

The determination of ferrous and ferric iron in rocks and minerals; and a note on sulphosalicylic acid as a reagent for Fe and Ti

M. H. HEY

British Museum (Natural History), Cromwell Road, London SW7

SYNOPSIS

INSTRUMENTAL methods of chemical analysis, including electron and ion-probes, X-ray fluorescence, atomic absorption, and plasma-source spectrometry, have largely replaced classical wet-chemical analysis except for 'referee' analyses, but have not so far proved able to determine the net state of oxidation of a rock or mineral with reasonable accuracy. Mössbauer spectroscopy can indeed give fairly accurate Fe^{2+} and Fe^{3+} estimates in favourable circumstances, but fails when the $\text{Fe}^{2+} : \text{Fe}^{3+}$ ratio is very small or very large or when the iron is present in several different lattice positions with different surroundings; and it cannot arrive at the net state of oxidation when other elements of variable valency are present. The term 'net state of oxidation' calls for some comment, and is dealt with in the full paper; for the moment we note as an example that Mössbauer spectroscopy shows that much of the iron in ludlockite is ferric, whereas a 'ferrous iron' determination corresponds to an arsenate of lead and ferrous iron, from which it follows that part of the arsenic must be trivalent, a result that could not have been arrived at from either the 'ferrous iron' or the Mössbauer data alone. Thus in the present state of the art a wet-chemical method for net state of oxidation is a necessity.

In this paper the development of methods from the determination of the net state of oxidation ('ferrous iron') is shortly reviewed; each of the methods currently in use has its own field of usefulness and its own specific weaknesses, but all are ill-suited to the determination of small amounts of ferric iron in presence of large amounts of ferrous.

A new technique is described in detail that allows separate determinations of Fe^{2+} and Fe^{3+} in a single small sample (1 to 10 mg or less). It depends on extraction of the Fe^{3+} from a citrated solution of the mineral, buffered to pH c.4, with the Fe^{2+}

complexed by *o*-phenanthroline and the Fe^{3+} by 8-hydroxyquinoline, by a chloroform solution of 8-hydroxyquinoline ('oxine'); Fe^{3+} in the chloroform extract is determined colorimetrically, as is Fe^{2+} in the aqueous solution after replenishment of the *o*-phenanthroline (largely extracted by the chloroform).

Acid-soluble minerals are dissolved in 8N H_2SO_4 on the water-bath with complete exclusion of air (HCl has been found to be unsatisfactory; a ferrous salt dissolved in 6N HCl and heated 3 hours on the water-bath with exclusion of air was largely oxidized).

Silicates (including rocks) are dissolved in a 10:1 mixture of 8N H_2SO_4 and 40% HF in screw-capped PTFE vessels, and the special reagent (*o*-phenanthroline + 8-hydroxyquinoline) is saturated with H_3BO_3 to complex excess HF and protect the separator and colorimeter cells.

The iodine monochloride method for the determination of the net state of oxidation in acid-soluble materials has also been adapted for use on silicates by use of *M*/25 ICl in 6N HCl together with 1/10th its volume of 40% HG, using a PTFE vessel and adding an equal volume of 6N HCl saturated with H_3BO_3 before extraction with CCl_4 . This technique has two advantages: air need not be excluded during solution, and the acid layer after extraction of the iodine by CCl_4 can be used for other determinations; but it has two disadvantages: iodine in CCl_4 has a relatively weak absorption, about 1/8th that of Fe^{3+} -*o*-hydroxyquinolate and 1/20th that of Fe^{2+} -*o*-phenanthroline; and sulphides, including pyrite, are readily oxidized by the ICl as are any organic contaminants. For rocks, the first of these disadvantages is unimportant, since a fairly large sample is normally necessary to ensure proper sampling; the latter is, however, serious, though in some rocks the sulphides could probably be attacked by pure dry chlorine without oxidation of the silicates.

Finally, a procedure is described for the determination of titanium and total iron, or of manganese, titanium, and total iron after a determination of Fe^{2+} by the ICl technique.

The new techniques, here shortly described, are dealt with more fully in the Miniprint section.

Procedure for acid-soluble minerals. Reagents: H_2SO_4 , c.8N, de-aerated and stored under N_2 or CO_2 .

NaOH, adjusted to a normality 0.9 that of the H_2SO_4 .

$\frac{1}{2}\%$ *o*-phenanthroline in water.

20% sodium acetate in water.

1% 8-hydroxyquinoline ('oxine') in CHCl_3 .

Dual reagent: 1 g oxine, $\frac{1}{2}$ g *o*-phenanthroline, 10 g sodium citrate, in 12 ml glacial acetic acid and 88 ml H_2O .

The sample should if possible contain $\leq 10 \mu\text{g}$ of FeO or Fe_2O_3 , whichever there is least of, and not more than 1 mg Fe_2O_3 . It is weighed into a glass-stoppered tube of 4 ml capacity, 3.0 ml H_2SO_4 added, the air displaced by N_2 or CO_2 , and the tube heated on the water-bath until solution is complete. The solution is poured into a 25 ml separator containing 3.0 ml NaOH, 2 ml 20% sodium acetate, and 2 ml dual reagent, rinsing the tube with the minimum of water, and the ferric oxine complex extracted with 5 ml (or more) 1% oxine in CHCl_3 , shaking vigorously for 30 sec; if the CHCl_3 layer appears black after a few seconds shaking, add a further 5 or 10 ml 1% oxine. Separate, add 1 ml $\frac{1}{2}\%$ *o*-phenanthroline to the aqueous layer and extract with a smaller volume of 1% oxine. For $< 100 \mu\text{g}$ Fe_2O_3 extractions with 5, 2, 1, 1 ml oxine will be satisfactory; for more Fe_2O_3 increase the volumes; the fourth extract should be completely colourless (if the second appears colourless, make only three). Add extra *o*-phenanthroline after each extraction, including the last.

Bulk the aqueous and CHCl_3 layers appropriately and colorimeter against standards and a blank, the aqueous layer at λ 508 nm for FeO, the CHCl_3 layer at 579 nm for Fe_2O_3 (if Al and Cu are absent, the CHCl_3 layer may be colorimetrically at 467 nm with a gain in sensitivity of about 1.5 times). The pH of the aqueous layer should be about 4.0 to 4.5.

Procedure for rocks and minerals insoluble in 8N H_2SO_4 . The 4 ml glass tubes are replaced by 7 ml screw-capped polytetrafluorethylene (PTFE)

capsules, and 5.0 ml 8N H_2SO_4 and $\frac{1}{2}$ ml 40% HF used for solution. The NaOH is increased to 5.0 ml, and the dual reagent is modified, being saturated with H_3BO_3 to complex the HF; a saturated solution of H_3BO_3 is used to rinse out the PTFE capsule. Otherwise the procedure is as for acid-soluble minerals.

Modified iodine monochloride method. For rocks and minerals insoluble in 1:1 HCl, the procedure of Hey (1974) for acid-soluble minerals is followed, except that: the solvent is a mixture of 9 parts *M*/25 ICl in 1:1 HCl and 1 part of 40% HF, duly stabilized; solution takes place in a PTFE capsule, which must be stoppered, but displacement of air is unnecessary; and the solution is transferred to the separator with 5 ml 1:1 HCl saturated with H_3BO_3 . (Note: The *M*/12 ICl solution recommended in Hey (1974) is unnecessarily strong; 4 ml *M*/25 ICl are enough to oxidize 5 mg FeO).

Sulphosalicylic acid as a reagent for Fe and Ti. The deep purple colour given by sulphosalicylic acid (phenol-2-carboxylic-4-sulphonic acid) with Fe^{3+} in weakly acidic solution is not suitable for determination of Fe^{3+} , but in alkaline solution iron (Fe^{3+} or Fe^{2+}) reacts to give a yellow colour, peak at λ 425 nm; interference by Mn or Co (which undergo air-oxidation) is suppressed by ascorbic acid, added after the solution is made alkaline, and the only other slightly interfering metal is V, which gives an absorbance about 1/70 that of Fe at λ 425 nm; for the small amounts of V present in rocks, a correction is hardly necessary. Interference by large amounts of acetic acid or citric acid is suppressed by extra sulphosalicylic acid.

In weakly acidic solution, pH 3.6-4.3, sulphosalicylic acid gives an intense absorption, peak λ 395 nm, with Ti; the purple Fe^{3+} colour can be bleached by ascorbic acid. It is thus practicable to determine total Fe in the aqueous layer after a Fe^{2+} determination by the ICl method, and then Ti in the same solution. If the solution is then evaporated with nitric acid and either sulphuric or perchloric acid, the picric acid formed from the sulphosalicylic acid does not interfere with determination of Mn as MnO_4^- .

REFERENCE

Hey, M. H. (1974) *Mineral. Mag.* **39**, 895-8.

[Manuscript received 31 March 1981]

[Note added in proof: The observations on the decay of the ferric *o*-phenanthroline complex, mentioned on p. 115 and in fig. 5, will appear as a note later in this volume.]

THE DETERMINATION OF FERROUS AND FERRIC IRON IN ROCKS AND MINERALS; AND A NOTE ON SULPHOSALICYLIC ACID AS A REAGENT FOR FE AND TI.

M. H. HEY

British Museum (Natural History), Cromwell Road, London, SW7

The last two decades have seen the development of several useful instrumental methods for the chemical analysis of rocks and minerals. X-ray fluorescence has revolutionized rock analysis; large numbers of analyses can now be obtained in a short time and many trace elements can be determined with comparatively little trouble, though it is still desirable to use with any batch of rocks to be analysed a similar rock of well-established composition as a standard.

The electron-probe and ion-probe will supply analytical data on minute areas of minerals and are invaluable in their proper field, but are, unfortunately, often misused - e.g. for the analysis of a hydrated mineral that will most certainly decompose under the beam and of which adequate material is available for a classical microanalysis; this misuse is largely due to the rarity of competent wet-chemical analysts, and even in some cases to lack of the simple facilities needed for these techniques.

But whether we are considering rocks or minerals, there is one important determination that cannot be made satisfactorily by any current instrumental methods - the determination of the net state of oxidation of a rock or mineral. The Mossbauer technique gives useful data on the state of oxidation of iron, provided that the $Fe^{2+}:Fe^{3+}$ ratio is neither very small nor very great, and provided the iron is not distributed over several lattice sites with different surroundings; but if there are any other elements present with variable valency, as Mn, Ti, V, or Cu, this information needs to be supplemented by a knowledge of the net state of oxidation.

Some reason for the use of this last term is, perhaps, desirable. In dilute acid solution, and in the absence of any complex-forming agents, the equilibria $Fe^{2+} + Ti^{4+} \rightleftharpoons Fe^{3+} + Ti^{3+}$, $Mn^{2+} + Fe^{3+} \rightleftharpoons Mn^{3+} + Fe^{2+}$ et sim. favour the left-hand side of each equation by a very large factor, and it has often been assumed that this will also be the case in minerals, and that any consumption of an oxidant by a solution of an iron-bearing mineral in acid represents Fe^{2+} present in the mineral.

That this is not necessarily the case was recognized some 70 years ago by Hillebrand who suggested that the vanadium in rocks is present as V^{3+} in pyroxenes, and that the FeO should be corrected accordingly. More recently, it has been shown that the presence of 'incompatible' pairs of ions in minerals is not unusual; and in such cases no chemical analysis can ever arrive at the proportions of the several ions present, since they will immediately react when taken into solution. Thus the net state of oxidation of a rock or mineral is measured by the amount of an oxidant, or in some cases of a reductant, consumed by a dilute acid solution of the rock or mineral, and is not necessarily a measure of the amount of Fe^{2+} or Mn^{3+} actually present; it is a somewhat indefinite term, since the final state of oxidation of such elements as As, Sb, and V will depend on the oxidant or reductant used; but it avoids the implicit assumption involved in speaking of such a procedure as a ferrous iron determination.

Nevertheless, no chemical analysis of a mineral containing an element of variable valency is complete without a determination of its net state of oxidation, and this can only be obtained by the methods of classical analysis.

Attempts are often made to meet this deficiency in electron-probe and similar analyses by calculations based on an assumption of exact stoichiometry, but are inevitably unreliable, partly because this assumption is often unjustified, and partly because all the analytical errors are summed into this one figure.

The history of 'ferrous iron' determinations. There are a wide variety of methods available for the determination of net states of oxidation; it may be of interest to trace their development, and perhaps some of the forgotten techniques might still prove useful in special circumstances.

H. Rose (1829, p.199) describes two methods for the determination of the oxidation state of magnetic iron ore. The less accurate is simply to dissolve the weighed mineral in acid, oxidize the solution, precipitate the iron with ammonia, ignite and weigh the ferric oxide; after correction for insolubles and any other oxides, the proportion of FeO necessary to account for the observed increase in weight is calculated. His second, more accurate, method is to reduce the mineral in a current of dry hydrogen and weigh the water formed; the remaining metallic iron may also be weighed, and in any case must be dissolved in acid and a correction made for insolubles and any other oxides.

In the same textbook, Rose describes (p.207) two wet-chemical methods, one for the determination of Fe^{2+} and one for Fe^{3+} , and adds: "Mit sehr vielen Schwierigkeiten ist die Trennung der Eisenoxyd vom Eisenoxydul verbunden. Die Schwierigkeiten können, wenn die Substanz von Säuren nicht aufgelöst wird, gar nicht überwunden werden", a statement that held good for 30 years. For Fe^{2+} Rose dissolved the mineral in acid under a protective cover of CO_2 , then added a small excess of $NaAuCl_4$, and after standing filtered off, dried and weighed the precipitated gold (he notes that solutions of H_2AuCl_4 are seldom, if ever, pure enough for use); $3Fe^{2+} + AuCl_4^- \rightarrow 3Fe^{3+} + 4Cl^- + Au$.

For the determination of Fe^{3+} , Rose again dissolved the mineral under CO_2 protection, then filled the vessel completely with a saturated solution of H_2S and stoppered it; after standing until the sulphur coagulated and settled, it was filtered off, dried and weighed; $2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + 2H^+ + S$. In another method for Fe^{3+} , due to Berzelius (1830), finely divided silver was employed as reductant; the mixture of Ag and AgCl resulting was weighed, the increase in weight being consequent on the reaction $Fe^{3+} + Cl^- + Ag \rightarrow Fe^{2+} + AgCl$.

That Fe^{2+} , like Mn^{2+} , Zn^{2+} , Ni^{2+} , and Co^{2+} , is a much stronger base than Fe^{3+} (or Al^{3+}) was already well known, and in 1831 Fuchs proposed a separation of Fe^{3+} and Fe^{2+} by dissolving the mineral in HCl under CO_2 protection and adding an excess of $CaCO_3$ or $BaCO_3$; when the precipitate of FeOH had settled the solution was decanted as far as possible and the precipitate washed; Fe^{3+} could then be determined in the precipitate and FeO in the solution. $BaCO_3$ had an advantage over $CaCO_3$ in that it is easier to separate the iron from Ba than from Ca. Liebig (1831), after referring to Fuch's work, notes that he prefers magnesium carbonate as precipitant for the Fe^{3+} .

Normandy (1849) mentions that J.W. Döbereiner used sodium formate to separate (as basic formate) Fe^{3+} , but I have failed to trace publication of this method in Döbereiner's numerous papers.

Döbereiner also proposed (1831) an unusual method for the determination of Fe^{3+} : to the acid solution, excess oxalic acid was added, and the solution exposed to a bright light; the CO_2 resulting from the photodecomposition $2Fe(C_2O_4)_3^{3-} \rightarrow 2Fe^{2+} + 5C_2O_4^{2-} + 2CO_2$ was collected over mercury and its volume measured.

In 1846, Margueritte introduced the first volumetric method for the determination of iron. He reduced an acid solution with zinc and titrated it with a standardized permanganate solution, so arriving at a total iron figure; he notes sulphite as a possible but less satisfactory reductant, but does not mention titration of an unreduced solution for Fe^{2+} . The new technique was quickly accepted, by industrial chemists in particular, both for total iron and for ferrous, but the older methods are still included in the last edition (6th) of Rose's Handbuch (1871).

Penny (1850) and Schabus (1851) both felt permanganate too unstable and too difficult to purify, and advocated potassium dichromate despite the need to use fericyanide as external indicator; dichromate not only has the advantage of stability, but can be purified enough to be used as a primary standard. Both reagents continue to be widely used, the choice being a personal one.

A third reagent, ceric sulphate, was shortly mentioned by Lange (1861), but he gave no experimental detail or test analyses, and it did not attract many users; while stable, it cannot be used as a primary standard, but is still favoured by some.

Until 1860, minerals insoluble in hot HCl or H_2SO_4 were intractable so far as determinations of the net state of oxidation goes, as Rose noted 30 years before, but in that year A. Mitscherlich found that many rock-forming minerals can be dissolved in 75 wt. % sulphuric acid in a sealed tube at 150 to 200°C; unfortunately this method leads to seriously high results for Fe^{2+} if even small amounts of sulphides are present, a fault it shares with many otherwise useful methods (see below).

Nevertheless, it remained a favourite method in many European countries for some 50 years, and if sulphides are absent it can give good results for Fe^{2+} ; it is not so satisfactory for many constituents of silicates, since there is always considerable attack on the glass. Jannasch (in Classen, 1900) sought to avoid this by using an inner tube of platinum, but this does not seem to have been widely used, perhaps because he preferred to use HCl for the attack, which meant very high pressures.

Hermann (in Rose, 1871, p.698) fused difficult minerals with borax, excluding air by placing the crucible inside a larger one filled with magnesite to provide a CO_2 atmosphere; this technique seems to have found few users.

The technical difficulties of the sealed-tube method were avoided by Cooke (1867), who attacked silicates with a mixture of HF and H_2SO_4 on the water-bath, excluding air by a current of CO_2 ; he used a fairly large platinum dish, inverted a large funnel over it, and took steps to provide a water seal to bar ingress of air. This apparatus had one advantage over the arrangements of Treadwell (1913) and Barneby (1915) - a stout platinum wire, passed down through the truncated stem of the funnel, could be used to stir the mixture and to feel for gritty undissolved particles. Soule (1928) proposed to use a pyrex flask for the attack, weighing it before and after use, so that a correction could be made for the dissolved glass.

Pratt (1894) simplified the arrangement; using a large platinum crucible, heated directly over a small flame, the boiling acid keeps the mixture in motion and speeds solution, while the steam largely or wholly replaces CO_2 as a protective cover. This technique, which is probably the best today for 0.1 to 1 g. scale analyses, is fully described by, e.g. Hillebrand and Lundell, 1929, 1953.

By the 1890s, it had become apparent that both the sealed-tube and the HF- H_2SO_4 methods occasionally gave high and erratic results. The experiments of Vogt (1899), Hillebrand and Stokes (1900), and Stokes (1901) showed that this is due to reduction by sulphides, traces of which in a rock, or as impurities in a mineral, can produce large errors, since reactions as disadvantageous as $8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + SO_4^{2-} + 8H^+$ are possible.

The sealed-tube method is more severely affected than the HF- H_2SO_4 techniques; with the latter, much of the sulphur escapes as H_2S without reducing iron, and, as Hillebrand and Stokes showed, pyrite is hardly attacked unless there is much Fe^{3+} present and solution is prolonged (here the Pratt method has a distinct advantage).

Users of the HF- H_2SO_4 techniques had three further troubles: They soon noticed that the permanganate end-point is unstable, fading quickly; Miller and Koppe (1910) showed that this is because MnF_2 is largely ionized, favouring the reaction $MnO_4^- + 4Mn^{2+} + 8H^+ \rightarrow 4H_2O + 5Mn^{3+}$, but Barneby (1915) suppressed this by complexing the HF with boric acid ($4F^- + BO_3^{3-} + 6H^+ \rightarrow BF_4^- + 3H_2O$). Secondly, there was (and still is) the problem of finding the optimum grinding time; a coarse powder will be too slow dissolving, while very fine grinding results in partial oxidation (Mauzelius, 1907; Hillebrand, 1908). And thirdly, there was always a suspicion that a little air might have reached the solution - and as Peters (1898) showed, Fe^{2+} is extremely readily oxidized in presence of F^- (because of the formation of FeF_6^{3-} ions) Sarver (1927), using the Pratt method, cooled the crucible with a current of CO_2 , passing, then added excess dichromate and back-titrated the excess with a standard ferrous sulphate solution.

Other analysts sought to oxidize the ferrous iron as soon as it was dissolved. Reichen and Fahy (1962) simply dissolved HF + H_2SO_4 plus a measured excess of dichromate, which was then back-titrated with standard ferrous sulphate; sulphides interfere seriously, and as Sarver

(1927) had shown, there is some reaction between $Cr_2O_7^{2-}$ and HF. A better protective oxidant was advanced by MacCardle and Scheffer (1951), who dissolved a slag in HF plus HCl, with an addition of a measured excess of a solution of V_2O_5 in dilute H_2SO_4 ; Wilson (1955) modified this by using a weighed amount of NH_4VO_2 as oxidant and cold 40% HF as solvent, adding H_2SO_4 and H_3BO_3 after solution, which is slow, was complete. Since V^{5+} is not a powerful oxidant, while V^{4+} is not oxidized by air, this technique is probably particularly suitable for sulphide-rich rocks. After solution the excess V^{5+} is back-titrated with ferrous ammonium sulphate; titration by an oxidant of the V^{4+} produced is less attractive because of the large amount of F^- .

For completeness, it should be mentioned that the principal disadvantage of dichromate as oxidant, the use of an external indicator, has been overcome, first by the use of oxidation-reduction indicators such as diphenylamine (Knop, 1924), and then by the application of potentiometric methods for the detection of the end-point (Kiss, 1967); and dichromate has the advantage of serving as a primary standard.

Direct determination of ferric iron. All the above volumetric methods have been directed to a determination of the ferrous iron in a solution of a rock or mineral. The alternative procedure, a determination of the ferric iron with a suitable reductant, as advanced by Knecht (1903), who used $TiCl_3$, or by Thornton and Chapman (1921), who preferred $Ti_2(SO_4)_3$, has been little used, mainly because the reductant has to be stored under nitrogen or hydrogen (and I have found it seems to encourage accumulations of grease in the burette), but has been modified by Cleney and Hagner (1961); their technique does not seem to have attracted much attention, perhaps because it requires the setting up of special apparatus for a determination that may not often be required.

Resistant minerals; the Rowledge fusion. While the HF- H_2SO_4 and sealed-tube techniques for solution of a mineral were a great advance on simple acid solution, a few minerals, including some of great interest, remained recalcitrant. In 1934, Rowledge showed that most of these minerals are attacked by a fused mixture of 2 parts NaF and 1 part B_2O_3 at 900°C, and that this fusion does not attack pyrex glass sufficiently to give trouble; the mineral is fused with this special flux in a sealed pyrex tube, and the fused mass dissolved in hot dilute sulphuric acid under protection of a current of CO_2 and titrated with permanganate. Partial oxidation of the FeO by air in the tube may easily be avoided by evacuation or by replacing the air with N_2 . The fused mass does not dissolve easily, and it may be advantageous to crush it in an agate mortar. The most serious disadvantage of the method is that sulphides exert their full reducing power on the ferric iron; most minerals that are not attacked by HF- H_2SO_4 are also unattacked by dry, HCl-free chlorine at 250 to 300°C, so this could be used to destroy sulphides before a Rowledge fusion (cf. Hey, 1973, p.10).

Microanalytical "ferrous iron" techniques. Microanalytical methods were soon applied to the determination of the net state of oxidation of rocks and minerals. Hueber (1932) describes procedures for a complete rock analysis on the 10 mg scale (except for very glassy or fine-grained rocks, 10 mg is about the smallest sample that can be relied on to be a representative sample); these include a "ferrous iron" determination on 7 to 8 mg, dissolved in HF- H_2SO_4 , to which a measured excess of permanganate was added and the solution diluted to a definite bulk and colorimetrically against a blank.

Hey (1941) describes an adaptation of Rowledge's method to the 10 mg scale; an evacuated tube is used, the fusion mass is coarsely crushed along with adhering glass, and dissolved in a cold M/200 solution of ICl in 1:1 HCl (solution is slow, but there is no danger of air oxidation) and titrated with M/2000 KIO_3 , using a globule of CCl_4 as indicator, a method due to Heisig (1928); the disappearance of free iodine, formed by the reaction $2Fe^{2+} + 2ICl \rightarrow 2Fe^{3+} + 2Cl^- + I_2$, from the CCl_4 indicates the end-point of the reaction $2I_2 + IO_3^- + 5Cl^- + 6H^+ \rightarrow 5ICl + 3H_2O$. The end-point is difficult to observe owing to the presence of the broken glass, and it would be preferable to speed solution by heating in a stoppered flask on the water-bath, then filter off the glass on a coarse sinter-glass disk, extract the liberated iodine with CCl_4 , and colorimeter it (cf. Davis, Hey, and Kingsbury, 1965).

Colorimetric techniques. While a number of ingenious methods have been devised for carrying out titrations on a micro-scale, they mostly call for specialized apparatus, and are, for the most part, not readily adaptable to the wide variety of conditions the mineral analyst must be prepared to meet. On the other hand, if a good modern spectrophotometer

is available, colorimetric methods do not call for any great manipulative skill and little other specialized apparatus. They have long been used for the determination of trace constituents, but only recently for major constituents, though precisions of the order of 1 to 2% of the amount present can often be attained. And as the optimum concentration of the element being determined is commonly 1 to 5 $\mu\text{g/ml}$ in the solution metered, samples of 1 mg or less are often adequate.

There are many colorimetric reagents for iron, some specifically for ferrous iron, some for ferric; two methods have been proposed for the determination of Fe^{2+} and total iron in the same solution, and one for Fe^{3+} and total iron. Alten et al. (1933) determined ferric iron in weakly acid solution (pH 2) with sulphosalicylic acid (phenol-2-carboxylic-4-sulphonic acid) as a purple complex, Fe^{2+} giving no colour or a very weak red (almost certainly due to traces of Fe^{3+} in their ferrous ammonium sulphate); the solution was then made alkaline and oxidized with H_2O_2 to determine the total iron as the yellow Fe^{3+} complex; this they found sensitive to pH and subject to interference by organic acids and especially by Mn. Thiel and Peter (1935) proposed a very similar procedure, but the reagent has not become popular; however, I have found it very satisfactory for the determination, not only of total iron, but also of titanium (see below).

Harvey et al. (1955) observed that o-phenanthroline, besides its well-known red ferrous complex with peak absorption at λ 512 nm, gives a yellow ferric complex with peak absorption at 360 nm (at which wavelength, however, o-phenanthroline itself absorbs appreciably). The two complexes have equal absorption at 396 nm, and Harvey et al. measure the absorbance at 512 nm (Fe^{2+}) and at 396 nm (total Fe); acetate, citrate, and oxalate interfere by complexing the Fe^{3+} ; they also observed that the yellow ferric complex is not stable, but slowly breaks down to the red ferrous complex (this will not affect the total iron determination, and the Fe^{2+} can readily be measured before any reaction is appreciable).

The most satisfactory adaptation of the HF- H_2SO_4 technique to the micro-scale appears to be that of Riley and Williams (1958), in which the mineral, after solution in a stoppered polytetrafluorethylene (PTFE) tube on the water bath, is complexed with 2:2'-dipyridyl and colorimetric. Air-oxidation is avoided by simply filling the tube completely, and an acetate buffer provides a suitable pH; o-phenanthroline may be substituted for dipyridyl (the absorption characteristics of the complexes are very similar). The fluorine content of the final solution must be kept below 0.4 g/ml; sulphides interfere more than in the Pratt method, since any H_2S cannot escape. After measuring the absorbance, the solution may be reduced with quinol and total iron determined.

If the ratio $Fe^{3+}:Fe^{2+}$ is very high, the breakdown of the ferric o-phenanthroline complex noted by Harvey et al. can lead to high results for Fe^{2+} ; Fadrus and Maly (1975) seek to prevent this by complexing the Fe^{3+} with nitrilotriacetic acid. A blank including an aliquot of sample material but no o-phenanthroline has to be used because of the absorption of the Fe^{3+} nitrilotriacetic complex.

Hey (1974) describes the use of the iodine monochloride method for acid-soluble minerals. Iodine liberated by the reaction $2Fe^{2+} + 2ICl \rightarrow 2Fe^{3+} + 2Cl^- + I_2$ is extracted by $CHCl_3$ and colorimetric. There is no danger of air oxidation, but sulphides exert their maximum effect. The M/12 ICl solution there recommended is stronger than necessary; 1000 μg Fe^{2+} only require 1/50 meq ICl for their oxidation, so that 2 ml M/25 or 4 ml M/50 ICl provides an ample excess.

Some new data relevant to the "ferrous iron" problem. In all the methods summarized above, except the photochemical method of Döbereiner (1831), the gravimetric method of Fuchs (1831), and the titanometric method of Clemency and Hägner (1961), ferrous iron is determined in a solution of the mineral, and ferric iron obtained by difference from a determination of total iron; this gives reasonable results so long as ferrous iron is not too greatly in excess of ferric, but it is desirable to have a method for the separate determination of Fe^{2+} and Fe^{3+} , in the same portion of material if possible, and the method now described provides this.

Assuming that the mineral can be dissolved without oxidation of any of the Fe^{2+} (either present as such in the mineral, or formed by reduction of Fe^{3+} by V^{3+} , Ti^{3+} , etc), we could seek either to determine Fe^{2+} and Fe^{3+} separately in two aliquots of the solution, or to complex the Fe^{2+} and Fe^{3+} by two reagents and colorimeter the two complexes in the same solution, or to separate them for determination.

The first option is not very promising: the danger of oxidation of the Fe^{2+} during the Fe^{3+} determination is high, and twice as much mineral will be used. Attention was first directed to the second option, which would call for the least manipulation; unfortunately, it has not so far proved possible to find two suitable reagents: they must give stable complexes with Fe^{2+} and Fe^{3+} respectively, but neither may be so stable as to rob iron from the other; the absorption curves of the two complexes must not overlap to the extent of either having appreciable absorption at the wavelength of the other's absorption peak; and the reagents must not give appreciable absorption at either complex's absorption peak. Combinations of o-phenanthroline with tiron (1:2-dihydroxybenzene-3:5-disulphonic acid), with EDTA (ethylenediamine tetracetic acid), with nitrilotriacetic acid, or with sulphosalicylic acid (phenol-2-carboxylic-4-sulphonic acid) all proved unsatisfactory for one or other of the above reasons.

After a few false starts, a successful procedure proved possible using o-phenanthroline to complex Fe^{2+} and 8-hydroxyquinoline to complex Fe^{3+} , and extracting the ferric complex with $CHCl_3$ (it is practically insoluble in CCl_4). Tests were made first to check whether Fe^{3+} can be completely extracted by 1:8-hydroxyquinoline (oxine) from solutions containing citrate and o-phenanthroline at pH 4 and at pH 8; from these it appeared that there was always a little Fe^{2+} formed; in one experiment, using 2.02 mg Fe^{3+} , only 2.00 mg were recovered, and 125 μg were found in the aqueous layer.

This suggested that the breakdown of the ferric o-phenanthroline complex observed by Harvey et al. (1955) is rapid enough for some Fe^{2+} to be formed during the few minutes required to perform the extractions, and in fact the golden-yellow ferric o-phenanthroline solution was observed to take on an appreciably orange tint in 15 minutes (the rate of breakdown and its probable mechanism are discussed below). The difficulty was readily overcome by adding oxine as well as o-phenanthroline from the start, so that the ferric o-phenanthroline complex is never formed; a moderate excess of oxine is necessary, at least 2 ml 1% oxine for 1 mg Fe^{3+} expected (theory, 0.8 ml).

Further experiments showed that 30 seconds vigorous manual shaking is enough to establish equilibrium between the phases (mechanical shakers are much less efficient); 15 seconds is too short, longer than 30 seconds is unnecessary. With 2 mg Fe^{3+} in 25 ml of a solution containing citrate, o-phenanthroline, and 50 mg oxine, a first extraction with 10 ml 1% oxine in $CHCl_3$ removed over 95% of the iron; subsequent extractions appear to be less efficient, but three extractions remove well over 99% of the iron.

It was found early on that extraction of a solution containing the ferrous o-phenanthroline complex with 1% oxine in $CHCl_3$ results in a marked bleaching, 5% or more; further work showed that there is no extraction of iron, that the bleaching is simply due to extraction of o-phenanthroline by the $CHCl_3$, and that if it is replaced after each extraction there is no bleaching and no extraction of iron.

Thus we have established that Fe^{2+} and Fe^{3+} can be successfully separated and determined colorimetrically by adding the acid solution containing them to a mixture of sodium citrate, o-phenanthroline, and oxine in suitable proportions, bringing the pH to between 3.5 and 8, and extracting the ferric 8-hydroxyquinolate with 1% oxine in $CHCl_3$, then replacing the o-phenanthroline extracted by the $CHCl_3$ before colorimetry for Fe^{2+} at λ 508 nm. If no interfering elements are present, Fe^{3+} is advantageously colorimetric at λ 467 nm; $CHCl_3$ solutions of the complex are dark grey, and show two absorption peaks, but the second peak, at 579 nm, is only 2/3 the height of that at 467 nm (fig.1).

Interferences. Many other elements form 8-hydroxyquinolates extractable by $CHCl_3$ at suitable pH, but except for V they are all various shades of yellow and have no appreciable absorbance at λ 579 nm. However, if allowed to form they will consume oxine, so it is preferable to work at pH 3.5 to 4.5, when Fe^{3+} , Cu, and V will be completely extracted and Zn partially; if much Al is present, a little may be extracted. At λ 467 nm Cu and Zn will not interfere even in considerable amounts (their absorbances at λ 467 nm are approximately 0.003 to 0.004 for a solution in $CHCl_3$ containing 1 μg cm^{-2} Cu or Zn), but Ti has nearly half the absorbance of Fe^{3+} so interferes seriously, as does V. At λ 579 nm, only V interferes, having an absorbance half that of Fe^{3+} . For the small amounts of V usual in rocks, a correction is reasonable, assuming an absorbance at λ 579 nm of 0.030 for 1 μg cm^{-2} V as oxine complex in $CHCl_3$. Removal of the V from the $CHCl_3$ by dilute alkali (Talvitie, 1953) was not found satisfactory.

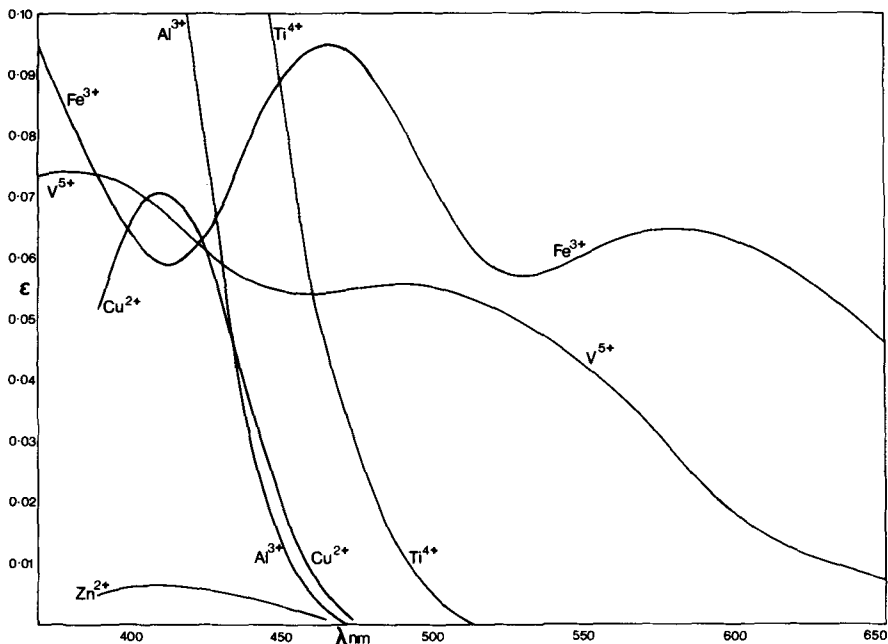


Fig. 1. Absorption spectra, at a concentration of $1 \mu\text{g cm}^{-2}$ of metal, of the 8-hydroxyquinoline complexes of Fe^{3+} , Al^{3+} , Ti^{4+} , V^{5+} , Cu^{2+} , and Zn^{2+} ; these complexes can all be extracted by chloroform at pH 5.5 to 6.5

An unexpected phenomenon. When an attempt was made to apply the dual-reagent procedure to childrenite, which is only slowly soluble in hot acid, much less Fe^{2+} was found than by the ICL technique. In a search for the cause of this result, 1.1 and 7.6 mg portions of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were heated for 2 to 3 hours on the water-bath with de-aerated 1:1 HCl in stoppered tubes from which air had been expelled by N_2 , then poured into a mixture of 2 ml 10% sodium citrate, 10 ml 20% sodium acetate, and 2 ml 1% o-phenanthroline, and extracted with 1% oxine in CHCl_3 ; large amounts of Fe^{3+} were found to be present. When the experiment was repeated except for the heating, a 2.6 mg portion of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was found to contain 365 $\mu\text{g Fe}^{2+}$ and 10.8 $\mu\text{g Fe}^{3+}$, in line with earlier observations on the same sample of this salt. And when H_2SO_4 (1:3 by volume, approximately 8N) was substituted for HCl, only 9.0 $\mu\text{g Fe}^{3+}$ were found from 2.6 mg of the salt after heating.

It is clear that ferrous salts, digested 2 to 3 hours with 1:1 HCl on the water-bath, with exclusion of air, undergo very substantial oxidation. A search of the literature brought to light an observation by Erdmann (1910), who found that when a solution of ferrous chloride was heated for long periods in sealed tubes hydrogen was formed. Whether the $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ equilibrium is sufficiently disturbed by formation of the complex ion FeCl_4^- to lead to reduction of water is a matter for study, but clearly hot strong HCl is not a suitable solvent for iron minerals in which the net state of oxidation is wanted.

Procedures for acid-soluble minerals and for silicates, based on the experiments described above, are detailed in the Synopsis, and will not be repeated here, but a few comments may be useful. If the alkali is adjusted to 0.9 times the normality of the acid and both are measured to 0.1 ml, the pH of the final solution will be between 4.0 and 4.4; the pH of the blank can easily be checked if desired.

2:2'-dipyridyl could almost certainly be substituted for o-phenanthroline, though this point has not been tested.

Using 10 ml of 1% oxine in CHCl_3 as extractant and metering the extract in a 4 cm cell at 4467 nm, 1 $\mu\text{g Fe}^{3+}$ should give an absorbance of approximately 0.038; accordingly, it should be possible to determine Fe^{3+} in 100 μg of a mineral with a precision of the order of 0.2%. Similarly, if the bulk of the aqueous layer is kept below 30 ml and a 4 cm colorimeter cell used, 1 $\mu\text{g Fe}^{3+}$ should give an absorbance of about 0.036.

There can be no doubt that this technique could be further developed, using special apparatus to avoid the transfers and using micro-cells, and it ought to be possible to determine the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio on a few micrograms of mineral.

Sulphosalicylic acid as a reagent for total Fe and for Ti.

The procedures of Alten *et al.* (1933) and of Thiel and Peter (1935) for determination of Fe^{3+} by sulphosalicylic acid in weakly acid solution (pH 2) followed by a determination of total iron in alkaline solution (see above) have not been generally adopted, with good reason. The purple colour in acid solution, while highly sensitive, is very dependent on pH; in too acid solutions it is weakened, at pH > 3 the hue begins to change. The yellow colour in alkaline solution is subject to interference by organic acids, and particularly by Mn. A re-examination of this reagent shows that these difficulties can easily be circumvented. The addition of H_2O_2 to the alkaline solution to ensure oxidation of Fe^{2+} is not only unnecessary, but ensures maximum interference by Mn (also, oxygen bubbles are liable to form in the colorimeter cell and give rise to spurious readings); a colourless, weakly acid solution containing Fe^{2+} and sulphosalicylic acid develops the full yellow Fe^{3+} complex in a few seconds when made alkaline; the dissolved oxygen in the air-saturated aqueous solution is enough to oxidize 20 to 30 $\mu\text{g ml}^{-1}$ of Fe^{2+} .

Interference by organic acids can be overcome simply by increasing the amount of sulphosalicylic acid. The divalent metals Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+} give rise to complexes with very low absorbance at 4425 nm, which is the peak of the curve for the Fe^{3+} complex (all 0.0005 or less for 1 $\mu\text{g cm}^{-2}$), but Co^{2+} and Mn^{2+} complexes readily undergo air-oxidation, leading to deeply coloured Co^{3+} and Mn^{3+} complexes (both deep brown). This oxidation is readily suppressed by hydroxylamine hydrochloride, or preferably by ascorbic acid, as the use of hydroxylamine leads to formation of nitrogen bubbles as it is oxidized, the Mn or Co acting as catalyst; if ascorbic acid is added before the solution is made alkaline, the full iron colour does not develop, but if the solution is made alkaline first, moderate concentrations of ascorbic acid (up to c. 8 mg ml^{-1} , which is sufficient to suppress the oxidation of 20 $\mu\text{g ml}^{-1}$ Mn^{2+} for an hour or more) do not interfere.

In weakly acid solution (pH 3.6 to 4.3) Ti^{4+} gives a pale greenish-yellow colour with sulphosalicylic acid, but the absorbance in the near ultraviolet is intense; at its peak, 4360 nm, its absorbance is 0.205 for 1 $\mu\text{g cm}^{-2}$ Ti. The only interfering metal

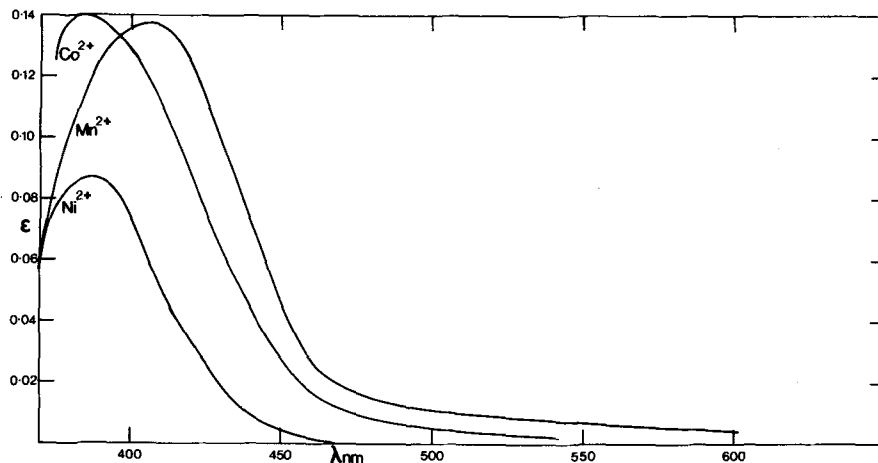


Fig.2. Absorption spectra, at a concentration of $1 \mu g \text{ cm}^{-2}$ of metal, of the 8-hydroxyquinoline complexes of Co^{2+} , Mn^{2+} , and Ni^{2+} ; these complexes can only be extracted by chloroform at $pH > 7$.

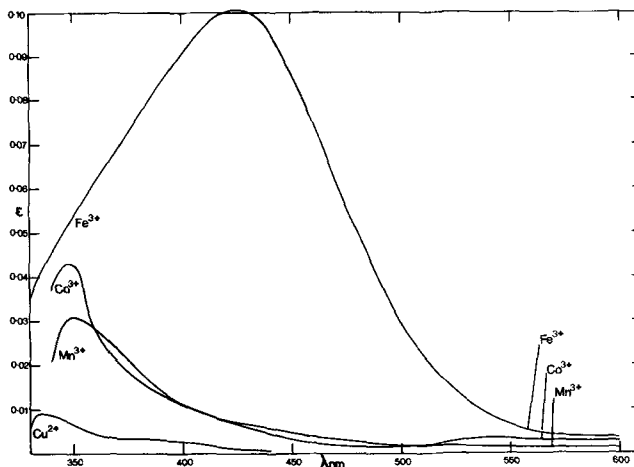


Fig.3. Absorption spectra, at a concentration of $1 \mu g \text{ cm}^{-2}$ of metal, of the sulphosalicylic acid complexes of Fe^{3+} , Mn^{3+} and Co^{3+} in alkaline solution ($pH 7$ to 9).

appears to be Fe^{3+} , and this is easily reduced with ascorbic acid. It is, however, necessary to measure the sulphosalicylic used accurately, to avoid too great an excess, and to use the same amount in a blank, because sulphosalicylic acid has an appreciable absorbance at 360 nm (a solution with 8 mg ml^{-1} gave an absorbance of 0.145).

These observations suggest a useful procedure following a state-of-oxidation determination by the ICL method: after extraction of the liberated iodine with CCl_4 , the solution is evaporated to dryness (in Pt if HF was used; and in this case, to avoid attack on the Pt, the ICL must be reduced by a slight excess of KI before evaporation); the residue is redissolved in HCl or H_2SO_4 , a measured amount of sulphosalicylic acid added (5 ml of 4% will normally be adequate), ammonia till the solution turns yellow, then ascorbic acid, 1 ml of 10% for 25 ml final volume of solution, bulk and colorimeter at 425 nm for total Fe. The solution is now acidified with acetic acid, when the purple ferric complex will normally develop, 10% ascorbic acid added till it is only weakly coloured (complete bleaching is not necessary), and metered at 360 nm against a blank that must contain the same amount of sulphosalicylic acid as the test solution.

After Ti determination, the solution may be evaporated with nitric and sulphuric acids, nitric and perchloric acids, or nitric acid and H_2O_2 . Part of the sulphosalicylic acid will end up as picric acid, but

this does not interfere with a manganese determination by the periodate method.

Destruction of organic reagents. Organic reagents have customarily been destroyed by evaporation with sulphuric and nitric acids, sometimes with nitric acid followed by nitric plus perchloric acid. With some reagents such as tartaric acid, this is apt to lead to a dishful of carbon, very difficult to get rid of. In many cases, evaporation with nitric acid, with addition of 30% H_2O_2 , to the covered beaker when the nitric acid has become fairly concentrated, has been found more efficient. But whichever oxidant is employed, part at least of any reagent that contains a benzene ring is liable to end up as picric acid, and it would appear that this will inevitably interfere with any subsequent colorimetric measurements. However, a study of the absorbance of picric acid shows that this is not necessarily true. While absorption by the $C_6H_2(NO_2)_3O^-$ ion is very strong, a solution containing 4.9 mg ml^{-1} (nearly saturated) in water showed no appreciable absorption at wave lengths longer than 520 nm ; with 4.9 mg ml^{-1} in 10% nitric acid, which will tend to reduce the ionization of the picric, appreciable absorption (0.02 for a 1 cm cell) starts about 505 nm . Hence picric acid should not interfere with determinations of Mn as MnO_4^- , which is metered at 425 or 545 nm . In alkaline solution, when ionization will be complete, absorption is much stronger (for a solution with 4.9 mg ml^{-1} , made alkaline with NH_3 , 0.370 at 545 nm , 0.079 at 700 nm).

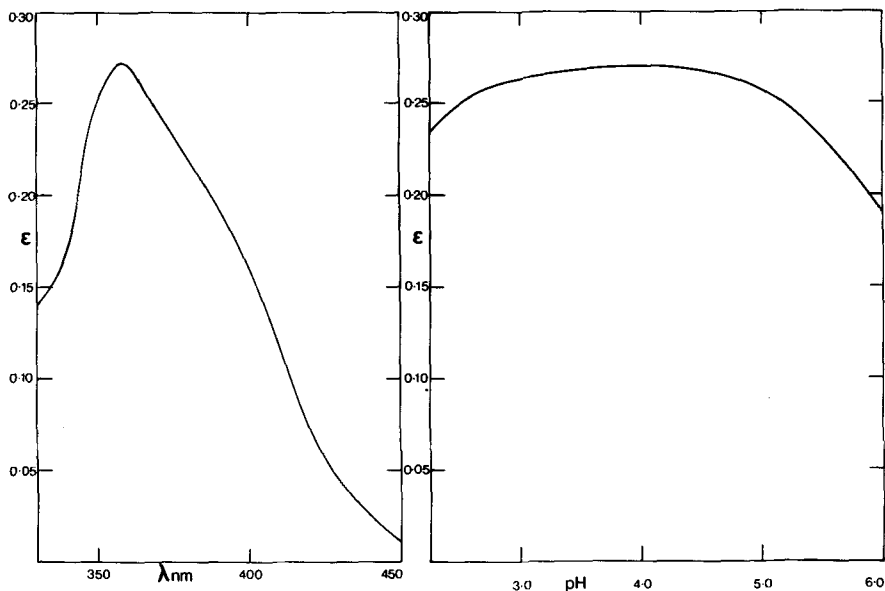


Fig. 4. Left: Absorption spectrum of the sulphosalicylic acid complex of Ti^{4+} at pH 4.0 and a concentration of $1 \mu g \text{ cm}^{-2} Ti$. Right: Variation of the absorption of the Ti^{4+} complex at $\lambda 359 \text{ nm}$ with pH.

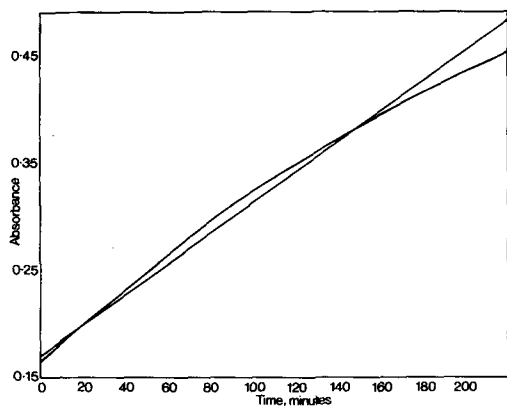


Fig. 5. Absorbance, at $\lambda 508 \text{ nm}$, of a solution initially containing 2 mg Fe^{3+} as *o*-phenanthroline complex in 25 ml , plotted against time after mixing; for significance of the lines, see text.

REFERENCES

- 1829 H. Rose, *Handb. anal. Chem.* 199 and 207
 1830 J. J. Berzelius, *Ann. Chem. Phys.* (Poggendorff), **20**, 541.
 1831 J. W. Döbereiner, *J. Chem. Phys.* (Schweigger), **62**, 94.
 1839 J. N. Fuchs, *J. Chem. Phys.* (Schweigger), **62**, 184.
 1831 J. von Liebig, *Ann. Chim. Phys.*, ser. 2, **48**, 290.
 1831 J. N. Fuchs, *J. prakt. Chem.* **17**, 140.
 1846 F. Margueritte, *Ann. Chim. Phys.*, ser. 3, **18**, 244.
 1849 A. Normandy, *Pract. Treat. Chem. Anal.* (transl. of H. Rose, *Handb. anal. Chem.*, 4th edn), **2**, 111, fn.
 1850 F. Penny, *Chem. Gazette*, **8**, 330.
 1851 J. Schabus, *Sitzungsber. Akad. Wiss. Wien*, **6**, 396.
 1860 A. Mitscherlich, *J. prakt. Chem.* **81**, 116.
 1861 L. Th. Lange, *J. prakt. Chem.* **82**, 129.
 1867 J. P. Cooke, *Am. J. Sci.*, ser. 2, **44**, 347.
 1871 H. Rose, *Handb. anal. Chem.*, 6th edn, **2**, 120-31.
 1894 J. H. Pratt, *Am. J. Sci.*, ser. 3, **48**, 149.
 1898 R. Peters, *Z. physikal. Chem.* **26**, 193.
 1899 J. H. L. Vogt, *Z. prakt. Geol.* 250.
 1900 W. F. Hillebrand and H. N. Stokes, *J. Am. Chem. Soc.* **22**, 625. *Z. anorg. Chem.* **25**, 326.
 1900 A. Classen, *Handb. quantit. chem. Anal.*, 5th edn, **2**, 193.
 1901 H. N. Stokes, *U.S. Geol. Surv. Bull.* 186; *Am. J. Sci.*, ser. 4, **12**, 414.
 1903 E. Knecht, *Ber. deut. chem. Ges.* **36**, 166.
 1907 R. Mauzelius, *Sver. Geol. Undersök.*, Arsbok I, no. 3.
 1907 W. F. Hillebrand, *U.S. Geol. Surv. Bull.* **302**, 22.
 1908 W. F. Hillebrand, *J. Am. Chem. Soc.* **30**, 1120.
 1910 E. Müller and P. Koppe, *Z. anorg. Chem.* **68**, 160.
 1910 E. Erdmann, [Kali, **4**, 73, cited by J. W. Mellor, *Compr. Treat. Inorg. Theor. Chem.* **14**, 21 (1935)].
 1913 J. H. Hillebrand, *J. Am. Chem. Soc.* **35**, 871.
 1913 F. P. Treadwell, *Kurzes Lehrb. anal. Chem.*, 6th edn, **2**, 425.
 1915 O. L. Barneby, *J. Am. Chem. Soc.* **37**, 1481.
 1921 W. M. Thornton and J. E. Chapman, *J. Am. Chem. Soc.* **43**, 91.
 1924 J. Knop, *J. Am. Chem. Soc.* **46**, 263.
 1927 L. A. Sarver, *J. Am. Chem. Soc.* **49**, 1472.
 1928 G. B. Heisig, *J. Am. Chem. Soc.* **50**, 1687.
 1928 B. A. Soule, *J. Am. Chem. Soc.* **50**, 1961.
 1929 W. F. Hillebrand and G. E. F. Lundell, *Applied inorganic analysis*, 769-86.
 1933 F. Alten, H. Weiland and E. Hille, *Z. anorg. Chem.* **215**, 81.
 1934 H. P. Rowledge, *J. R. Soc. Western Australia*, **20**, 165.
 1935 A. Thiel and O. Peter, *Z. anal. Chem.* **102**, 161.
 1941 M. H. Hey, *Mineral. Mag.* **26**, 116.
 1951 L. E. MacCardle and E. R. Scheffer, *Anal. Chem.* **23**, 1169.
 1953 W. F. Hillebrand and G. E. F. Lundell, *Applied inorganic analysis*, 2nd edn, 907-22.
 1953 N. A. Talvitie, [*Anal. Chem.* 25, 604], cited by E. B. Sandell. *Colorim. Determ. Traces Elem.*, 3rd edn, 1959, 925.
 1955 A. E. Harvey, jr., J. E. Smart, and E. S. Amis, *Anal. Chem.* **27**, 26.
 1955 A. D. Wilson, *Bull. Geol. Surv. G.B.* **2**, 56.
 1958 J. P. Riley and H. D. Williams, *Mikrochim. Acta*, **4**, 516.
 1961 C. V. Clemency and A. F. Hagner, *Anal. Chem.* **33**, 888.
 1962 L. E. Reichen and J. J. Fahy, *U.S. Geol. Surv. Bull.* **1144B**.
 1965 R. J. Davis, M. H. Hey, and A. W. G. Kingsbury, *Mineral. Mag.* **35**, 79.
 1967 E. Kiss, *Anal. Chim. Acta*, **22**, 223.
 1973 M. H. Hey, *Mineral. Mag.* **39**, 4.
 1974 M. H. Hey, *Mineral. Mag.* **39**, 895.
 1975 H. Fadrus and J. Maly, *Chem. Soc., Exp. Synops. J. Mark II*, 3.