyst is his ability to choose the proper line of attack for the analysis of the material on hand, to modify existing methods of analysis or devise new ones if necessary, to carry the analysis through, and to put the proper interpretation on the result that is obtained.'

Volumetric methods have found little use in mineral analysis, partly because prominent analysts, including Berzelius, Rose, and Fresenius, regarded the early techniques

---

[1] Some were discussed shortly in an appendix in later editions.

as of inadequate accuracy,[1] partly because there were, and are even now, no really satisfactory methods for the determination of the major rock-forming elements with the exception of iron; most volumetric methods still call for larger samples than are normally used for gravimetric methods, the principal exceptions, so far as mineral analysis is concerned, being iron, chromium, manganese, and antimony when these are principal constituents of a mineral.[2] But for one purpose volumetric methods have proved essential: the determination of the net state of oxidation[3] of a mineral or rock. For an acid-soluble mineral this is a straightforward matter nowadays, for which permanganate (Margueritte, 1846), dichromate (Penny, 1850; Schabus, 1851), or ceric sulphate (Lange, 1861) are usually employed, but as late as 1846 it was difficult; thus Rose (1829) recommends dissolving the mineral in acid under carbon dioxide, and either reducing the ferric iron with a saturated solution of H_2S, with exclusion of air, and weighing the sulphur formed, or oxidizing the ferrous iron with chlorauric acid and weighing the gold precipitated. Minerals insoluble in acid at 100 °C remained intractable until 1860, when A. Mitscherlich succeeded in dissolving a wide range of rock-forming minerals in 75 wt. % sulphuric acid in a sealed tube at 150 to 250 °C, but unfortunately this method leads to seriously high results for Fe^{2+} if even small amounts of sulphides are present;[4] Cooke's method of solution in a hydrofluoric–sulphuric acid mixture is superior in this respect, since pyrite (the commonest sulphide in rocks) is not appreciably attacked by the acid mixture unless large amounts of ferric iron are also present (Hillebrand and Stokes, 1900). But the modern variants on the Cooke technique, in which a measured excess of an oxidant (V^{5+}, Cr^{6+}, Ce^{4+}) is added at the start, to avoid any possibility of air-oxidation, are likely to give high results in the presence of appreciable sulphide, small amounts of which are present in most igneous rocks; in the attack by a mixture of sodium fluoride and boric oxide (Rowledge, 1934) also, sulphides or organic matter will lead to seriously high results. It is possible, too, that those techniques in which the ferrous iron is stabilized by a complex-forming agent such as dipyridyl or *o*-phenanthroline may be affected by sulphides. Fortunately it appears possible to attack the sulphides with pure dry chlorine at 250 to 300 °C without attack on or oxidation of a wide range of rock-forming minerals[5] (Moss, Hey, Elliott, and Easton, 1967).

Recent developments. A comparison of the precipitants and weighing forms recommended for the various elements by Fresenius (1853) and by Hillebrand and Lundell

---

[1] Gay-Lussac's procedure for the silver–chloride titration was accurate, but very tedious; and chloride is of little importance as a constituent of rocks and minerals.

[2] A calcium oxalate precipitate can be dealt with at least as accurately by permanganate titration as by ignition to the oxide or carbonate, but it is then impossible to determine coprecipitated manganese, and very troublesome to determine strontium.

[3] For hyperoxidized rocks or minerals such as the chromates, the higher oxides of manganese, piemontites, and the like, this is usually referred to as an available oxygen determination. For under-oxidized rocks and minerals it is generally called a ferrous iron determination; but since Fe^{2+} and Mn^{3+}, or Fe^{3+} and Ti^{3+}, or Fe^{3+} and Cu^{+} can coexist in the same crystal structure, it is desirable to avoid this term, though we conventionally continue to report the result as Fe^{2+} so far as is possible.

[4] $8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + SO_4^{2-} + 8H^{+}$.

[5] Magnetite is an exception, being oxidized to maghemite and part of the iron volatilizing; $6Fe_3O_4 + 3Cl_2 \rightarrow 8Fe_2O_3 + 2FeCl_3$.

(1929) will reveal few changes; the most important are the virtual disappearance of sulphides as weighing forms and the introduction of electrolytic methods for a few metals (Gibbs, 1864; Luckow, 1865) and of electrolysis with a mercury cathode for the removal of many metals from solutions (Cain, 1911); also the introduction of a small number of more or less specific organic precipitants: α-nitroso-β-naphthol, as a reagent for cobalt (Ilinski and Knorre, 1885); phenylhydrazine, for the separation of iron and aluminium (Hess and Campbell, 1899); dimethylglyoxime, for nickel and palladium (Chugaev, 1905); cupferron, for iron, tin, vanadium, uranium, titanium, zirconium, tantalum, and niobium (Baudisch, 1909); tannin, for the separation of tantalum and niobium (Powell and Schoeller, 1925); and 8-hydroxyquinoline, for a wide variety of metals (Berg, 1927).[1]

Dimethylglyoxime is often referred to as the first organic reagent for quantitative analysis, but this is incorrect, though it appears to have been the first organic reagent to give complexes that could be used as weighing forms; but apart from those already mentioned, sodium succinate was in use to separate iron from the divalent cations by 1808 (Accum), while Hisinger (1811) used sodium benzoate for the same separations.[2] That tartaric acid inhibits the precipitation of many metals by alkali was known to Aikin (1807), and probably much earlier, but I have not been able to trace the first use of this property in analysis; Otto (1833) seems to refer to it as a well-known procedure.

The success of 8-hydroxyquinoline started off a flood of new organic reagents, many of which were inadequately studied—one more reagent that will precipitate copper quantitatively from neutral solutions is of little interest to the busy analyst if there are no data on the pH range over which the precipitation is complete, or on what other ions may be present. Most of the useful survivors, plus some that do not seem entirely satisfactory, will be found in such collections as Flagg (1948), Johnson (1955, 1964), and Prodinger (1957), but it is likely that some of the casualties could prove valuable if more carefully studied. There can be little doubt that one of the greatest needs in quantitative work today is a thorough re-examination of many of the techniques currently available;[3] there is scope here for a good many Ph.D. theses!

Perhaps the biggest advantage the analyst of today enjoys over his colleague of 100 years ago is the availability of reliable, pure reagents. Berzelius and his contemporaries had to purify every reagent, and often to prepare them as well. In the 1920s corrections for filter-paper ash and reagent blanks (especially alkali in the calcium carbonate used

---

[1] It will be noticed that the lists of cations for which the reagents mentioned have been found useful differ from the lists for which they were originally proposed.

[2] Kolthoff, Stenger, and Boskovitz (1934) proposed the use of ammonium benzoate; I have not seen their paper in the original, and am not clear whether they were aware of Hisinger's work.

[3] For example, the original (and satisfactory) recipe of Berg for the precipitation of aluminium by 8-hydroxyquinoline in weakly acid solution was incautiously modified by the replacement of sodium acetate by ammonium acetate and by immediate filtration instead of digestion for an hour on the water-bath, and was found to give low results. It seems probable that the first of these modifications results in too low a *p*H, with incomplete precipitation of the aluminium; when this is corrected, low results may still be obtained although the filtrate may now contain no aluminium, because the digestion period was necessary to convert to its 8-hydroxyquinolate colloidal alumina, normally present in a solution that has been neutralized to incipient precipitation and then just 'cleared' with acid.

for the Lawrence Smith alkali determination) were still important; and a large platinum still for the purification of hydrofluoric acid had only just gone out of use at the British Museum.

Microchemical and semi-micro gravimetric analysis. In the eighteenth century Klaproth used 5 to 10 g of a mineral or rock for analysis. Berzelius reduced this to 1 g, largely through improvements in the analytical balance, and this remained the standard quantity for some 130 years.[1] Occasionally, smaller amounts had to be used because no more material was available—Laspeyres' (1896) analysis of cosmochlore on 3 mg must be accounted a good one, considering that his balance only weighed to 0·1 mg. Any major reduction in the amount of material used had to await the advent of more sensitive balances and of techniques that avoid the mechanical transfer of precipitates. When the Kuhlmann microbalance, weighing to 10 μg, or with suitable precautions to 1 μg, became available, mineral and rock analyses on 100 mg became a simple matter (Guthrie and Miller, 1933), and with the Stahler 'filterstick' (Emich, 1933) and the King–Miller microfilter[2] (1939) the way was open to the development of microanalysis of minerals, and even of rocks[3] (Hueber, 1932; Hecht, 1940). Microchemical analysis is by no means as difficult as is often imagined, nor is it as rapid as has sometimes been suggested; it is usual to avoid hydroxide and sulphide precipitates because they do not filter easily, and to seek weighing forms with a favourable conversion factor; when, as is often the case, little material is available, a special separation scheme must be worked out for each new mineral studied, and tested on a synthetic mixture; repeated evaporations are necessary to keep the bulk of the solutions down to the capacity of a microbeaker; and as organic reagents are largely used, the removal of excess reagent can be troublesome.[4] The main needs of the microanalyst are patience, a modicum of manipulative skill, and the widest possible knowledge of the available reagents and their deficiencies.

The most serious weakness of mineral microanalysis is in the determination of water, which all too often has to be done by loss on ignition, in air or better in nitrogen. Absorption-tube techniques, as used in organic microanalysis, are a difficult technique to acquire and the blank is usually large. We need a more stable reagent than Lindner's α-naphthyl phosphoric acid chloride (1922) or the methyl-ethylglutaryl chloride of

---

[1] Some analysts sought to simplify their calculations by trying to weigh out exactly 1·0000 g; this is a stupid procedure in an analysis aspiring to any claim to accuracy, since it is very probable that a quantity of material differing from 1 g by 0·2 mg or even more will be accepted as '1·0000 g'— and the saving of time in the calculations is far outweighed by the time taken to weigh out an exact amount.

[2] This simple device originated by King and perfected by Miss Miller is none too well known; it allows the analyst to filter off a precipitate that must be ignited, in the precipitation vessel, using a small wad of filter paper and pulp that is burnt with the precipitate, so avoiding any transfer of the precipitate.

[3] With non-homogeneous materials like rocks, the problem of a representative sample arises: a 10 to 20 mg sample of a fine powder will be adequately representative of the major minerals of a rock, but may not be for minor components.

[4] Many organic reagents can conveniently be destroyed with strong nitric acid and hydrogen peroxide, but those containing a benzene nucleus are liable to end up as picric acid and interfere with subsequent colorimetric procedures. Extraction of the excess reagent with chloroform or carbon tetrachloride at a suitable pH is often possible.

Belcher *et al.* (1960), and preferably one converting the water to a compound more readily determined by colorimetric techniques than is chloride.

A procedure that has considerable possibilities is the extraction of metal complexes with an organic solvent. Ether extraction of the autocomplex ferric chloride has long been used to remove the bulk of the iron from a suitable solution (Rothe, 1892) at all scales of working—macro-, semi-micro-, and micro-, and extraction of suitable complexes is widely used in the determination of trace constituents (see, e.g., Sandell, 1959), but has yet to find its proper place in the microchemist's armoury. I have found extraction of the Sn^{iv} cupferron complex by chloroform, followed by evaporation of the extract and ignition to stannic oxide, a very satisfactory procedure for the estimation of tin (Leavens *et al.*, 1970).

Beyond the milligram. With a microbalance weighing to one microgram, 3 to 5 mg of a mineral are normally necessary for a good gravimetric analysis—and often this amount is not available. If a balance weighing to 0·1 μg, such as the Oertling decimicro-balance, is available, simple gravimetric determinations on samples weighing 1 mg or even less are possible, but there are difficulties in such operations as filtration, and owing to the low capacity of such balances the vessels for much of the work will be very small, often only 0·2 to 0·3 ml. However, very satisfactory analyses can be made for the major constituents (other than water) on samples of 1 mg or less by colorimetric methods; these have been very largely applied to trace constituents, working on 100 to 500 mg samples, but if we note that the optimum concentration in the final solution is of the order of 5 μg/ml for most oxides, and that 5 ml is more than enough to fill a standard 1-cm colorimetric cell, it will be evident that, provided the test solutions of the unknown and of the standard are made by weight rather than relying on pipettes or measuring flasks, no more than 25 μg of an oxide need, as a rule, be present for it to be determined with a precision limited mainly by the sensitivity of the colorimeter. It follows that a one-quarter aliquot of a 1-mg sample is adequate for a good determination of a constituent present to the extent of 10 %, provided a good colorimetric technique is available, and provided any interfering elements can be separated or masked.

Colorimetric methods are, in fact, available for almost all the elements, but vary greatly in precision, and while some are highly specific, others require extensive preliminary separations. Generally speaking, methods involving colloidal lakes, such as the aluminon method for aluminium, are to be avoided, since small variations in *p*H, electrolyte content, and even temperature may have serious effects. For the common anions sulphate, carbonate, chloride, and bromide, only indirect methods of relatively low precision are available, but for most elements, provided aliquots are taken by weight, the precision is at present only limited by that of the colorimeter, which for a good spectrophotometer is around 1 % of the amount present—and could almost certainly be improved on.

At present colorimetric techniques are widely used for minor and trace elements (see, e.g., Sandell, 1959), but it is clear that selected methods could find increasing use for major constituents in micro and semi-micro analyses.

Flame photometry[1] has had a chequered career since its first introduction by Champion *et al.* (1873) for sodium, its development by Lundegårdh (1929–34), and the attempts of Stahl (1931) to use it for the determination of boron. In recent years it has largely replaced the Lawrence Smith method (1853, 1871) for the alkalis, but the older method remains a useful stand-by and 'referee' method for alkali-rich minerals.[2] Flame photometry is valuable for all the alkalis, provided narrow-pass interference filters are used to isolate the appropriate wave-lengths, and provided interfering ions have been removed, but has proved less satisfactory for the alkaline earths. The main difficulty with many forms of apparatus is in maintaining steady flame conditions, and better instrumentation could improve the precision.

Atomic absorption spectrometry. In flame photometry dilute solutions of the unknown and of a series of standards are fed alternately to a suitable flame and the emission spectrum photometered. In atomic absorption methods, a flame similarly fed absorbs radiation emitted by the element being determined in a suitable lamp. The range of elements that can be determined is considerable, but an appropriate lamp is needed for each element. Interference by anions or by cations other than the one being determined is often serious, and suitable preliminary separations are often necessary, though it is sometimes possible to suppress interference by the addition of excess of some other ion to both unknown and standard. The sensitivity of the technique is, in general, high, and with a suitable instrument the precision is similar to that of the better colorimetric methods, but in the present state of knowledge it appears essential to check possible interference by other elements. The method is particularly useful for the alkaline earths, magnesium, zinc, and lead, for which colorimetric and gravimetric methods, especially micro-methods, are either unsatisfactory or tedious; the working dilutions for these elements are such that the technique is applicable to analyses on the sub-milligramme scale.

Emission spectrography, using arc or spark sources, has undergone much development since its introduction by Hartley (1884) and de Gramont (1895). For routine studies of large numbers of samples of very similar composition it is a valuable technique, but the intensities of the emission lines of most elements are dependent on the exact composition of the sample, as well as on the excitation conditions; it is therefore necessary to know the composition of the unknowns fairly closely (e.g. by a preliminary run), and to use synthetic standards of closely similar composition. The technique has been widely used for minor and trace elements, but in my opinion is less reliable than colorimetric or atomic absorption methods. The main uses I have

---

[1] There is a considerable literature on this and most of the techniques considered in the following paragraphs. I have included one or two books on each in the references, not to recommend these books in particular, but solely to give some lead into the literature on the subject.

[2] It is, however, essential to dry the residue from which the alkalis have been leached, add to it the dried precipitate produced by ammonium carbonate (essentially calcium carbonate), add a further dose of ammonium chloride, and repeat the sintering and leaching if results of high accuracy are to be obtained. This is especially the case in potash-rich rocks or minerals; I have occasionally found as much as 5 % of the total alkali, and that mainly potash, in the second leachings of an alkali-rich rock.

found for the method are: for a qualitative or semi-quantitative analysis on a sma sample, around 1 mg or less, as a help in planning a microchemical analysis; to determine the approximate proportions of the rare earths in a separated rare-earth precipitate; and in certain cases to check whether a weighed precipitate contains any unsuspected constituent—e.g. beryllia or rare earths in an alumina precipitate.

X-ray fluorescence appears superior to emission spectrography as a quantitative method, but it also is sensitive to the exact composition of the sample; though this and some other troublesome effects can be largely suppressed by dilution of the sample in a suitable flux (at some loss of sensitivity), the most useful field for the method appears to be in rock analysis. Here, if two or three representative members of a series of rocks are analysed by classical methods they can serve as standards for the rest of the series. The technique is quicker and, if standardized in this way, more accurate than any of the 'rapid methods' of wet-chemical rock analysis; water, carbon dioxide, and the net state of oxidation ('ferrous iron') must, however, still be determined by classical methods. Most users of X-ray fluorescence for rock analyses determine only a very limited range of major constituents, but there can be little doubt that a considerable number more minor constituents could be determined with little additional time or trouble, and the gain from such an extended programme would be very great.

The electron micro-probe has proved invaluable in tracing variations in composition across a suitably prepared section, and in providing analyses on crystals as small as about 2 to 5 μm in diameter. It has, however, its own troubles; not only are numerous corrections to the raw results necessary, especially if the unknown and standards differ considerably in composition, but some minerals are liable to alteration under the bombardment of the electron beam.

Infra-red spectrography has not, so far, proved very satisfactory as a quantitative analytical technique, but is very valuable qualitatively: water, hydroxyl groups, and a considerable range of XO_4 and XO_3 anions can be identified in small samples, and if a pressed KBr disc is used it may be possible to recover the sample for identification of the cations by emission spectrography, or to use it for a quantitative microanalysis, knowing what constituents to look for.

Other techniques. Radiochemical methods are widely employed for trace-element determinations, and could well be adapted, in suitable cases, to the analysis of very small samples. They will not be further considered here, nor do I propose to deal in any detail with polarographic or chromatographic methods or with Mössbauer spectrography, all of which are useful analytically in special cases, simply because I have had little or no experience of them. It may, however, be mentioned that a chromatographic technique is now available for the separation of niobium and tantalum, in place of the tedious tannin fractionation (it is possible that this latter might be adapted to a chromatographic procedure); a chromatographic separation of zirconium and hafnium has also been described. Mössbauer spectroscopy is admirably suited to decide on the valency of certain ions where this is doubtful (e.g. to decide whether delafossite is essentially $Cu^{+}Fe^{3+}O_2$ or $Cu^{2+}Fe^{2+}O_2$), and to determine the ferrous: ferric ratio in highly resistant minerals, but it is doubtful if all the claims made for it as a method for the determination of ferrous: ferric ratios in general can be justified (see, e.g., Herr and Skerra, 1969; Sprenkel-Segel, 1969; Hogg and Meads, 1970).

Assessing a chemical analysis

The problem of deciding whether or not a given analysis from the literature is of acceptable accuracy is not a simple one. It is, unfortunately, not uncommon for mineralogists, petrologists, or meteoriticists to accept all analyses made after some arbitrary date and reject all earlier ones: such an attitude can only arise from laziness or ignorance. While the date of an analysis must always be borne in mind, there are analyses 150 years old as accurate as any made today, and analyses published recently that are not worth the paper they are printed on.[1] With few exceptions, the older techniques, while more tedious, or requiring more skill on the part of the analyst, were capable of giving as good separations as the modern ones; the biggest change since 1810 is that the analyst rarely has to purify his reagents himself. Indeed, some modern methods and reagents have simplified the determination of one constituent while leaving the rest of the analysis as tedious as before.[2]

Often, especially with early analyses or with modern ones made by specially planned techniques, the analytical procedures are shortly described, and may sometimes indicate that the analysis is likely to be of inferior accuracy (e.g. the original analysis of phoenicochroite (1833) was made by a method that is clearly unreliable; rocks and silicates analysed by 'rapid methods', or analyses made mainly by emission spectroscopy, should be treated with some reserve); but on the other hand, a sound method does not necessarily mean a good analysis.

The summation, too, may be a guide: in rock analyses, Hillebrand regarded a ummations less than 99·75 % or greater than 100·50 % as indicative of a second-grade analysis (Hillebrand and Lundell, 1929, p. 645), though Washington (1019, p. 23) preferred the limits 99·50 to 100·75 %; for most mineral analyses, these wider limits seem suitable, while for microanalyses they may be extended somewhat, to about

---

[1] As W. F. Hillebrand wrote (Hillebrand and Lundell, 1929, p. 645): 'The composition of the ultimate ingredients of the earth's crust . . . was the favorite theme of the great workers in chemistry of the earlier half of the nineteenth century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others the mineralogists and geologists of today have reason to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvelous. As an outgrowth of and closely associated with the analysis of minerals came that of . . . rocks, to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness.'

[2] For example, dimethylglyoxime offers a far simpler and quicker separation of nickel and iron than the old basic acetate separation, though the latter is an excellent one in competent hands; but in meteorite analysis cobalt is left associated with at least 100 times its weight of iron. When I joined the British Museum in 1928, there were about a score of beakers in a cupboard, containing the evaporated filtrates from determinations of nickel in meteoritic iron made by Dr. G. T. Prior; they were awaiting an improved method for cobalt in presence of much iron. Cupferron could, of course, have been used, but the iron complex does not filter at all well, and its extraction with chloroform was not known at that date.

99·0 to 101·0 %. There is always the possibility that the analytical procedures in an analysis summing outside these limits were sound but that an unsuspected constituent was present; thus Plattner's (1846) analysis of Elba pollucite gave the impossibly low summation of 92·75 %, though his technique was sound and ably executed; he could not repeat his analysis for lack of material. After the discovery of caesium by Bunsen and Kirchhoff (1860), Pisani (1864) re-examined Elba pollucite, and found it to be a casieum mineral; he noted: 'il n'y a qu'à calculer en cœsium le chloro-platinate supposé de potasse qu'il [Plattner] obtint, pour retrouver presque exactement les mêmes nombres que m'a donné mon analyse',[1] showing that Plattner's was in fact a fairly good analysis.

A summation of exactly 100·00 %, without comment, is suspect (since some analysts recalculate an analysis to 100 %, or determine a constituent by difference, without saying so), and so is an analysis in which major constituents are cited to three or more decimal places.

Fortunately, with many analyses there is useful internal evidence. Thus if a rock analysis cannot be interpreted in terms of the mode, one or the other must be in error. In the analysis of an ionic mineral, anion and cation valencies must balance; but in sulphides and similar (non-ionic) structures extensive lattice vacancies are common, and in many other groups the possibility of unusual substitutions must always be borne in mind. In general, however, we may assume that in an aluminosilicate with network structure, such as a feldspar, feldspathoid, or zeolite, the other cations will balance the alumina plus ferric iron to within an acceptable analytical error.[2] X-ray data by Bannister (1950) suggested that ashtonite is a true zeolite, closely related to mordenite, and accordingly threw doubt on the original analysis, which does not balance in this way; a new analysis (Reay and Coombs, 1971) confirms this conclusion. Similar considerations may be applied in many other groups, such as the pyroxenes, the amphiboles (Phillips, 1963, 1966; Phillips and Layton, 1964; Borg, 1967), the uranites, and the apatite family.

If the unit-cell dimensions and density are available, the empirical unit-cell contents should always be calculated (Hey, 1939, 1954); failure of the large anions (usually O, OH, F, and Cl) to approach an integral figure within an acceptable allowance for the errors of density and the analysis suggests something wrong (often a water determination, still the most troublesome constituent), but of course Σ (O, OH, F, Cl) may really be non-integral, as in schwartzembergite.

---

[1] Brush (1864), abstracting Pisani's paper, apparently failed to notice this sentence; he recalculated Plattner's analysis independently, showing that if the chloroplatinate was the pure caesium salt the summation would become 103·18 %.

[2] As an example of the power of this type of check, we may consider three analyses of pollucite from Elba: Plattner's analysis, as interpreted by Pisani and by Brush and discussed above, balances within 6 % (if we assume that Plattner missed the CaO reported in both the other analyses, the balance is even better), whereas Pisani's has a marked excess of cations, giving

$$(\mathrm{Cs}+\mathrm{Na}+2\mathrm{Ca})/(\mathrm{Al}+\mathrm{Fe}) = 1{\cdot}2.$$

The more recent analysis by Gossner and Reindl (1932) balances very well, and a comparison of the three suggests that Pisani's imbalance and high summation (101·70 %) is due to too high Na_2O, while the high summation of Plattner's reinterpreted analysis is probably fairly evenly distributed over the major constituents.

There are a number of internal tests applicable to meteorite analyses: Mason (1965) has proposed a useful set of criteria applicable to analyses of the common chondrites, while Moore, Lewis, and Nava (1969) have suggested criteria for analyses of siderites;[1] Moore's criteria are, however, a little too strict: there are a few meteorites with less than 5 % Ni, so that analyses with such low nickel figures, while suspect, cannot be rejected out of hand; and while the cobalt figures for those analyses giving an anomalous Co:Ni ratio can almost certainly be rejected, the nickel figures may well be reasonably close to the truth.

All too often, however, no internal evidence is available—indeed, this is usually the case with rock analyses, and we have to fall back on the reputation of the analyst as our sole guide, together with the date of the analysis, since analyses published early in an analyst's career may not be up to his later standard.[2] Thus any analysis by Berzelius, Fletcher, C. Friedel, Hillebrand, J. B. Mackintosh, Pisani, Prior, Raoult, H. Rose, J. Lawrence Smith, Washington, Winkler, or Wöhler must be taken seriously, as must meteorite analyses made in Cohen's laboratory, especially those by Fahrenhorst and Sjöström—and some other names could certainly be added. On the other hand, while Rammelsberg's own analyses are usually trustworthy, his compilation (2nd edn, 1875–95) includes many indifferent ones by his students;[3] A. H. Church, too, included a number of poor-quality student analyses in his publications. T. Thomson appears to have been a sound analyst, but none too careful in his selection of material; many of his analyses appear to have been made on impure material or even on gross mixtures. Heddle's analyses are erratic, and are often given to more decimal places than can possibly be significant.

A few analysts had very characteristic failings in otherwise sound work: thus S. von Waltershausen regularly over-estimated potassium, whereas his total alkalis appear to be correct; Bechi regularly overestimated magnesia at the expense of lime; and Jakob's determinations of the net state of oxidation are not reliable. As might be expected, analyses by a commercial laboratory such as Whitfield's are of variable quality. Fortunately, few analysts seem to have been as unlucky as E. Herrero Ducloux, none of whose analyses of South American meteorites are to be trusted.

The scope of rock analyses

There are a considerable number of analyses in the literature in which only 10 constituents are reported: silica, alumina, ferric and ferrous oxides, magnesia, lime, soda, potash, and water lost at and above 105 or 110 °C. These analyses can only be

---

[1] It may be of some interest to note that while the Co:Ni ratios in the metal phase of three olivine-hypersthene chondrites (Moss *et al.*, 1967) fit well to Moore's line, the metal of an olivine-bronzite chondrite and that of an enstatite chondrite are markedly poor in cobalt (ibid.).

[2] Washington (1904, 1917) made a careful survey of most of the rock analyses published between 1869 and 1913. As Hillebrand remarks (Hillebrand and Lundell, 1929, p. 646, fn.): 'After a systematic critical examination he has assigned to each analysis a certain value on a scale of 5. Many of these values may be incorrect, but most of them undoubtedly give a fairly true measure of the weight to be attached to the respective analyses.'

[3] It should be noted that while Doelter's *Handbuch der Mineralchemie* (1911–31) is very useful, it contains numerous misprints, both in the analyses and in the references quoted; a check in the original literature is essential.

regarded as seriously deficient, since manganese and titanium are almost invariably present in significant amounts. Yet the great bulk of rock analyses are only a little better in respect of completeness—the above 10 constituents plus TiO_2, MnO, P_2O_5, CO_2, and total sulphur usually completes the list, and a large proportion of the numerous analyses currently being made by X-ray fluorescence methods are restricted to these 15 constituents at most—and sometimes without water or CO_2 or a net state of oxidation. Yet it is now nearly 80 years since Hillebrand wrote *A plea for greater completeness in chemical rock analysis* (1894); this is, to my mind, so important a paper that a longish quotation may not be out of place:

> The valuelessness to the mineralogist and geologist of many of the analyses of mineral substances made in earlier times is a fact too well-known to need substantiation. Defective methods of analysis, the difficulty of procuring pure reagents, and want of time for exhaustive examination have been largely responsible for this condition, but lack of appreciation of the fact, now so well established, that substances present in small amounts may have an important bearing on the discussion of results, has no doubt contributed in no small measure to it.
>
> Whatever the causes, the result has been the necessity for a vast amount of repetition in analytical work, and it behooves the present generation of chemists to heed well the warning and to work with a two-fold purpose in view, that of lightening the labors of those who come after us by enabling them to use our work with less supplementary examination, and of thereby enhancing our own reputations by meriting encomiums on work that has stood the test of time.
>
> This monition applies to the lithologist as well as to the chemist, and the former should seek to make or to have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water; even going so far sometimes as to ask the chemist to omit tests for other constituents that may be present in small quantity for the sake of getting a greater number of more or less incomplete analyses accomplished. The latter, it is true, may serve the immediate purpose for which they were intended, but their incompleteness may on the other hand not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analyses made for purely scientific purposes.
>
> [Here follows a comparison of two pairs of analyses, in which TiO_2, MnO, SrO, BaO, CO_2, SO_3, P_2O_5, F, and Cl remained undetermined in one of each pair.]
>
> While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I do maintain that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis . . . should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0·02 or 0·06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

> Finally, whenever possible, a thorough microscopical examination of the rock in thin section should *precede* the chemical analysis [my italics]. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.

There can be very little doubt that the older methods (as in, e.g., Hillebrand and Lundell, 1929) for zirconium, barium, strontium, lithium, sulphide, and chloride could be improved and simplified appreciably (the methods for fluorine have already been greatly improved). All these constituents will usually be found if looked for, and could be of help in tracing petrological relations if the necessary data were available; but until these determinations are made as a matter of course on at least a few members of every suite of rocks studied, the data will not be there; the data for even the major constituents were of little value until a large number of rocks had been analysed, and it is a short-sighted policy to restrict the analyses to those constituents whose significance is obvious today.

The 'ore-forming' metals nickel, cobalt, copper, lead, zinc, chromium, and vanadium can readily be determined colorimetrically (see, e.g., Sandell, 1959), and they too will usually be found if looked for.[1] For the last century there has been a tendency among petrologists to lump all the oxides and sulphides in a silicate rock together under the heading 'Opaques' and to neglect them; indeed, petrology and ore mineralogy (including ore genesis) for long drifted so far apart as to be essentially separate and unrelated disciplines[2]—a very unfortunate example of 'drift'. It is now readily possible to follow the variations in the 'ore-forming' metals through a suite of rocks accurately enough for the data to help with such questions as assimilation. Moreover, the development of ore-mineralogy and micro-scale X-ray powder photography has rendered it relatively simple to identify the opaque minerals in rocks, while the electron-probe can provide analytical data, and the chlorination technique developed for meteorites (Moss *et al.*, 1967) could in favourable cases enable the distribution of the 'ore-forming' and other chalcophile elements between the sulphides and the silicates to be determined. The tools for a reunification of petrology and ore mineralogy are available, and work in the borderline field could be highly rewarding.

It therefore seems highly desirable that a few selected members of any extended suite of rocks should be analysed for all the 30 constituents mentioned above, and, in potash-rich rocks at least, rubidium too should be looked for. Methods are also available for beryllium and boron, which are likely constituents of some granites, but have rarely, if ever, been determined in rocks (if ignored, beryllium will be counted as aluminium in a classical rock analysis; boron will be partly lost, partly counted with silicon, and partly counted with aluminium, the proportions varying according to the composition of the material and the precise course of the analysis).

---

[1] There have been some trace-element studies in rocks by emission spectroscopy, but most of this has been of relatively poor accuracy—often only qualitative or semi-quantitative.

[2] T. Crook (1933) wrote: 'They allowed the science of petrology to degenerate for all practical purposes into a study of silicate rock masses . . ., whereas it should have been applied to mineral deposits generally, including ore deposits . . .' (p. 6). '. . . not until all mineral deposits come within the purview of rock studies will petrology become a fully fledged science' (p. 161).

The future of wet-chemical analysis

With the development of instrumental methods of analysis—emission spectroscopy, X-ray fluorescence, atomic absorption, electron-probe, etc.—both the classical macroscale gravimetric methods and the more recent gravimetric and colorimetric microchemical methods have become increasingly neglected, and it is not uncommon to meet a young analyst who has never done a simple gravimetric analysis in his life.

In my opinion, this is a very dangerous position, for many reasons. Reliance on a single technique is always a mistake; in qualitative analysis it has led to such absurdities as the devising of spot tests for sodium and of crystal micro-tests for manganese, and the neglect of borax-bead and microcosmic-salt-bead tests and of blowpipe analysis—a versatile tool in experienced hands.

Gravimetric methods, on macro or micro scale, must always remain the final court of appeal: they alone can escape the doubt associated with correction factors; and only by quantitative separation of all the constituents, together with a check of the purity of the separated components, for example by the spectrograph, can we be certain that no constituent has been overlooked and that the separations were effective (good analysts have reported 'alumina' that included beryllia or rare earths; several per cent of boric oxide have been missed, distributed over silica and alumina). And although nothing more than a modicum of manipulative skill and a strict adherence to the textbook instructions is needed to make a sound rock analysis (unless the rock happens to contain an unusual mineral such as beryl, tourmaline, or pyrochlore—and it is the responsibility of the petrologist to warn his analyst of such a possibility), the mineral analyst should have the widest possible acquaintance with various reagents and techniques, and his success will largely depend on his judgement in selecting a suitable procedure for the problem on hand.

If many analysts are ignorant of the classical methods, even more mineralogists, petrologists, and meteoriticists know little or nothing of them. Petrologists have been known to attach great significance to 1 % of normative corundum, though it is well within the probable error of a good rock analysis; on the other hand, mineralogists have been known to pass a 5 % imbalance in an analysis of an ionic mineral without comment. Perhaps some words of Klaproth's are still apposite today (*Beitr. chem. Kenntn. Min.* **1**, iv (1795)): 'Wenn aber mit einigem Zweifel ob man seinen eigenen Augen trauen dürfe, liest, wie einer [Chemist] einen Edelstein in destillirtem Wasser aufzulösen sucht — wie ein anderer eine Erde mehrere Stunden lang in einigen Unzen Blutlauge kocht, um ihren Eisengehalt zu erforschen — oder wie ein dritter ein Mineral mitsammt dem zufällig beygemischten Gestein pulvert, und dann der Zerlegung unterwirft, u.s.f. — und wenn man dann siehet dass Mineralogen, die von dergleichen Chemisten angegebenen Resultate ihrer Zerlegungen in ihr System aufgenommen haben, ohne auch nur den mindesten Zweifel über die Richtigkeit der Zerlegung zu äussern: so kann man, meines Erachtens, sich dieses wohl nicht leicht anders erklären, als — dass es diesen Mineralogen entweder gleichfalls an hinlänglichen chemischen Kenntnissen gefehlet haben möge, oder dass sie jene Zerlegungen nicht selbst zu

Gesichte bekammen, sondern sich begnüget haben, die Resultate derselben aus den davon vorhandenen Tabellen auf Treu und Glauben auszuziehen.'[1]

REFERENCES

1768 [Lavoisier (A. L.), *Analyse du Gypse*, Mém. sav. Étrang. **5**].
1774 Bergman (T.), De mineris ferri albis, *Opuscula* **2**, 228 (collected works, 1784).
1777 —— De terra gemmarum, ibid. 96.
1780 —— De praecipitatis metallicis, ibid. 349.
1782 —— De terra asbestina, ibid. **4**, 160.
1787 Kirwan (R.), *Elements of Mineralogy*, London.
1787 Klaproth (M. H.), *Schr. Gesell. naturf. Freunde*, Berlin, **7**, 141; transl. by J. G. Groschke as *Observations relative to the mineralogical and chemical history of the fossils of Cornwall*, 1787.
1792 Hochheimer (C. F. A.), *Chemische Mineralogie*, Leipzig, **1**, iv.
1792 [Richter (J. B.), *Anfangsgründe der Stöchyometrie*, Breslau]; cited by Szabadváry, 1966.
1792–1815 Klaproth (M. H.), *Beiträge zur chemischen Kenntniss der Mineralkörper*, **1–6**, Posen and Berlin; **1** and **2** translated as *Analytical Essays towards promoting the Chemical Knowledge of Mineral Substances*, London, 1801.
1799 Proust (J. L.), (≡ An viii^{e}), *Ann. Chim.* **32**, 31.
1801 [Lampadius (W. A.), *Handbuch zur chemischen Analyse der Mineralkörper*]; cited by Szabadváry, 1966.
1803 [Berthollet (C. L.), *Essai de statique chimique*, Paris]; cited by Szabadváry, 1966.
1804 Accum (F. C.), *A practical essay on the analysis of minerals*, London.
1805 Dalton (J.), *Mem. Manchester Lit. Phil. Soc.* **1**, 244; *Alembic Club Reprints*, no. 2 (1948).
1807 Aikin (A.) and Aikin (C. R.), *Dict. Chem. Min.*, London, **2**, 408.
1807 Thomson (T.), *A System of Chemistry*; *Alembic Club Reprints*, no. 2 (1948).
1808 Accum (F. C.), *A manual of analytical mineralogy*, 2 vols., London.
1808 Dalton (J.), *A New System of Philosophy*; *Alembic Club Reprints*, no. 2 (1948).
1808 Thomson (T.), *Phil. Trans.* **98**, 63; *Alembic Club Reprints*, no. 2 (1948).
1808 Wollaston (W. H.), Ibid. 96; ibid.
1811 Hisinger (W.), [*Afhl. Fys. Kemi Min.* **3**, 152]; *Phil. Mag.* **40**, 258 (1812).
1811 Gay-Lussac (J. L.), *Ann. Chim.* **78**, 86; **80**, 205.
1816 Fuchs (J. N.), *Journ. Chem. Phys.* (*Schweigger*), **18**, 288.
1818 —— Ibid. **24**, 121.
1819 Berzelius (J. J.), *Ann. Chim. Phys.*, ser. 2, **12**, 12.
1821 [Pfaff (C. H.), *Handbuch der analytischen Chemie*, Altonah]; cited by Szabadváry, 1966.
1826 Guillemin (J.), *Ann. Mines*, ser. 1, **12**, 390.
1829 Rose (H.), *Handbuch der analytischen Chemie*, Berlin.
1833 Otto (F. J.), *Journ. Chem. Phys.* (*Schweigger*), **67**, 148.
1841 [Berzelius (J. J.), *Lehrbuch der Chemie*, 10, Dresden and Leipzig]; cited by Szabadváry, 1966.
1841 [Fresenius (C. R.), *Anleitung zur qualitativen chemischen Analyse*]; cited by Szabadváry, 1966.
1846 [—— *Anleitung zur quantativen Analyse*]; cited by Szabadváry, 1966.
1846 Margueritte (F.), *Ann. chim. phys.* **18**, 244.
1846 Plattner (C. F.), *Ann. Phys. Chem.* (*Poggendorff*), **69**, 443.
1850 Penny (F.), [*Chem. Gazette*, **8**, 330]; *Brit. Assoc. Ann. Rept.* 1851 (for 1850), pt. 2, 58.
1851 Reynoso (A.), *Compt. Rend. Acad. Sci. Paris*, **33**, 385.
1851 Rose (H.), *Ausführliches Handbuch der analytischen Chemie*, **2**, Braunschweig.

---

[1] This passage is omitted from the translated preface in Analytical Essays (1801), from which the other translations of Klaproth's remarks cited in this paper have been taken. A free translation is: One may well doubt one's own eyes when one reads how one chemist sought to dissolve a gemstone in distilled water, how a second boiled an ore in potassium ferrocyanide solution for several hours in order to determine its iron content, how a third powdered a mineral together with the adherent matrix and then proceeded to analyse the mixture, and so forth: and when one sees how some mineralogists incorporate the results published by such chemists in their Systems without expressing the least doubt of their accuracy, one can only conclude, to my mind, that either these mineralogists are equally lacking in the appropriate chemical knowledge, or that they have never seen the actual analyses, but have been satisfied to accept the tabulated results as correct.

1851 Schabus (J.), *Sitzungsber. kais. Akad. Wiss. Wien, Mat.-nat. Cl.* **6**, 396.

1851 Sonnenschein (F. L.), *Journ. prakt. Chem.* (*Erdmann*), **53**, 339.

1853 Fresenius (C. R.), *Anleitung zur quantitativen Analyse*, 3rd edn.

1853 Smith (J. Lawrence), *Amer. Journ. Sci. and Arts*, ser. 2, **15**, 234; **16**, 53.

1860 Bunsen (R. W.) and Kirchhoff (G. R.), *Monatsber. Akad. Berlin*, 221.

1860 Mitscherlich (A.), *Journ. prakt. Chem.* **81**, 116.

1861 Lange (Th.), Ibid. **82**, 129.

1864 Brush (G. J.), *Amer. Journ. Sci. and Arts*, ser. 2, **38**, 115.

1864 Gibbs (W.), *Zeits. anal. Chem.* **3**, 334.

1864 Pisani (F.), *Compt. Rend. Acad. Sci. Paris*, **58**, 714.

1865 [Luckow (C.), *Dinglers polytechn. Journ.* **177**, 43, 296]; cited by Szabadváry, 1966.

1867 Cooke (J. P.), *Amer. Journ. Sci. and Arts*, ser. 2, **44**, 347.

1871 Smith (J. Lawrence), Ibid., ser. 3, **1**, 269.

1873 Champion (P.), Pellet (H.), and Grenier (M.), *Compt. Rend. Acad. Sci. Paris*, **76**, 707.

1875–95 Rammelsberg (C. F.), *Handbuch der Mineralchemie*, 2nd edn.

1884 Hartley (W. N.), *Phil. Trans.* **175**, 49, 325.

1885 Ilinski (M.) and Knorre (G.), *Ber. deut. chem. Gesell.* **18**, 699.

1894 Hillebrand (W. F.), *Journ. Amer. Chem. Soc.* **16**, 90.

1895 de Gramont (A.), *Bull. Soc. franç. Min.* **18**, 171.

1896 Lacroix (A.), *Min. de France*, **2**, 274.

1896 Laspeyres (H.), *Zeits. Kryst. Min.* **27**, 586.

1899 Hess (W. H.) and Campbell (E. D.), *Journ. Amer. Chem. Soc.* **21**, 776.

1900 Hillebrand (W. F.) and Stokes (H. N.), *Zeits. anorg. Chem.* **25**, 326.

1904 Washington (H. S.), *U.S. Geol. Surv. Prof. Paper* **28.**

1905 [Chugaev (L.)] Tschugaeff (L.), *Zeits. anorg. Chem.* **46**, 144.

1909 Baudisch (O.), *Chem. Zeitung*, **33**, 1298.

1910 Washington (H. S.), *Manual of the Chemical Analysis of Rocks*, 2nd edn, New York (Wiley).

1911 [Cain (J. R.), *Journ. Ind. Eng. Chem.* **3**, 476]; abstr. *Zeits. anal. Chem.* **51**, 255 (1912).

1911–31 Doelter y Cisterich (C. A.), *Handbuch der Mineralchemie*, **1–4.**

1917 Washington (H. S.), *U.S. Geol. Surv. Prof. Paper* **99.**

1922 [Lindner (J.), *Ber. deut. chem. Gesell.* 55, 2025]; abstr. *Zeits. anal. Chem.* **65**, 335 (1925).

1925 [Powell (A. R.) and Schoeller (W. R.), *Analyst*, **50**, 485]; in Schoeller (W. R.), *The analytical chemistry of tantalum and niobium*, London (Chapman and Hall), 1937.

1927 Berg (R.), *Journ. prakt. Chem.* **115**, 178; *Zeits. anal. Chem.* **70**, 341.

1929 Hillebrand (W. F.) and Lundell (G. E. F.), *Applied inorganic analysis*, New York (Wiley).

1929–34 Lundegårdh (H.), *Die quantitative Spektralanalyse der Elemente*, 2 vols., Jena (Fischer).

1931 Stahl (W.), *Zeits. anal. Chem.* **83**, 268.

1932 Emich (F.), trans. Schneider (F.), *Microchemical laboratory manual*, New York (Wiley).

1932 Gossner (B.) and Reindl (E.), *Centr. Min., Abt. A*, 330.

1932 Hueber (H.), *Tschermaks min. petr. Mitt.* **43**, 84.

1933 Crook (T.), *History of the Theory of Ore Deposits*, London (Murby).

1933 Guthrie (W. C. A.) and Miller (C. C.), *Min. Mag.* **23**, 405.

1934 [Kolthoff (J. M.), Stenger (V. A.), and Moskovitz (B.), *Journ. Amer. Chem. Soc.* **56**, 812]; abstr. *Zeits. anal. Chem.* **98**, 355 (1934).

1934 Rowledge (H. P.), *Journ. Roy. Soc. Western Australia*, **20**, 165 [M.A. 6–191].

1939 Hey (M. H.), *Min. Mag.* **25**, 402.

1939 Miller (C. C.), *Journ. Chem. Soc.* 1962.

1940 Hecht (F.) and Donau (J.), *Anorganische Mikrogewichtsanalyse*, Wien (Springer).

1943 Fenton (H. J. H.), *Notes on qualitative analysis*, 2nd edn, Cambridge (University Press).

1945 Vogel (A. I.), *A textbook of qualitative analysis*, 3rd edn, London (Longmans).

1948 Flagg (J. F.), *Organic reagents used in gravimetric and volumetric analysis*, New York and London (Interscience).

1950 Bannister (F. A.), In Hey (M. H.), *Chemical Index of Minerals*, London (British Museum (Natural History)).

1952 Kolthoff (I. M.) and Lingane (J. J.), *Polarography*, 2nd edn, 2 vols., New York and London (Interscience).

1954 Hey (M. H.), *Min. Mag.* **30**, 481.

1955 Johnson (W. C.), editor, *Organic reagents for metals*, 5th edn, **1**, Chadwell Heath, Essex (Hopkin and Williams).

1957 PRODINGER (W.), *Organische Fällungsmittel in der quantitativen Analyse*, Stuttgart (Enke).
1958 BOLTZ (D. F.), *Colorimetric determination of non-metals*, New York (Interscience).
1959 SANDELL (E. B.), *Colorimetric determination of traces of metals*, 3rd edn, New York (Interscience).
1960 BELCHER (R.), OTTENDORFER (L.), and WEST (T. S.), *Talanta*, **4**, 166.
1963 BOWEN (H. J. M.), *Radioactivation analysis*, Oxford (Clarendon Press).
1963 DAVIES (MANSEL), editor, *Infra-red spectroscopy and molecular structure*, Amsterdam (Elsevier).
1963 PHILLIPS (R.), *Min. Mag.* **33**, 701.
1964 JOHNSON (W. C.), editor, *Organic reagents for metals*, 5th edn, **2**, Chadwell Heath, Essex (Hopkin and Williams).
1964 PHILLIPS (R.) and LAYTON (W.), *Min. Mag.* **33**, 1097.
1965 MASON (B.), *Amer. Mus. Novitates*, no. 2223.
1966 PHILLIPS (R.), *Min. Mag.* **35**, 945.
1966 SZABADVÁRY (F.), trans. SVEHLA (G.), *History of analytical chemistry*, 2nd edn, Oxford (Pergamon).
1967 BORG (L. Y.), *Min. Mag.* **36**, 583.
1967 MOSS (A. A.), HEY (M. H.), ELLIOTT (C. J.), and EASTON (A. J.), Ibid. **36**, 101.
1968 GOLDANSKII (V. I.) and HERBER (R. H.), editors, *Chemical applications of Mössbauer spectroscopy*, New York and London (Academic Press).
1969 DEANS (J. A.) and RAINS (T. C.), *Flame Emission and Atomic Absorption Spectroscopy*, New York and London (Marcel Dekker).
1969 HERR (W.) and SKERRA (B.), In *Meteorite Research* (P. M. MILLMAN, editor), 103, Dordrecht (Reidel).
1969 MOORE (CARLETON B.), LEWIS (C. F.), and NAVA (D.), In *Meteorite Research* (P. M. MILLMAN, editor), 738, Dordrecht (Reidel).
1969 SPRENKEL-SEGEL (E. L.), Ibid. 93.
1970 HOGG (C. S.) and MEADS (R. E.), *Min. Mag.* **37**, 606.
1970 LEAVENS (P. B.), WHITE (J. S., *jr.*), and HEY (M. H.), *Mineralog. Record.* **1**, 92.
1970 MAVRODINEANU (R.), editor, *Analytical Flame Spectroscopy*, London (Macmillan).
1971 REAY (A.) and COOMBS (D. S.), *Min. Mag.* **38**, 383.

[*Manuscript received 20 January 1972*]