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Analytical Methods used in the Complete Analysis of a Complex Uraniferous Titanium Ore Concentrate.

by

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Analytical Methods used in the Complete Analysis of a Complex Uraniferous Titanium Ore Concentrate

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ABSTRACT.

A complete analysis has been made of a standard Radium Hill concentrate. Both Chemical and Spectrographic techniques were used and an outline is given of the methods used and developed during the analysis.

1. Summary.

An analysis of a standard Radium Hill Concentrate, mark U3/40324, assay no. 9879 10/1/56, was undertaken. Standard analytical procedures were not readily adaptable and difficulties had to be overcome in carrying out the full scheme of group separations. Following modern trends (26, 36) the constituents were preferably sought individually with the minimum of chemical separations using specific methods of determination.

Although the analysis totals 99.96 per cent, the allotting of oxygen to vanadium, uranium and iron was made on an empirical basis and does not necessarily represent the natural oxidation states of these constituents. The presence of metallic iron in the sample made the calculation of the ferric-ferrous iron ratio also somewhat arbitrary.

The complete analysis is given in the appendix.

2. Introduction.

This report is an outline of the methods of analysis used for a complex uraniferous titanium ore, Radium Hill Concentrate, and sets out the procedures used with discussion relating to the reasons for their adoption.

Introduction cont.

Where standard analytical methods were used only an outline of the method is given but when a new method was developed or one adopted which deviated from existing practice, a more detailed procedure is outlined.

3. Analytical Procedures.

3.1. Silica (SiO_2)

The ore was fused with potassium bisulphate, leached and filtered. The residue was fused with sodium carbonate and followed by a double evaporation with HCl. The crude silica was weighed, treated with HF and the loss in weight reported as silica.

Procedure.

Weigh 0.5 g of ore into a silica crucible and fuse with 5 g of prefused $KHSO_4$. When cool leach the melt in 50 ml water containing 5 ml HCl and 10 ml H_2SO_4, warming only a little to aid solution. Rinse crucible and filter through Whatman 44 papers and wash with 5 per cent H_2SO_4. Ignite paper in a platinum crucible and fuse with Na_2CO_3 equal to 10 times the weight of residue or at least 1 g whichever is the greater. Evaporate the silica twice as usual (21). Ignite silica at 950°C and weigh. Treat with a few ml of HF - H_2SO_4 and reweigh reporting loss in weight as silica. Fuse residue with $KHSO_4$, leach and add both this and the silica filtrate to the original solution.

3.2. General Analysis scheme.

3.2.1. Group 2.

The volume of the solution was diluted to 250 ml to give a 2N solution with respect to H_2SO_4. H_2S was passed, sulphides allowed to stand overnight and then H_2S repassed next morning. The precipitate was filtered on Whatman 44 papers, washed with 1 per cent

HCl - H_2S water and the paper digested with nitric acid (17 ml) and perchloric acid (7 ml). After the reaction was complete 5 ml of 1-1 H_2SO_4 was added and the whole evaporated to dryness. The residue was dissolved in 5 ml of ammonium acetate (50 per cent) and polarographed. Very little lead was detected indicating too high an acidity for quantitative PbS precipitation. Lead was then determined separately on another sample.

3.2.2. Group 3.

The filtrate volume was 350-400 ml H_2S was boiled off and 1 g of ammonium persulphate added to oxidise iron and boiled for 15 minutes to decompose excess persulphate. The volume was evaporated to 200 ml and Group 3 was precipitated with ammonia. The precipitate was filtered and washed once, redissolved in 10 ml HCl and 10 ml 1-1 H_2SO_4, diluted to 50 ml and reprecipitated, filtered and washed six times with 2 per cent ammonium chloride.

3.2.2.1. Group 3 residue.

The residue was dissolved in 10 ml of 1-1 H_2SO_4, neutralised with 10 per cent NaOH solution and poured into 20 ml water containing 1 g Na_2CO_3 and 0.5 ml H_2O_2 (100 volume) boiled for 1 minute, settled, filtered, and washed with 2 per cent Na_2CO_3. This was repeated twice (making a total of three precipitations in all). The residue was dissolved in 10 ml of 1-1 H_2SO_4 and the iron and titanium determinations made. The combined filtrates were set aside for chromium, vanadium determinations.

3.2.2.2. Group 3 filtrate.

The combined filtrates were evaporated to 200 ml, 10 ml excess ammonia was added to make a 5 per cent ammoniacal solution and 40 ml of bromine water added, boiled for 5 minutes and the manganese dioxide filtered off and washed with warm water. The filtrate was acidified and boiled for $\frac{1}{2}$ hour to remove bromine. Ammonium oxalate (10 ml) was added, the solution made ammoniacal, simmered and allowed to stand overnight. No precipitate of calcium was observed, indicating its precipitation in Group 3 as sulphate.

3.3. Magnesia (MgO)

To the above solution was added 20 ml of ammonium phosphate, 30 ml ammonia (to give 10 per cent solution) and the magnesium ammonium phosphate allowed to precipitate for 24 hours, stirring at intervals for the first 6-7 hours. The precipitate was reprecipitated and ignited as usual (17).

3.4. Lime (CaO)

A separate determination was made by taking 0.5 g of ore in a platinum dish. Nitric acid (10 ml) and 10 ml HF were added and evaporated to dryness on a steam bath. A further 2 ml HNO_3 and 5 ml HF were added and the solution re-evaporated. This treatment decomposed the silicates leaving a residue of rutile and ilmenite.

The residue was fumed with 5 ml $HClO_4$, dissolved in 5 ml HCl and 20 ml water and filtered. A double precipitation of group 3 was made, followed by the usual double oxalate precipitation (16) and ignition to lime. A spectrographic examination of the ore residue showed 0.02 per cent CaO and MgO less than 0.005 per cent. Magnesia could be then determined on the lime filtrate if desired.

3.5. Strontia (SrO).

The ignited lime precipitate was submitted for spectrographic determination of strontia and showed 0.02 per cent SrO.

In general the analysis scheme 3.2.1., 3.2.2. was found to be long, cumbersome and on the whole unsatisfactory. Where sufficient sample is available, it is preferable to determine lead, titanium, iron, chromium, vanadium &c. on separate samples. The lime, magnesia and strontia could also be determined from one sample. Methods for direct determination were subsequently developed and used, thus rendering the above scheme of analysis unnecessary in future work.

3.6. Alumina (Al_2O_3)

This presented the most difficult problem and a direct determination with the necessary separations was made.

The ore was fused with potassium bisulphate and the alkali salts removed with an ammonia precipitation. The precipitate was dissolved in 10 per cent H_2SO_4 and Ti, Fe, V and part of the rare earths removed with cupferron precipitation. The filtrate was adjusted to pH 5 and a further cupferron precipitation made. This contained Al, Cr, U, and remaining rare earths. The paper and organic matter were destroyed with HNO_3 and $HClO_4$. Cr and U were removed by 8-hydroxyquinoline separation with ammonium carbonate and hydrogen peroxide. The precipitate contained Al and rare earths and was digested with HNO_3 and $HClO_4$ to destroy organic matter. The Aluminium and rare earths were precipitated with ammonia, dissolved in HCl and the rare earths removed by oxalic acid. The filtrate was evaporated and oxalic acid destroyed by HNO_3 and H_2SO_4 and a precipitation of aluminium was made with ammonia followed by ignition and weighing as Al_2O_3.

Procedure.

Weigh 0.5 g of ore into a silica crucible and fuse with 5 g of prefused $KHSO_4$. When cool leach with 50 ml of 10 per cent H_2SO_4. Filter into a 400 ml beaker transferring all the residue to filter paper. Wash with 5 per cent H_2SO_4 and finally with water. Ignite residue in a platinum crucible and remove silica with HF plus a few drops H_2SO_4. Ignite and fuse residue with 2 g of $KHSO_4$ and leach into the original solution. Rinse and remove crucible.

Bring to the boil, make just ammoniacal (2 drops excess) and filter, washing once with 2 per cent NH_4Cl to remove most of the alkali salts. Rinse the precipitate from paper and dissolve in 100 ml of 1 in 5 H_2SO_4 and dilute to 200 ml. Cool and chill to 5^oC in ice water.

Add a freshly prepared and chilled 6 per cent cupferron solution to precipitate (10) all Ti, V, Fe, Nb, Mo, Sn, Ta, Zr (Rare earths and Thorium partially). 65 ml of cupferron solution was required. Add pulp and filter through a 12.5 cm paper washing with cupferron wash solution (10 per cent H_2SO_4 containing 1.5 g/l cupferron). The precipitate is dried and ignited in an iron crucible and used for the subsequent determination of titanium.

Adjust the filtrate to pH5, (11), cooling in ice water to keep the temperature low. The solution is chilled in ice water to 5^oC and more cupferron solution added. The precipitate consists of Be, Al, Cr, U and rare earths and Th left in the original filtrate. Filter and wash with chilled water containing 1.5 g/l cupferron. Reject the filtrate and place the precipitate and paper in original beaker and destroy organic matter by adding 20 ml HNO_3 and 20 ml $HClO_4$. Evaporate to fumes and then reflux to oxidise Cr to chromate. As an alternative, the filtrate from the first cupferron precipitation can be evaporated, organic matter destroyed with 25 ml HNO_3 and H_2SO_4 and evaporated to fumes. This procedure was found to be much longer, difficulty was found in dissolving rare earth sulphates, and the double cupferron procedure was found to be superior.

Dilute to 75-100 ml, make just ammoniacal then acid with HCl. Add 10 ml of 3 per cent H_2O_2 (for Cr removal) and 15 ml of 2.5 per cent 8 hydroxyquinoline dissolved in HCl. Pour with stirring into 20 g of ammonium carbonate dissolved in 100 ml water for U removal (13). Heat to 50°C and stand 1 hour. Cool, filter and wash with 2.5 per cent ammonia, 2.0 per cent ammonium carbonate, and 10 ml of 8 hydroxyquinoline per 400 ml as wash solution. The precipitate consists of Al and rare earths, whilst the filtrate contains U, Cr, and any P, B and F not previously removed.

Add the paper back to the original beaker and destroy organic matter with 20 ml HNO_3 and 15 ml $HClO_4$ and evaporate to fumes. Dilute to 50 ml, add 5 ml HCl and filter and wash with 1 per cent HCl to remove silica introduced from filter paper ash and chemicals. Reject the residue. Make the filtrate just ammoniacal (2 drops excess), filter and wash a few times to remove perchlorates.

The rare-earths are removed by dissolving the precipitate in a few ml of HCl and evaporating to near dryness (29) diluting to 20 ml and when boiling add 1.5 g oxalic acid dissolved in 5 ml hot water. Simmer and allow to stand overnight. Filter through a 9 cm 44 Whatman paper washing with 0.5 per cent oxalic acid wash solution . Discard precipitate and evaporate filtrate. Add 15 ml HNO_3 and 10 ml $HClO_4$, to destroy oxalic acid and evaporate to fumes.

Dilute to 50 ml, add 5 ml HCl, filter and wash with 1 per cent HCl if necessary. Boil and make the filtrate just ammoniacal (2 drops excess) and filter, washing with 2 per cent ammonium chloride to remove perchlorates. Ignite in a tared platinum crucible and weigh as Al_2O_3. Carry a blank determination through on the entire procedure.

To economise on sample, the silica and alumina determinations could be carried through on the same sample, rendering the preliminary solution operations outlined in the method above unnecessary.

3.7. Total Iron.

The total iron was checked by two slightly different techniques. In the first one 0.5 g of ore was fused with prefused $KHSO_4$, leached in 10 per cent H_2SO_4, filtered and the ignited residue treated with HF and refused with $KHSO_4$ which was leached into the original solution. The solution was made 10 per cent with respect to HCl and passed through a silver reductor (9) and washed with 10 per cent HCl. The reduced iron was titrated with N/20 $K_2Cr_2O_7$ after adding 5 ml of phosphoric acid and 4 drops of barium diphenylamine sulphonate indicator.

In the second technique the sulphuric acid solution of the Group 3 residue obtained in 3.2.2.1. was diluted to 200 ml and 100 ml aliquot taken (equivalent to 0.25 g of ore), made 10 per cent with respect to HCl and passed through a silver reductor, washed and titrated as above. The two techniques gave exactly the same result.

3.7.1. Ferrous Oxide (FeO)

This was determined by a modification of the Method of Pratt (22) taking 1 g samples and boiling with the H_2SO_4-HF mixture for 15 minutes. The solution was rinsed into 75 ml of saturated boric acid and titrated with N/20 $K_2Cr_2O_7$ after adding 5 ml phosphoric acid and barium diphenylamine sulphonate as indicator.

Whilst the titration itself was satisfactory, in such a complex ore a number of assumptions and corrections must be made which makes the resulting corrected figures of approximate value only.

Depending on the state of oxidation of the vanadium and uranium, varying corrections could be applied to the ferrous iron value, but, owing to the uncertainties of such corrections, none were made.

The presence of free metallic iron introduced from grinding operations does cause a positive error. 1 mol. of metallic iron reduces 2 mols. of ferric iron to give 3 mols. of ferrous iron.

$$Fe^{0} + 2Fe^{+3} = 3Fe^{+2}$$

Hence 0.61 per cent metallic iron titrates as the equivalent of 1.83 per cent ferrous iron, making the ferrous iron high by that amount. Therefore a titrated ferrous iron value of 6.48 per cent becomes 4.65 per cent when allowance is made for 0.61 per cent metallic iron, thus giving 5.98 per cent FeO in the ore.

3.7.2. Metallic iron.

This was determined by taking 2 g of ore, adding 20 ml of copper sulphate solution (25 g/l) and allowing to stand with intermittent shaking for 3 hours. The metallic iron will dissolve, displacing an equivalent weight of copper from solution. The solution after standing was filtered, washed and the copper dissolved from the residue by boiling with 4 ml of 1-1 HNO_3.

The solution was again filtered and the filtrate received in 100 ml volumetric flask made just ammoniacal and then 20 per cent excess. After centrifuging, the cupramine color was read spectrophotometrically at 620 mμ. The copper value originally present in the ore was deducted and the difference reported as the equivalent value of metallic iron (0.61 per cent).

3.7.3. Sulphide iron.

The sulphide sulphur was calculated to FeS_2 and an equivalent iron percentage reported as iron disulphide (0.32 per cent Fe).

3.7.4. Ferric Oxide (Fe_2O_3)

This value was calculated as the total iron minus the sum of the ferrous iron, metallic iron and sulphide iron and reported as Fe_2O_3.

$$18.74 - (4.65 + 0.61 + 0.32) = 13.16 \equiv 18.80 \text{ per cent } Fe_2O_3.$$

3.8. Titanium dioxide (TiO_2)

The second 100 ml aliquot of the group 3 residue (see 3.2.2.1. and 3.7) was passed through a Jones reductor, the iron value deducted and the difference calculated as titanium. However, the aliquot was cloudy due to some slight hydrolysis of titanium during the preceding separations and the results obtained were high and erratic, indicating an inefficient separation of Cr, V, U.

Titanium was subsequently determined by two methods, one colorimetric and the other volumetric which agreed exactly.

3.8.1. Colorimetric method.

The colorimetric procedure was made by weighing 0.25 g of ore into an iron crucible, adding 4-5 g of Na_2O_2 and fusing. When cool the melt was extracted with water, the crucible policed and rinsed, set aside and the solution filtered and washed with 2 per cent NaOH solution. The filtrate contained the U, V and Cr, while the residue consisted of iron and titanium. The filtrate was discarded and the residue dissolved in 1-4 H_2SO_4. The inside of the crucible was cleaned with H_2SO_4 and the whole diluted to 500 mls, any ferrous iron from crucible attack being oxidised with $KMnO_4$, the H_2SO_4 concentration being kept at 10 per cent. A second dilution was made taking 50 ml and diluting to 250 ml in 10 per cent. H_2SO_4. The solution was peroxidised by adding ~~Na~~$_2O_2$ to a small portion of the solution in a beaker and reading spectrophotometrically at 408 mμ against the original solution as reference to compensate for the iron present. On adding HF to the peroxidised solution to check for V, none was found.

3.8.2. Volumetric method.

In the volumetric method, the cupferron precipitate from the aluminium determination (3.6) having been freed from Cr and U, but containing V, was ignited in an iron crucible and fused with 10 g Na_2O_2, extracted with water, filtered and washed with 2 per cent NaOH solution. The Vanadium passed into the filtrate. The hydroxides of Fe and Ti were dissolved in 5 per cent H_2SO_4, and the iron removed on a mercury cathode. The solution was diluted to 250 ml and a 200 ml aliquot (equivalent to 0.4 g of original sample) passed through a Jones reductor, (15) the reduced titanium being collected under ferric phosphate solution and the equivalent of liberated ferrous iron titrated with N/20 $K_2Cr_2O_7$. The residual iron in the solution was determined on a separate aliquot by the o-phenanthroline method (34).

In a second volumetric procedure 0.25 g was fused with Na_2O_2, water extracted, filtered and washed with 2 per cent NaOH solution. The iron was removed by mercury cathode electrolysis, the volume made to 250 ml and the determination made in a manner similar to the above volumetric procedure. Results were 0.6 per cent higher than given by the two preceding methods probably indicating an incomplete removal of uranium. Previous experience has shown that on Radium Hill residues containing little uranium this third procedure can give good results for titanium. However, in the presence of more than traces of uranium, a preliminary cupferron separation would possibly be desirable.

3.9. Soda (Na_2O) - Potash (K_2O)

Soda and Potash were determined by flame photometry but owing to the large number of other metal ions present in solution it was decided to do a preliminary J. Lawrence Smith (23) fusion, taking 0.5 g of ore. Most of the calcium was removed with an ammonia-ammonium carbonate separation, the filtrate being evaporated to dryness and carefully heated to remove ammonium chloride. The remaining salts were dissolved in 2.5 ml HCl and diluted to 50 ml. This solution was sprayed into a Beckman D.U. flame photometer and the alkalies determined against suitable standards, using as reference a standard solution containing 100 p.p.m. K_2O - Na_2O to which the instrument was set at 100 per cent transmission. A blank was carried through with the assays.

3.10. Water at 100°C.

A sample of 5 g was dried overnight at 105°C and the loss in weight recorded. Further drying caused no more loss.

3.11. Total Water.

This was determined by the Penfield method (20) by heating over a Meker burner for 10-15 minutes.

3.12. Phosphorus pentoxide (P_2O_5)

This was a method developed for titaniferous ores of a refractory nature and was based on the colorimetric phosphovanadomolybdate complex method given by Snell (32).

The phosphate was removed from the bases by a sodium carbonate fusion in the presence of excess silica (0.5 g ore, 0.5 g SiO_2, 8 g Na_2CO_3), followed by water extraction, filtration and washing with a 2 per cent Na_2CO_3 solution. The excess silica was necessary to give a quantitative separation with one fusion and extraction.

The solution was acidified with nitric acid to liberate CO_2, made ammoniacal and warmed to precipitate silicic acid. The ammonia was neutralised and 10 ml excess perchloric acid added. Then 20 ml of saturated boric acid was added to complex fluorine and the volume made to 200 ml. This was filtered on a dry paper and two 20 ml aliquots taken. To one (A) was added by pipette 5.0 ml of 10 per cent $HClO_4$ and to the other (B) 5.0 ml of vanadatemolybdate reagent. The colour was allowed to develop for only 5-10 minutes and read immediately before development of the silicomolybdate color. Readings were made spectrophotometrically at 470 mμ using (B) as color reading solution and (A) as reference to correct for chromate colour.

3.13. Chlorine (Cl).

The chlorine was determined by taking 10 g of ore and digesting with 100 ml of 25 per cent H_2SO_4 under reflux for at least 6 hours. After filtration, the chlorine was precipitated with silver nitrate and allowed to stand for 4 hours. The silver chloride was filtered off, washed and dissolved in 20 ml of 1:1 ammonia and diluted to 100 ml. A 20 ml aliquot was taken and a silver sulphide colloid developed giving a golden brown colour by adding 0.5 ml Na_2S (2.5 per cent solution) and 1 ml gelatin (0.4 per cent solution). (3, 24). The solution was diluted to 50 ml, allowed to stand for 15 mins. and read spectrophotometrically at 410 mμ. The colorimetric determination of the chlorine was preferred to gravimetric determination as AgCl because of the contamination sometimes experienced due to hydrolysed titanium.

3.14. Total Sulphur

Two grams of ore were taken and treated with KBr-Br mixture and the method of Allen & Bishop (18) followed. The dried salts were taken up in 10 ml HCl (instead of usual 4 ml) to avoid titanium hydrolysis. The ferric iron was reduced with 0.2 g of aluminium powder and the solution was filtered, and the paper washed with 2 per cent HCl. The solution was diluted to 250 ml and $BaSO_4$ precipitated. To correct for titanium hydrolysis, the weighed $BaSO_4$ precipitate was fused with Na_2CO_3, extracted with H_2SO_4, diluted to 50 ml, filtered through a dry paper and the peroxide-titanium color read spectrophotometrically at 408 mμ and the amount of titanium found deducted from the original weight of precipitate.

3.14.1. Sulphur Trioxide (SO_3)

Two grams of ore were boiled for 20 minutes with 20 ml 1-1 HCl, filtered, washed and $BaSO_4$ precipitated. The weighed precipitates were again corrected for any titanium hydrolysis.

3.14.2. Iron disulphide (FeS_2)

The total sulphur minus sulphur trioxide was assumed to be sulphide sulphur and calculated to FeS_2 for convenience in reporting.

3.15. Fluorine.

The ore was fused with Na_2CO_3, leached with water and the fluorine distilled by the usual Willard, Winter distillation (19) and titrated with thorium nitrate using sodium alizarin sulphonate as indicator in a buffered solution. However, hydrolysed titania, also silica and alumina considerably retard the distillation rate and 1 litre of distillate was necessary for complete recovery of the very small amount of fluorine. The method was modified according to the procedure given by Grimaldi et al. (5).

Procedure. Fuse 0.5 g sample with a mixture of 1.2 g of zinc oxide and 6 g of sodium carbonate in a nickel crucible. Cool. Place the crucible and contents in a beaker and add 30 ml water, cover and heat on a steam bath until the cake has softened. Remove crucible, police and rinse. The volume should now be approximately 50 ml .

Break up any lumps with a stirring rod flattened at one end, and then bring the solution to boil, stirring to prevent bumping. Boil for several minutes, remove from the heat, and allow the residue to settle.

Filter the solution into a 100 ml volumetric flask and wash residue and paper with hot 2 per cent Na_2CO_3 and wash to a volume of 100 ml. Reject residue. Cool, mix solution and pipette 50 ml (equivalent to 0.25 g ore) into distillation flask. Add slowly 20 ml perchloric acid and 2 ml phosphoric acid, keeping the flask cool by immersing it in cold water. Distil by the usual Willard, Winter procedure. When the temperature reaches about 135°C pass in steam from an auxiliary flask. Increase the temperature to 140°C ± 3° and distil at the rate of 4 ml per minute collecting nearly 250 ml of distillate. Dilute to volume and mix.

Transfer 100 ml aliquots (equivalent to 0.1 g ore) to 250 ml beakers and continue with usual thorium nitrate -sodium alizarin sulphonate titration. Carry a blank through on the entire procedure.

It was found that following the above procedure all fluorine could be quantitatively distilled in 250 ml. Where larger amounts of fluorine are to be determined the titration of a 50 ml aliquot would be sufficient.

The fluorine was also determined colorimetrically in the distillate using the zirconium-alizarin method and whilst satisfactory the titration with thorium nitrate was quicker and required less manipulation and the results were found to be quite satisfactory.

3.16. Arsenic trioxide (As_2O_3).

This was determined by the Gutzeit method (12). One gram of ore was attacked with Br-KBr mixture, followed by nitric acid, evaporated and fumed with H_2SO_4. The salts were dissolved in water, filtered and diluted to 100 ml in a volumetric flask. A 10 ml aliquot (equivalent to 0.1 g ore) was taken and the usual Gutzeit procedure followed.

3.17. Manganous oxide, (MnO)

The ore was attacked with a bisulphate fusion and diluted to 100 ml. Two aliquots were taken and the chromium oxidised to chromate with a preliminary treatment of ammonium persulphate. One solution was used as reference and the other as reading solution after the manganese had been oxidised by potassium periodate (35). Large precipitates of titanium phosphate were formed which necessitated centrifuging before the assays could be read spectrophotometrically.

Procedure.

Fuse 0.5 g of ore with 5.0 g of prefused $KHSO_4$ in a silica crucible. When cool leach with 40 ml water containing 5 ml H_2SO_4. Filter, wash, ignite residue in a platinum crucible, remove silica with HF treatment and refuse residue with $KHSO_4$. Leach into the original solution, rinse crucible and dilute to 100 ml in a volumetric flask.

Pipette two 40 ml aliquots and to each add 0.5 ml of $AgNO_3$ (50 g/l) 1 g ammonium persulphate and boil for 10 minutes to oxidise chromium. Add sulphurous acid dropwise adding just sufficient to destroy the permanganate color, boil for a few minutes to remove SO_2 and cool.

Add 16 ml 1-1 H_2SO_4 5 ml phosphoric acid (AR) and to the assay solution 0.3 - 0.4 g potassium periodate. Boil both assay and reference solutions to oxidise manganese and coagulate the titanium phosphate. Boil for 15-20 minutes, cool and dilute to 100 ml. Centrifuge solutions for 5-10 minutes and read the assay solution against the reference solution spectrophotometrically at 545 mμ.

3.18. Vanadium Pentoxide (V_2O_5)

Vanadium was best determined by direct potentiometric titration and was adapted from the method given by Rodden(28).

The ore was fused with sodium peroxide, leached with water, acidified with H_2SO_4, boiled and excess peroxide destroyed by adding $KMnO_4$. On cooling all reducible elements were reduced to their lower valency states by adding $FeSO_4$ solution in slight excess. By using weak (N/20) $KMnO_4$ solution the vanadium only was reoxidised, chromium and cerium remaining reduced. The excess $KMnO_4$ was destroyed by adding sodium nitrite and the excess sodium nitrite was destroyed by adding urea. On chilling the assay solution to 5°C and titrating potentiometrically with ferrous sulphate a good end point was obtained.

Procedure.

Weigh 1 g of ore into an iron crucible, add 8 g sodium peroxide and fuse for 5 minutes. Cool, extract the melt with water, acidify with H_2SO_4 and make 10 per cent with respect to H_2SO_4. Boil and destroy excess peroxide by adding $KMnO_4$ solution in slight excess. Cool to room temperature.

Add N/10 $FeSO_4$ solution in slight excess. (This is shown by taking 1 drop of the solution and adding to a drop of potassium ferricyanide on a spot plate; a blue coloration indicates excess ferrous iron). Now add N/20 $KMnO_4$ in slight excess such that the pink color remains for a least 2 minutes. Vanadium (+4) is only oxidised slowly to (+5).

Add 0.1 N sodium nitrite dropwise until the permanganate color is discharged and then 4 drops excess. Rinse sides of beaker and add 2 g of urea, stir for half a minute and allow to stand 10 minutes. Add 20 ml of 1-1 H_2SO_4. Cool in ice water to 5°C and titrate potentiometrically using N/20 $FeSO_4$ as titrant. The ferrous sulphate is standardised daily against N/20 $K_2Cr_2O_7$.

3.19. Chromic Oxide (Cr_2O_3).

The determination of chromium was made by three independent methods:-

(1) Colorimetrically using diphenyl carbazide.

(2) Colorimetrically using chromate color after separation of uranium.

(3) Volumetric titration with $FeSO_4$ after ammonium persulphate oxidation.

3.19.1. Diphenyl carbazide method.

Diphenyl carbazide is almost a specific reagent for chromium (30,33). Iron and vanadium interfere but iron is removed by filtration of the alkaline fusion and the vanadium color fades quickly so that by allowing the color to stand 15 minutes before reading, vanadium interference is eliminated provided its concentration is not 10 times greater than Cr.

The procedure consisted of fusing 0.25 g of ore with 4 g of Na_2O_2 in a porcelain crucible for 5 minutes. The melt was extracted with water and boiled fifteen minutes to decompose peroxide. The solutions were diluted to 100 ml, cooled, mixed and filtered through a dry paper. Five ml aliquots were taken in 50 ml volumetric flasks, neutralised with H_2SO_4 and 10 ml of N H_2SO_4 added in excess to give a final solution of 0.2N with respect to H_2SO_4. Two ml of diphenyl carbazide solution (0.25 per cent in 1-1 water-acetone) was added, the volume diluted to 50 ml and the color allowed to stand 15 minutes before reading spectrophotometrically at 543 $m\mu$. The results obtained averaged 0.40 per cent Cr_2O_3.

3.19.2. Chromate method.

Uranium gives a color which interferes with the chromate color and so it was necessary to remove the uranium from the combined filtrates in 3.2.2.1. The combined acidified filtrates were evaporated to 150 ml and an excess of $FeSO_4$ added to reduce Cr and V. Excess $FeSO_4$ was oxidised by $KMnO_4$ and a group 3 precipitation made by adding ammonia to the boiling solution. The precipitate was filtered, washed with 2 per cent ammonium nitrate and dissolved in nitric acid. The excess nitric was removed by evaporation to dryness, the dry solids dissolved in 10 ml of 10 per cent nitric acid and the uranium removed by passing through a cellulose column. (37).

The cellulose wad was removed, dried, ignited in a platinum dish and the residue fused with 5 g Na_2CO_3 and 0.5 g $NaNO_3$. The melt was extracted with water and diluted to 100 ml. After filtering through a dry paper, the chromate color was read spectrophotometrically at 406 $m\mu$. The results obtained averaged 0.40 per cent Cr_2O_3.

3.19.3. Volumetric method.

The ore was attacked with a sodium peroxide fusion, leached with water and acidifiod with H_2SO_4. The chromium and vanadium were oxidised with ammonium persulphate and silver nitrate added as catalyst, the excess persulphate destroyed with boiling and permanganate destroyed by adding dilute HCl. The Cr and V were titrated by adding ferrous sulphate and determining the end point potentiometrically or alternativaly using ferroin as indicator.

Procedure.

Proceed with fusion etc. as for Vanadium using porcelain crucibles and destroying excess peroxide by boiling and adding $KMnO_4$. Filter and wash with water to a volume of 100 ml (a) and adjust the solution to contain 5 ml excess sulphuric acid. Add 2 ml AgNO3 (50 g/l) and 25 ml of 10 per cent ammonium persulphate and boil 10 minutes. Complete oxidation is shown by the persistence of the pink MnO_4^- color. Add 5 ml of 1-3 HCl and boil for a further 5 minutes to destroy MnO_4^- and coagulate AgCl. Cool to room temperature and add 20 ml of 1-1 H_2SO_4 to make the solution approximately 5N in H_2SO_4. Titrate with standard $FeSO_4$ using ferroin as indicator or chill to 5°C and titrate potentiometrically using $FeSO_4$ as titrant.

(a) As an alternative check the volume was diluted to 300 ml and the procedure given in Hillebrand et al.(14), was followed, back titrating the excess ferrous sulphate with N/20 $K_2Cr_2O_7$ using barium diphenylamine sulphonate as indicator. The vanadium titre was deducted and the difference reported as chromium.

The results obtained averaged at 0.38 per cent Cr_2O_3.

Of the three methods, the diphenyl carbazide method is preferred. It is relatively quick, simple and specific. The chromate method requires the long and cumbersome removal of uranium which limits its usefulness. The volumetric method is a difference method and is therefore subject to more errors than a direct, specific method.

3.20. Lead Oxide (PbO).

The sample was attacked with HNO_3 - HF and fumed with $HClO_4$, dissolved in HCl and filtered. The lead was precipitated from the filtrate with H_2S, the sulphides filtered and dissolved from the paper with bromine water-nitric acid and evaporated with H_2SO_4. Excess acid was neutralised, ammonium acetate added and the resulting solution polarographed.

Procedure.

Weigh 5 g ore into a platinum dish and digest with 10 ml HNO_3 and 20 ml HF and evaporate to dryness. Re-evaporate twice with 10 ml HF and 5 ml HNO_3. When dry, add 5 ml $HClO_4$ and fume. Rinse sides of dish and refume.

Add 10 ml HCl, dilute and warm to dissolve, rinse into a 250 ml beaker and boil for some minutes. Filter and wash with hot 2 per cent HCl and finally with hot water. Dilute to 500 ml to give a solution 0.2 N in acid as required for lead precipitation (25). Warm and pass H_2S for 15-20 mins. and stand. Warm and repass H_2S. Filter and wash with H_2S water. Rinse sulphides into the original beaker. Pour 10 ml of 1-1 HNO_3-Br water over paper, rinse and discard. Evaporate to small bulk adding more Br water if necessary to attack sulphides. Add 5 ml 1-1 H_2SO_4 and fume. Rinse sides and refume to incipient dryness.

Rinse sides and add ammonia until only just acid. Add 10 ml of 50 per cent ammonium acetate and boil to dissolve $PbSO_4$. Dilute to 100 ml in a volumetric flask, filter through a dry paper and polarograph.

A spectrographic examination showed that the residue contained less than 0.001 per cent Pb indicating the completeness of the acid attack.

3.21. Copper oxide. (CuO).

The method used was a colorimetric one using 2,2' Diquinolyl as developed by Guest (6).

The sample, 0.1 g, was weighed into a test tube and fused with 1 g of $KHSO_4$. The melt was leached with 4 ml of 2N HCl and rinsed into a beaker, hydroxylamine hydrochloride solution and tartaric acid solution were added and the determination completed by the method given by Guest.

3.22. Boron trioxide (B_2O_3).

The method used was the colorimetric procedure using carmine and developing the color in H_2SO_4. Fusion with sodium carbonate and direct acid solution of the melt proved unsatisfactory owing to titanium giving an interfering color. Consequently water extraction of the sodium carbonate melt was necessary. The method followed was essentially that given by Hatcher & Wilcox (8).

Procedure

Weigh 0.25 g of ore into a platinum crucible and fuse with 4 g Na_2CO_3 (A.R.). Extract the melt in a platinum dish on water bath. When extracted, rinse and remove crucible, filter and wash a few times with 2 per cent Na_2CO_3 solution. Add 10 ml HCl to filtrate, warm to 50°C, stirring to liberate CO_2. Boiling the solution may steam distil boric acid. Contact of the alkaline solution with pyrex glass must be kept to a minimum.

Dilute to 100 ml. Pipette a 2 ml aliquot into a dry 25 ml flask. Add 0.1 ml water and 2 ml conc. H_2SO_4, cool, then a further 8 ml H_2SO_4 and cool. The fluorine content of the aliquot must be kept below 10 micrograms otherwise significant bleaching of the color will occur. From a burette add 10 ml of carmine solution (0.05 per cent in conc. H_2SO_4) and dilute to mark with conc. H_2SO_4, cool, mix and allow to stand overnight. Carry through a blank and read spectrophotometrically at 610 mμ.

3.23. Uranium Oxide (UO_2).

The method used was an adaption of the ether-nitric acid-cellulose column method with colorimetric $NaOH$-Na_2O_2 finish given in "Handbook of Chemical Methods for the determination of Uranium in minerals and ores" (37). One gram of ore was fused with 8 g Na_2O_2 in an iron crucible, extracted with water and acidified with nitric acid and evaporated just to dryness. The salts were dissolved in 10 ml of 10 per cent HNO_3 and the uranium separated by the cellulose column technique.

3.24. Rare Earths - Thorium oxide.

The ore was attacked by a sodium peroxide fusion in a nickel crucible at low temperature, extracted and precipitated with ammonia. The hydroxides were dissolved in HF and the solution was evaporated to near dryness in a platinum dish. The dry salts were dissolved in a dilute HF-HCl solution and the insoluble fluorides were removed by centrifuging. The insoluble fluorides were then decomposed with H_2SO_4 and calcium removed with an ammonia precipitation. The hydroxides were dissolved, the excess HCl removed and the rare earths precipitated with oxalic acid and ignited. The thorium was determined colorimetrically after a mesityl oxide solvent extraction of the thorium.

Procedure

Take 1 g of ore and fuse at low temperature with 8 g Na_2O_2 in nickel crucible. When cool extract with water, acidify and adjust to 5 per cent acid with H_2SO_4. Warm to 60°C, neutralise with ammonia and add 5 per cent excess. Stand 15-30 minutes cooling to room temperature. Filter through an 11 cm 541 paper and wash with 5 per cent ammonia. Discard filtrate.

Rinse the hydroxides into a platinum dish, add 10 ml HF, stir to dissolve and evaporate on water bath to near dryness. Pour 1-1 HCl over paper into original beaker, rinse paper and add rinsings etc. to HF solution in platinum dish. When nearly dry add 40 ml of HF-HCl solution (2 ml HF + 2 ml HCl/100 ml) and warm until salts dissolve. Cool. Centrifuge in plastic tubes at 4000 R.P.M. Decant off liquor and recentrifuge with 2 per cent HCl-HF wash. Reject all solutions.

Rinse fluorides into the original platinum dish and evaporate off water. Add 3 ml of H_2SO_4 warming carefully at first (HF evolved) and finally fume to near dryness. Cool, add hot water and 2 ml HCl. Warm to dissolved and transfer quantitatively to 250 ml beaker. Boil to dissolve all sulphates adding 3 per cent H_2O_2 and more acid if necessary. The solution should be clear, but if not, filter, wash residue, ignite, fuse with $KHSO_4$ and add to original solution.

Warm to 60°C and add 5-10 per cent ammonia in excess. Stand 10 minutes and cool to room temperature. (Total standing time 15-30 minutes). Filter through an 11 cm 541 paper and wash with 5 per cent ammonia - 1 per cent NH_4Cl solution. If much Ca is present reprecipitate as before, dissolving the hydroxides in the minimum of HCl. If titanium is still present, hydrolysis will occur in the HCl solutions so rinse into a platinum dish and repeat fluoride separation.

When free from Ca and Ti dissolve the hydroxides in the minimum of HCl and evaporate to near dryness to remove HCl. Dilute to 80 ml with water, adding a few drops of HCl if necessary. The solution must be clear af this point. Neutralise excess acidity with 50 per cent ammonium acetate using bromphenol blue indicator (pH 3), bring to boil (neglect any hydrolysate) and add 5 g of oxalic acid dissolved in 20 ml hot water. Boil, simmer and allow to stand overnight.

Filter through a 9 cm 44 paper washing with 1 per cent oxalic acid. Ignite at 950°C to constant weight (usually half an hour is sufficient).

3.24.1. Thorium oxide (ThO_2)

Fuse the above precipitate with $KHSO_4$, extract with dilute 2 per cent H_2SO_4. Neutralise with NaOH and make 5 per cent with respect to NaOH. Boil a few minutes to precipitate hydroxides and decompose double sulphates. Filter through a 9 cm 541 paper and wash with water until fairly free from sulphates. Dissolve the precipitate in HNO_3 in original beaker, evaporate to dryness and dissolve in 20 ml of saturated $Al(NO_3)_3$ and extract the thorium with mesityl oxide separation (1) using "Thorin" as colour developing reagent and read spectrophotometrically at 545 mμ.

3.24.2. Spectrographic Determination of Rare Earths.

The preparation of a sample for spectrographic determination of individual rare earth members using a mothod suitable for uranic materials resulted in so much contamination with titanium from hydrolysis that it was rejected. A sample prepared by the above procedure was used, the mixed rare eartho oxides - thorium oxide being ignited. The mixed oxides were dissolved in nitric acid, a solution containing 10.0 mg of Fe_2O_3 added and a hydroxide precipitation made, using five percent excess ammonia. This proved very satisfactory except that the scandium was found to be only 0.01 per cent as against 0.06 per cent when estimated from an original spectrographic examination of the ore without preliminary separations. The low valuo for scandium might be expected owing to the solubility of its fluoride and oxalate the value 0.06 per cent was accepted.

3.25. Cobalt oxide (CoO).

The method used was the colorimetric procedure employing Nitroso R salt (4.7). A sample weighing 0.5 g was digested with 10 ml HNO_3, and 10 ml HF and evaporated to dryness in a platinum dish, then further treated with 5 ml HNO_3, and 10 ml 1-1 H_2SO_4 and evaporated to strong fumes. The sample was diluted with water, filtered, washed and diluted to 50 ml in a volumetric flask. Aliquots of 20 ml were taken and the color developed and read spectrophotometrically at 550 mμ.

3.26. Zinc oxide (ZnO).

This was determined by the method of Miller & Cowling (27,31) using dithizone (10). The filtrates from the lead determination (3.20) were boiled free from H_2S, oxidised with nitric acid and diluted to 500 ml. A 20 ml aliquot equivalent to 0.2 g sample was taken, buffered with ammonium citrate and extracted with dithizone. The final color was measured spectrophotometrically at 535 mμ.

3.27. Organic carbon (C) arising from flotation reagents

Attempts were made to extract the flotation reagent with solvents and to steam distil the volatile portion but both procedures were unsatisfactory. The linseed fatty acid probably forms a tough skin around the particles which will not allow the solvents to penetrate through and give complete extraction of the oil coating the minerals. The organic carbon was finally determined by standard procedures for ultimate analysis given in "British Standard Methods for the Analysis and Testing of Coal and Coke" (2).

The flotation reagent consists of two thirds fuel oil and one third mixed oxygenated organic materials. The hydrogen and oxygen could then account for a further 0.1 - 0.15 per cent making the total flotation reagent value 0.74 - 0.80 per cent. Only the organic carbon was reported as the total flotation reagent value could not be suitably determined.

3.28. Spectrographic Analyses.

Tin, niobium, zirconium and barium were found to be present in the ore and, being less than 0.05 per cent, no further chemical work was undertaken and they were reported as their spectrographic values.

4. Complete Analysis.

The Complete Analysis is as follows:-

Silica, SiO_2	11.84 %
Alumina, Al_2O_3	3.70
Ferric Oxide, Fe_2O_3	18.80
Ferrous Oxide, FeO	5.98

Complete Analysis Cont.

Metallic iron, Fe	0.61 %
Magnesia, MgO	2.48
Lime, CaO	1.32
Soda, Na_2O	0.17
Potash, K_2O	0.84
Water at 100°C	0.33
Water over 100°C	2.04
Titanium oxide, TiO_2	44.05
Zirconium oxide, ZrO_2	0.03
Phosphorus Pentoxide, P_2O_5	0.71
Sulphur trioxide, SO_3	0.01
Chlorine, Cl	0.05
Fluorine, F	0.20
Iron disulphide, FeS_2	0.69
Chromic oxide, Cr_2O_3	0.40
Vanadium pentoxide, V_2O_5	1.15
Manganous oxide, MnO	0.15
Strontium oxide, SrO	0.02
Barium oxide, BaO	0.03
Lead oxide, PbO	0.10
Tin oxide, SnO_2	0.04
Copper oxide, CuO	0.02
Boron trioxide, B_2O_3	0.06
Uranium oxide, UO_2	0.92
Scandium oxide, Sc_2O_3	0.06
Yttrium oxide, Y_2O_3	0.23
Lanthanon oxides	2.26
Thorium oxide, ThO_2	0.05
Niobium pentoxide, Nb_2O_5	0.03
Cobalt oxide, CoO	0.01

Complete Analysis Cont.

Zinc oxide, ZnO	0.03	%
Organic Carbon, C	0.64	
Nickel oxide (NiO) detected but less than	0.01	%
Arsenic Trioxide (As_2O_3) detected	1 p.p.m	
	100.05	
less oxygen equivalent of chlorine and fluorine.	0.09	
	99.96	

LANTHANON OXIDES.

Lanthanum oxide, La_2O_3	1.06	%
Cerium oxide, Ce_2O_3	0.89	
Praseodymium oxide, Pr_2O_3	0.02	
Neodymium oxide, Nd_2O_3	0.08	
Samarium oxide, Sm_2O_3	0.01	
Eurpium oxide, Eu_2O_3 detected less than	50 p.p.m	
Gadolinium oxide, Gd_2O_3	0.01	
Terbium oxide, Tb_2O_3	0.02	
Dysprosium oxide, Dy_2O_3	0.03	
Holmium oxide, HO_2O_3	0.01	
Erbium oxide, Er_2O_3	0.05	
Thulium oxide, Tm_2O_3	0.01	
Ytterbium oxide, Yb_2O_3	0.06	
Lutecium oxide, Lu_2O_3	0.01	
	2.26	%

The following elements could not be detected Spectrographically:-

Antimony, Beryllium, Bismuth, Cadmium, Gallium, Germanium, Indium, Molybdenum, Palladium, Thallium, Tungsten, Gold, Mercury, Iridium, Osmium, Platinum, Rhenium, Rhodium, Ruthenium, Silver, Tantalum, and Tellurium.

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