Methods for the chemical analysis of meteorites.
I. Siderites.

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Summary. Simple chemical procedures (colorimetric and gravimetric) for the determination of Co, Cr, Cu, Ga, Ni, P, and S in an iron meteorite or in the separated metallic phase of a pallasite are described; the minimum size of sample is discussed. A procedure for the quantitative removal of the metallic, sulphide, and phosphide phases from a stone or siderolite is described, and is applicable to the quantitative isolation of silicate and oxide inclusions from siderites (other than some very high in nickel).

ONE of the major difficulties in meteoritic studies is the variable quality of the chemical data. Work on the rocks G1 and W1 has shown that even when well-tried standard methods are available there is an uncomfortably wide spread in the results obtained by different analysts or even by the same analyst at different dates.[1] The meteoriticist is in a far worse position than the petrologist, for not only are there few standard, commonly accepted techniques, but the shortage of material and the gross inhomogeneity of many meteorites are apt to make it difficult to obtain a representative sample and the analytical problems are much more serious. Wahl[2] and others have shown that the figures for alkalis and alumina in stones are commonly gravely in error, and it is doubtful if any but the most modern figures for cobalt or copper in irons are satisfactory.

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[1] H. W. Fairbairn *et al.*, U.S. Geol. Surv. Bull. no. 980, 1951; H. W. Fairbairn and J. F. Schairer, Amer. Min., 1952, vol. 37, p. 744 [M.A. **12**–33]; H. W. Fairbairn, Geochimica Acta, 1953, vol. 4, p. 143 [M.A. **12**–264]; A. A. Smales, D. Mapper, and A. J. Wood, Analyst, 1957, vol. 82, p. 75 [M.A. **13**–250]; S. S. Goldich and E. H. Oslund, Bull. Geol. Soc. Amer., 1956, vol. 67, p. 811 [M.A. **13**–467]; A. A. Smales, Geochimica Acta, 1955, vol. 8, p. 300 [M.A. **14**–43]; J. P. Riley, Anal. Chim. Acta, 1958, vol. 19, p. 413 [M.A. **14**–87]; R. C. Chirnside, Journ. Soc. Glass Technol., 1959, vol. 43, p. 5 T [M.A. **14**–383]; J. P. Riley and H. P. Williams, Mikrochim. Acta, 1959, p. 804 [M.A. **14**–455].

[2] W. Wahl, Geochimica Acta, 1950, vol. 1, p. 28 [M.A. **11**–261]; W. Wahl and H. B. Wiik, ibid., p. 123 [M.A. **11**–437].

At their meeting at Mexico in 1956 the Permanent Commission on Meteorites of the International Geological Congress recognized the development of reliable methods for the chemical analysis of meteorites as an urgent need, and over the past four years we have sought to meet this need; the present paper will, it is hoped, be the first of several on analytical techniques particularly adapted to work on various classes of meteorites. Recent developments in physical and other specialized methods of analysis, particularly radioactivation and X-ray fluorescence and microanalyser methods, radioactive tracer techniques, and mass spectrography, provide invaluable methods for a very wide range of trace elements; but there are many laboratories where these techniques are not available, and our experience has shown that many trace elements can readily be determined by colorimetric and other methods that call for little or no special equipment beyond that available in any laboratory practising rock analysis. Little modification has been necessary to adapt many of the colorimetric methods used by E. B. Sandell and his fellow workers[1] to meteorite analysis, and these methods have in general proved outstandingly reliable.

Meteorites are in general far from uniform in composition even within a moderate-sized mass: the combination of white aubrite and black enstatite chondrite in Cumberland Falls is unique, but Wahl[2] has shown that many other stony meteorites are breccias, often on a fairly large scale, containing fragments of two or more different types; non-uniformity in irons is less spectacular, apart from the gradations from a pallasite to a pure siderite in some specimens of Brenham, but the distribution of inclusions is often far from uniform, and it is by no means certain that differences between two or more analyses of the same fall[3] are always due to analytical error.

In polymict brecciated stones we should expect the composition of many of the constituent minerals to vary from fragment to fragment, but variation has also been demonstrated in apparently monomict stones, for instance in the feldspar of Juvinas.[4] A detailed study of the chemistry (including trace elements) and physical properties of the

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[1] E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd edn, New York and London, 1959.

[2] W. Wahl, Geochimica Acta, 1952, vol. 2, p. 91 [M.A. **11**-526].

[3] See, for example, the entries in G. T. Prior, Catalogue of Meteorites, 2nd edn, London, 1953, under Cape York, Otumpa, Mount Joy, Glorieta Mountain, Prambanan, Cratheús, and Rodeo. On the other hand, the widely differing analyses for the different masses of Babb's Mill and of Staunton may indicate distinct falls.

[4] P. M. Game, Min. Mag., 1957, vol. 31, p. 656.

several distinct phases in a range of stony meteorites and, if possible, in the distinct fragments of a polymict brecciated stone may be expected to yield interesting results, and it is hoped to undertake such a study as soon as the necessary techniques have been perfected.

In the present article we consider a method for the determination of Co, Cr, Cu, Ga, Ge, Ni, P, and S in a siderite or in the separated metallic phase of a pallasite, and a method for the removal of the metallic, phosphide, and sulphide phases from a stone or a siderolite, or for the quantitative isolation of the silicate and oxide phases from a siderite.

Visible inclusions of troilite are often large and very irregularly distributed; and in some meteorites (e.g. La Primitiva) there are large drop-like inclusions of schreibersite, while others contain coarse lamellae of schreibersite. It seems preferable to avoid, as far as possible, all macroscopic inclusions; but where the inclusions are of small or moderate size and regularly distributed, then a sample large enough to ensure that they will be correctly represented must be taken (compare below). If the inclusions are coarse and can be avoided, and if a bulk composition is desired, a separate analysis of the inclusions and an areal analysis of as extensive a cut surface or surfaces as possible will be the most satisfactory procedure. But there seems little point in computing the bulk composition of a siderite with irregularly distributed inclusions.

DETERMINATION OF Co, Cr, Cu, Fe, Ga, Ge, Ni, P, AND S IN A SIDERITE.

A single sample of the meteorite will serve for the determination of these nine elements; the size of sample required depends on the class of siderite under investigation: for hexahedrites, ataxites, and finest octahedrites a 1-g. sample may be assumed to be representative; but with a very coarse octahedrite it will be obvious that a sample approximately 5 mm. cube may fail to include the true proportion of taenite.

A rough calculation of the minimum size of sample was made, assuming that the taenite lamellae are uniformly t mm. apart and contain 30% Ni: for a sample weighing $2t^3$ g., the standard deviation from the true mean nickel content, due to an excess or deficit of taenite in the sample, will be approximately $\frac{1}{3}$% of the amount present, or 0·02 to 0·03% Ni; thus for such a sample we can be reasonably certain that the sampling error of the nickel content will not exceed 0·1% Ni and will be less than the probable analytical errors. For the less abundan elements, the relative precision of the analytical methods is not so good, and a rather smaller sample, say of t^3 g., will be acceptable.

In the detailed procedure set out below three separate portions of 1 g. of meteorite serve for the determination of Ge, S, and P, and the residues from the distillations for the Ge and S are combined to give a solution derived from 2 g. of meteorite, which serves for the determination of the remaining elements, while aliquot parts from the solution used for P serve for check determinations. Thus there should be no appreciable error due to excess or deficit of taenite in the sample, unless the meteorite is an octahedrite with band width exceeding 1·0 mm.; for octahedrites coarser than this the size of sample must be increased and the scale of operation adjusted accordingly: each of the three portions should weigh at least t^3 g. Similar calculations apply to siderites bearing regularly distributed inclusions of small or moderate dimensions, t then being the spacing of these inclusions (in mm.).

It will in general be advantageous for the sample to be tabular in shape, provided the thickness is not less than about $2t$ mm.; for in a tabular sample macroscopic inclusions are less likely to be obscured. It will also be useful (though not essential) to polish, etch, and examine both faces of the tablet, to make sure that the structure and microscopic inclusions are representative of the main mass.

Preparation of the working meteorite solutions.

Assuming that we are dealing with an ataxite, hexahedrite, or octahedrite of band width less than 1 mm., a 3-g. sample, free from macroscopic inclusions, will have been obtained and will be sawn into three approximately equal pieces, *X*, *Y*, and *Z*. One of these, *X*, is used for the determination of phosphorus, and it has been found that in order to recover all the phosphorus this sample must be dissolved under oxidizing conditions; simple attack with 1:1 hydrochloric acid[1] is unlikely to dissolve all the schreibersite, and furthermore some of the phosphorus will be lost. This portion is therefore dissolved in aqua regia, evaporated to dryness, 5 ml. conc. HCl added and the solution again evaporated to dryness to destroy nitrates, and this second residue dissolved in 5 ml. conc. HCl and a little water, and diluted to 100 ml. in a volumetric flask;[2] this constitutes solution *A*. Reagent blanks must be prepared for solution *A*, and for solutions *B*1, *B*2, *C*, and *D* described

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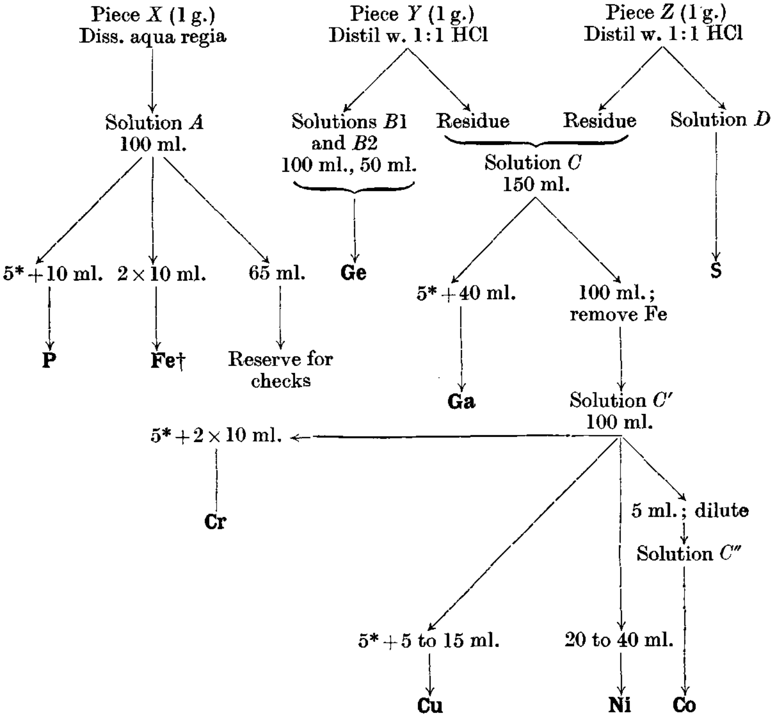
[1] That is, a mixture of equal parts conc. HCl, sp. gr. 1·18, and water.

[2] If larger samples than 1 g. are necessary, the amount of acid and final bulk of solution *A* should be increased proportionally. Similarly the scale of operation on the other two samples, and the bulk of solutions *B* and *C*, must be increased proportionally. But the size of the aliquots for the several determinations need not be increased.

below; these may be labelled solutions *a*, *b*1, *b*2, *c*, and *d*. The preparation and utilization of these working solutions is outlined diagrammatically in table I.

TABLE I. Schematic course of analysis for iron meteorites (larger samples are needed for coarsest, coarse, and some medium octahedrites).



* Portion for preliminary rough determination.

† Iron will usually be determined by difference.

A second piece, *Y*, of the meteorite is placed in a flask fitted with a tap funnel, still head, and condenser, and a 50-ml. cylinder is placed under the end of the condenser. Fifty ml. of 1:1 HCl are run into the flask, which is gently heated until the meteorite has dissolved; the heat is then increased and 20 ml. of acid are distilled over into the cylinder, 10 ml. 1:1 HCl run into the flask and a further 20 ml. of acid distilled over, making 40 ml. in all. Distillation is stopped and the distillate transferred to a 100-ml. volumetric flask and made to volume with water (solution *B*1). The cylinder is replaced, 15 ml. 1:1 HCl run into the flask, and a further 20 ml. of distillate collected, transferred to a 50-ml. volumetric flask, and made up with water (solution *B*2). The residue in the flask is transferred to a 150-ml. volumetric flask and reserved without dilution to volume (part of solution *C*).

The third piece, *Z*, of meteorite is placed in a 50-ml. flask fitted with a reflux condenser and a dropping funnel the stem of which reaches to the bottom of the flask. The upper end of the reflux condenser is connected by glass tubing to two bubblers in series, both containing absorbing solution (1 g. $ZnSO_4.7H_2O$ and 50 ml. ammonia sp. gr. 0·880, diluted to 1 litre); arrangements are made to lead a current of nitrogen[1] through the apparatus, via the dropping funnel, during the determination. The first bubbler should be a 250-ml. flask; it is charged with 100 ml. of absorbing solution and the second with 25 ml.; 20 ml. of 1:1 HCl are run into the 50-ml. flask, a slow nitrogen current started, and the flask heated gently until the meteorite has dissolved and then boiled gently for about 15 min. The residual solution in the flask is united with solution *C*, the residue from the other distillation (for Ge), and the combined solutions diluted to volume (150 ml.).

The contents of the second bubbler are added to the first (no rinsing is necessary), and the inlet tube of the first bubbler is rinsed; the combined solutions (solution *D*) are titrated for sulphide as described below.

Sulphide.

To solution *D* add 10 ml. of an iodate–iodide solution (130 mg. KIO_3 and 550 mg. KI in 200 ml. water) and, after mixing, 10 ml. conc. HCl; mix and cool by standing the flask in cold water and titrate with standard N/50 sodium thiosulphate, using starch as indicator. A reagent blank, solution *d*, is treated similarly, and the difference between the two titrations gives the sulphide sulphur in piece *Z* of the meteorite; $H_2S+I_2 \rightarrow S+2H^++2I^-$.

Germanium.[2]

A stock standard germanium solution is prepared by dissolving 72 mg. of GeO_2 in 10 to 15 ml. 0·4% NaOH and diluting to 50 ml. with water. This solution contains 1 mg. Ge per ml.; working standards (1 μg. Ge per ml.) are prepared by dilution as required.

A phenylfluorone reagent is prepared by dissolving 30 mg. of 9-phenyl-2:3:7-trihydroxy-6-fluorone in a mixture of 85 ml. ethyl alcohol and 5 ml. dilute sulphuric acid (1:6 by volume) and making up to

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[1] If nitrogen is not available carbon dioxide may be used.

[2] After H. J. Cluley, Analyst, 1951, vol. 76, p. 523.

100 ml. with alcohol. The approximate germanium content of solution *B*1 is first ascertained by a trial[1] on a 10-ml. aliquot, and then for the determination proper an aliquot containing between 5 and 30 μg. Ge is run into a 50-ml. volumetric flask, together with 5 ml. 0·5% gum arabic solution. The HCl content of the aliquot used is calculated, on the assumption that the 100 ml. of solution *B*1 contain 20 ml. conc. HCl (sp. gr. 1·18), and sufficient conc. HCl is added to make the total 5 ml., together with enough water to bring the total volume to about 30 ml. The solution is cooled below 20° C., if necessary, 15 ml. of phenylfluorone reagent run in from a pipette, and the flask filled to the mark; after standing for 30 min. the optical density is compared with a reagent blank made up from solution *b*1, at a wave-length[2] of 510 mμ, and with that of solutions of known germanium content made up in the same manner from the diluted standard solution.

The germanium content of 25 ml. of solution *B*2 is determined in the same way, and the total germanium content of the meteorite in parts per million can then be calculated; 100 ml. of solution *B*1 and 50 ml. of solution *B*2 were obtained from piece *Y* of the meteorite.

Phosphorus.

Standard phosphate and reagent solutions are prepared as follows— Phosphate: about 900 mg. KH_2PO_4 are weighed out accurately and dissolved in 200 ml. H_2O for a stock solution, which is diluted 1/100 for use, and will then contain approximately 10 μg. P per ml. Reagent: 2·0 g. ammonium molybdate are dissolved in 40 ml. water and mixed with 60 ml. of 1:1 (by volume) sulphuric acid to form a stock solution; immediately before use, 50 ml. of this stock molybdate solution are diluted to about 160 ml., 20 ml. of 0·15% aqueous hydrazine sulphate added, and the volume made up to approximately 200 ml.

Ten ml. of solution *A*, representing a tenth of piece *X* of the meteorite, are run in a 100-ml. beaker, and 10 ml. of the blank solution *a* in a second beaker. Ten ml. of 10% aqueous $Na_2SO_3.5H_2O$ are added to each of these beakers and the solutions boiled gently for 5 min. A third beaker receives 20 ml. water, and a fourth receives an amount of standard phosphate solution containing about as much phosphorus as 10 ml. of

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[1] It is usually convenient to make the preliminary estimates by reference to a standard curve, but the actual determination should be made against standard solutions prepared at the same time as the unknown. The same applies in the other colorimetric procedures described below.

[2] A spectrophotometer is the most suitable instrument for this and the other determinations described below, but a filter-type absorptiometer may be used.

solution *A* (as determined by a trial run on 5 ml. of solution *A*), together with enough water to make up 20 ml.

Twenty-five ml. of freshly prepared molybdate–hydrazine reagent are run into each of the four beakers, which are covered and placed on a boiling-water bath for 40 min., then removed and allowed to cool to room temperature, after which they are made up to 100 ml. or 50 ml. in volumetric flasks according to the intensity of the colour. The optical density of each solution is measured against the appropriate blank at a wave-length of 650 mμ.

Gallium.

The method is based on the extraction of gallium from hydrochloric acid solution by *iso*-propyl ether, extraction of iron being prevented by reduction to the ferrous state; the extracted gallium is complexed with Rhodamine B, and the lake extracted by a mixture of monochlorbenzene and carbon tetrachloride.[1] The extraction of the Rhodamine B lake is not complete, and for accurate results it is essential that the conditions should be closely adhered to, especially the strengths of acid. Accordingly, the concentration of the 7N hydrochloric acid and of the 6N hydrochloric acid + $TiCl_3$ prescribed below must be checked by titration and adjusted if necessary.

The stock standard gallium solution is prepared by dissolving 27 mg. pure Ga_2O_3 in 6N HCl and making up to 200 ml. with 6N HCl; this solution contains about 100 μg. Ga per ml., and should be diluted with 6N HCl to prepare working standards.

The approximate gallium content of solution *C*, the 150 ml. of which were obtained by combining pieces *Y* and *Z* of the meteorite, is first ascertained by a trial on a 5-ml. aliquot, and for the determination proper an aliquot not exceeding 40 ml. and containing, if possible, between 5 and 20 μg. Ga is run into a 100-ml. beaker and evaporated to dryness on the water bath. An equal volume of solution *c* is evaporated in a second beaker to serve as a blank. An appropriate amount of gallium standard is evaporated in a third beaker, and an equal amount of 6N hydrochloric acid in a fourth. The residue in each of the four beakers is dissolved in 5 ml. of 7N hydrochloric acid and transferred to a 100-ml. separating funnel, using a further 10 ml. of acid for washing out the beaker.

About 2 ml. 15% w/v titanous chloride are added to reduce the iron, followed by 15 ml. of *iso*-propyl ether, and the separator is gently shaken

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[1] F. Culkin and J. P. Riley, Analyst, 1958, vol. 83, p. 208.

for 1 min. The aqueous phase is run into a second separator, shaken for 1 min. with 10 ml. of *iso*-propyl ether, and the aqueous phase discarded. The combined ether extracts are washed by shaking for 10 sec. with 3 ml. of 7N hydrochloric acid and a drop of titanous chloride, then run into a 100-ml. beaker, covered and placed on a hot water bath until all the ether has evaporated. To each of the evaporated gallium extracts is added 5 ml. of 6N hydrochloric acid containing about 1% titanous chloride; the covered beaker is allowed to stand on the water bath for 10 min., cooled, and the solution transferred to a 10-ml. volumetric flask and made up to volume with 6N hydrochloric acid + titanous chloride. Five ml. of this solution are transferred to a 50-ml. separating funnel, 0·5 ml. of a 0·5% solution[1] of Rhodamine B in 6N hydrochloric acid are added, and the gallium lake extracted with 10 ml. of a mixture of 50 ml. carbon tetrachloride and 150 ml. chlorbenzene by shaking for 5 min. on a mechanical shaker. After standing for 10 min. a few drops of liquid are run out of the funnel, the stem is dried out with filter paper, and some of the extract run into a 1-cm. photometer cell and its optical density measured against the CCl_4–C_6H_5Cl solvent at a wave-length of 562 mμ. The appropriate blank should be run through at the same time so that all readings are comparable, since the optical densities of both sample and blank alter with time.

Iron.

It is usually adequate to obtain the iron content of a siderite by difference, but if for any reason a direct determination is desired, two 10-ml. portions of solution *A*, each representing a tenth of piece *X* of the meteorite, may be reduced and titrated.

Removal of iron from the working solutions.

The determinations of Co, Cr, Cu, and Ni are best made on iron-free solutions, and accordingly a large aliquot of solution *C* is taken and the iron removed by extraction with *iso*-propyl ether from 8N hydrochloric acid solution.[2]

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[1] The proportion of dyestuff in the Rhodamine B bought from different suppliers of chemicals varies, and in order to obtain the maximum extraction of the complex it may be necessary to double or even quadruple the concentration prescribed below; preliminary experiments with 0·5%, 1%, and 2% solutions and standard gallium solution should be made with each new batch of dyestuff to ascertain the appropriate strength.

[2] E. H. Swift, Journ. Amer. Chem. Soc., 1936, vol. 58, p. 2573.

A hundred ml. of solution C are evaporated to dryness on the water bath, dissolved in 8N hydrochloric acid, and transferred to a 100-ml. separating funnel, using about 20 ml. acid in all. Twenty ml. *iso*-propyl ether are added and the funnel shaken for about 1 min., then the aqueous layer is run into a second funnel, rinsing the stopper and delivery tube of the first funnel with small amounts of 8N hydrochloric acid; the ethereal layer is washed with 10 ml. of 8N acid, shaking for about 20 sec. and the aqueous layer combined with that from the first extraction. The combined aqueous solutions are extracted with a further 20 ml. of ether and the ethereal layer washed with acid as before. The second ether extract should be nearly colourless, and the aqueous layer a clear green; if this is not the case, a third ether extraction will be needed. The final aqueous layer is run into a 150-ml. beaker, evaporated to dryness, dissolved in 1 ml. hydrochloric acid and a little water and made up to 100 ml. in a volumetric flask to form solution C', derived from two-thirds of the combined pieces Y and Z of meteorite. A reagent blank, solution c', is prepared similarly from 100 ml. of solution c.

The final ether layers are accumulated in a residue bottle, washed with water to remove ferric chloride, and the ether recovered by distillation after destroying any peroxides by shaking with a little ferrous sulphate solution.

Nickel.

The approximate nickel content of the meteorite will be known unless it is a nickel-rich ataxite. An aliquot of solution C' containing not more than 30 mg. Ni is run into a 250-ml. beaker, 1 g. ammonium chloride and 0·5 g. tartaric acid added, and the solution diluted to 200 ml.; 5 ml. of a 1% alcoholic solution of dimethyl glyoxime are added for every 10 mg. of nickel present, the solution heated to boiling-point and ammonia added until it is alkaline. The beaker is covered and left 2 hrs. on the water bath, filtered on a porosity grade 3 silica or glass filter crucible, washed with hot water, dried at 110 to 120° C., and weighed.

Cobalt.

Five ml. of solution C' are diluted to 100 ml. in a volumetric flask to give a dilute working solution C'', 10 ml. of which represent 1/300 of the two pieces Y and Z of meteorite. A preliminary estimation on 10 ml. of solution C'' is made to ascertain the approximate cobalt content, and an aliquot containing 20 to 40 μg. is run into a 15-ml. beaker and evaporated to dryness on the water bath. In a second beaker 5 or 10 ml. of diluted standard cobalt solution (about 4 μg. per ml., prepared by dilution of a stock solution containing about 1 mg. Co per ml.) are evaporated, while a third beaker will receive the reagent blank diluted from solution *c′*. A buffer solution is prepared, containing 0·62 g. boric acid, 7·2 g. $Na_2HPO_4.12H_2O$, and 2·0 g. NaOH in 100 ml., and to each beaker is added 1·5 ml. 4·2% citric acid, 1·8 ml. buffer solution, and then 4·0 ml. of 0·2% nitroso-R-salt solution. The beakers are covered and replaced on the boiling water bath and left there for 10 to 15 min., then 1·5 ml. of nitric acid, sp. gr. 1·42, are run into each beaker, and the beakers are left on the water bath for a further 10 to 15 min., placed in the dark till cool, transferred to 15-ml. volumetric flasks, and made to volume. The optical densities of the standard and meteorite solutions are measured against the reagent blank at wave-length 550 mμ.

Copper.

After a trial run on 5 ml. of solution *C′* to ascertain the approximate copper content, an aliquot containing not more than 40 μg. Cu (usually 5 to 15 ml.) is run into a separating funnel; 1 ml. of 10% hydroxylamine hydrochloride and 1 ml. of 10% tartaric acid are added, and the solution diluted to about 35 ml. and mixed well. The pH is adjusted to 5·5 with 1:1 ammonia, using narrow-range indicator papers, and diluted to 40 ml.; 5 ml. of an 0·05% solution of 2:2′-diquinolyl in *iso*-amyl alcohol are added and the funnel shaken for 2 min. (preferably mechanically). After standing for 4 min. the aqueous layer and a few drops of the alcohol are drained off and discarded, the stem of the funnel is dried with filter paper and a 1-cm. spectrophotometer cell filled with the alcoholic layer.

The same aliquot of the blank solution *c′* and a suitable amount of a standard copper solution are treated in the same way (the stock copper standard may conveniently contain 1 mg. Cu per ml. and be diluted to 5 μg. Cu per ml. for the working standard).

The optical densities of the meteorite solution, standard, and blank are measured against 2:2′-diquinolyl reagent at wave-length 545 mμ.

Chromium.

Direct photometric comparison of the diphenyl carbazide colour from a meteorite solution with a standard does not give satisfactory results, but the following technique proved reliable.

A trial run is made on a 5-ml. aliquot of solution *C′* (representing 1/30 of pieces *Y* and *Z* of the meteorite), comparing directly against the standard chromium solution (a stock solution is prepared by reducing a sulphuric acid solution of potassium dichromate with sulphur dioxide, boiling off the sulphur dioxide, and diluting to about 4 mg. Cr per ml. with dilute sulphuric acid; this is diluted to 4 μg. Cr per ml. for a working standard).

Two 10-ml. aliquots of solution *C′* are run into two beakers, and to one is added an amount of standard chromium solution containing about as much chromium as is already present in the 10-ml. aliquot; 10 ml. of the blank solution *c′* are run into a third beaker. To each beaker 1·7 ml. of 6N H_2SO_4 is added, and the solutions evaporated as far as possible on the water bath, the sides of the beakers rinsed and the solutions re-evaporated to expel chlorides thoroughly. Twenty ml. of water, 5 drops of 1·7% silver nitrate solution, and about 0·5 g. ammonium persulphate are added to each beaker and the liquid level marked; the beakers are then covered and boiled gently for 10 min., adding water occasionally to maintain the original level of liquid. The sides of the beakers are then rinsed and the boiling repeated. The solutions are cooled, transferred to 50-ml. volumetric flasks, and diluted to about 45 ml.; 1 ml. of a 0·25% solution of diphenyl carbazide in acetone is added and the solutions made up to volume and well mixed. The optical densities of the meteorite solution and of the meteorite solution plus added chromium are measured against the blank prepared from solution *c′* in 1-cm. cells, at wave-length 540 mμ; the measurements should be made as quickly as possible as the colour fades. If N μg. of chromium were added, and if the optical densities of the meteorite aliquot and of the meteorite aliquot with added chromium are P and Q respectively, the chromium content of the meteorite aliquot (1/15 of pieces Y and Z of meteorite) is $NP/(Q-P)$ μg.

Check determinations.

Sixty-five ml. of solution *A* have been held in reserve; this can be used for check determinations of Ni, Co, Cu, or Cr, and for the determination of certain other elements when suitable techniques have been devised.

THE ACTION OF DRY CHLORINE AT 250 TO 350° C. ON METEORITES.

In 1932 one of the authors[1] showed that pure dry chlorine at 250 to 300° C. attacks the metal, sulphide, and phosphide phases of a stony meteorite completely but does not affect the olivine or pyroxene. With

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[1] M. H. Hey, Min. Mag., 1932, vol. 23, p. 48; cf. idem, ibid., p. 12; J. Kokta, Coll. Czech. Chem. Comm., 1937, vol. 9, p. 471 [M.A. 7-173].

siderites having up to at least 18% Ni the attack is equally successful, and the specimen may be in the form of lumps or tablets up to at least 5 mm. thick; but a siderite having 34% Ni was not attacked by chlorine. Iron, sulphur, phosphorus, and germanium distil quantitatively and although no direct experiments have yet been made, other evidence[1] suggests that gallium too will be found in the distillate. Nickel, cobalt, chromium, and copper are known to remain as chlorides.

Recent work has confirmed and extended these results: feldspars, apatite, magnetite, and chromite are not attacked provided the chlorine is dry and free from HCl. Traces of HCl give rise to an attack on the oxides, on olivine, and to a lesser extent on pyroxene; contrary to expectation, the attack on olivine resulting when the chlorine contains a trace of HCl does not lead to sublimation of ferric chloride, the only cation released being magnesium, which appears as chloride.[2]

The chlorine attack is particularly valuable in the study of stony meteorites, where it permits of a much cleaner removal of metal than is possible by magnetic separation[3] or the mercuric ammonium chloride method;[4] it is hoped to discuss its use in this connexion in a future paper. As applied to siderites, its principal value lies in the fact that there is no attack on acid-soluble silicates or oxides, enabling inclusions of these materials to be isolated conveniently.

The apparatus used for the treatment with chlorine is shown in figs. 1 and 2. The chlorine is well washed with water and thoroughly dried in a series of bubblers and then passed in a fairly rapid stream over the meteorite. The reaction tube, which is heated in a small electric furnace, consists of two parts connected by a ground joint. The chlorine enters through the side-tube of part *A*, the straight inner tube being a thermocouple well;[5] to the right of the ground joint, as shown in the figures, part *A* is a fairly close fit in the outer part *B*, the annular space between the two being no more than ½ to 1 mm.; thus the chlorine, leaving part *A* by four holes near its right-hand end, passes through the last ½ inch of the annular space in a rapid stream, to prevent back-diffusion of

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[1] L. M. Dennis and J. A. Bridgeman, Journ. Amer. Chem. Soc., 1918, vol. 40, p. 1534.

[2] 0·7 g. of olivine heated to 310° C. for 40 hrs. in a current of chlorine containing a little HCl gained 2 mg. in weight and was then very hygroscopic. There was no sublimate of $FeCl_3$; leaching of the residue with water gave a solution containing Mg together with chlorine corresponding to 1·5 mg. $MgCl_2$, but no iron.

[3] G. T. Prior, Min. Mag., 1913, vol. 17, p. 24.

[4] L. Fletcher, ibid., 1894, vol. 10, p. 287.

[5] This well is placed eccentrically, near the top of part *A*, rather than centrally as drawn, so that a larger boat can be accommodated.

$FeCl_3$, which can be troublesome. The horizontal part of the outer tube, *B*, is 1 inch in internal diameter and 11 inches long; it turns sharply down, the vertical part being ½ inch in internal diameter and 9 inches long overall, the last 4½ inches projecting into a 250-ml. conical flask, to which section *B* is connected by a ground joint. Most of the ferric chloride collects in the conical flask and the vertical part of section *B*, the rest, together with the more volatile halides, being collected in a couple of water-charged bubblers.

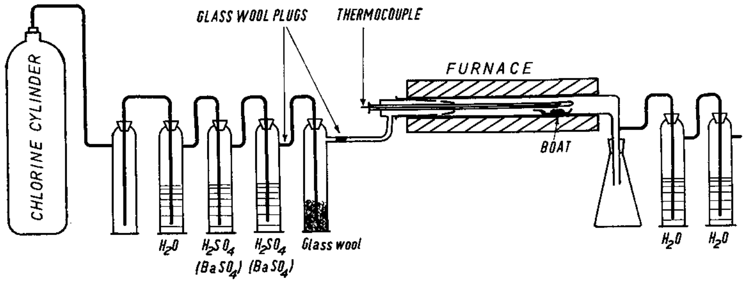

FIG. 1. Apparatus for the chlorine attack on meteorites. The sulphuric acid in the wash-bottles is saturated with barium sulphate; the appearance of a deposit or cloudiness indicates that the acid is becoming diluted and inefficient as a drying agent.

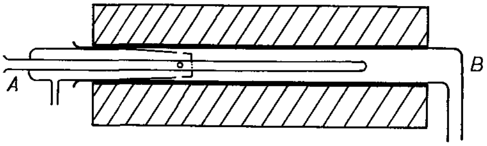

FIG. 2. Detail of the chlorination tube.

The weighed piece of meteorite, carefully cleaned from rust and grease, is placed in a porcelain boat in the reaction tube. A stony meteorite must be crushed fairly fine, but a siderite can be successfully attacked in the lump. A rapid current of chlorine is passed through the apparatus until the air has been displaced, then the reaction tube is heated gradually until reaction begins and ferric chloride starts to sublime. The heat is increased when the reaction slows down, and is raised finally to about 350° C. and maintained there for at least an hour (a large lump of a siderite, a coarsely crushed stone, or a stone in which silicate and metal or sulphide are intimately intergrown, may take up to 2 hours for the whole reaction). The reaction tube is allowed to cool below 100° C. with a slow current of chlorine still passing. The boat is withdrawn, cooled in a desiccator, and weighed.

The residue in the boat is now leached with water; if there is a large bulk of insoluble materials, as with a stony meteorite, the insolubles can be filtered off on a glass filter-crucible, porosity grade 4, washed, dried, and weighed; but if there is very little insoluble material, as with most siderites, it should be separated by centrifuging, withdrawing the bulk of the solution with a narrow-bore siphon (turned up at the intake end to avoid disturbing the solids), and washing by dilution and centrifuging, then washed out into a small weighed dish, evaporated, dried, and weighed.

With most siderites, the insoluble residue is very small in amount but sufficient for X-ray and optical study. The aqueous solution obtained by leaching the residue in the boat contains all the Ni, Co, Cu, and Cr, with at most traces of Fe. It can be used for the determination of all these elements by the methods described in the first part of this paper, using suitably sized aliquots.

Work on the best utilization of the distillate is still proceeding. Preliminary tests suggest that phosphorus may be determined on a suitable aliquot by the method described above, but it is not yet certain whether the receiver and traps collect germanium quantitatively, and the fate of any silicide or carbide present is still under investigation. Graphite remains unattacked and is collected with the insoluble matter.