AMERICAN JOURNAL OF SCIENCE

MAY 1934

QUANTITATIVE METHODS OF MICRO-ANALYSIS WITH SPECIAL REFERENCE TO THE GORDONIA URANINITE.

FRIEDRICH HECHT.

A. INTRODUCTION.

In the following pages a description will first be given of the various appliances and pieces of apparatus which are necessary for the carrying out of analyses of minerals by micro methods[1]; this is followed by a detailed account of the procedure adopted in the analysis of specimens of Gordonia uraninite, collected by the late Dr. P. Wagner for Professor Arthur Holmes, at whose suggestion this work has been carried out.

B. GENERAL DESCRIPTION OF APPARATUS AND METHODS OF PROCEDURE.[2]

In all my work crucibles and filtersticks (for inverted filtration by Emich's method[3]) made of platinum or porcelain were used. The platinum vessels and filtersticks (which latter were fitted with a Munro filter disc) were manufactured by Heraeus at Hanau, Germany, the porcelain ones by the Berlin State Porcelain Manufactory. The porcelain crucibles had an external diameter of 33 mm. at the top, and 19 mm. at the bottom; their height was 43 mm., and their capacity 25 cc. The measurements of the platinum crucibles were: upper diameter 28 mm., lower diameter 17 mm., height 40 mm., capacity 20 cc. The area of the bottom was fairly small, so as to permit of the

[1] Cf. Hecht, F., Mikrochemie, **10**, 45 (Microanalysis of Morogoro pitchblende), 1931; Mikrochemie, **12**, 193 (Microanalysis of Ceylon Thorianites), 1932; Hecht, F., and Reich-Rohrwig, W., Mikrochemie, **12**, 281 (Microanalysis of pitchblendes), 1933; Hecht, F., Mitt. Inst. Ra-Forschung Wien, Nr. 281, 1931.

[2] A description of all apparatus mentioned in the present paper has been previously published by W. Reich-Rohrwig and the author in Mikrochemie **12**, (l. c.) 1933.

[3] Emich, F., and Schneider, F., Microchemical Laboratory Manual, Wiley, N. Y., 1932.

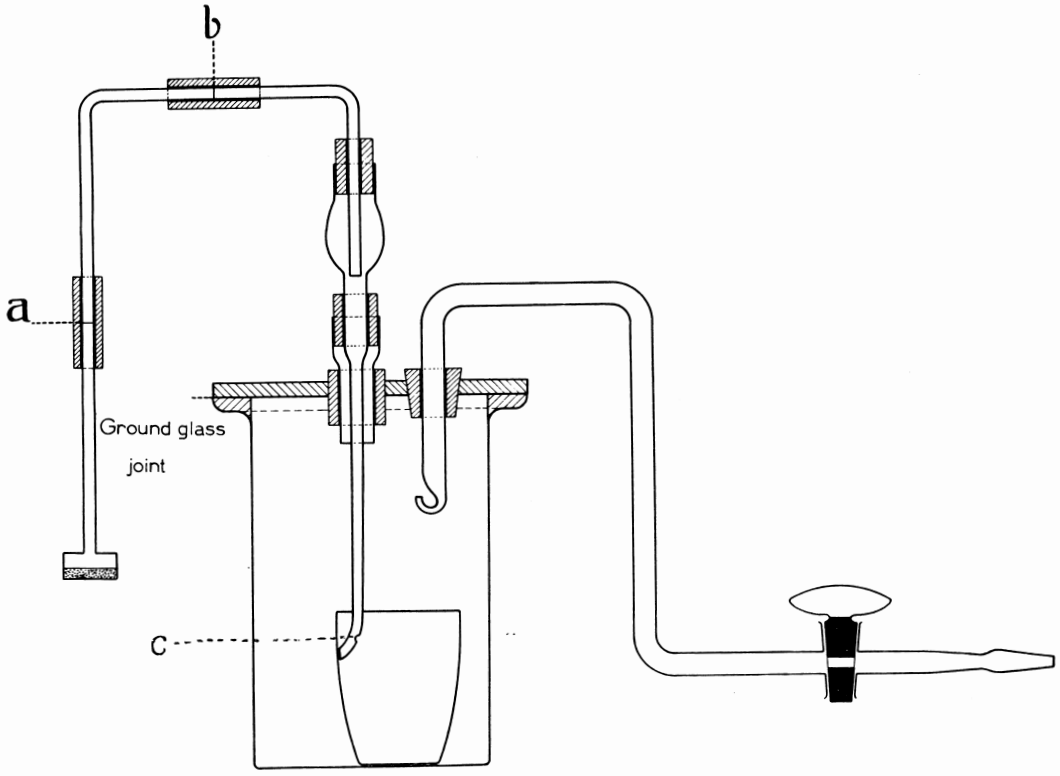


Fig. 1

use of small quantities of potassium pyrosulphate for the fusion of insoluble substances. Fig. 1 depicts a filterstick (left-hand side, below *a*), also the apparatus necessary for filtering a solution through the stick into another crucible. The terminal capillary tube has a small hole at *c*, close to its lower end, in order to prevent loss of solution through the formation and bursting of air-bubbles. This apparatus was devised by R. Dworzak and W. Reich-Rohrwig after the pattern of a macro apparatus of Professor A. Franke, which was employed

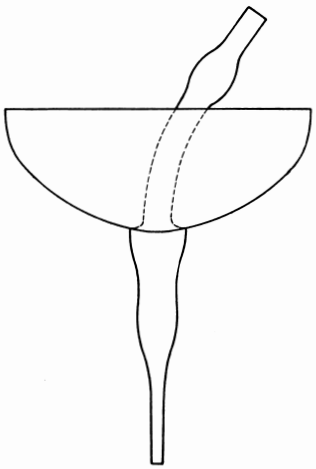


Fig. 2

for filtering a solution through a Gooch crucible directly into a beaker; it is an improved model of J. Donau's filter bell jar.[4] The introduction of hydrogen sulphide is effected by means of a curved clock glass with a capillary tube fused through it (see Fig. 2). The clock glass can be weighted if necessary with pieces of metal or with water. If the lower part of the capillary tube is made shorter and bent at an angle, the apparatus can be used to pass a stream of HCl gas over carbonate solutions in order to neutralize them. In order to prevent loss due to effervescence the crucibles are covered with a hollow glass ball having a projection on its lower side which serves to return the condensed liquid to the crucible (see Fig. 3).[5] The ball is filled with water to act as a condenser.

[4] Emich, F., and Schneider, F., l. c.
[5] Ibid.

As a water bath, the following apparatus (Fig. 4)[6] proved quite satisfactory. A Jena glass vessel containing distilled water was heated by means of an electric hot plate. The upper portion of the apparatus (which fits on to the lower portion by means of a ground glass joint) has two openings on which dishes or crucibles can be placed. Inverted funnels clamped above these openings and connected with a filter pump enable the vapours from the solutions evaporated in the dishes or crucibles to be drawn off. The distilled water in the lower por-

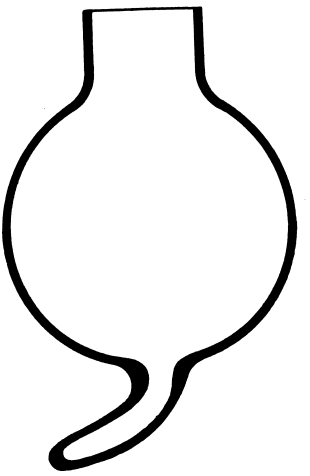


Fig. 3

tion of the apparatus is condensed and returned by the reflux condenser A. Openings not in use can be closed by a glass cover (*a*, Fig. 4). Interchangeable insets (*b*, Fig. 4), permit of the employment of crucibles and dishes of different sizes. The apparatus described prevents contamination of the liquids being evaporated by the flame gases, dust from the air, or metallic particles derived from the usual forms of metal water baths, and the exterior of the dishes and crucibles always remains perfectly clean. In addition, as the vapours of the liquids evaporating are drawn off by a pump, the micro balance may be set up in the same room in which the chemical work is carried out, and where the water bath is in use, this arrangement effecting a considerable saving of time.

[6] Reich-Rohrwig, W., Mikrochemie, **12**, 189, 1932.

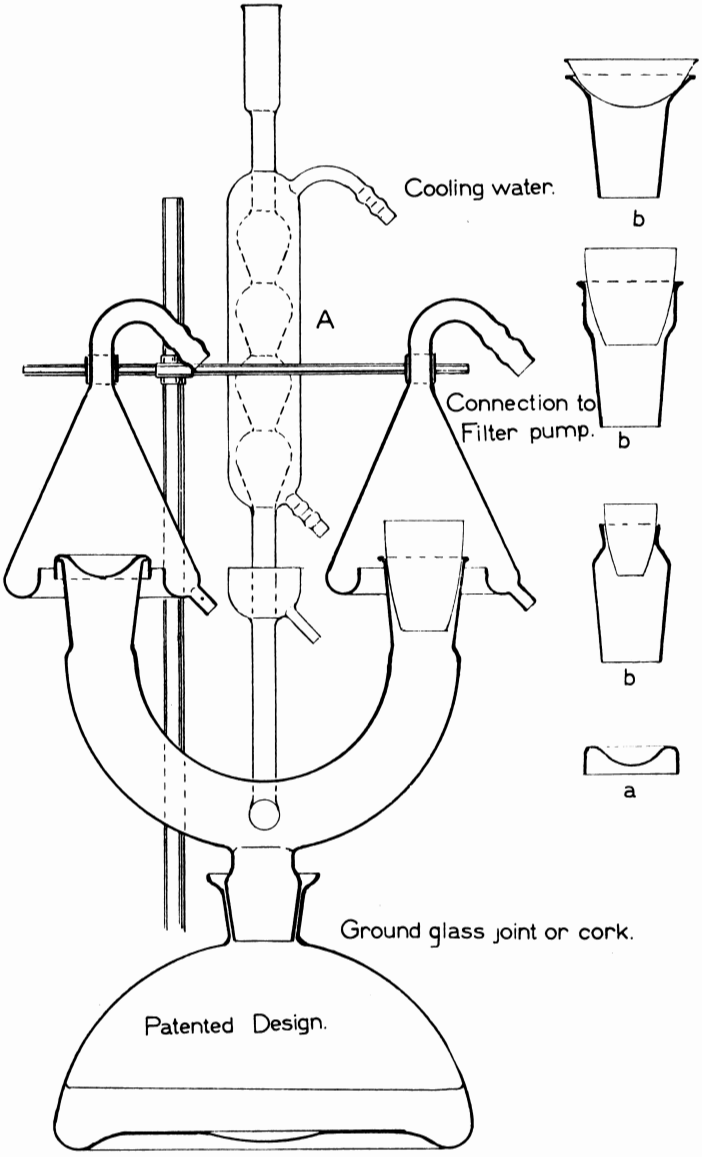

Cooling water.
A
Connection to
Filter pump.
b
b
b
a
Ground glass joint or cork.
Patented Design.

Fig. 4

Precipitates which do not require ignition can be precipitated in the micro filterbeaker made by Schott u. Gen., Jena, Germany, of Jena glass.[7] This beaker (Fig. 5) is a vessel in which both precipitation and filtration can be carried out, the

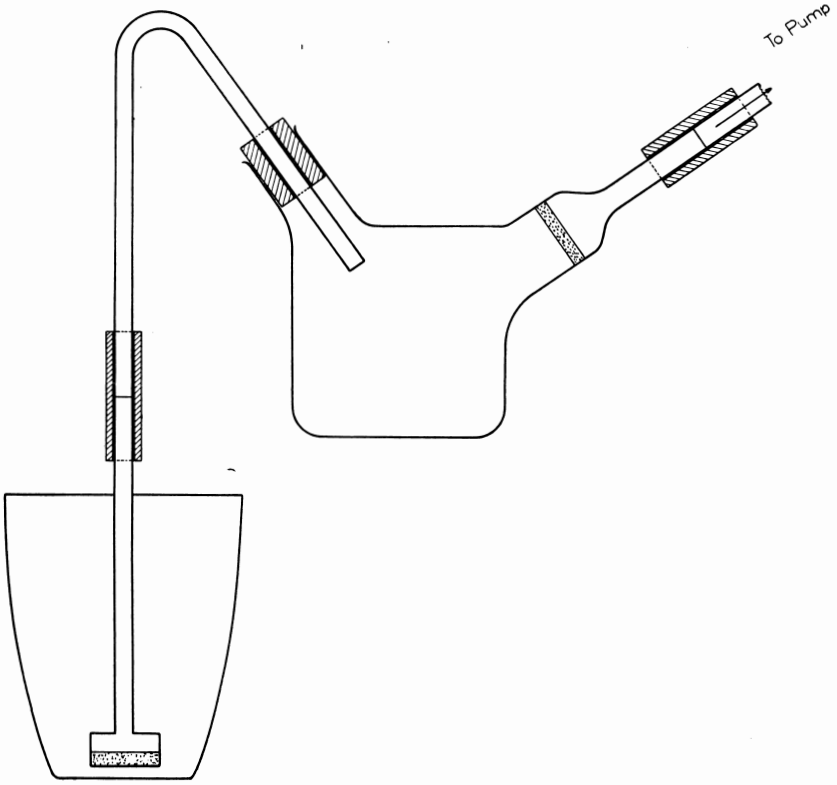


Fig. 5

latter operation being effected by means of a sintered glass disc fixed in a projecting side tube. After filtration and washing have been completed, the beaker and contents are dried at a definite temperature and weighed. In Fig. 5 is shown the transference of a solution to a micro filterbeaker through a porcelain filterstick.

[7] Schwarz-Bergkampf, E., Zeitschr. analyt. Chem., **69**, 336, 1926.

For adding drops of reagents small capillary pipettes were used, which were kept in a glass holder (Fig. 6).

The upper portions of the wash bottles and the covers of the weighing bottles fitted over the lower portions with ground glass joints, in order to prevent contamination by abraded glass powder.

The platinum crucibles and filtersticks were cleaned by fusion with potassium pyrosulphate, followed by solution of the melt in nitric or hydrochloric acid, and washing with water under suction. The "insoluble residue" was removed by fusing it with sodium carbonate. The porcelain and glass vessels and filtersticks were cleaned with chromic-sulphuric acid.

C. Analytical Procedure.

A platinum crucible and a platinum filterstick were wiped on the outside with a moist chamois leather, and then heated for 5 minutes to about 1000° in an electric oven, after which they were cooled to room temperature upon a copper block placed under a glass bell jar. After 5 minutes the crucible and filterstick (which were handled throughout with platinum-tipped forceps—never with the fingers) were placed inside the open case of the micro balance, and weighed after standing there for 20 minutes. The filterstick was then removed from the crucible in which it had been placed during the weighing, and placed beside it on the balance pan. About 30 mg. of the mineral were weighed into the crucible, 15 drops of 1:1 nitric acid added by means of a capillary pipette (1 drop = 0.05 cc.), the crucible covered with the hollow glass ball previously described, and the whole heated on the water bath for 30 minutes. After rinsing back the liquid condensed on the lower part of the glass ball, the solution was carefully sucked through the platinum filterstick into a second platinum crucible which had been previously weighed together with a platinum filterstick. The small insoluble residue was washed three times with 1 cc. of hot water containing a little nitric acid. (Filtrate F_1, residue R.) The rinsing of the crucible with the above small quantities of wash liquid is accomplished by inclining and rotating it. The stem of the filterstick and the outer side of the crucible are then wiped with a moist chamois leather, and the two are then dried in an oven at 110°, and then heated in the electric oven for 5 minutes at 1000°. After cooling

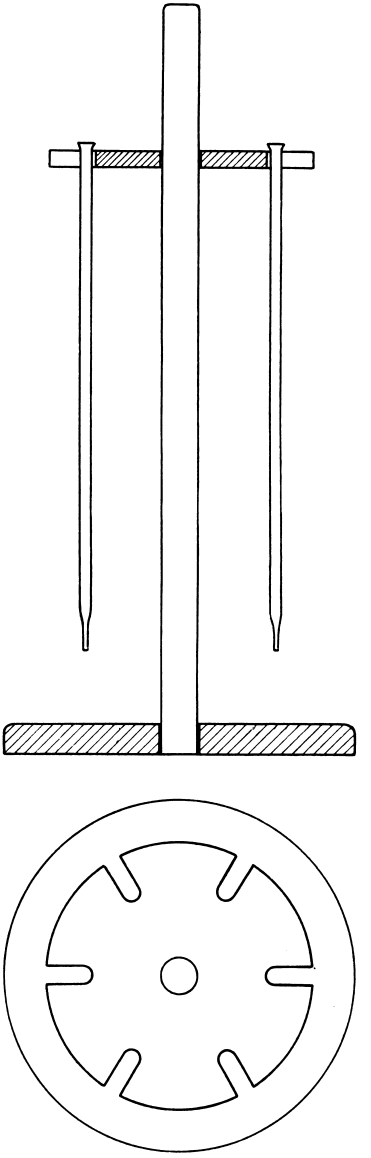


Fig. 6

on the copper block, and standing in the balance case for 20 minutes, as previously described, the crucible and filterstick are weighed. The difference between this weight and the previous weight of the empty crucible and filterstick gives the insoluble residue. Ten drops of hydrofluoric acid (previously distilled in platinum) and 1 drop of sulphuric acid were added, the HF evaporated off on the water bath and the sulphuric acid removed by heating on an electric hot plate covered with an inverted funnel through which the fumes were sucked away by means of a pump. On reweighing the crucible and filterstick the amount of silica present in the insoluble residue is given by the difference between this and the previous weighing. Filtrate F_1 was evaporated to dryness on the water bath, a few drops of nitric acid added, and the whole again evaporated. A little more nitric acid was then added, and the evaporation to dryness repeated. The residue was taken up with 2 cc. of hot 10% nitric acid, and the solution filtered into a porcelain crucible through the platinum filter. The residual silica was washed twice with hot 10% nitric acid, and then once with hot water, after which the crucible and filterstick were ignited and weighed as before. In the case of the analyses dealt with in this paper the amount of silica obtained here was so small as to render a treatment with HF and sulphuric acid unnecessary. The filtrate, F_2, was evaporated to dryness, and the residue treated repeatedly with a few drops of HCl and water followed by evaporation, care being taken that no marked evolution of gas took place during the process. The dry residue was finally taken up with 3 drops of HCl, and the solution diluted to 6 cc. Hydrogen sulphide was then passed into the solution for 30 minutes, using the apparatus depicted in Fig. 2 for the purpose. The precipitate of sulphides was filtered through a porcelain micro filterstick, the filtrate being collected in a porcelain crucible (F_3). The filterstick with the adhering precipitate was treated in the crucible with a few drops of ammonium polysulphide. After heating for a few minutes on the water bath, the residual lead sulphide was filtered through the same filterstick, the filtrate being received in a second porcelain crucible (F_4). The residue R_2 was heated with 1 cc. of dilute nitric acid (1 : 3), then 0.5 cc. of hot concentrated nitric acid was added, and the solution filtered through the porcelain filterstick into a previously weighed platinum crucible, followed by three washings, using 0.5 cc. of hot 1 : 1 nitric acid each time. The

solution in the platinum crucible was evaporated to dryness after the addition of 2 drops of pure sulphuric acid, first on a water bath and finally on the electric hot plate. The dry residue was ignited for 5 minutes in the electric oven at 600°-700°. After weighing, the residue was again treated with 1 drop each of nitric and sulphuric acids, the acid evaporated, and the lead sulphate again weighed after ignition as before.[8] An alternative procedure consists in precipitating the lead sulphate by dilute sulphuric acid and alcohol after the nitric acid has been removed by evaporation. The lead sulphate is filtered through a platinum filterstick, previously weighed with the platinum crucible, and weighed after drying in an oven followed by ignition for 5 minutes at 600°-700°. Filtrate F_4 was acidified with a few drops of HCl, diluted with water to 2 cc., and hydrogen sulphide passed in. The precipitate of sulphur together with a very small amount of sulphides was filtered through a porcelain filterstick, and washed several times with a little H_2S water, the filtrate being rejected. The mixture of sulphur and sulphides was treated in the crucible with hot HCl (1 : 1), the solution filtered through the filterstick into a porcelain crucible (previously ignited and weighed) followed by several rinsings with hot water. After evaporation of the solution to dryness, the chlorides in the residue are treated repeatedly with nitric acid, and the whole finally evaporated, ignited and weighed. This residue was always so small in amount that it was not possible to confirm the presence of Sn or Sb in it.[9]

Filtrate F_3 was evaporated to dryness in the porcelain crucible, and the residue moistened with a few drops of water. After adding 2 drops of nitric acid to oxidise it, the solution was again evaporated, the residue taken up with 8 cc. of water and 5 drops of HCl, and 0.5 g. of hydroxylamine hydrochloride added to the solution which was warmed on the water bath. After 20 minutes heating, ammonia (recently distilled, and free from carbon dioxide) was added in large excess, and the covered crucible and contents heated for a further period of 30 minutes. A few more drops of ammonia were added, until the liquid had a distinct odour of ammonia, and the precipitate produced was filtered through a porcelain filterstick into a porcelain crucible, the residue being washed with hot water con-

[8] No other element of the H_2S group was present.
[9] This is given in the analysis as "SnO_2."

taining ammonium chloride and a small amount of ammonia. The precipitate so obtained consists of the hydroxides of Fe, Al, Th, and the rare earths. The filtrate F_5 contains the uranium as a dark yellow complex salt, and also calcium and magnesium.[10] The above separation with hydroxylamine is due to P. Jannasch,[11] but has rarely been applied to the analysis of pitchblende. It was employed for the first time in the separation of uranium from the rare earths by the author and one of his co-workers, H. Krafft-Ebing.[12]

The hydroxides were dissolved in a few drops of hot water and HCl, and the solution filtered through the filterstick into a porcelain crucible. This procedure is necessary in order to recover that portion of the solution which was in the stem of the filterstick, and would otherwise have escaped the subsequent treatment. A better procedure, however, is as follows: The capillary tube (see Fig. 1) is cut above the point *c* and directly connected with the filterstick by means of a rubber tube, without the filterstick being removed from the crucible in which precipitation originally took place. Acid is then sucked through the capillary tube from the end *a*, followed by several rinsings with water. This procedure obviates the necessity for using a second crucible, as the reprecipitation is carried out in the crucible originally employed. 0.5 g. of the hydroxylamine hydrochloride was added to the solution of the hydroxides, the whole warmed for 20 minutes and carbonate-free ammonia added. The liquid was then heated for 30 minutes on the water bath, a little more ammonia introduced, and the liquid filtered into the same crucible previously used to collect filtrate F_5; this filtrate had in the meantime been partially evaporated. The whole operation was repeated a third time, using 0.3 g. of hydroxylamine hydrochloride, and the united filtrates, F_5, concentrated on the water bath until bubbles of gas appeared, due to the decomposition of the hydroxylamine. The crucible was then covered with the glass ball (shown in Fig. 3) and nitric acid added little by little to the solution (which was heated meanwhile continuously on the water bath) until the evolution of gas ceased. The glass ball was then removed and rinsed,

[10] Komarowsky, A. S., and Goremykin, W. J., Ztschr. analyt. Chem., **87**, 339, 1932.

[11] Jannasch, P., and Schilling, J., Journ. prakt. Chem., **72**, *26*, 1905; Jannasch, P., l. c. 35; Becker, A., and Jannasch, P., Jahrbuch für Radioakt. u. Elektronik, **12**, 9, 1915.

[12] These experiments are not yet published.

and the solution again concentrated. So soon as fresh evolution of gas commenced, the ball was replaced in position and nitric acid carefully introduced. When, after the lapse of some time, the evolution of gas finally ceased, the ball was removed and the solution could then be evaporated to dryness without risk of loss through effervescence. The procedure described is somewhat tedious, but on its completion not only the hydroxylamine but also the greater part of the ammonium salts present have been destroyed.

The residue was evaporated twice with a few drops of HCl, dissolved in 6 cc. of water and 5 drops of HCl, 0.5 g. of hydroxylamine hydrochloride added, and the separation repeated once more in order to remove small quantities of the hydroxides which had passed into the filtrates containing the uranium during the three previous treatments. A reprecipitation of small amount of hydroxide obtained is unnecessary; it can be regarded as free from uranium for practical purposes. The filtrate was treated with nitric acid in the manner previously described in order to remove hydroxylamine and ammonium salts.

The third precipitate of hydroxides, together with the small additional precipitate mentioned above, were heated in the crucibles together with the filtersticks with 5 drops of nitric acid and a little water in each case. The solutions were both sucked over into the same platinum crucible (previously weighed together with its filterstick), washing being carried out with hot dilute nitric acid. The volume of the solution was reduced to 6 cc., and 1.5 cc. of a cold saturated solution of oxalic acid was added drop by drop, whereby a precipitate of the oxalates of thorium and a part of the rare earths was obtained. After standing overnight the solution was filtered into a platinum crucible which had previously been weighed together with its filterstick. The wash liquid employed consisted of a mixture of 1 part of a cold saturated solution of oxalic acid and 3 parts of water; it was used hot, washing being carried out with three portions of 1 cc. each time. The crucible, filterstick and precipitate were first dried in an oven at 110°, and then gradually heated in an electric oven, finally being ignited at 1000° for 5 minutes. The weighted residue represented the oxides of thorium and the rare earths. The filtrate F_6 was rendered feebly ammoniacal, neutralised with nitric acid in the presence of phenol phthaleine as indicator (the

volume being 6-8 cc.) and 6 drops of acid in excess added, and the whole heated on the water bath for some time, when a fresh precipitate, consisting of the remainder of the rare earths present, generally appeared; whenever possible, this precipitate was allowed to stand overnight. Next day, the solution was sucked over into a porcelain crucible, and the residue washed several times with the dilute oxalic acid solution previously mentioned (this solution was partially neutralised with ammonia in this case before use). The crucible, filterstick and precipitate were ignited as in the previous case, and the weight obtained represented the remainder of the rare earths.

The ignited oxides of thorium + the first portion of the rare earths were subjected to the following treatment in order to separate the thorium from the remaining earths. A small quantity of potassium pyrosulphate was placed in the crucible containing the filterstick and the oxides, and the whole heated, at first gently, and finally to redness. Any particles of oxide which had adhered to the sides of the crucible were brought into contact with the molten pyrosulphate by carefully moving the filterstick up and down the sides by means of platinum-tipped forceps, so that complete attack on the oxides was thus attained. After cooling, the crucible was half filled with water, 15-20 drops of nitric acid were added, and the whole heated on the water bath until complete solution resulted. The resulting solution was transferred by suction to a porcelain crucible, followed by several rinsings with hot water, and the whole heated on the water bath after having been made strongly ammoniacal. The hydroxides separated under these conditions in a flocculent state, and could be readily filtered. They were filtered through a porcelain filterstick, washed with hot water containing a little ammonia and ammonium nitrate, and redissolved in the same crucible by sucking in hot dilute nitric acid from the end *a* of a capillary tube (Fig. 1) in the manner previously described. After rinsing several times with hot water and evaporation to a volume of 3 cc., the precipitation by ammonia followed by filtration and washing was repeated. The second precipitate was redissolved by warming with water and a few drops of nitric acid, and the solution transferred through a filterstick into another porcelain crucible. The oxides of the second portion of rare earths were dissolved by warming with 1 cc. of 1:1 nitric acid, and the solution sucked over through the platinum filterstick into the porcelain

crucible containing the nitrates of thorium and the first portion of the rare earths; no thorium is, however, likely to be present in this second portion of rare earths. The nitric acid solution was evaporated to dryness, the residue moistened with water, and the whole again evaporated; this process was then carried out a third time, in order to ensure complete expulsion of the acid. Twenty drops of a 10% solution of ammonium nitrate were added, and after warming on the water bath for a short time 7-10 drops of 3% hydrogen peroxide were introduced, whereupon a gelatinous precipitate of hydrated thorium peroxide formed, which filtered extremely readily. The solution was transferred through a porcelain filterstick into a platinum crucible (previously weighed together with its filterstick), and the residue washed with a hot, 10% solution of ammonium nitrate (Filtrate F_{10}). The precipitate of thorium peroxide was dissolved in dilute nitric acid, the solution transferred to a platinum crucible (previously weighed together with its filterstick), and evaporated to dryness. The residue was twice re-evaporated after being moistened with water each time, and finally taken up with 10% ammonium nitrate solution and the thorium reprecipitated with hydrogen peroxide, etc., in the manner given above. The filtrate was added to F_{10}. The crucible, filterstick and precipitate were dried first at 110°, and then heated in an electric oven, the temperature being gradually increased until the precipitate had been maintained for a few minutes at 1000°.

The weight of the ignited residue gave the thoria. The united filtrates can be further treated in the following way, if one does not wish to obtain the value for the rare earths from the difference between the total weight of oxides and that of the thoria determined as above. They are diluted to 4 cc., and 2 drops of nitric acid and 10 drops of a cold saturated solution of ammonium oxalate are added. After standing for 12 hours, the precipitate of rare earth oxalates is filtered off, ignited to oxides, and weighed.

The filtrate F_7, which contains Fe and Al, was concencentrated on the water bath so far as possible, and treated with 10 drops each of perhydrol and HCl, and a few drops of water. The crucible was at once covered with the glass ball, which was only removed and rinsed when all evolution of gas had ceased. The solution was evaporated so far as possible, 10 drops of nitric acid were added, the solution

evaporated, more nitric acid introduced, and the whole evaporated to dryness. The crucible was then placed in a drying oven and kept at 190°-200° for some time, and finally heated on an electric hot plate. In the majority of cases the ammonium salts and the greater portion of the oxalic acid will have been already removed by the treatment on the water bath, but by the method described above the whole of the remaining oxalic acid can be destroyed without risk of loss. The residue is dissolved in a few drops of HCl and water, the liquid evaporated to dryness, the residue taken up with 4 drops of nitric acid and a little water, evaporated to dryness, and once more moistened with a few drops of nitric acid and hot water. The solution is transferred through a porcelain filterstick to a platinum crucible (previously weighed together with its filterstick) and diluted to 2 cc. Ammonia is added until its odour just persists, and the whole is warmed on the water bath for 10 minutes when a further drop of ammonia is added. The liquid is filtered through the platinum filterstick, and the precipitate washed with a hot 1% solution of ammonia, containing a little ammonium nitrate; the filtrate is rejected. The crucible, filterstick and precipitate are first dried at 110° and then ignited for 5 minutes in the electric oven at 1000°; the ignited precipitate consists of ferric oxide and alumina. The above two constituents may be separated if desired by the following method. Fusion with potassium pyrosulphate, followed by solution in 5 drops of HCl and 3 cc. of hot water, transference of the solution to a porcelain crucible, and saturation of the liquid with hydrogen sulphide. The precipitated platinum sulphide is filtered off through a porcelain filterstick, and the solution received in another porcelain crucible which has previously been weighed together with its filterstick. 0.1 g. of tartaric acid is added, and hydrogen sulphide passed in. Ammonia is added until its odour definitely persists, and more hydrogen sulphide introduced. The solution is filtered through the porcelain filterstick, and the residue washed three times with a very dilute solution of yellow ammonium sulphide. The residue is dried at 110°, ignited for 5 minutes at 1000°, and weighed as ferric oxide.

The filtrate F_5 was further treated as follows: After removal of the hydroxylamine, the residue from the evaporated solution, which contained nitrates of U, Ca and Mg, was dissolved in the least possible amount of hot water, and the solu-

tion transferred with the aid of a bent capillary tube through a porcelain filterstick into a Jena micro filterbeaker (Fig. 5) which had previously been dried at 110° to constant weight. It was washed with hot water, care being taken to see that the total volume of the filtrate and washings did not exceed 3 cc. The employment of a filter is necessary when transferring the solution to the micro beaker, as the evaporation of the ammoniacal solution liberates small amounts of silica, probably derived from the porcelain crucible. Furthermore, the employment of a filterstick in this and similar cases permits of a very slow and undisturbed transference of the solution, and obviates the possible introduction of accidental impurities. These, and similar refinements of procedure, which may perhaps seem to be of little importance to the reader who has no practical experience of micro-gravimetric analysis, exert in reality a very great influence on the success of a micro-analysis which is so complicated as the one under discussion.

Five drops of a concentrated solution of ammonium acetate were introduced into the micro filterbeaker, and after heating to 80° a large excess of the 8-hydroxyquinoline reagent was added drop by drop.[13] The amount of free acetic acid must not exceed 2%. After cooling to room temperature the beaker was connected with the suction apparatus and the solution drawn over into a porcelain crucible, the residue being rinsed three times with hot water whilst rotating the beaker. In order to exclude dust, a Jean glass filter (with sintered plate) was fitted by means of a cork into the wide neck of the beaker (Fig. 5, left-hand side). The beaker was placed in a drying oven at 110°, and a rapid current of air aspirated through it for 20-30 minutes. It was then wiped, first with a moist and then with a dry chamois leather, allowed to stand in the open balance case for 30 minutes, and then weighed. The weight of the precipitate gave that of the "oxine" of uranium (abbreviation for hydroxyquinolate) which is multiplied by 0.3386 to give the corresponding amount of uranium.

The filtrate F_8 was evaporated to dryness in a porcelain crucible, the residue covered with sublimed oxalic acid, and gently ignited. It was then moistened with a few drops of dilute nitric acid, evaporated to dryness, the residue dissolved

[13] Determination of uranium with 8-hydroxyquinoline; Hecht, F., and Reich-Rohrwig, W., Monatshefte für Chemie, **53** and **54**, 596, 1929; see also Hecht, F., Mikrochemie, **10**, 49, 1931.

in hot water and the solution transferred to a micro filterbeaker with the aid of a bent capillary tube, as previously described. The beaker in question had been previously weighed after drying at room temperature whilst a current of dust-free air was aspirated through it. The volume of solution in the beaker must not exceed 2 cc.; if it does, it must be reduced to this volume by heating at 80° in a drying oven in a current of dust-free air, a Jena glass filter tube being meanwhile inserted into the wide neck as previously mentioned. The calcium was then precipitated by the addition, drop by drop, to the solution heated to 50°, of twice the theoretical amount of the picrolonic acid reagent.[14] The precipitate was allowed to stand for some hours in an ice-chest or refrigerator, and was then filtered and washed twice with 0.2-0.3 cc. of ice-cold water each time. The precipitate was dried at the ordinary temperature by aspirating a rapid current of air through the beaker with the dust filter in position. The weight of the dried precipitate multiplied by 0.05641 gives the calcium.

The filtrate F_9 which had been collected in a porcelain crucible was evaporated to dryness, the residue carefully ignited, and dissolved in 2 drops of HCl and 0.5 cc. of hot water. The solution was sucked over into a Jena micro filterbeaker (previously dried to constant weight at 105°), a few drops of a saturated solution of ammonium chloride and 3 drops of ammonia were added, the whole heated to 70° and the magnesium precipitated by an excess of a 1% alcoholic solution of 8-hydroxyquinoline.[15] The precipitate was filtered after standing for 30 minutes, washed alternately with water containing a little ammonia, and alcohol, and finally with alcohol alone. The beaker and precipitate were then dried for 30 minutes at 105°, and the magnesium determined by multiplying the weight of the dried precipitate by 0.0698.[16]

[14] Determination by the method of R. Dworzak and W. Reich-Rohrwig, Ztschr. analyt. Chem., **86**, 98, 1931. In order to obtain a N/100 solution of picrolonic acid, 2.64 g. of Merck's or Kahlbaum's preparation was dissolved in 1 litre of water with the aid of heat, and the solution cooled to room temperature. A small residue—presumably picrolonic acid—is filtered off, and a saturated (N/100) solution of the reagent is thus obtained.

[15] Determination by the method of R. Strebinger and W. Reif, Mikrochemie, Pregl-Festschrift, 319, 1929.

[16] In previous analyses Mg was precipitated as $MgNH_4PO_4$, ignited and weighed as $Mg_2P_2O_7$. The determination by means of 8-hydroxyquinoline is preferable, and the former method is consequently not described here.

Determinations of moisture were carried out in a very small porcelain crucible, 5-10 mg. of the mineral being dried in an oven at 110° to constant weight (which usually required 2 hours). The crucible was then heated in an electric oven at 300° until constant in weight (usually 2 hours). Finally it was ignited at 1000° for 10-15 minutes in order to determine the loss on ignition.

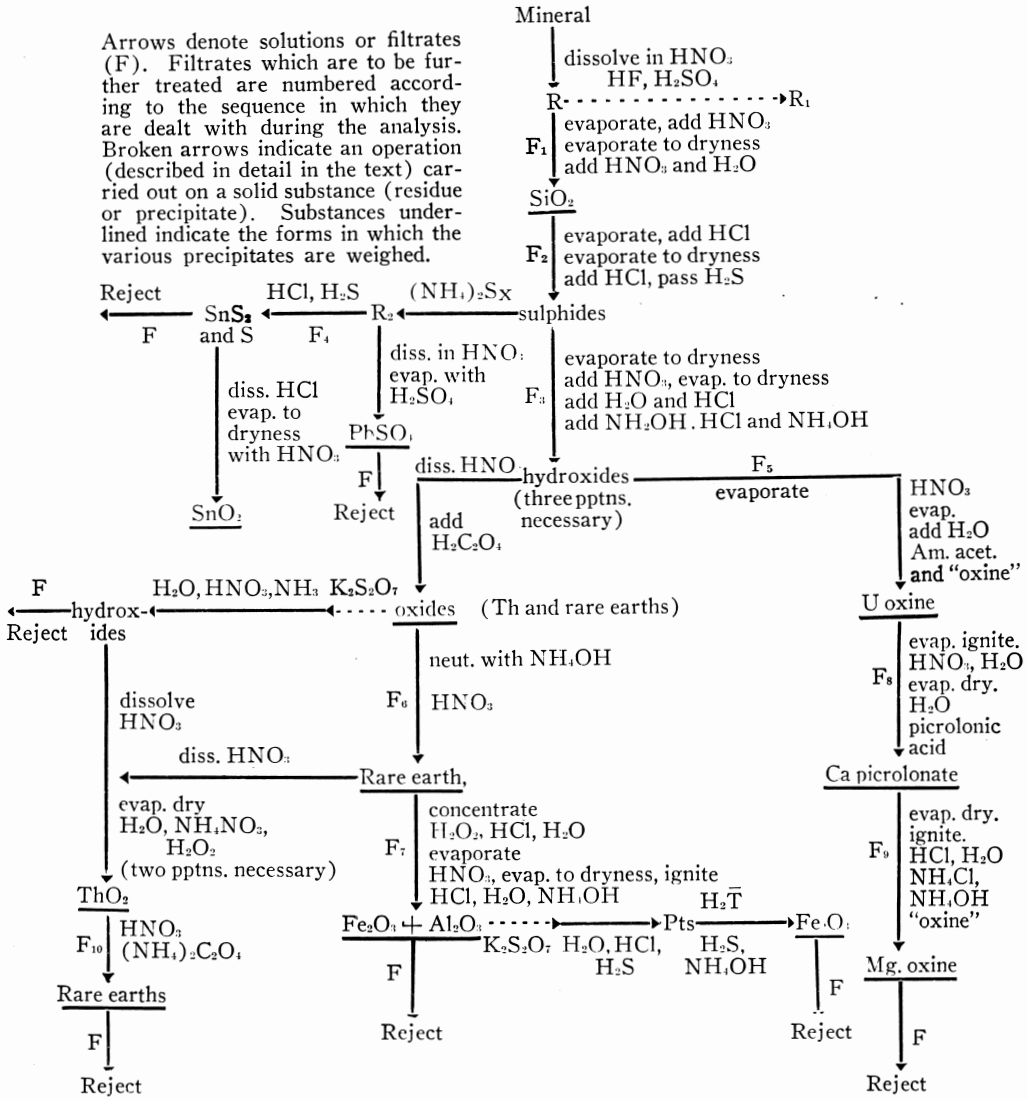
In order to determine the ratio UO_2/UO_3 4-6 mg. of the mineral were placed with dilute sulphuric acid (1 : 6) in a glass tube closed at one end. The air was displaced by CO_2. The tube was sealed whilst introducing CO_2 and heated in a micro bomb oven at 175°; 2-3 hours were sufficient to ensure complete attack. After cooling to the ordinary temperature the tube was opened and the uranium determined as rapidly as possible by titration with N/100 potassium permanganate. A more detailed description of this method, which has been worked out by the author and his co-worker, H. Krafft-Ebing, will be published shortly in another journal. (The above volumetric method was described by W. F. Hillebrand[17] for *macro*-analysis in 1891.)

It is evident that the micro methods just described will yield good results only in the hands of an analyst who has acquired considerable experience in this specialised branch. On this account it seemed necessary to me to give a detailed account of the procedure. All the operations must be carefully carried out with the greatest possible precautions. If this is done, however, then micro-analysis shows a great saving of time, labour, materials and reagents as compared with the usual macro methods.

Furthermore, it must be mentioned that my collaborators and myself have for some time past been working on the application of micro methods to the analysis of other radioactive minerals, such as kolm-ash, cyrtolite, thucholite, monazite, allanite and wiikite. A certain amount of preparatory work on the last-named mineral was carried out by Dr. L. Lokka and myself two years ago.

[17] Hillebrand, W. F., Bull. Geol. Survey, U. S. No. 88, p. 49, 1891.

Scheme for the Analysis of a Pitchblende.



Arrows denote solutions or filtrates (F). Filtrates which are to be further treated are numbered according to the sequence in which they are dealt with during the analysis. Broken arrows indicate an operation (described in detail in the text) carried out on a solid substance (residue or precipitate). Substances underlined indicate the forms in which the various precipitates are weighed.

D. Analyses of Gordonia Uraninite.

The powdered mineral A was treated for 5 hours with HCl (1 : 1), and the insoluble part (sample A′) was finely powdered and dried at 110° to constant weight. The analysis of the HCl extract (sample A″) was referred to the sum total of the oxides contained in the solution after removal of insoluble silica (which constituted about 4% of the whole); these oxides were: soluble SiO_2, PbO, Fe_2O_3, Al_2O_3, ThO_2, rare earths, U_3O_8, CaO, MgO. In order to determine these, two portions of 5 cc. each of the extract were converted to nitrates in a porcelain crucible, and then ignited to oxides; the weights obtained in both cases coincided almost absolutely. Portions of 5 cc. of solution were also employed for the analyses. Determinations of the hygroscopic water and loss on ignition were carried out on separate weighed quantities of material. The macro-analyses used as a check were carried out by M. v. Mack.

	A′ (residue after treatment with HCl)		A″ (HCl-extract)	
	Micro	Macro	Micro	Macro
Weight of sample	32 mg.	1.02 g.	45 mg.	2.17 g.
Insoluble residue	8.45%	8.34%	.....%	.....%
(of which SiO_2)	(6.92)	(6.94)	.....	.....
SiO_2 soluble	0.35	0.10	0.41	0.32
PbO	10.99	11.04	10.17	10.25
(Pb)	(10.20)	(10.25)	(9.44)	(9.51)
SnO_2?	0.20	0.13	.....	.....
Rare earths	3.00	3.10	1.92	2.55
ThO_2	13.29	13.55	6.26	5.98
(Th)	(11.68)	(11.91)	(5.50)	(5.26)
$Fe_2O_3 + Al_2O_3$	7.26	n.d.*	1.41	1.54
UO_2 ..... 26.45)	50.70†		75.30†	75.85†
UO_3 ..... 23.60)				
(U)	(42.96)	(43.00)	(63.85)	(64.32)
CaO	1.75	1.45	2.40	2.38
MgO	0.39	0.24	0.07	0.24
H_2O (–300° C)	2.58	2.19	.....	.....
Loss on ignition (300-1000° C)	2.02	1.79	.....	.....
Total	100.33%	.....%	97.94%	99.11%

* Not determined.
† Calculated as U_3O_8.

	B Micro	B′ Micro	B′ Micro
Weight of sample	23 mg.	24 mg.	26 mg.
Insoluble residue	2.76%	0.46%	
(of which SiO_2)	(1.41)	n.d.	
SiO_2 soluble	1.92	0.02	
PbO	10.13	11.13	10.87
(Pb)	(9.40)	(10.33)	(10.09)
SnO_2?	.....	0.31	
Rare earths	1.05	2.81	16.32
ThO_2	9.17	13.37	
(Th)	(8.06)	(11.75)	
Fe_2O_3	0.35	0.42	
Al_2O_3	0.81	1.83	
UO_2	17.40	31.99	64.85
UO_3	51.50	32.20	
(U)	(58.20)	(55.00)	(55.00)
CaO	1.11	3.00	
MgO	0.11	traces	
H_2O (-110°)	0.94	0.05	
H_2O (110-300°)	2.23	0.09	
Loss on ignition (300-1000°)	0.82	0.73	
Total	100.27%	98.41%	

B—original sample, untreated with HCl, finely powdered.
B′—handpicked material, untreated with HCl, finely powdered.

Control Analysis of an "Artificial Pitchblende."

For the purpose of obtaining an exact check on the methods, an "artificial pitchblende" was made up by mixing accurately standardised solutions, and the resulting final solution was analysed by the micro methods previously described. A slight modification was introduced, in that the Fe and Al were not determined together as oxides after ignition of the ammonia precipitate, but the two metals were weighed together as 8-hydroxyquinolates,[18] the Fe being then separated by ammonium sulphide in presence of tartaric acid. The FeS was dissolved in HCl, the solution evaporated, filtered from separated sulphur, and the Fe precipitated and weighed as 8-hyroxyquinolate in a Jena micro filterbeaker, the Al being then obtained by difference. It may be pointed out in this connection that the Jena micro filterbeaker permits of a perfectly satisfactory filtration of the Fe oxine precipitate (either alone or in conjunction with the Al oxine), a turbid filtrate never being obtained. SiO_2 or silicates were not used in this arti-

[18] Benedetti-Pichler, A., Mikrochemie, Pregl-Festschrift, p. 6, 1929; Benedetti-Pichler, A., and Schneider, F., Mikrochemie, Emich-Festschrift, p. 1, 1930.

ficial mixture, as the presence of appreciable quantities of alkalis interferes with the precipitation of the Ca as picrolonate, and renders a preliminary separation as oxalate necessary. The reliability of the method used for the determination of the silica is, however, evident from a comparison of the results afforded by the micro- and macro-analyses of specimens A′ and A″ (page 340).

	Present		Found		Present		Found	
	mg.	mg.	mg.	mg.	%	%	%	%
PbO	2.890		2.879		9.96		9.91	
Rare earths ...	1.978	5.879	5.882	1.901*	6.82	20.26	20.26	6.55*
ThO_2	3.901			3.957*	13.44			13.63*
Fe_2O_3	0.823	2.074	2.073	0.850*	2.84	7.15	7.15	2.93*
Al_2O_3	1.251			1.223†	4.31			4.22†
U_3O_8	17.842		17.920		61.47		61.74	
CaO	0.287		0.393‡		0.99		1.36‡	
MgO	0.052		0.093‡		0.18		0.32‡	
Total	29.024		29.240‡		100.01%		100.74%	

Analysts; F. Hecht and H. Krafft-Ebing.

* After separation.

† Calculated from the oxine determinations of Fe and Fe + Al.

‡ Owing to the rather considerable discrepancy in these values for CaO and MgO, a further determination of these two constituents was carried out in another portion of material, with the following results:

CaO	0.286 mg., corresponding to 0.985%
MgO	0.037 mg., corresponding to 0.13%
Total	29.077 mg.

E. Acknowledgments.

It is a pleasure for me to express my indebtedness to Professor A. Franke, Director of the Analytical Laboratory of Vienna University, for the great interest he has shown in all my work, and for placing all the necessary laboratory facilities at my disposal; also to the Elizabeth Thompson Science Fund in Boston for a grant which defrayed the cost of a micro balance and accessories, and to Professors A. C. Lane, G. P. Baxter, and G. Kirsch, for having kindly recommended this grant. I wish to thank the Editors and Publisher of *Mikrochemie* for permission to reproduce the diagrams and also the Editors of this Journal for having had them specially redrawn and lettered in English. A special word of acknowledgment is due to Dr. H. F. Harwood (Imperial College of Science and Technology, London), who most kindly undertook the arduous task of translating this paper into English. For his friendly coöperation I am deeply grateful.

Vienna, Austria.