THE ESTIMATION OF INDIUM IN ZINC ORES, WITH SPECIAL REFERENCE TO THE INDIUM CONTENT OF SOUTHERN AFRICAN SPHALERITES.

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THE ESTIMATION OF INDIUM IN ZINC ORES, WITH SPECIAL REFERENCE TO THE INDIUM CONTENT OF SOUTHERN AFRICAN SPHALERITES.

Introduction.

(a) Aim: Up to comparatively recently, it was extremely difficult to procure even a few grams of indium, but, since 1932, considerable quantities of this element have been produced by the Indium Corporation of America.

Most of the pioneering work in this connection, has been done by W. S. Murray (1) and (2), who carried out an extensive survey of American Zinc Ores and who placed the commercial production of indium on a firm basis.

Metallic Indium of 99.98% purity can be purchased to-day, for approximately $ 30.0 per troy ounce, in America.

Amongst the uses to which indium has been put (1), (2), (3), (4), (5), (6), the following are the most important:-

(1) In electroplating
(2) In bearing metals
(3) In jewellery
(4) In dental alloys
(5) In thermometry
(6) In medicine
(7) In radio and television

No work has been done on the indium content of Southern African Zinc Ores and it is the basic idea of this research to analyse typical Southern African Sphalerites in order to determine the indium content.

In the Union of South Africa, there are no extensive Zinc deposits, although in the Marico district of Western Transvaal, fairly rich sphalerite deposits are found and were worked for Zinc up to 1921 (7).

The Rhodesian deposits are economically more important.

With this basic idea in view, that is, the estimation of the indium content of typical Southern African Sphalerites, the next consideration was the analytical process to be used. It was decided to use a purely chemical method and one that could be readily applied in any average laboratory.

It was found that the basic reaction in nearly all the existing chemical methods, was the displacement of indium by means of metallic zinc (6), (8), (9), (10), (11), (12), (13). Displacement methods, whereby one metal is precipitated by means of another, are usually open to loss of some of precipitated element, except, when that element is highly insoluble in acids, etc. This loss may become relatively appreciable, when the precipitated element is present in small proportions, which is usually the case with indium in typical Sphalerites and Smithsonites.

Moreover, displacement methods are uncommon and are usually not recommended in quantitative analysis in general except, of course, when the precipitated element is highly insoluble, as in the case of gold, platinum, selenium, etc. Cadmium is occasionally estimated this way, but, the American Society for Testing Materials (14) clearly points out that there is a slight loss of Cadmium, when using this method. The solubility of Indium in acids is somewhat similar to that of Cadmium.

Again, most impure zinc contains indium and there is always the chance of introducing small amounts of indium in this way. Very pure zinc could be used, but it reacts rather slowly with dilute acids.

When using ordinary zinc as the precipitant, a blank test should be carried out.

With regard to the quantitative chemical methods, no data could be found in connection with the quantitative recovery of indium from comprehensive synthetic mixtures, using the zinc precipitation scheme, or in fact any other chemical scheme.

It was thus decided firstly to evolve a chemical method for estimating indium in zinc ores and secondly to estimate the indium in typical Southern African Sphalerites, using this method.

For the description and discussion of the existing methods of estimating indium in zinc ores, concentrates and similar materials, see Section (1) (pages 4 - 9).

The analytical method was not intended so much for ores carrying small traces of Indium (less than 0.001%), as it was for indiferous ores carrying in excess of 0.001%.

The Indium Corporation of America, which is the most important producer of indium, recovers this element from ores containing 2 oz. per ton (approximately 0.005%) and upwards. (1).

It follows then, that an analytical method, which could be applied to ores carrying from 0.001% indium upwards, would be very useful, especially if the method could be readily carried out in a normally equipped laboratory.

(b) ABUNDANCE AND DISTRIBUTION OF INDIUM.

According to Professor Goldschmidt (15), the concentration in grams per ton of Indium in the earth's crust is 0.1.

Similar concentrations are shown by Silver (0.1), Mercury (0.5) Thallium (0.3), Bismuth (0.2) and Selenium (0.6). (16).

For details regarding the distribution and concentration of indium in different parts of the world, refer to "Gmelins Handbuch der Anorganischen Chemie" (17).

No specific indium mineral has yet been discovered. (18).

(c) CHEMICALS AND SPECIAL SOLUTIONS USED THROUGHOUT THE RESEARCH.

In all cases, where high purity chemicals were necessary, British Drug Houses "Analar" reagents were used.

Metallic indium (99.98%), indium trichloride and indium sesquioxide, were obtained from "The Indium Corporation of America" and metallic gallium and thallium from the British Drug Houses.

The following solutions were prepared:-

(1) STANDARD INDIUM CHLORIDE SOLUTIONS.

1 Gram of metallic indium (99.98%), weighed accurately to 0.1 mgrm., was dissolved in 5N. hydrochloric acid and made up to 1 litre.

A Weaker standard was prepared in a similar manner, by dissolving 0.1 gram metallic indium in hydrochloric acid and making up to 1 litre.

(2) INDIUM CHLORIDE SOLUTION FOR QUALITATIVE PURPOSES.

Approximately 6 grams of indium sesquioxide were dissolved in 2N hydrochloric acid and made up to 500 ml.

This gave an approximately 1% indium solution.

SECTION 1.

EXISTING CHEMICAL METHODS OF ESTIMATING INDIUM IN ZINC ORES.

(a) Method used by W. R. Schoeller and A. R. Powell (Metallurgical Chemists, London). (9).

100 Grams of the blende are dissolved in hydrochloric acid, with the addition of some nitric acid, if necessary.

This is filtered and the filtrate boiled with metallic zinc until nearly neutral.

The precipitate is dissolved in hydrochloric acid (with Pot. Chlorate, if necessary) and copper and bismuth precipitated from the boiling solution with iron wire.

The filtrate is again boiled with zinc and the precipitate digested with nitric acid to eliminate tin.

The filtrate is evaporated to fumes with sulphuric acid and lead sulphate filtered off.

This filtrate is treated with ammonia and filtered on pulp, the precipitate dissolved in hydrochloric acid, the acidity adjusted to less than 0.05N. and the Indium precipitated as sulphide by bubbling hydrogen sulphide for two hours at 70°C.

The sulphide is either weighed as such, or converted to nitrate using nitric acid, precipitating the hydroxide with ammonia and then igniting gradually.

(b) METHOD DESCRIBED BY W. R. SCHOELLER AND A.R. POWELL. (9).

100 Grams of the blende are dissolved in hydrochloric acid with the addition, if necessary, of nitric acid.

Excess nitric acid must be destroyed. The filtered solution is digested with metallic zinc, thereby precipitating all the Indium, together with lead, copper, cadmium etc.

The precipitate is dissolved in nitric acid and the solution evaporated to fumes with sulphuric acid.

The lead sulphate is filtered off and the filtrate treated with ammonia, boiled and filtered.

The precipitate is dissolved in a minimum of hydrochloric acid, the solution neutralised with ammonia, an excess of sodium bisulphite added and boiling continued for some time.

A white crystalline precipitate is thrown down, which may be dissolved in hydrochloric acid and indium estimated as oxide by adding ammonia, boiling, filtering and ashing the hydroxide.

(c) METHOD USED BY GEORGE L. ROYER, CORNELL UNIVERSITY, ITHACA, N.Y. (10)

The blende is dissolved in hydrochloric acid and nearly neutralised with ammonium carbonate.

One Gram of ammonium chloride is added and the volume made up to about 50 ml. sulphur dioxide is passed into the solution and iron reduced to the ferrous state.

The solution is then made slightly acid by adjustment with 6N. ammonium carbonate and hydrochloric acid.

A freshly prepared suspension of barium carbonate is added in excess and allowed to stand with occasional shaking for several hours and then filtered.

This procedure separates the Indium and Aluminium from most of the Zinc, Manganese and Ferrous Iron.

The precipitate is dissolved in 6N. Hydrochloric Acid and Bromine added to oxidise any sulphite to sulphate.

Sulphuric Acid is then added until all the Barium is precipitated as barium sulphate.

This precipitate is digested, filtered and washed with hot water.

One Gram of Ammonium Chloride is added to the filtrate and the volume made up to 50 ml. with water.

Ammonium Hydroxide is added in excess and the solution boiled for a short time.

The precipitated hydroxides are removed and dissolved in 6N. Sulphuric Acid.

The sulphuric acid solution is made up to 50 ml.

To remove any remaining iron, 25 ml. of 0.6% cupferron is added.

After standing about an hour, the precipitate is filtered off and washed.

The filtrate is concentrated by evaporation and indium is determined by electrodeposition in the small cell.

In the development of this method, all discarded precipitates and filtrates were tested spectroscopically to show the absence of indium.

For the details of the electrolytic procedure, see (10).

(d) EARLY METHOD DEVELOPED BY F. REICH AND TH. RICHTER (11) & (12).

The pulverised blende is dissolved in a mixture of nitric and hydrochloric acids and lead, copper, cadmium, arsenic, tin and molybdenum precipitated by means of hydrogen sulphide in acid solution.

The filtrate is oxidised and ammonia added in excess, whereby most of the zinc remains in solution.

The ferric hydroxide precipitate is dissolved in acetic acid and indium sulphide precipitated by bubbling in hydrogen sulphide.

The sulphide is dissolved in hydrochloric acid, the solution oxidised with nitric acid and indium precipitated as hydroxide with ammonia.

This last process is repeated a few times to remove the last traces of zinc.

The hydroxide is dissolved in acetic acid and the sulphide precipitated with hydrogen sulphide.

This sulphide is dissolved in hydrochloric acid, the solution oxidised with nitric acid and indium reprecipitated with ammonia or sodium carbonate.

(e) EARLY METHOD DEVELOPED BY C. WINKLER. (13).

The roasted blende is dissolved in hydrochloric acid and indium, together with certain other elements, precipitated by means of metallic zinc.

The metallic sponge is dissolved in a mixture of nitric and hydrochloric acids and hydrogen sulphide bubbled into the solution.

The sulphides are filtered off and the filtrate freed from hydrogen sulphide.

Sodium sulphite is added to reduce ferric to ferrous iron and barium carbonate added in an atmosphere of carbon dioxide.

Iron remains in solution, whilst indium, together with excess barium carbonate, is found in the precipitate.

This precipitate is treated with dilute dulphuric acid and barium removed as sulphate.

The filtrate is treated with ammonia and indium hydroxide precipitated.

This is converted to oxide.

(f) METHOD USED BY R. E. LAWRENCE AND L. R. WESTBROOK.(8).

The blende or process residue is digested with dilute sulphuric acid. Insoluble silica, gangue, and lead sulphate are filtered off and zinc shavings added to the filtrate until all the iron has been reduced and practically all the free acid neutralised.

The precipitated metals, with the excess zinc, are dissolved in dilute nitric acid and ammonia added in excess, together with ammonium chloride.

The whole is boiled until only faintly ammoniacal, filtered and the precipitate dissolved in dilute hydrochloric acid.

The ammonia treatment is repeated, the hydroxides dissolved in hydrochloric acid, the acidity adjusted to 2N and hydrogen sulphide bubbled in.

The sulphides are filtered off, hydrogen sulphide removed from the filtrate, potassium hydroxide added in excess and the whole boiled.

The hydroxide precipitate is dissolved in acetic acid, ammonium acetate added and indium precipitated as sulphide with hydrogen sulphide.

This sulphide is dissolved in hydrochloric acid and reprecipitated as hydroxide as before.

The final precipitate of indium hydroxide is then ignited to indium sesquioxide at 700°C. and the purity of the oxide determined spectrographically.

COMMENTS ON ABOVE METHODS.

METHOD (a):

(1) The basic reaction is the precipitation of indium by means of zinc and as stated on page 1 , this method is open to slight loss of indium, which loss, might be relatively appreciable, when the indium is present in small proportions.

Impure zinc may contain indium in greater or lesser proportions and this may give rise to the introduction of extraneous indium.

This difficulty is obviously overcome by running a blank test on the zinc, but this introduces another process.

In this particular method, the zinc precipitation is repeated.

With a view to quantitatively investigating this zinc displacement method, the follwwing recoveries were made.

Five lots of 50 Grams each of zinc chloride were dissolved in 300 ml. water and varying proportions of 1.18.S.G. - G.R. hydrochloric acid added to each.

0.0050 Gram of indium (as chloride) was added to each and then metallic zinc, according to the table below.

The zinc used, was neither chemically pure nor commercial quality, but ordinary laboratory pure zinc.

The metal was of fairly thin gauge and presented a fair surface area.

It was specially chosen from a kilogram lot of granulated zinc.

The following table gives the details of weights of zinc and volumes of acid:-

TABLE 1.

Test.	Wt. of Zinc.	Vol. of Acid.
1	20 Grams.	70 ml.
2	15 "	50 "
3	10 "	35 "
4	10 "	35 "
5	5 "	20 "

The solutions were brought to the boil and allowed to simmer, until the volume was reduced to about 50 ml.

Water was then added to bring the volume back to 300 ml.

This procedure was carried out over two complete days, in order to precipitate as much indium as possible under the conditions.

Finally, the solutions were filtered in the presence of residual zinc and the residues dissolved in 5N. hydrochloric acid.

Ammonia was then added in moderate excess and the solutions allowed to simmer until they were only faintly ammoniacal.

The indium hydroxide was filtered off, washed and then dissolved in 5N. hydrochloric acid.

This ammonia precipitation was repeated another three times in order to remove all zinc and the final indium hydroxide ignited to oxide at 800°C.

Following ar e the results:-

TABLE 2.

Test.	In. Added.	In. Recovered.
1	0.0050 Gram.	0.0030 Gram.
2	"	0.0038 "
3	"	0.0036 "
4	"	0.0039 "
5	"	0.0025 "

Another two recoveries by means of displacement were made, but in these cases, a higher concentration of acid was used, resulting in a more vigorous evolution of hydrogen and the reactions were allowed to proceed for six hours.

Excess Zinc was present during the filtration.

These recoveries were:-

TABLE 3.

Test.	In. Added.	In. Recovered.
1	0.0050 Gram.	0.0010 Gram.
2	" "	0.0018 "

The above seven results are certainly very unsatisfactory from a quantitative aspect.

It is quite feasible that better recoveries are possible, using the zinc displacement method, but the above data indicate that there is always a grave danger of loss.

A more vigorously reacting zinc may give better results, but, vigorously reacting zinc is usually impure and may introduce extraneous indium.

Copper is frequently present in sphalerites and smithsonites and this would give rise to a superficial zinc - copper couple, which, would result in a continuous, fairly vigorous reaction and in this case, the recovery might be noticeably better.

The data in tables 2 and 3 are sufficient, however, to demonstrate the errors to which this type of analytical method is subject.

(2) Tin is removed as metastannic acid.

If the tin percentage is considerably greater than the indium, there is a distinct danger of loss of indium through adsorption.

Metastannic acid is highly adsorptive.

If antimony were present, the same would apply to this element.

(3) Indium is precipitated as sulphide from a hydrochloric acid solution, in which the normality is less than .05N.

In quantitative work, one has to be very careful in adjusting the acidity when precipitating indium as sulphide from mineral acid solutions.

It appears as if the acidity should be controlled to within .03 - .05N, otherwise there is danger of loss of indium with higher normality, or of the inclusion of other sulphides with lower normality.

With acetic acid solutions, on the other hand, there is a much greater range of normality, in which indium sulphide is quantitatively precipitated and in which many other elements remain in solution, (19), (20), (21). (See also "Recovery of indium in presence of zinc by hydrogen sulphide treatment in different acetic acid concentrations" - Pages20-21).

Moreover, when the indium percentage is low, it is advisable to have an adsorptive medium, such as zinc sulphide, at this stage, otherwise, there is danger of loss of indium.

(4) The zinc displacement has an obvious advantage in so far as the major portion of the iron is removed in solution.

METHOD (b):

The remarks appearing under "Method (a) (1)", pages 6 - 8 also apply here.

SECTION 2.

IMPORTANT REACTIONS UNDERLYING THE ANALYTICAL METHOD DEVELOPED IN THIS RESEARCH.

(a) The quantitative precipitation of indium hydroxide, by means of ammonia. (22), (23), (24), (25), (26).

Although much work has been done on this fundamental reaction, it was considered advisable to gain experience, by carrying out qualitative and quantitative work on the hydroxide precipitation by means of ammonia.

The quantitative results are recorded in Section 4. Page 44 - 45.

(b) The quantitative precipitation of indium sulphide from acetic acid solution, by means of hydrogen sulphide (26), (27), (28), (29).

For the quantitative recovery of indium through indium sulphide in the presence of zinc, using different concentrations of acetic acid, see Section 4. Pages 20 - 21.

(c) The quantitative precipitation of indium hydroxide, by means of sodium hydroxide. (28), (30).

Recoveries of indium, using sodium hydroxide in different concentrations, are shown on page 35-36 Section 4.

(d) The quantitative adsorption of indium hydroxide by ferric hydroxide in relatively high concentrations of ammonia.

See Section 4., Pages 26/27 for recovery data.

(e) The inhibition of the precipitation of ferric hydroxide by means of Tartrate Ion.

(f) The solubility of indium sulphate in water and dilute sulphuric acid. (31), (32).

(g) The solubility of indium sulphide in weak mineral acid. (28), (33).

See also "Recovery of indium in the presence of moderate proportions of Bismuth", Section 4., Pages 42 - 43.

(h) The quantitative conversion of indium hydroxide to indium sesquioxide on ignition. (22), (23), (34), (35), (36).

SECTION 3.

OUTLINE OF THE ANALYTICAL SCHEME.

The group scheme presented below is an outline of the analytical method evolved, as a result of considerable qualitative work and also as a result of the quantitative recoveries shown throughout Sections 4. and 5.

The scheme is shown in group form, mainly in order to simplify the setting out of Section 4, which deals with each group separately and also to clarify Section 7., which presents the whole scheme in diagrammatic form.

The precise analytical and manipulative details are not given here, but are described later in Section 8.

GROUP 1.

Dissolve the finely crushed ore in concentrated hydrochloric acid, followed by a minimum of nitric acid.

Dilute, if necessary, to about 250 ml., allow to settle and filter, preferably through pulp.

GROUP 2.

Add a strong solution of sodium hydroxide to the filtrate from Group 1, until a slight permanent precipitate remains.

Then add ammonia in excess until nearly all the zinc hydroxide dissolves. (It is desirable at this stage to leave a comparatively small proportion of the zinc hydroxide undissolved).

The whole is filtered and without washing, the precipitate is dissolved from the filter paper with hot dilute hydrochloric acid, the filtrate being caught in the original precipitation beaker.

In certain instances, it is necessary to repeat this precipitation and solution in acid.

If the iron percentage in the ore is very low, ferric chloride should be added just before proceeding with this group separation, in order to bring up the weight of iron to about 0.5 Gram.

GROUP 3.

Add 4 - 10 grams of tartaric acid to the final solution obtained in Group 2. and then ammonia, until the solution is very faintly ammoniacal.

Then add strong acetic acid until the solution is approximately 1.5N, warm to 70 - 80°C and bubble hydrogen sulphide for 15 - 20 minutes.

Sufficient zinc sulphide must be present at this stage for purposes of adsorption.

If insufficient zinc sulphide is present, add slightly acidic zinc acetate solution drop by drop, with constant agitation, until sufficient zinc sulphide has been formed for satisfactory adsorption.

It is advisable to have between 0.2 and 0.5 gram Zinc sulphide in approximately 250 ml. of solution at this stage.

Allow to settle and filter.

Wash a few times with hot water and then dissolve the precipitate in hot, dilute hydrochloric acid, catching the solution in the precipitation container.

Remove the hydrogen sulphide by boiling and finally with a few drops of nitric acid, neutralise with ammonia, add very small excess of ammonia and then acetic acid until 1.5N.

Repeat the hydrogen sulphide bubbling, settling, filtering and solution in hydrochloric acid, as stated above.

If much iron is present, three hydrogen sulphide treatments may be necessary.

In the final precipitation the sulphides must be thoroughly washed in order to remove all traces of tartaric acid.

The final sulphide precipitate is dissolved in hot, dilute hydrochloric acid, the solution freed from hydrogen sulphide, a few drops of nitric acid added and then evaporated down to about 50 ml.

GROUP 4.

Neutralise the solution obtained from Group 3. with ammonia and add a slight excess.

Boil for a short time, filter, wash a few times and dissolve in hot, dilute nitric acid.

GROUP 5.

Add sulphuric acid to the solution obtained from Group 4, and evaporate down to fumes.

Cool, dilute, filter and wash thoroughly.

GROUP 6.

Add sodium hydroxide solution in slight excess to the filtrate from Group 5, and boil for a few minutes.

Filter and wash a few times and dissolve in hot, dilute hydrochloric acid.

GROUP 7.

(a) Neutralise the solution obtained from Group 6, with Sodium Hydroxide and then add hydrochloric acid intil the acidity is 0.5N.

Warm and bubble in hydrogen sulphide for a few minutes.

If no precipitate forms, boil off hydrogen sulphide, oxidise with nitric acid and pass on to 7 b.

If a precipitate forms, filter, wash thoroughly, remove hydrogen sulphide from filtrate, neutralise with sodium hydroxide solution and add hydrochloric acid until 0.5N.

Bubble in hydrogen sulphide for a few minutes and refilter and wash.

Remove hydrogen sulphide from filtrate, oxidise with nitric acid and pass on to 7 b.

(b) Neutralise solution with sodium hydroxide solution and add slight excess.

Boil for a few minutes, filter and wash.

Dissolve precipitate in hot, dilute nitric acid or hydrochloric acid.

GROUP 8.

Add ammonia in slight excess to the solution obtained from Group 7, and boil for a few minutes.

Filter through ashless paper, wash thoroughly, dry and ignite to the oxide.

BRIEF TABULATION OF ANALYTICAL SCHEME.

TABLE 4.

Group.	Treatment.	Indium found in.
1.	Ore dissolved in HCL with minimum HNO_3, diluted and filtered.	Filtrate
2.	$FeCl_3$, added, if necessary, followed by NaOH and then NH_4OH in excess.	Precipitate
3.	$H\bar{T}$, followed by NH_4OH, followed by $H\bar{A}$, followed by H_2S.	Precipitate
4.	NH_4OH in faint excess.	Precipitate
5.	Concentrating with H_2SO_4 to fumes, diluting and filtering.	Filtrate
6.	Na OH in slight excess.	Precipitate
7.	(a) Na OH to neutralise, followed by HCl in moderate excess and then H_2S.	Filtrate (a)
	(b) Na OH in slight excess to oxidised filtrate.	Precipitate (b)
8.	NH_4OH in faint excess.	Precipitate.

SECTION 4.

QUALITATIVE AND QUANTITATIVE SIGNIFICANCE OF THE DIFFERENT ANALYTICAL GROUPS OR STAGES DESCRIBED IN SECTION 3.

In this section, the different groups will be treated separately, and in each case, brief mention will be made of the elements eliminated and this will be followed by a detailed description, including recovery tables, of the quantitative recoveries of indium in the presence of the more important elements, which are eliminated in the particular group under consideration.

In the case of Group 3, a detailed record of qualitative work is also included.

The analytical method detailed in Section 6, together with the group outline in Section 3, was elaborated as a result of the work recorded in this section and in Section 5.

GROUP 1.

In this group, free quartz, gangue matter, and refractory silicates are removed.

Most of the silver is removed here and much of the lead is eliminated as chloride.

Most of the arsenic and germanium are volatilised and the greater portion of selenium and tellurium removed.

Indium remains in solution as the trichloride.

GROUP 2.

In this group, nearly all copper, Cadmium, Nickel, Cobalt, magnesium and alkaline earths are eliminated.

Much manganese and the greater portion of the zinc are also eliminated.

Residual Silver from Group 1 will be removed here.

Indium remains in the precipitate.

QUANTITATIVE WORK.

The main function of this group separation, is the removal of the major portion of the zinc, which is obviously always present in relatively large proportions when dealing with Sphalerites or Smithsonites.

The method finally adopted was, the addition of ferric chloride, if necessary, the neutralisation of most of the acidity from Group 1, with sodium hydroxide, followed by the addition of an appreciable excess of ammonia.

This was developed in the following stages:-

(1) Neutralisation with ammonia only, followed by an appreciable excess of that reagent.

(2) Neutralisation of the greater portion of the acidity with ammonia, followed by complete neutralisation with potassium cyanate in excess.

(3) Neutralisation of the greater portion of the acidity with sodium hydroxide, followed by complete neutralisation with potassium cyanate, followed by the addition of ammonia in excess to bring most of the zinc in solution.

(4) The addition of ferric chloride, followed by the procedure described under (3) above.

(5) The addition of ferric chloride followed by the addition of sodium hydroxide, until the solution is almost neutralised, followed by the addition of ammonia in appreciable excess.

Here, the cyanate hydrolysis was excluded.

RECOVERIES.

(a) RECOVERY OF INDIUM IN PRESENCE OF COMPARATIVELY LARGE PROPORTIONS OF ZINC, BY MEANS OF AMMONIA PRECIPITATION.

Four lots of 50 grams each of zinc (all the metallic zinc used throughout the work recorded in this section was G. R. purity), were dissolved in pure hydrochloric acid and 20 ml. of standard indium chloride solution (0.0214 gram of indium) added to each.

This represents approximately one part of indium in 2,400 parts of zinc, or the equivalent of one part of indium in 3,600 parts of zinc sulphide.

This proportion is found in high grade indiferous sphalerites.

Considerable quantities of ammonium chloride (sufficient to keep the zinc in solution) were added and then ammonia in fair excess.

The whole was brought to the boil and allowed to simmer for about one hour.

The indium hydroxide was at first manifested by an opalescence, which later flocculated.

Each lot was filtered through two 15 cm. filter papers.

The zinc complex and indium hydroxide remaining in the beaker, were dissolved in 5N. hydrochloric acid, the solution transferred to a 250 ml. beaker, ammonia added in moderate excess and the whole boiled.

The precipitate was quantitatively added to the original precipitates and the whole dissolved in hot 5N. hydrochloric acid, the solutions being caught in 250 ml. beakers.

The indium was reprecipitated with ammonia and the hydroxide filtered through 11 cm. filter papers.

This procedure was repeated another twice and filtered finally through a 9 cm. ashless filter paper.

After washing with water and drying, the hydroxide was ignited at about 800°C.

(For quantitative results in connection with the precipitation of indium hydroxide by means of ammonia, and ignition to the oxide, see page 44/45 and also refer to (21), (22), and (23).

The results were:-

TABLE 5.

Test.	In. Added.	In. Recovered.
1.	0.0214 grm.	0.0087 grm.
2.	" "	0.0080 "
3.	" "	0.0025 "
4.	" "	0.0044 "

This is obviously very unsatisfactory.

This method of estimating indium is very satisfactory in the presence of small and moderate proportions of zinc, but as outlined above, not quantitative in the presence of large proportions of zinc, such as is the case with solutions of zinc ores.

The next stage in the development of the quantitative aspect of Group 2, was the precipitation of indium by means of Potassium Cyanate.

(b) RECOVERY OF INDIUM IN PRESENCE OF COMPARATIVELY LARGE PROPORTIONS OF ZINC BY MEANS OF CYANATE HYDROLYSIS. (21), (22) and (25).

Four lots of 50 grams each of zinc were dissolved in hydrochloric acid and 0.0214 gram Indium (as chloride) added to each.

The acidic solution was neutralised with ammonia, using methyl orange as indicator, and then made faintly acidic with hydrochloric acid.

A freshly prepared 10% solution of potassium cyanate was then added, until the indicator showed alkaline and the whole brought to the boil and allowed to simmer for about half an hour.

On allowing to stand, a distinct granular precipitate settled.

This was filtered off and dissolved in 5N. hydrochloric acid.

The filtrate was again treated with potassium cyanate and refiltered.

This precipitate, which was very slight in two cases and hardly noticeable in the other two, was filtered off, dissolved in 5N. hydrochloric acid and the solution added to the main solution.

Indium hydroxide was precipitated by means of ammonia and the hydroxide ignited to oxide.

The Results were:-

TABLE 6.

Test.	In. Added.	In. Recovered.
1.	0.0214 Grm.	0.0101 Grm.
2.	" "	0.0084 "
3.	" "	0.0085 "
4.	" "	0.0025 "

As these results are very variable and unsatisfactory, a second series of recoveries, making use of the same cyanate method, was carried out.

These results were:-

TABLE 7.

Test.	In. Added.	In. Recovered.
1.	0.0214 grm.	0.0112 grm.
2.	" "	0.0078 "
3.	" "	0.0098 "
4.	" "	0.0059 "

These are again very unsatisfactory.

It appears as if the cyanate hydrolysis method is not quantitative under these conditions of a high proportion of zinc.

It seems feasible, moreover, that in method (a) above, indium was lost owing to its low concentration in the absence of a satisfactory adsorptive medium.

This argument may also apply to the cyanate method.

With this in view, it was decided to adopt another method of neutralisation and precipitation.

(c) RECOVERY OF INDIUM IN PRESENCE OF COMPARATIVELY LARGE PROPORTIONS OF ZINC BY MEANS OF SODIUM HYDROXIDE NEUTRALISATION AND CYANATE HYDROLYSIS.

Six lots of 50 grms. each of zinc were dissolved in hydrochloric acid and 0.0214 gram Indium (as chloride) added to each.

200 ml. of concentrated acid were used for dissolving the zinc and 200 ml. of water were added after solution.

Methyl orange was added as indicator.

A strong solution of sodium hydroxide (30-40%) was added little by little with constant agitation, until the indicator just changed.

At this stage, a fair amount of flocculated zinc hydroxide was present.

Hydrochloric acid was then added until, on shaking, the pinkish methyl orange colour did not change back to yellow.

Care was taken at this juncture, to have only a very slight excess of acid.

The whole was then warmed and solid potassium cyanate (about 2 grams at a time) was added with vigorous agitation, until the solution reacted alkaline.

About 20 grams of potassium cyanate were necessary to effect this change.

At this stage, a distinct opalescence was observed and on boiling for about a quarter of an hour, some zinc hydroxide settled out.

The beaker was then removed from the source of heat and allowed to cool for about a quarter of an hour.

During this period, more zinc hydroxide precipitated.

Ammonia was then added until most, but by no means all, of the zinc hydroxide had dissolved.

The whole was then filtered as quickly as possible, using two filters for each lot.

When the beakers were empty, about 40 - 50 ml. of a slightly ammoniacal ammonium chloride solution was added and the whole boiled for a few minutes.

This was then filtered through the original filters.

The precipitate on the filters was not washed, but dissolved by pouring hot 5N. hydrochloric acid directly onto the precipitates on the filters and catching the solutions in 500 ml. conical beakers.

The original precipitation beakers were washed with about 30 ml. of hot 5N. hydrochloric acid, the resulting solutions being added to the 500 ml. beakers containing the main solutions.

The solutions were concentrated to about 100 ml., cooled, and ammonia added in moderate excess and the whole boiled for a short time.

The hydroxide was filtered off, washed a few times and then dissolved by pouring hot 5N. hydrochloric acid on to the precipitate on the filter and catching the solution in the precipitation beakers.

Indium hydroxide was again precipitated by means of ammonia and filtered through ashless filters.

The hydroxide was ignited to oxide in the usual way.

The final oxide ash was contaminated with ferric oxide.

This was determined colorimetrically as ferric thiocyanate, the indium oxide being calculated by difference.

The results were:-

TABLE 8.

Test.	wt. of Fe_2O_3 and In_2O_3.	wt. of Fe_2O_3.	wt. of In_2O_3.	In. Recov.	In. Added
1.	0.0271 grm.	0.0017 grm.	0.0254 grm.	0.0210 grm.	0.0214g
2.	0.0269 "	0.0014 "	0.0255 "	0.0211 "	" "
3.	0.0299 "	0.0042 "	0.0257 "	0.0212 "	" "
4.	0.0307 "	0.0042 "	0.0265 "	0.0219 "	" "
5.	0.0290 "	0.0032 "	0.0258 "	0.0213 "	" "

Average Indium Recovered = 0.0213 grm.
Indium Added = 0.0214 "

These results are quite satisfactory and indicate that the sodium hydroxide - potassium cyanate - ammonia method is quantitatively sound.

At this stage, it appeared as if the presence of a certain amount of undissolved zinc hydroxide, just prior to filtration may have been an essential condition for quantitative precipitation and adsorption of indium hydroxide.

Considering that the great majority of sphalerites contain iron, the ordinary varieties containing from about 0.2% to 4.0% and the ferruginous sphalerites or marmatites containing 10% and over (37), it was imperative to ascertain the quantitative nature of Group 2 in the presence of moderate proportions of Iron.

As iron is removed in Group 3, the recovery of indium in the presence of iron and zinc will be dealt with under that heading below.

For recovery of indium in presence of cadmium, nickel, cobalt, magnesium, manganese, calcium, barium and strontium, see Section 5 - Page 46 - 49.

GROUP 3.

In this group, Iron, Aluminium, Chromium, Manganese, Gallium, Tungsten, Beryllium, Vanadium, Uranium, Thorium, Zirconium, Rare Earths, Phosphate, Fluoride and Borate are removed in the filtrate from the hydrogen sulphide treatment.

It must be borne in mind, that this group is invariably duplicated in practice, i.e., the hydrogen sulphide treatment in acetic solution is always carried out at least twice.

The small proportion of any of these elements remaining in the precipitate (after washing) by adsorption, will be completely removed in the second process.

It might appear incautious to state that after two hydrogen sulphide treatments, these elements (or radicals) are "completely" removed, but, one must realise, that, with the exception of iron and manganese and possibly aluminium, the solution obtained by dissolving a typical zinc ore in acid, will contain very small proportions of these elements.

Residual manganese, moreover, is eliminated in Group 4 and aluminium in Group 6.

Residual iron is ignited with the indium and estimated colorimetrically.

On dissolving the precipitate from the hydrogen sulphide treatment in 6N. hydrochloric acid, almost all mercury, arsenic, molybdenum, platinum, palladium and gold remain undissolved.

Also, residual (from previous groups) magnesium, calcium, barium, strontium, lithium, selenium and tellurium will be removed in this group.

QUANTITATIVE WORK.

The main function of this group is the removal of iron.

Besides this important function, the Group 3 separation eliminates more elements than any other group separation.

The quantitative work in this group has been divided up as follows:-

(1) Influence of increase in acetic acid concentration on the quantitative precipitation of indium sulphide.

(2) Recovery of indium in the presence of iron.

(3) Recovery of indium in the presence of iron, omitting the cyanate hydrolysis in Group 2.

(4) Recovery of indium in the presence of iron and aluminium.

(5) Recovery of indium in the presence of rare earths.

(6) Recovery of indium in the presence of iron and manganese.

Special mention is also made of certain important qualitative reactions.

(a) RECOVERY OF INDIUM IN THE PRESENCE OF ZINC BY HYDROGEN SULPHIDE TREATMENT IN DIFFERENT ACETIC ACID CONCENTRATIONS. (20),(28),(29),(38).

The higher the acetic acid concentration, the more efficacious is the scheme of elimination in this particular group.

Furthermore, zinc sulphide is precipitated in a more filtrable form from strongly acetic solutions than from weakly acetic.

Qualitatively, 10% (approximately 1.6N.) acetic acid solutions gave a zinc sulphide, which was easily filtrable.

In this particular quantitative work, 5%, 10% and 20% acetic solutions were investigated.

Six lots, each containing 0.25 gram Zinc and 0.0051 gram Indium (as chlorides) were prepared and then made acetic, two with a concentration of 5%, two 10% and two 20% (approximately 0.8N, 1.6N and 3.3N. respectively).

The solutions were warmed to 70°C and hydrogen sulphide bubbled for twenty minutes.

The sulphides were allowed to settle for ten minutes and then filtered and washed with hot water.

The sulphides were then dissolved by pouring hot 5N. hydrochloric acid onto the filters and catching the filtrates in the precipitation beakers.

Hydrogen sulphide was destroyed in the solutions and indium hydroxide precipitated with ammonia.

This ammonia precipitation was made three times in all, the final hydroxides being ignited to oxides and weighed.

The results were:-

TABLE 9.

Test.	Acetic Acid Concentration.	In. Added.	In. Recovered.
1.	0.8N.	0.0051 grm.	0.0049 grm.
2.	0.8N.	" "	0.0050 "
3.	1.6N.	" "	0.0053 "
4.	1.6N	" "	0.0053 "
5.	3.3N.	" "	0.0044 "
6.	3.3N.	" "	0.0047 "

The 0.8N. and 1.6N. concentrations gave satisfactory results, although the 3.3N. shows signs of loss of Indium.

As a result of these recoveries, it was decided to adhere to an approximately 1.5N. concentration of acetic acid.

0.25 gram of zinc was chosen, because this is quite a usual weight of zinc remaining after the Group 2 separation.

(b) RECOVERY OF INDIUM IN THE PRESENCE OF IRON.

Considering that zinc blendes are usually fairly rich in iron, it is obvious that iron should be eliminated in solution and not as a precipitate.

The following methods of separating iron from indium have been described:-

(1) L. MOSER AND F. SIEGMENN (39).

Hydrogen sulphide is bubbled into a 0.03 - 0.05N. hydrochloric acid solution. Iron remains in solution and indium sulphide is precipitated.

Great care must be exercised here, otherwise, with a slight increase in acidity, small amounts of indium sulphide will not be quantitatively precipitated.

A very much greater concentration of acetic acid may be used with quantitative results.

Moreover, using hydrochloric acid, there will be very little, if any, precipitation of zinc sulphide and hence, there will be little or no adsorbent sulphide medium for adsorption of indium sulphide, which is necessary when the indium percentage is low. See also (41).

(2) F.C. MATHERS. (40).

The iron is precipitated from strong acetic acid solution with α Nitroso - B. Naphthol.

This method is obviously suitable for small amounts of iron and not for the comparatively large amounts found in typical sphalerites.

There is likely to be a serious loss of indium by adsorption.

(3) F.C. MATHERS AND C.E. PRICHARD (42).

The iron is precipitated with ammoniumnitrosophenylhydroxylamine (cupferron).

This method is only applicable to small amounts of iron.

(4) R.E. MEYER. (43).

This method depends on the formation of potassium ferrocyanide from potassium cyanide, but is not recommended by Sinecke(41).

(5) L.M. DENNIS AND W.C. GEER. (44).

This method depends upon the solubility of Ferric Thiocyanate in ether.

Indium thiocyanate is, however, not completely insoluble in ether and when dealing with small amounts of this element, there may be relatively serious losses. Sinecke (41) points out this disadvantage.

(6) K. J. BAYER. (45).

Indium is precipitated with Sodium hydrosulphide.

According to Mathers (40) and Thiel (46), this method is impracticable.

(7) A.A. Noyes and W. C. Bray (81).

This method depends on the solubility of an hydrochloric acid solution of ferric chloride in ether and the insolubility of a similar solution of indium chloride.

On thoroughly shaking the mixed chlorides with ether, practically all of the indium chloride remains in the aqueous layer and the ferric chloride passes into the ethereal layer.

It is very doubtful, however, whether two or three of these extractions would quantitatively separate the iron from the indium.

Moreover, a separation of this type is inapplicable in this particular analytical scheme.

The most satisfactory way of eliminating iron in solution and not as a precipitate is to treat an acidic solution of iron with hydrogen sulphide.

The iron solution should be faintly acidic with hydrochloric acid (0.03 - 0.05N.) (39), or moderately acidic with acetic acid (approximately 1.5N.) for the removal of iron and the quantitative precipitation of indium sulphide.

The hydrochloric acidity has to be very carefully controlled for quantitative precipitation of indium as sulphide, hence, in this group 3 separation, acetic acid was chosen.

In the presence of large quantities of iron, there is the danger of the precipitation of the basic acetate of iron.

This difficulty however, is overcome by the addition of tartaric acid to the hydrochloric acid solution obtained from Group 2, just prior to neutralising with ammonia and adding acetic acid for the Group 3 precipitation.

In the presence of sufficient tartrate, iron remains in solution, under both acidic and ammoniacal conditions.

The actual procedure adopted for recovering indium in the presence of iron, was as follows:-

3 Grams of ferric chloride were dissolved in dilute hydrochloric acid and 0.0204 grm. indium (as chloride) added.

About 5 grams of tartaric acid were then added and the whole just neutralised with ammonia. (The volume at this stage was approximately 150 ml.)

17 ml. of strong acetic acid were added, the solution warmed to 70°C. and hydrogen sulphide bubbled in for twenty minutes.

The indium sulphide was allowed to settle for about ten minutes and then filtered and washed.

The sulphide was dissolved by adding hot 5N. hydrochloric acid to the precipitate on the filter and catching the solution in the precipitation beaker.

The solution was boiled to remove hydrogen sulphide and then oxidised with a few drops of nitric acid. One gram of Tartaric acid was added to this solution and then ammonia until very faintly ammoniacal.

(The volume of the solution at this stage was 150 ml.)

17 ml. of strong acetic acid were added, the solution warmed to 70°C and hydrogen sulphide again bubbled in for twenty minutes.

This sulphide was filtered and thoroughly washed.

It is very essential at this point to wash thoroughly, so as to remove the tartrate.

The sulphide was dissolved in hot 5N. hydrochloric acid, hydrogen sulphide removed by boiling and oxidation with nitric acid and indium hydroxide precipitated by ammonia in the usual way.

The hydroxide was converted to oxide and weighed.

The following recoveries were recorded:-

TABLE 10.

Test.	In. Added.	In. Recovered.
1.	0.0204 grm.	0.0204 grm.
2.	" "	0.0207 "
3.	" "	0.0204 "
4.	" "	0.0203 "

Average recovered - 0.0205.
Added - 0.0204.

The data in the "In. Recovered" column were calculated after deducting Fe_2O_3, which was estimated colorimetrically. The Fe_2O_3 was very low, being 0.15, 0.10, 0.15 and 0.20 mgrm. in tests 1, 2, 3 and 4 respectively.

These results indicate that the tartaric - acetic scheme for removing iron is very satisfactory and that indium is quantitatively precipitated as sulphide.

(c) RECOVERY OF INDIUM IN PRESENCE OF LARGE PROPORTIONS OF ZINC AND MODERATE PROPORTIONS OF IRON.

(1) 34 Grams of zinc were dissolved in hydrochloric acid and 3 grams of ferric chloride and 0.00204 gram indium (as chloride) added. This was done in quadruplicate.

It will be noted that this mixture approximates to a 50 gram sample of sphalerite, containing 0.004% of indium and a typical proportion of iron.

This mixture was treated in the standard way as described under Group 2 (pages 17/18) with sodium hydroxide - potassium cyanate - ammonia and the final hydrochloric acid solution treated according to the Group 3 method described on page 11 - 12.

After removing most of the zinc by Group 2 and iron by Group 3, indium was precipitated three times by ammonia and finally, the hydroxide ignited to oxide.

Just prior to the hydroxide precipitation, pairs of solutions were combined, so that two lots, each containing 0.0041 grm. indium, were dealt with.

The Results were;-

TABLE 11.

Test.	In. Added.	In. Recovered.o
1.	0.0061 grm.	0.0060 grm.
2.	" "	0.0060 "

o After deducting the iron.

(2) Two series of recoveries were made previous to the one just described, but, in each case, during the Group 2 treatment ammonia was added in sufficient excess to dissolve all the zinc hydroxide.

It will be noted that in the description of this portion of Group 2 (page 11), it is emphasised that some zinc hydroxide must remain undissolved.

The mixtures analysed contained each:-

Zinc - 20 grms.
Ferric Chloride - 3 "
Indium - 0.0061 grm.

In Group 3, it was observed that only a slight precipitate formed.

The indium was estimated in the usual way and the recoveries were:-

TABLE 12.

Test.	In. Added.	In. Recovered.
1.	0.0061 grm.	0.0060 grm.
2.	" "	0.0060 "
3.	0.0061 "	0.0056 "

It seems very feasible, that indium was lost in Group 3, owing to a deficiency of zinc sulphide. (The concentration of indium was only 1 in 40,000 in this group).

Although the ammonia concentration was high in Group 2, indium should not have been lost there, by virtue of the comparatively large proportion of ferric hydroxide functioning as an adsorbing medium. In the work done on the recovery of indium in the presence of iron, but in the absence of zinc, very good results were recorded, but, there, the weight of indium was noticeably greater (0.0005 grm against 0.0061 grm) and the concentration of indium just prior to bubbling hydrogen sulphide 1 in 6,000 (8 times stronger).

It would appear therefore, that a fair weight of zinc should be present in Group 3, especially when the weight of indium is less than, say 0.01 grm, and in the absence of other adsorbing media, such as lead sulphide, bismuth sulphide, etc.

(3) Another three recoveries were made, using in each case 25 grms. of zinc, 3 grams ferric chloride and 0.0061 grm indium.

The usual Group 2 and 3 procedure was adopted, except that two Group 2 separations were made instead of one and that zinc acetate (prepared from metallic zinc) was added in sufficient quantity in Group 3 to give a satisfactory proportion of sulphide for adsorption. Three ammonia precipitations were made.

The recovery was as follows:-

TABLE 13.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram	0.0051 gram
2.	" "	0.0050 "
3.	" "	0.0051 "

Average Indium recovered = 0.0051 gram
Indium Added = 0.0051 gram

Considering that <u>two</u> precipitations were made in Group 2, the above results appear to confirm the inference drawn in the last series of recoveries (C (2) - Page 24), i.e., that the loss was due to the Group 3 procedure and not to the Group 2 separation.

(4) At this stage, the following question naturally suggests itself, i.e.,

Is not the Group 2 separation scheme quantitatively sound in the <u>absence</u> of Potassium Cyanate, but in the presence of sufficient Ferric Hydroxide, functioning as an adsorbent?

This question is dealt with here because iron is removed in Group 3.

With this question in view, five lots were prepared, each containing 25 grams of zinc, 3 grams ferric chloride (approx. 1 gram iron) and 0.0051 gram indium.

The procedure was similar to that described under Group 2 (c), (Page 17), except that sodium hydroxide was added until there was a slight permanent precipitate of zinc hydroxide (no indicator was included) and that this was followed almost immediately by the addition of ammonia, until only a slight precipitate of zinc hydroxide remained.

The cyanate hydrolysis was omitted.

The Group 2 scheme was repeated, Group 3 separation carried out twice (with addition of approximately 0.2 grm. of zinc as zinc acetate) and then finally, three ammonia separations made.

The results were:-

TABLE 14.

Test.	In. Added.	In. Recovered.
1.	0.0051 grm.	0.0053 grm.
2.	" "	0.0053 "
3.	" "	0.0050 "
4.	" "	0.0049 "
5.	" "	0.0053 "

Average Indium recovered = 0.0052 grm.
Indium added = 0.0051 grm.

These results are very pleasing and clearly indicate that the analytical scheme is quantitatively perfect in the <u>absence</u> of the cyanate hydrolysis, provided, ferric hydroxide is present as an adsorbent.

(d) RECOVERY OF INDIUM IN PRESENCE OF LARGE PROPORTIONS OF ZINC AND VARYING PROPORTIONS OF IRON.

The last series of recoveries clearly show that indium is quantitatively precipitated from comparatively large proportions of zinc, in the presence of ferric hydroxide, as adsorbent.

These recoveries were made in the presence of 1 gram of iron.

It was considered advisable, however, to carry out a further series of recoveries, using smaller proportions of iron.

By these means, a minimum weight of iron may be found for the satisfactory quantitative recovery of indium, in the presence of large proportions of zinc.

The following mixtures were prepared:-

(1) Zinc ..... - 25 grams.
Iron (as ferric chloride) - 1.0 grams.
Indium ..... - 0.0050 gram.

(2) Zinc ..... - 25 grams.
Iron ..... - 0.40 gram.
Indium ..... - 0.0050 gram.

(3) Zinc ..... - 25 grams.
Iron ..... - 0.10 gram.
Indium ..... - 0.0050 gram.

(4) Zinc ..... - 25 grams.
Iron ..... - 0.04 gram.
Indium ..... - 0.0050 gram.

The analytical procedure was the same as in the last series of recoveries, except that the Group 2 separation was made once and as a result of this, no zinc acetate was added in Group 3.

Three ammonia separations were made.

The results were as follows:-

TABLE 15.

Test.	Fe. Present.	In. Added.	In. Recovered.
1.	1.0 gram.	0.0050 grm.	0.0051 grm.
2.	0.40 "	" "	0.0050 "
3.	0.10 "	" "	0.0051 "
4.	0.04 "	" "	0.0047 "

The recoveries in tests 1, 2 and 3 are obviously excellent and in test 4, the somewhat low result may be due purely to a normal experimental error, but may indicate, that, in the presence of less than 0.1 grm. iron, the adsorption is not quantitatively satisfactory. In any case, it seems advisable to have considerably more than 0.04 gram iron in the Group 2 separation.

One will find, that, in a volume of about 500 - 600 ml., 1 gram of iron, as ferric hydroxide, will present no filtration difficulties.

0.1 Gram Iron, as ferric hydroxide, is obviously very much easier to filter than 1.0 gram, but, in the presence of considerable proportions of zinc (which is always the case in the analysis of sphalerites and blende concentrates), where the ammonia concentration is necessarily high, there is always the

danger of loss of some indium, unless there is ample ferric hydroxide present to hold the indium as indium hydroxide.

Another advantage in having moderate and not small proportions of iron in Group 2, is to be found in the fact, that the ferric hydroxide adsorbs fair proportions of zinc, which zinc, is carried on to Group 3, where the zinc sulphide functions as an adsorbent of the indium sulphide.

It was found that the most convenient weight of iron for the Group 2 separation was 0.5 - 1.0 gram.

The above results in Table 15 do, however, indicate that considerably smaller proportions of iron may be present, thereby, making the Group 2 separation scheme less restricted.

In analysing sphalerites according to this group separation scheme, it will be found, that approximately 1.0 gram of iron is quite a usual weight, when dealing with 40 - 50 gram lots.

(e) RECOVERY OF INDIUM IN PRESENCE OF LARGE PROPORTIONS OF ZINC AND MODERATE PROPORTIONS OF IRON AND ALUMINIUM.

The recognised method of separating aluminium from indium, has been developed by Moser & Siegmann (47) and has also been described by Einecke (41).

In this method, sulphosalicylic acid is added to the solution and then ammonium carbonate, until neutral to methyl orange.

Acetic acid is then added and hydrogen sulphide bubbled in.

Indium sulphide is thus quantitatively precipitated.

Aluminium remains in solution.

Dennis and Bridgman (48) separated aluminium from indium by means of sodium hydroxide.

In Moser and Siegmann's method, the sulphosolicylic acid is used to keep the aluminium in solution.

Considering that tartaric acid is added to the solution in the Group 3 separation described here, it is not necessary to add sulphosalicylic acid, as tartrate ion inhibits the precipitation of aluminium hydroxide and basic acetate of aluminium.

Moreover, any residual aluminium will be completely removed in the sodium hydroxide groups (Groups 6 and 7).

The following recovery scheme was adopted:-

Three lots were prepared, each containing 20 grams of zinc, three grams of ferric chloride and 5 grams of A.R. Ammonia Alum.

0.0082 gram indium was added to one lot and 0.0041 gram to each of the others.

These solutions were treated in the usual manner, according to Group 2 (omitting the cyanate hydrolysis).

Two Group 3 separations were made. These were followed by one ammonia precipitation, one sodium hydroxide precipitation (in 0.5N alkalinity) and finally one more ammonia precipitation.

The hydroxide was ignited to oxide in the usual manner.

The results were as follows:-

TABLE 16.

Test.	In. Added.	In. Recovered.
1.	0.0082 grm.	0.0086 grm.
2.	0.0041 "	0.0040 "
3.	0.0041 "	0.0040 "

Results 2 and 3 indicate that aluminium is satisfactorily eliminated by the Group 3 method, followed by sodium hydroxide treatment.

It seems feasible that almost all the aluminium is eliminated in Group 3 and that residual aluminium is removed as aluminate in the sodium hydroxide filtrate (48).

Result 1. is slightly high and may be due to the retention of a small amount of aluminium.

(f) RECOVERY OF INDIUM IN PRESENCE OF MODERATE PROPORTIONS OF ZINC AND SMALL PROPORTIONS OF CERIUM AND OTHER RARE EARTHS.

Considering that small amounts of indium in indiferous zinc ores, may be associated with similarly small amounts of the rare earths, it was deemed advisable to carry out a special recovery of indium in the presence of these metals.

Furthermore, by virtue of the fact that the rare earth hydroxides are insoluble in ammonia and sodium hydroxide (49) and also that the rare earth sulphides are not precipitated by dil hydrogen sulphide in weak mineral acid or acetic acid solution (49). Group 3 is the only stage in the whole analytical scheme, where these elements can be eliminated.

Four solutions were prepared. Two included cerium chloride (not free from other earths) and the other two included a hydrochloric acid solution obtained by suitably treating the mineral monazite.

The finely crushed monazite was fused with potassium pyrosulphate (50).

The mixtures were:

(1) Zinc ..... - 0.25 gram.
Cerium ..... - 0.005 "
Indium ..... - 0.0050 "

(2) Zinc ..... - 0.25 gram.
Rare Earth Metals.. - 0.005 - 0.007 gram.
Indium ..... - 0.0050 gram.

In the latter case, the rare earths were introduced as sulphates from the monazite treatment and were approximately 0.005 - 0.007 grm.

In this particular recovery, the Group 3 hydrogen sulphide treatment was carried out twice and was followed by one ammonia precipitation, one sodium hydroxide precipitation and finally another ammonia treatment.

The indium was weighed as oxide in the usual way.

The results were as follows:-

TABLE 17.

Test.	In. Added.	In. Recovered.
1.	0.0050 gram.	0.0052 gram.
2.	" "	0.0052 "
3.	" "	0.0052 "
4.	" "	0.0051 "

3 and 4 were the "Monazite" recoveries.

The 0.25 gram of zinc in the mixtures is quite characteristic of the amount of zinc in Group 3 during the analysis of a typical ore.

The Group 3 separation was made only twice, thus, the above recoveries must be considered quite satisfactory.

In the presence of abnormally high proportions of rare earths, the hydrogen sulphide separation scheme would obviously have to be carried out at least three times.

Most monazite deposits are thoriferous, (79), (up to 20% as ThO_2), hence, it follows that thorium is also quantitatively removed in this Group, when in small proportions. (See also "Qualitative work on Group 3" below).

(g) Recovery of Indium in the presence of large amounts of zinc and moderate amounts of iron and manganese.

Most sphalerites are manganiferous, containing up to 2½% of manganese (37), hence, it was considered necessary to run a series of recoveries of indium in the presence of manganese as well as ofcourse zinc and iron.

The following mixture was prepared in quadruplicate:-

Zinc	-	20 grams.
Iron	-	1 gram.
Manganese	-	0.5 gram.
Indium	-	0.0051 gram.

The zinc was dissolved in hydrochloric acid and the iron (as ferric chloride), manganese (as manganous chloride), and indium (as chloride) added.

One Group 2 separation and two Group 3 separations were made and these were followed by three ammonia separations.

The final hydroxide was ignited to oxide in the usual way.

The recoveries were as follows:-

TABLE 18.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0051 gram.
2.	" "	0.0051 "
3.	" "	0.0053 "
4.	" "	0.0052 "

Average Indium recovered - 0.0052 gram.
Indium Added - 0.0051 gram.

These results are very satisfactory and show that manganese (in the presence of iron) is satisfactorily eliminated, by the standard Group 2 and 3 separations, followed by ammonia precipitations. (See also Section 5).

The recognised method of separating indium from manganese, depends on the reaction of hydrogen sulphide in acetic acid solution, whereby indium sulphide is precipitated and manganese remains in solution.

This method has been described by Moser and Siegmann (47) and Einecke (52).

It was considered advisable however to carry out the above series of recoveries, by virtue of the fact that in the actual analysis of a sphalerite, large proportions of zinc and moderate proportions of iron are present, which were the conditions of the above recoveries.

QUALITATIVE WORK ON GROUP 3.

(a) With a view to investigating the behaviour of certain elements, which one would expect to be eliminated in Group 3, the following qualitative tests were made:-

The solution of the element (usually about 0.2 - 0.3 gram in 5 0 ml.) was acidified with hydroxhloric acid, about 1 gram of tartaric acid added, the solution rendered faintly ammoniacal and then correctly acidic (1.5N) with acetic acid.

The solution was warmed to about 70°C and hydrogen sulphide bubbled in for about 10 minutes.

If a precipitate formed, it was filtered off, washed and treated with hot 5N. hydrochloric acid. The resulting filtrate was boiled to remove hydrogen sulphide (when present), oxidised with a drop or two of concentrated nitric acid and then treated in the same way as described above.

If a precipitate again appeared, it was treated with hot 5N. hydrochloric acid, the filtrate boiled to remove hydrogen sulphide, oxidised with a drop or two of nitric acid, cooled and then rendered slightly ammoniacal. Any precipitate or opalescence was noted.

The following are the results in tabular form:-

TABLE 19.

Element.	1st H_2S Treatment.	2nd. H_2S Treatment.	Ammonia Treatment.	Remarks.
Cr from $CrCl_3$	No. Pr.	-	-	Note. 1.
Mn from $MnCl_2$	No Pr.	-	-	Note. 1.
W from Sod. Tungstate	No Pr.	-	-	
Metallic W in Aqua Regia.	Slight Opalescence	No Pr. or Opalescence	-	
Zr. from $Zr(NO_3)_4$	No Pr.	-	-	
Th from $Th(NO_3)_4$	No Pr.	-	-	
Mo from Ammon. Molybdate	Heavy Pr.	No Pr. but Slight discol-oration.	No Pr.	Note. 2.

TABLE 19 Continued.

Element.	1st H_2S Treatment.	2nd H_2S Treatment.	Ammonia Treatment.	Remarks.
Metallic Mo in Aqua Regia	Heavy Pr.	No Pr. but slight discoloration.		Note 2.
Be from $BeCl_2$	No Pr.	-	-	
V from Sod.	Slight	Slight		
Orthovanadate	Turbidity	Turbidity	No Pr.	Note 3.
V from Sod. metavanadate	Turbidity	Slight Opalescence	No Pr.	Note 3.
V from Vanadyl Chloride	Turbidity	No Pr.	-	
U from Uranyl Nitrate	No Pr.	-	-	
Ti from $TiCl_3$	Moderate Pr.	Slight Pr.	No Pr.	
Ti from Pot. fluotitanate	No Pr.	-	-	Note 4.
Pt. from $PtCl_4$	Distinct Pr.	No Pr.	-	
Pd. from $PdCl_2$	Distinct Pr.	No Pr.	-	Note 5.
Au from Sod. Chloraurate	Distinct Pr.	No Pr.	-	
Se from Na_2SeO_3	Heavy Pr.	Slight discoloration	No Pr.	
Te from Na_2TeO_3	Heavy Pr.	Slight discoloration	No Pr.	

Notes:

(1) In the case of Chromium and Manganese, the concentration was considerably greater; approximately 1.0 gram in 50 ml.

(2) The discoloured solution was boiled, oxidised with nitric acid and then ammonia added in slight excess.

No precipitate formed.

(3) The turbidity appeared to be due mainly to sulphur.

(4) The solution treated with hydrogen sulphide was obtained by acting upon the potassium fluotitanate with Aqua Regia and driving off excess chlorine.

(5) Some Palladious Chloride was oxidised with Chlorine, excess Chlorine removed and the resulting solution treated in the usual way.

The results were the same as for unoxidised Palladious Chloride.

All these tests were done in the absence of Zinc.

In the presence of zinc, there would obviously be adsorption difficulties, but, considering that none (with the exception of manganese and possibly molybdenum, selenium and tellurium), of these elements is likely to be present in anything but small traces and also that the Group 3 separation is invariably carried out two or three times, it seems as if these elements will be satisfactorily eliminated at this stage.

Moreover, it is interesting to note that the "ammonia" column shows "no precipitate" for each element.

In the case of manganese, any traces passing beyond Group 5 will be removed in Groups 4 and 8.

Traces of residual molybdenum, selenium and tellurium will be eliminated in Groups 4, 6, 7 and 8. (See also Section 5).

(b) ELIMINATION OF PHOSPHATE, ARSENATE, FLUORIDE & BORATE.

(1) PHOSPHATE.

Qualitative work was done on solutions containing phosphate, iron and tartrate.

It was found that with comparatively small proportions of phosphate, hydrogen sulphide gave no precipitate in 1.5N. acetic acid concentration.

Phosphate remained in solution.

When the phosphate (as disodium hydrogen phosphate) was in excess of 0.5%, there was a tendency for phosphate to precipitate during the hydrogen sulphide treatment. (A large excess of tartaric acid would probably avoid this).

This tendency does not materially affect the group separation scheme, because any residual phosphate would ultimately be eliminated in the sodium hydroxide groups, namely, groups 6 & 7.

This would, however, result in an abnormal amount of iron passing on with the indium and ultimately being included in the sesquioxide ash.

This condition however would be exceptional in practice, but, if it arose, the iron could be weighed with the indium and estimated colorimetrically in the usual way or else, the precipitate in Group 7 could be dissolved in hydrochloric acid, approximately 0.2 gram zinc (as chloride) and 0.5 gram tartaric acid added and the whole made up to 100 ml. Ammonia would then be added until neutrality was reached and then acetic acid until 1.5N.

The usual hydrogen sulphide treatment would then be carried out and this would be followed by the routine Group 4 - 8 separations.

This would rarely be necessary and would only arise in cases of phosphatically veined sphalerites and phosphatised smithsonites.

Zinc phosphates are uncommon in nature.

(2) ARSENATE.

The behaviour of arsenate in the presence of iron, would be almost identical to that described under phosphate above.

There would be a strong possibility, however, of arsenic being precipitated in Group 3 as sulphide.

In this case, owing to the insolubility of the sulphide in 5N. hydrochloric acid, arsenic would be almost entirely eliminated in Group 3.

Residual arsenic would, ofcourse, be removed in Groups 6 & 7.

(3) FLUORIDE.

A solution was prepared containing 2.0 grams sodium fluoride, 2.0 grams ferric chloride, 3.0 grams tartaric acid and 5 ml. hydrochloric acid in a total volume of 200 ml.

This was rendered very faintly ammoniacal (no precipitate formed at this stage) and then acetic acid was added up to 1.5N.

This gave a clear solution, which was warmed to 80°C and then treated with hydrogen sulphide for 15 mins.

The whole was filtered, washed and dissolved in hot 5N. hydrochloric acid.

The filtrate contained only a trace of fluoride and very little iron.

It is obvious, therefore, that with only one hydrogen sulphide treatment, nearly all the fluoride passes into the Group 3 filtrate. Two of these separations should remove all fluoride.

Greater proportions of fluoride may have to be specially dealt with, but, the above proportion represents approximately 2% of fluorine (i.e., working on a 40-50 gram sample of zinc ore) or 4% of fluor-spar.

It is very doubtful whether fairly pure specimens of zinc blende or smithsonite could contain fluor spar (or apatite) in excess of this proportion.

Small amounts of residual fluoride would be removed in Group 5.

(4) BORATE.

A test very similar to that described under "Fluoride" was conducted and the results found to be similar to the fluoride results.

Borates are not likely to accompany sphalerite or smithsonite, although sussexite (a zinciferous borate) has been found associated with zincite and willemite (51).

Traces of residual borate would be removed in Groups 6 & 7.

For quantitative recoveries of indium in presence of phosphate, arsenate and fluoride, see "Section 5".

Quantitative work in the presence of arsenic is also given under "Groups 4 and 6" - page 39A - 40.

GROUPS 4 and 6: For sake of convenience, these groups will be described under one heading.

Group 4.

The important function of this group is the elimination of almost all of the residual zinc from Group 2.

Besides this, residual copper, cadmium, nickel, cobalt, manganese and possibly molybdenum, vanadium and tungsten will be eliminated here. Probably all thallium is removed in this group.

Group 6.

Traces of zinc escaping Group 4 are entirely removed here.

Any residual Thallium, Gallium, Molybdenum, Vanadium and Tungsten will be eliminated in this group. Also residual arsenic, phosphate, borate and aluminium will be removed with this treatment.

Tin and Antimony are almost entirely eliminated by this sodium hydroxide treatment.

Residual silica acid will be removed here.

QUANTITATIVE WORK:

(a) INFLUENCE OF VARYING AMOUNTS OF TARTRATE ON THE QUANTITATIVE PRECIPITATION OF INDIUM HYDROXIDE BY MEANS OF AMMONIA.

Considering that comparatively large amounts of tartaric acid are deliberately added to the solution just prior to the hydrogen sulphide treatment in Group 3, it seems expedient to investigate the maximum tartrate ion concentration for the satisfactory quantitative precipitation of indium hydroxide by ammonia.

Reich, Richter & Wyrouboff have done work in connection with the inhibition of the precipitation of indium hydroxide by tartrate ion (and similar ions).

Reich & Richter (28) found that in the presence of tartrate ion, no indium hydroxide was precipitated by alkali hydroxide.

Wyrouboff states, however, that tartrate ion does not inhibit the precipitation (53).

Reich & Richter also state, that no indium hydroxide is precipitated by ammonia in the presence of tartrate ion (54).

The Group 3 precipitation is usually carried out twice. After the first, the greater portion of the tartrate is removed in the filtrate.

It is seldom necessary to add more tartaric acid just before the second hydrogen sulphide bubbling, because the concentration of iron has been greatly diminished by the first treatment.

Hence, it follows that the precipitate from the second treatment will contain only a small amount of tartaric acid and this should be entirely eliminated on washing with many lots of hot water (which is the recognised procedure in practice).

Nevertheless, there is a remote possibility of small amounts of tartrate being present in the final filtrate from Group 3 and hence in the solution for the Group 4 treatment.

The following recoveries were thus made, with a view to establishing whether the presence of small amounts of tartrate seriously affect the precipitation of indium hydroxide by ammonia.

Five lots of indium chloride (each representing 0.0050 grm. Indium) were made up to 50 ml., 1 ml. of concentrated A.R. Nitric Acid and the correct amount of A.R. Tartaric acid added.

The solutions were boiled for fifteen minutes, the hydroxide allowed to settle for thirty minutes and then filtered and washed three times to remove most of the sodium hydroxide.

The precipitates were then dissolved in 5N. nitric acid, and the hydroxide reprecipitated with ammonia and ignited to the oxide in the usual manner.

The results of these tests were as follows:-

TABLE 21.

Test.	NaOH Concentration.	In. Added.	In. Recovered.
1.	0.02N.	0.0050 grm.	0.0050 grm.
2.	0.02N.	0.0050 "	0.0050 "
3.	0.25N.	" "	0.0052 "
4.	0.25N.	" "	0.0051 "
5.	0.25N.	" "	0.0052 "
6.	0.25N.	" "	0.0050 "
7.	0.25N.	" "	0.0050 "
8.	0.5N.	" "	0.0050 "
9.	0.5N.	" "	0.0049 "
10.	0.5N.	" "	0.0050 "
11.	0.5N.	" "	0.0051 "
12.	0.5N.	" "	0.0051 "
13.	0.5N.	" "	0.0052 "
14.	N.	" "	0.0042 "
15.	N.	" "	0.0039 "
16.	2N.	" "	0.0019 "
17.	2N.	" "	0.0018 "

It appears, therefore, that concentrations of sodium hydroxide up to 0.5N. are quite safe for the quantitative precipitation of indium hydroxide.

Noyes and Bray found that with 1.7N. Sodium hydroxide, 1 mgrm. of indium was recovered from 1 mgrm. (30).

Presumably, conditions were different from those under which the above recoveries were made.

In practice, however, it will be wise to limit the sodium hydroxide concentration to 0.5N., which concentration is sufficient to hold appreciable amounts of tin and antimony in solution.

Of the elements (or groups) that may be present in Group 6, tin and antimony are likely to be in the greatest proportion. (see (e) Page 39 - 39A for the recovery of indium in presence of tin and antimony).

(c) RECOVERY OF INDIUM IN THE PRESENCE OF SMALL PROPORTIONS OF GALLIUM AND MODERATE PROPORTIONS OF ZINC.

Einecke (56) states that the separation of gallium from indium is a difficult one and cites Crookes' method (57), in which, sodium hydroxide is used as the medium of separation.

By these means, indium hydroxide is precipitated and sodium gallate remains in solution.

The objections made appear to be that the indium hydroxide adsorbs some gallium hydroxide and that some indium remains in solution with the sodium gallate.

The former objection is obviously of little significance in the group separation scheme devised here, owing to the fact that there are invariably two sodium hydroxide treatments.

Traces of gallium hydroxide remaining with the indium hydroxide after the first sodium hydroxide treatment, will be entirely removed during the second treatment.

Moreover, it must be remembered, that the major portion of the gallium is removed in Group 3.

Gallium like aluminium does not form a sulphide in the wet way. (58).

Considering, however, that some gallium may be adsorbed by the zinc sulphide in Group 3, it is necessary to investigate the removal of gallium by means of sodium hydroxide.

Gallium is always likely to be present in sphalerites and occasionally, its concentration may be greater than that of indium.

The latter objection mentioned above, does not appear to be serious in this particular separation scheme, when one studies the recoveries recorded on page 36

In an alkaline environment of 0.5N. and less, there appears to be no significant loss of indium.

The following series of recoveries of indium in the presence of zinc and gallium, appears to confirm this.

The following mixture was analysed in quadruplicate.

Zinc (as chloride)	-	0.25 gram.
Gallium (as chloride)	-	0.022 "
Indium (as Chloride)	-	0.0051 "

The Group 3 treatment was carried out twice and the final filtrate therefrom was oxidised with a few drops of nitric acid (after boiling to remove greater portion of the hydrogen sulphide).

The solution was concentrated to 50 ml. and then made moderately ammoniacal.

This was gently boiled until faintly ammoniacal, the precipitate allowed to settle, filtered and washed and then dissolved in 5N. hydrochloric acid.

To this solution was added a 6N. solution of sodium hydroxide until exact neutrality.

Sodium hydroxide was then added in excess, until the alkalinity was 0.5N., the solution boiled for about five minutes, the precipitate allowed to settle and then filtered and washed.

This precipitate was dissolved in 5N. hydrochloric acid and the sodium hydroxide treatment repeated.

The precipitate in this case was again dissolved in 5N. hydrochloric acid and the solution rendered moderately ammoniacal.

Excess ammonia was removed by boiling and the precipitate allowed to settle, filtered and washed and then ignited to the oxide.

The results were as follows:-

TABLE 22.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0050 gram.
2.	0.0051 "	0.0050 "
3.	0.0051 "	0.0051 "
4.	0.0051 "	0.0052 "

Average Indium Recovered - 0.0051 gram.
Indium Added - 0.0051 "

The Group3separation was included, because, in practice, much, if not most of the gallium will be removed there.

(d) RECOVERY OF INDIUM IN THE PRESENCE OF SMALL PROPORTIONS OF THALLIUM AND MODERATE PROPORTIONS OF ZINC.

One of the most satisfactory ways of separating thallium from indium is by agitating the mixed bromides, inthe presence of free hydrobromic acid, with ether.

Indium bromide is insoluble.

This method is described by Wada and Ishii (59). Noyes and Bray (80), (81), have also done work in this connection.

In the analytical method developed in this research, this method is obviously inapplicable.

By virtue of the fact that thallous hydroxide is soluble in water (60) and in excess alkali, it appears quite feasible that thallium will be eliminated in Groups 4, 6 and 7.

Böttger describes a separation using ammonia (61).

Hence, the following recoveries were made.

The following mixture was analysed in quadruplicate.

Zinc (as chloride - 0.25 gram.
Thallium (as thallous nitrate) - 0.022 "
Indium (as chloride - 0.0051 "

One Group 3 and one Group 4 separation were carried out and these were followed by one sodium hydroxide and finally, one more ammonia precipitation.

The results were as follows:-

TABLE 23.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0049 gram.
2.	" "	0.0052 "
3.	" "	0.0050 "
4.	" "	0.0049 "

Average Indium Recovered - 0.0050 gram.
Indium Added - 0.0051 "

It is interesting to note that thallous nitrate was used in this recovery.

Thallic solutions give precipitates with alkalies (62) insoluble in excess, hence, since the thallium appears to have been eliminated in Groups 4 and 6. (Thallium is precipitated as sulphide in Group 3 and this sulphide is soluble in 6N. hydrochloric acid), it follows, that the regular nitric acid treatment does not oxidise thallous ion to thallic ion.

Noyes and Bray in their "Qualitative analysis for the Rare Elements", record that thallous chloride is oxidised to thallic chloride by chlorine and bromine, but do not mention the action of nitric acid (63). Presumably, nitric acid does not oxidise thallous to thallic thallium, nor apparently a low concentration of chlorine produced by the action of a few drops of nitric acid on approximately 250 ml. of a dilute hydrochloric acid solution, such as obtains on oxidising the filtrate from Group 3.

Moreover, if thallium is in the thallic condition prior to Group 3, the hydrogen sulphide treatment will precipitate thallous sulphide (63).

(e) RECOVERY OF INDIUM IN THE PRESENCE OF MODERATE PROPORTIONS OF TIN AND ANTIMONY AND THE USUAL AMOUNT OF ZINC.

No specific data could be found with regard to the quantitative recovery of indium in the presence of antimony and tin, although, Wada and Ato have done general work on the precipitation of sulphides insoluble in dilute hydrochloric acid, in the presence of indium (64).

By removing elements such as tin, antimony, copper, lead, cadmium, mercury, bismuth, etc., by precipitating their sulphides in dilute mineral acid solution, there is definite danger of loss of indium by adsorption.

This loss may be relatively appreciable, when one or more of these elements is in fair proportion and indium in low concentration.

One of the main objects in this research, is to develop an analytical group scheme, whereby, indium is, as far as possible, in the precipitates and not in the solutions, thus, minimising loss by adsorption.

This aim is fulfilled by introducing an ammonia and then sodium hydroxide separations, after Group 3.

It will be found that antimony and tin are satisfactorily eliminated by sodium hydroxide, except, possibly when in abnormally high concentrations.

The following mixture was analysed in quadruplicate:-

Zinc (as chloride	-	0.25 gram.
Antimony (as antimonious chloride	-	0.05 "
Tin (as stannous chloride)	-	0.05 "
Indium (as chloride)	-	0.0051 "

With this mixture, one Group 4, two Group 6, and one final ammonium hydroxide precipitation were carried out.

The sodium hydroxide concentration in the first treatment was 0.6N. and the second treatment, 0.3N.

The recoveries were as follows:-

TABLE 24.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0050 gram.
2.	" "	0.0049 "
3.	" "	0.0050 "
4.	" "	0.0050 "

Average Indium Recovered - 0.0050 gram.
Indium Added - 0.0051 "

These results are very satisfactory and show that tin and antimony up to 0.1 gram are completely removed by two sodium hydroxide treatments.

If tin and/or antimony are in greater proportions than this, then three sodium hydroxide precipitations would, in all probability, remove all traces of these elements.

It will be noted that stannous and antimonious chlorides were used for this recovery.

During the oxidation of the final Group 3 filtrate by means of a few drops of nitric acid (in a total volume of 200 ml.), stannous ion will oxidise to stannic ion, but, it is very doubtful whether antimonic ion will result.

Moreover, if antimony is present in the antimonia condition in the filtrate from Group 1, it may be precipitated as the pentasulphide in Group 3.

In this case, it might still be in the antimonic form in Group 6.

This, however, will not negative the efficacy of Group 6 with respect to antimony, since sodium antimonate forms just as readily as the antimonite and is soluble in excess alkali. Sodium stannate is also soluble in excess sodium hydroxide.

(f) RECOVERY OF INDIUM IN PRESENCE OF MODERATE PROPORTIONS OF ARSENIC AND THE USUAL PROPORTION OF ZINC.

It is very doubtful whether any, but traces of arsenic will pass into the filtrate from Group 3, owing to the insolubility of the sulphides of arsenic in 5N. hydrochloric acid.

The following analysis, however, was made and is worthy of record. The mixture analysed was:-

Zinc (as chloride) - 0.25 gram.
Arsenic (as disodium hyd. arsenate) - 0.10 gram.
Indium (as chloride) - 0.0051 "

One ammonia and two sodium hydroxide separations were made and these were followed by a final ammonia precipitation.

Group 3 was omitted.

The results were as follows:-

TABLE 25.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0049 gram.
2.	" "	0.0049 "
3.	" "	0.0053 "
4.	" "	0.0052 "
5.	" "	0.0050 "

Average Indium Recovered - 0.0051 gram.
Indium Added - 0.0051 "

(g) RECOVERY OF INDIUM IN THE PRESENCE OF MODERATE PROPORTIONS OF SILICIC ACID AND THE USUAL PROPORTION OF ZINC.

All refractory silicates and free silica, will be removed in Group 1, and the greater portion of the silicic acid, derived from silicates readily acted upon by hydrochloric acid, will also be removed in this separation.

Residual silicic acid will pass on to Group 3, where it may or may not be eliminated, depending on conditions.

Of the residual silicic acid which escapes both the Group 1 and 3 separations, most will be eliminated along with lead in Group 5.

If traces still persist, however, the sodium hydroxide treatment in Groups 6 and 7 should entirely eliminate these last traces.

It was thus considered advisable to run a quantitative recovery of indium in the presence of silicic acid, using the Group 3 and sodium hydroxide separations only and omitting the sulphuric acid treatment (Group5).

By introducing 0.1 gram of silica and omitting Group 5, conditions were obviously extreme.

The mixture used was:-

Zinc (as chloride) - 0.25 gram.
Silica (as sodium silicate) - 0.1 "
Indium (as chloride) - 0.0050 "

The hydrogen sulphide treatment was carried out once, followed by one Group 4, two group 6 and finally, one ammonia precipitation.

The results were as follows:-

TABLE 26.

Test.	In. Added.	In. Recovered.
1.	0.0050 gram.	0.0051 gram.
2.	" "	0.0051 "
3.	" "	0.0050 "
4.	" "	0.0049 "

Average Indium Recovered - 0.0050 gram.
Indium Added - 0.0050 gram.

For work done on other elements removed in these Groups, see Section 6.

Group 5.

The filtrate from Group 4 is carefully evaporated to fumes with sulphuric acid copied, diluted and filtered and the precipitate thoroughly washed.

The filtrate is retained for Group 6.

The obvious function of this group is the removal of lead.

Lead is partly removed in group 1, but much passes on to the sulphuric acid group.

Besides lead, residual silicic acid will be almost entirely removed in this group.

Traces of fluoride would also be eliminated here.

QUANTITATIVE WORK:

RECOVERY OF INDIUM IN THE PRESENCE OF MODERATE PROPORTIONS OF LEAD AND THE USUAL PROPORTIONS OF ZINC.

The following mixture was analysed in triplicate:-

Zinc (as chloride)	-	0.25 gram.
Lead (as nitrate)	-	0.50 gram.
Indium (as chloride)	-	0.0061 "

The procedure was as follows:-

The above mixture was made up to 100 ml., 5 ml. of nitric acid added and the whole brought to the boil. After, cooling slightly, ammonia was added in moderate excess and the whole boiled until the solution was faintly ammoniacal.

The hydroxides were filtered off, washed three times and then dissolved in hot 5N. nitric acid, the filtrate being caught in the precipitation beaker.

5 ml. of concentrated C.P. sulphuric acid were added and the whole carefully evaporated to fumes, cooled and 50 ml. of water added.

After standing for two hours the sulphate was filtered off and washed thoroughly.

Sodium hydroxide was added to the filtrate to neutralise the sulphuric acid and then added in excess, until the solution was 0.3N.

This was brought to the boil and allowed to simmer for about 15 minutes.

The precipitate was then allowed to settle and was filtered.

The hydroxide was dissolved in 5N. hydrochloric acid and indium hydroxide precipitated by means of ammonia.

The hydroxide was ignited to oxide in the usual way.

Along with this triplicate recovery, two blanks were run, the conditions being precisely the same as those of the recovery analyses, except, that lead was omitted.

The results were as follows:-

TABLE 27.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0053 gram.
2.	0.0051 gram.	0.0052 "
3.	0.0051 gram.	0.0053 "
4. *	0.0051 gram.	0.0051 "
5. *	0.0051 gram.	0.0048 "

* Tests 4 and 5 were the blanks.

These results are fairly satisfactory.

If any lead sulphate remains in solution in Group 5, it will be removed in Group 6 by being converted to sodium plumbite, which will be eliminated in the Group 6 filtrate.

Group 7.

The term "Group" here might be deemed a misnomer, as this stage was introduced into the analytical scheme purely in order to eliminate bismuth.

The group however, includes a sodium hydroxide treatment and this eliminates the last traces of zinc. Moreover, if an unusually high proportion of antimony and/or tin is present, this group is essential.

Traces of residual mercury would also be removed here.

It is interesting to note that if bismuth is present in the ore, it will remain quantitatively with the indium throughout Groups 1 - 6.

In the presence of bismuth, therefore, this group is indispensable.

QUANTITATIVE WORK:

RECOVERY OF INDIUM IN THE PRESENCE OF MODERATE PROPORTIONS OF BISMUTH.

(a) PRECIPITATION BY HYDROGEN SULPHIDE IN 2N. HYDROCHLORIC ACID SOLUTION.

The following mixture was treated:-

Bismuth (as chloride) - 0.10 gram.
Indium (as chloride) - 0.0051 gram.

The procedure was as follows:-

The bismuth chloride and indium chloride were made up to 50 ml. with water and 13 ml. of concentrated C.P. hydrochloric acid added.

The solution was warmed to 80°C. and hydrogen sulphide bubbled in for five minutes.

The sulphide was allowed to settle and then filtered and thoroughly washed, firstly with three washings of 0.5N. hydrochloric acid and secondly with five lots of water.

The filtrate was evaporated down to about 50 ml. and oxidised with a few drops of nitric acid.

The indium was precipitated with ammonia in the usual manner and weighed as oxide, after ignition.

The results were:-

TABLE 28.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0049 gram.
2.	" "	0.0050 "
3.	" "	0.0063 "
4.	" "	0.0053 "

Excluding the outside result, the average of tests 1, 2 and 4 is 0.0051 gram.

It seems probable that the high result in test 3, was due to the incomplete precipitation of bismuth as sulphide, although all four were conducted under the same conditions.

A further series was analysed, using 0.5N. instead of 2N. hydrochloric acid.

(b) PRECIPITATION BY HYDROGEN SULPHIDE IN 0.5N. HYDROCHLORIC ACID SOLUTION.

The same weights of bismuth and indium were taken as before and the general procedure was the same, except that the acidity was 0.5N. instead of 2N.

The results in this case were:-

TABLE 29.

Test.	In. Added.	In. Recovered.
1.	0.0051 gram.	0.0053 gram.
2.	" "	0.0051 "
3.	" "	0.0051 "
4.	" "	0.0052 "

Average Indium Recovered - 0.0052 gram.
Indium Added - 0.0051 gram.

These results show that no indium was lost in the 0.5N. acid treatment and also that all bismuth was removed.

It appears advisable, therefore, to remove bismuth in 0.5N. instead of 2N. acid solution.

Noyes and Bray (33) seem to favour 0.3N. acid for the complete precipitation of bismuth, without danger of loss of indium.

Wada & Ato (65) state that 0.3 gram of bismuth in 50 ml. of 0.6N. Nitric Acid is completely precipitated as sulphide with hydrogen sulphide treatment.

It seems, therefore, that 0.5N. acid is quite suitable for this group (See also Section 5).

Group 8.

Group 8.

As in the case of Group 7, this can hardly be considered a "Group Separation" in the strict sense of the term.

The function of this group is merely to precipitate indium as hydroxide, in preparation for the actual estimation- Gravimetric, Volumetric, Electrolytic or Potentiometric.

The filtrate from Group 7 will be almost free from all other metals, with the exception of small amounts of sodium, which, ofcourse will not affect the purity of the indium hydroxide after suitable washing.

It is undesirable to ignite the hydroxide formed from the sodium hydroxide treatment, as there is always the possibility of the retention of small amounts of sodium salts.

The presence of small amounts of ammonium nitrate on the other hand is not deleterious to the quantitative conversion of indium hydroxide to indium sesquioxide.

One must guard against the presence of chlorides, including ammonium chloride, except in the smallest traces, as there is a tendency for indium to be lost as the chloride, which sublimes at about 500°C at ordinary atmospheric pressure (22), (66).

As this final ammonia group is so vital in the gravimetric estimation of indium as oxide through hydroxide, a series of determinations was made, in which, ammonia was added to indium chloride solution, in the absence of other metals. (22), (23), (24), (25), (26).

The analytical details were as follows:-

The indium chloride was made up to 50 ml. with water, 1 ml. of concentrated nitric acid added and then ammonia in moderate excess (about 2 - 3 ml. of the 880 ammonia in excess in a total of 50 ml. of solution).

The solution was boiled until only faintly ammoniacal, the precipitate allowed to settle and then filtered through ashless filters, thoroughly washed, dried and ignited to the oxide.

The results were as follows:-

TABLE 30.

Test.	In. Added.	In. Recovered.
1.	0.0050 gram.	.0051 gram.
2.	.0050 "	.0051 "
3.	.0050 "	.0051 "
4.	.0050 "	.0050 "
5.	.0050 "	.0051 "
6.	.0050 "	.0050 "
7.	.0101 "	.0103 "
8.	.0101 "	.0102 "

A second series of estimations was made but in this case, hydrochloric acid was added instead of nitric acid.

These results were:-

TABLE 31.

Test.	In. Added.	In. Recovered.
1.	.0050 gram.	.0050 gram.
2.	.0050 "	.0050 "
3.	.0050 "	.0051 "
4.	.0050 "	.0052 "
5.	.0050 "	.0050 "
6.	.0050 "	.0052 "
7.	.0101 "	.0102 "
8.	.0101 "	.0100 "

In the case of Table 30, the average for the 5 mgrm. lots is .0051 grm. and in the case of Table 31, .0051 grm. The overall average is ofcourse .0051 gram.

The overall average for the 10 mgrms. lots is .0102 gram.

Considerable work has been done by Moser & Siegmann (22) and by Thiel and Koelsch (23), (24), on the quantitative determination of indium as oxide, by means of the precipitation of the hydroxide with ammonia, but, considering that this final stage is so vital to the estimation of indium in zinc ores, it was decided to gain first hand experience by conducting the above series of tests.

SECTION 5.

CONFIRMATION OF THE EFFICACY OF THE ANALYTICAL SCHEME BY THE RECOVERY OF INDIUM FROM COMPREHENSIVE SYNTHETIC MIXTURES.

The results recorded in Section 4, pages 14 - 45 indicate that indium can be satisfactorily and quantitatively isolated from the elements which are likely to accompany it in nature, by means of the analytical scheme outlined in Section 3, pages 11 - 13.

In Section 4, however, the various elements, from which indium was recovered, were given individual treatment in the relevant groups and it now remains to establish the method by attempting to recover indium quantitatively from comprehensive mixtures.

With this in view, three series of analyses were conducted, namely:-

(a) Recovery of indium from a mixture of elements, which are likely to accompany it in nature.

(b) Recovery of indium from a mixture of elements, which are not likely to accompany it (except, possibly in small traces) in nature.

(c) Recovery of indium from a mixture more comprehensive than either (a) or (b).

(a) The following mixture was prepared in triplicate:-

TABLE 32.

Element.	How Introduced.	Wt. of Element.
Zinc	Zinc in hydrochloric acid	25 grams.
Iron	Ferric chloride	1.0 "
Gallium	Gallium chloride	0.005 gram.
Thallium	Thallous nitrate	0.005 "
Silicon	Sodium metasilicate	0.1 "
Calcium	Calcium Carbonate in hydrochloric acid	2.0 "
Manganese	Manganous chloride	0.2 "
Copper	Cupric oxide in hydrochloric acid	0.2 "
Arsenic	Sodium arsenite	0.1 "
Selenium	Sodium Selenite	0.05 "
Tellurium	Potassium Tellurite	0.05 "
Silver	Silver Nitrate	0.005 "
Cadmium	Cadmium Chloride	0.5 "
Tin	Stannic Chloride	0.05 "
Antimony	Antimonic Chloride	0.05 "
Mercury	Mercuric Chloride	0.1 "
Lead	Lead Oxide in Aqua Regia	0.5 "
Indium	Indium Chloride	0.0050 "

The indium was accurately pipetted from a standard solution.

This mixture was made up to 400 mls. and treated in the following way:-

Group 1 - Omitted
Group 2 - One Separation
Group 3 - Two Separations
Group 4 - One Separation
Group 5 - One Separation

Group 6 - One Separation
Group 7 - One Separation
Group 8 - One Separation

The groups mentioned here refer of course to those described in Sections 3 and 4.

The "Brief Tabulation of Analytical Scheme" on page 13 Section 3, should be referred to at this juncture.

Group 1 was omitted on account of the absence of gangue material refractory silicates, etc.

The results were as follows:-

TABLE 33.

Test.	In. Added.	In. Recovered.
1.	0.0050 gram.	0.0047 gram.
2.	" "	0.0048 "
3.	" "	0.0048 "

In a mixture of this nature, the recovery must be considered as being quite satisfactory.

The slightly low results do, at least, appear to indicate that the other elements were eliminated.

(b) The mixture chosen in this instance was:-

TABLE 34.

Element.	How Introduced.	Wt. of Element.
Zinc	Zinc in Hydrochloric acid	25 grams.
Iron	Ferric Chloride	1.0 gram.
Zirconium	Zirconium Nitrate	0.05 "
Titanium	Sodium Fluotitanate	0.05 "
Beryllium	Beryllium Chloride	0.05 "
Tungsten	Sodium Tungstate	0.05 "
Vanadium	Sodium Orthovanadate	0.05 "
Uranium	Uranyl Nitrate	0.05 "
Indium	Indium Chloride	0.0050 "

This was prepared in triplicate.

The group separation was as follows:-

Group 1 - Omitted
Group 2 - One Separation
Group 3 - Two Separations
Group 4 - One Separation
Group 5 - Omitted
Group 6 - One Separation
Group 7 - One Separation
Group 8 - One Separation

Group 1 was omitted for the same reason as that given under (a) above, and Group 5 was omitted, because lead and silicon were not introduced into the mixture.

The results of the recovery were as follows:-

TABLE 35.

Test..	In. Added.	In. Recovered.
1.	0.0050 gram.	0.0051 gram.
2.	" "	0.0051 "
3.	" "	0.0051 "

These results are excellent and in this particular mixture emphasise the efficacy of Group 3.

Of the nine elements in the mixture the greater portion of seven of them is removed in Group 3.

(e) The mixture treated in this case was:-

TABLE 36.

Element.	How Introduced.	Wt. of Element.
Zinc	Zinc in Hydrochloric Acid	25 grams.
Iron	Ferric Chloride	1.0 Gram.
Fluorine	Sodium Fluoride	0.2 "
Magnesium	Magnesium Oxide in Hydrochloric Acid	1.0 "
Aluminium	Aluminium Chloride	0.05 "
Silicon	Sodium Silicate	0.1 "
Phosphorus	Disodium Hyd. Phosphate	0.2 "
Calcium	Calcium Carbonate in Hydrochloric acid	2.0 "
Manganese	Manganous Chloride	0.1 "
Cobalt	Cobaltous Chloride	0.05 "
Nickel	Nickelous Chloride	0.05 "
Copper	Cupric Oxide in Hydrochloric Acid	0.5 "
Gallium	Gallium Chloride	0.005 "
Arsenic	Disodium Hyd. Arsenate	0.2 "
Selenium	Sodium Selenite	0.05 "
Strontium	Strontium Chloride	0.1 "
Molybdenum	Ammonium Molybdate	0.05 "
Silver	Silver Nitrate	0.005 "
Cadmium	Cadmium Chloride	0.5 "
Tin	Stannic Chloride	0.05 "
Antimony	Antimonic Chloride	0.05 "
Tellurium	Potassium Tellurite	0.05 "
Barium	Barium Carbonate in Hydrochloric acid	0.5 "
Cerium	Cerous Chloride (not free from other rare earths)	0.005 "
Mercury	Mercuric Chloride	0.1 "
Thallium	Thallous Nitrate	0.005 "
Lead	Lead Oxide in Hydrochloric Acid	0.5 "
Bismuth	Bismuthous Chloride	0.05 "
Chromium	Chromic Chloride	0.05 "
Indium	Indium Chloride	0.0050 "

This analysis was carried out in duplicate and the results were:-

TABLE 37.

Test.	In. Added.	In. Recovered
1.	0.0050 gram.	0.0051 gram
2.	0.0050 gram.	0.0053 gram

The Group Separations were:-

Group 1 - Omitted
Group 2 - Two Separations
Group 3 - Four Separations
Group 4 - One Separation
Group 5 - One Separation
Group 6 - One Separation
Group 7 - One Separation
Group 8 - One Separation

By virtue of the relatively high proportion of elements partly eliminated in Group 2, this separation was made twice and by virtue of the presence of 0.2 gram of phosphorus, four separations of Group 3 were necessary.

It is interesting to note, that the final oxide ash contained only 0.5 mgrm. of ferric oxide in each case.

It must be remembered that this recovery was made from a mixture containing 30 elements (excluding, ofcourse, chlorine, oxygen, nitrogen, sodium, etc.) and the above two results are very reassuring. In these special recoveries from comprehensive mixtures, it is worthy of note, that the average of the eight results is 0.0050 gram, which is the theoretical recovery.

The greatest positive error is 0.3 mgrm. (only once) and the greatest negative error, 0.3 mgrm. (only once).

In the circumstances, this maximum error of 6% cannot be considered serious.

SECTION 6.

BLANK TEST ON THE ESSENTIAL REAGENTS USED IN THE ANALYTICAL RESEARCH.

With a view to running a blank test on the essential reagents used in the analytical research, four lots of 30 grams of G.R. Zinc were dissolved in G.R. hydrochloric acid, 3 grams of G.R. Ferric Chloride added to each and the solution taken through the complete group separation scheme.

The final hydroxide precipitate from Group 8 was ignited to oxide in the usual way and the ferric oxide estimated colorimetrically.

The reagents used in these blank tests were:-

	Metallic Zinc	- Analar.
	Ferric Chloride	- Analar.
	Hydrochloric Acid	- Analar.
	Sodium Hydroxide	- Analar.
x	Ammonium Hydroxide	- Ordinary C.P. and Analar.
	Tartaric Acid	- Ordinary C.P.
	Acetic Acid	- Ordinary C.P.
	Hydrogen Sulphide	- Generated from ordinary ferrous sulphide and commercial hydrochloric acid.
	Nitric Acid	- Analar.
	Sulphuric Acid	- Analar.

x Ordinary C.P. Ammonia was used in Group 2 and analar purity in Groups 4 and 8.

The above reagents were used throughout the work detailed in Sections 4 and 5.

The results of these blank tests were as follows:-

TABLE 38.

Test.	Wt. of Oxide	Ferric Oxide (colotimetric)	Difference.
1.	0.2 mgrm.	0.18 mgrm.	0.0 mgrm.
2.	0.2 "	0.16 "	0.0 "
3.	0.1 "	0.12 "	0.0 "
4.	0.6 "	0.38 "	+ 0.2 "

In the "Wt. of Oxide" column, the weights are ± 0.1 mgrm. and in the "Ferric Oxide" column, ± 0.02 mgrm.

In the "Difference" Column, the results are therefore ± 0.1 mgrm.

SECTION 7.

DIGRAMMATIC SCHEME AND NOTES IN CONNECTION WITH THE ELIMINATION OF ELEMENTS IN THE GROUP SEPARATION PROCESS.

(a) DIAGRAMMATIC SCHEME:

The diagram on page 51A gives one a concise representation of the group separation scheme and indicates how and where the different elements are eliminated.

The following explanatory notes appertain to the scheme:-

(1) An "E" against a vertical line indicates, that the elements appearing below are entirely, almost entirely or mainly removed in that particular group.

(2) A "P" against a vertical line indicates, that the elements appearing below are only partly removed in that particular group.

(3) Symbols appearing in brackets, represent those elements, which have been mainly or partly, but not entirely removed in a previous group (or groups).

(4) The reagents appearing across the long verticals, are those which are salient in the respective groups.

(5) Across each long vertical, is an indication, as to whether indium appears in the filtrate or precipitate in the particular group.

(b) NOTES:

In the following notes, the elements are dealt with in order of increasing atomic number.

The different type forms and bracketing indicate:-

(1) BLOCK TYPE: Elements which are invariably or usually present in typical zinc ores.

(2) ORDINARY TYPE: UNBRACKETED: Elements which are occasionally present.

(3) ORDINARY TYPE: BRACKETED: Elements which are infrequently or rarely present.

The special symbols appearing immediately after the chemical symbols represent:-

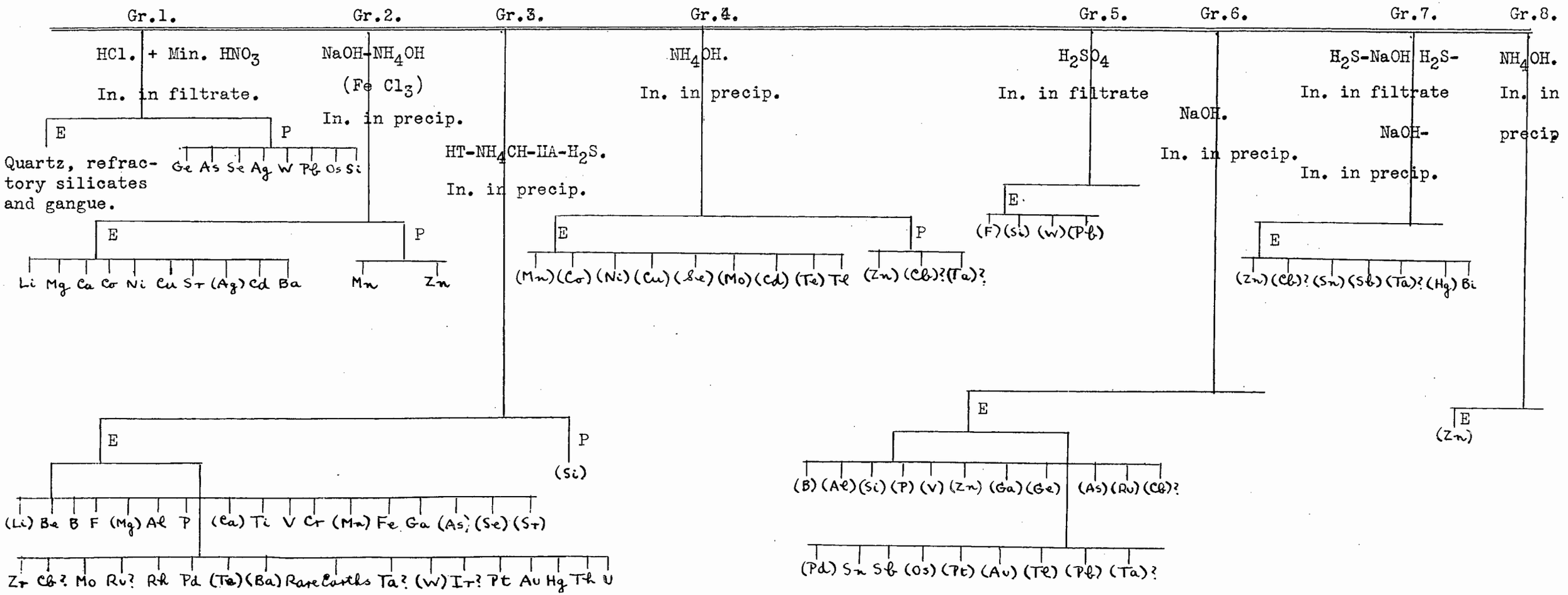
(1) "E" Entirely, almost entirely or mainly eliminated in the group, the number of which is postfixed.

(2) "P" Partly eliminated in the group, the number of which is postfixed.

Elements which obviously do not enter into the group separation scheme, such as hydrogen, nitrogen, chlorine, etc. and also the alkalies, have not been included.

(Lithium) E.2., E.3.
(Beryllium) E.3. - (See page 31)
(Boron) E.3., E.6. - (see page 33)
Fluorine E.3., E.5. - (See page 33)
Magnesium E.2., E.3.
Aluminium E.3., E.6. - (see page 27)
SILICON. P.1., P.2., E.5., E.6. - (See page 40)

DIAGRAMMATIC ELIMINATION SCHEME.



Phosphorus	E.3., E.6. - (See page 32)
CALCIUM	E.2., E.3. (When rich in Ca., P.2., E.3., E.4.)
(Titanium)	E.3. - (See page 31)
(Vanadium)	E.3., E.6. - (See page 31)
Chromium	E.3. If Cr. is present in fairly high proportions, which incidentally is most unlikely, then traces may pass beyond Gr.3, through adsorption in the ZnS. In this case, it will be found with the final In_2O_3. This, however, may be avoided by dissolving the combined hydroxides from Gr. 7 in HCl and reprecipitating with Na_2O_2. Under these conditions, indium is quantitatively precipitatedm(65) and Cr. remains in solution as Na_2CrO_4. One may then pass on to Gr. 8. This condition will, however, be rare, since chromates are not common in nature and since the relatively commonly occurring mineral chromite is not readily acted upon by strong acids.
MANGANESE	P.2., E.3., E.4. - (See page 29)
IRON	E3. Traces of iron invariably pass through with the indium and are found as Fe_2O_3 in the final ash. This residual iron is probably beneficial to the precipitation of indium by hydroxide in Grs. 4, 6, 7 and 8 and is estimated colorimetrically.
Cobalt	E.2., E.4.
Nickel	E.2., E.4.
COPPER	E.2., E.4.
ZINC	P.2., P.4., E.6., E.7., E.8.
GALLIUM	E.3., E.6. Gallium is usually present, but seldom in anything but small traces. (See page 36)
Germanium	P.1., E.6.
Arsenic	P.1., E.3., E.6. - (See page 39A)
Selenium	P.1., E.3., E.4.
Strontium	E.2., E.3.
(Zirconium)	E.3. - (See page 30)
(Columbium)	Doubtful, but probably eliminated in Groups 3, 4, 6 and 7.
Molybdenum	E.3., E.4. - (See page 30)
(Ruthenium)	E.3?., E.6. In the HCl - H_2S treatment, Ru will probably behave like Pt and Pd. It should definitely be removed in Group 6, considering that sodium ruthenate is soluble in water (82)
(Rhodium)	E.3. Rhodium sesquisulphide and rhodium hydrosulphide are insoluble in acids. (83)

(Palladium)	E.3., E.6. - (See page 31)
Silver	P.1., E.2.
CADMIUM	E.2., E.4.
INDIUM	Quantitatively retained throughout the scheme.
Tin	E.6., E.7. - (See page 39)
Antimony	E.6., E.7 - (See page 39)
Tellurium	P.1., E.3., E.4.
Barium	E.2., E.3.
(Rare Earths)	E.3. - (See page 28)
(Tantalum)	Doubtful, but probably eliminated in Groups 3, 4 6 and 7.
(Tungsten)	P.1., E.3., E.5. - (See page 30)
(Osmium)	P.1., E.6. Sodium osmate is soluble in water (84)
(Iridium)	E.3.
(Platinum)	E.3., E.6. - (See page 31)
Gold	E.3., E.6. - (See page 31)
Mercury	E.3., E.7.
THALLIUM	E.4., E.6. Thallium is usually present, but seldom in anything but small traces (See page 38)
LEAD	P.1., E.5., E.6. - (See page 41)
Bismuth	E.7. If bismuth is present in relatively appreciable proportions the H_2S section of Group 7 must be repeated. (See page 42)
(Thorium)	E.3. - (See page 30)
(Uranium)	E.3. - (See page 31)

The rare metals Hafnium, Masurium, and Rhenium have not been dealt with. Hafnium is chemically very similar to zirconium and it is thus highly probable, that this element would be eliminated in Group 3.

The oxides of Rhenium are more acidic than basic, hence, it appears as if this element would be eliminated in the sodium hydroxide groups.

Rhenium would tend to precipitate in Group 3, either as Re_2S_7 or ReS_2.

Not sufficient is known about Masurium to speculate on its elimination in this analytical scheme.

Owing to their extreme rarity, Radium and its associates need not be considered here.

Most of the above elements were introduced into the comprehensive synthetic mixtures described in Section 5, pages 46 - 49.

SECTION 8.

DETAILED ANALYTICAL PROCEDURE IN CONNECTION WITH THE ANALYSIS OF ZINC ORES.

Finely crush the ore and weigh out four lots of 40 - 50 grams each. If the indium percentage is very low, say below 0.001%, eight lots of 40 - 50 grams each should be treated.

These are ultimately combined and reduced to duplicate estimations.

Transfer to litre conical flasks and add 200 ml. concentrated hydrochloric acid to each.

In the case of sulphide ores, allow to simmer on a hot-plate, without vigorous boiling, until most of the ore has dissolved.

This usually takes 3 - 4 hours with typical sphalerites, but may take longer.

It is frequently necessary to add a further 50 - 100 ml. of acid in order to dissolve the majority of the ore.

Remove from hot-plate, allow to settle a few minutes and then decant into litre conical beakers.

Add a further 50 - 100 ml. concentrated hydrochloric acid to the residue (which should not be excessive) and then sufficient concentrated nitric acid to dissolve any residual sulphide.

A minimum of nitric acid should be added.

Bring the decanted solution to the boil and very carefully add nitric acid, drop by drop, in order to oxidise ferrous to ferric ion.

Care must be taken here, especially when the iron is over 2%.

Avoid excess of nitric acid.

Combine the major solution and the residual solution and dilute or concentrate to about 300 ml. cool and allow to stand in order to precipitate insoluble matter (gangue, insoluble silicates, silicic acid, lead chloride, etc.)

Filter (preferably through paper pulp) into litre conical beakers. If there is much gelatinous silicic acid present, it must be specially treated in order to remove any adsorbed indium chloride.

Transfer the gelatinous precipitate to a 300 ml. beaker, add 10-30 ml. concentrated nitric acid (depending on the volume of the precipitate), carefully evaporate to dryness and then bake. Cool, add about 20 ml. 5N. nitric acid, warm and filter into 300 ml. beakers.

Evaporate to dryness again, bake and take up with 10 - 20 ml. 2N. hydrochloric acid.

If any lead is present, allow the lead chloride to settle out and filter.

Add the acid solution to the main bulk.

This is the completion of stage 1 (The "Groups" will be termed "Stages" in the detailed analytical procedure).

Whilst Stage 1 is in progress, a special quantitative analysis on a separate portion of the finely crushed ore, should be carried out in order to determine the iron percentage.

If a carbonate ore is being analysed, there is less difficulty in getting the material into solution with hydrochloric acid and less acid will be required.

If the iron percentage is exceptionally low, i.e. below 0.5% it is advisable at this juncture to add C.P. ferric chloride solution in sufficient quantities to bring up the weight of iron in each lot to approximately 0.5 gram.

Add 6N - 7N sodium hydroxide to the filtrate from Stage 1, until a permanent brownish precipitate results.

An excess of sodium hydroxide must be avoided and the liquid must not react alkaline after this treatment.

The sodium hydroxide is added to neutralise the greater portion of the free acid and to bring down some of the iron and zinc, but not all of the iron and not sufficient to redissolve zinc as sodium zincate.

Now add .880 ammonia with thorough agitation, until nearly, but not all the zinc hydroxide has dissolved.

The zinc hydroxide is usually plainly visible at the bottom of the beaker after allowing to settle for a few minutes.

If all the zinc is dissolved at this stage, there will be insufficient zinc sulphide in Stage 3 for satisfactory adsorption, Allow the hydroxides to settle for about 15 - 30 minutes and then filter through 15cm. filters.

Each lot should be filtered through two 15 cm. filters, to avoid too great a volume of hydroxides in each paper.

When the iron percentage is excessive, i.e., greater than 5%, three filters (or two larger filters) should be used, for each lot.

When all the precipitate has been transferred to the filters and filtration has ceased, place each funnel in turn in the correct beaker and add hot 5N. hydrochloric acid to the contents of the filter paper.

The chlorides will thus be received in the precipitation beakers.

It will not be necessary at this stage to wash the hydroxide precipitates prior to dissolving in acid.

This is the end of Stage 2.

Transfer the contents of the litre beakers from Stage 2 to 500 ml. conical beakers.

The most suitable volume at this point is 250 ml.

If the iron percentage is greater than 5%, a somewhat larger volume is preferable.

Add 4 - 10 grams of Tartaric acid (the actual weight of tartaric acid to be added, depends mainly on the volume of the solution and the concentration of iron) and then .880 ammonia, until the solution is very faintly ammoniacal.

The sense of smell is probably the best indicator here.

If ferric hydroxide precipitates at this juncture, acidify with hydrochloric acid, add more tartaric acid and then render very faintly ammoniacal.

Then add glacial acetic acid until the acidity is 1.6N. Warm to about 80°C and bubble in hydrogen sulphide for 15 - 20 minutes.

Allow the sulphides to settle and then filter through 15 cm. filters, again using two filters for each lot.

If too much zinc had been removed in Stage 2, zinc acetate solution (containing approximately 1% of zinc) should be carefully added drop by drop to the acetic solution during the hydrogen sulphide treatment, until a satisfactory volume of zinc sulphide is present. 0.4 - 0.6 gram appears to be the optimum weight of zinc sulphide in this particular process.

If the zinc sulphide is much in excess of this, difficulty might be experienced in filtering and washing the sulphides.

If very much lower, there is a possibility of loss of indium, especially if the indium is present in very small proportions.

Experience should be gained, by passing hydrogen sulphide into specially prepared acetic solutions containing the usual amounts of iron and varying proportions of zinc.

One will then become acquainted with the appearance of 0.4 - 0.6 gram of zinc sulphide.

The sulphide precipitates are then washed two or three times with hot water and during this washing, a few ml. of hydrochloric acid should be added to the precipitation beakers (the bubbling tubes must be placed in the beakers during this procedure) in order to dissolve adhering sulphides.

The funnels are then placed in the correct beakers and warm 5N. hydrochloric acid added to the sulphides on the papers.

It is necessary to place a watch glass over the funnel immediately after adding the acid, in order to avoid loss by spraying, due to the evolution of hydrogen sulphide.

The filtrates are boiled to expel the hydrogen sulphide and are then carefully oxidised with a minimum of concentrated nitric acid, added dropwise.

Concentrate the solutuions, if necessary, to about 250 ml. add ammonia until very faintly ammoniacal and then acetic acid until 1.5N. and repeat the hydrogen sulphide treatment.

It is usually not necessary to add tartaric acid just prior to the second hydrogen sulphide bubbling.

The iron concentration has been greatly reduced and there is usually sufficient tartaric acid carried through from the first precipitation to keep this iron in solution.

If the iron percentage in the ore is over 5%, it may be necessary to make three precipitations in Stage 3.

The final sulphide precipitates are thoroughly washed with hot water in order to remove all traces of tartaric acid and are then dissolved by adding hot 5N. hydrochloric acid to the filter papers and the solutions being received in the precipitation beakers.

Boil the solutuions to remove hydrogen sulphide, oxidise with a minimum of concentrated nitric acid and evaporate down to about 50 ml.

Transfer to 250 ml. beakers.

This ends Stage 3.

Add ammonia in moderate excess to the solution obtained from Stage 3 and boil until slightly ammoniacal.

Allow to settle and filter through 11 cm. filters.

Wash, place the funnels in the precipitation beakers and dissolve the hydroxides in hot 5N. nitric acid.

This ends Stage 4.

Add 5 ml. of concentrated sulphuric acid to the nitric acid solution obtained from Stage 4 and concentrate to fumes.

Cool, add 50 ml. water and allow to settle.

It is advisable at this point to allow the precipitate to settle over night.

Filter and wash into 250 ml. beakers.

This ends Stage 5.

Add 5N. sodium hydroxide in excess until the alkalinity is about 0.4N (it is not advisable to exceed 0.5N), bring to the boil and allow to simmer for about 15 minutes.

Remove from hot-plate and allow to stand for about 20 - 30 minutes.

If the precipitates are very small at this stage, pairs should be filtered through one filter paper, thus reducing the estimation from quadruplicate to duplicate.

The solutions are filtered through 11cm. filters and washed.

The funnels are then placed in the precipitation beakers and hot 5N. hydrochloric acid added to the hydroxides on the filter papers.

This ends Stage 6.

Neutralise the solution obtained from Stage 6 with 5N. sodium hydroxide solution and then add hydrochloric acid until the solution is 0.5N. in acidity.

Warm the solution to about 80°C and bubble hydrogen sulphide for 5 minutes. Allow the sulphide to settle and then filter through 11cm. filters.

Wash a few times with 0.5N. hydrochloric acid and finally with water.

Catch the filtrates in 250 ml. beakers. Boil the filtrates to remove hydrogen sulphide and then oxidese with a few drops of concentrated nitric acid.

Add 5n. sodium hydroxide in excess, until the alkalinity is about 0.4N., bring to the boil and allow to simmer for about 15 minutes. Remove from hot-plate and allow to stand for about 20-30 minutes.

Filter through 11cm. filters and wash. Place the funnels in the precipitation beakers and add hot 5N. hydrochloric acid to the hydroxides.

If, during the bubbling of hydrogen sulphide, no precipitate or distrinct brownish colour appears, it will obviously not be necessary to proceed with the filtration and the solution may be boiled and oxidised immediately and then sodium hydroxide

added.

This is the end of Stage 7.

Add ammonia in moderate excess to the solution obtained from Stage 7, allow to simmer on the hot-plate until slightly ammoniacal, then, allow to settle and filter through 11cm. ashless filter paper.

Wash thoroughly, transfer to tared crucibles, dry in an oven, place in a cold muffle and gradually bring the temperature up to about 850°C.

When ashed, place in desiccator, cool and weigh.

Transfer the ash to 100 ml. beakers dissolve in a few drops of C.P. hydrochloric acid, transfer this solution to 100 ml. graduated flasks, take suitable aliquots and estimate the iron colorimetrically.

The thiocyanate method is very suitable here.

The ferric oxide weight is deducted from the total ash and the indium percentage calculated.

The indium sesquioxide - indium factor is .827.

The atomic weight of indium is taken as 114.76.

This atomic weight was decided upon by the Atomic Weight Commission of the International Union of Chemistry. (67).

If the indium percentage is very low, i.e., less than .001%, it is advisable to unite all four precipitates in Stage 6 (see page 57).

By these means, ores containing down to approximately.0005% indium can be evaluated.

With the extreme case of .0005%, beginning with 4 lots of one, each weighing 50 grams, the final weight of indium oxide (if quite free from iron) will be .0012 gram.

Provided this can be weighed $\pm$ 0.1 mgrm., the relative error is < 10% and the absolute error < .00005%.

There is much evidence in the various recovery tables appearing in Sections 4 and 5 - pages 14 - 49, that the errors due to analytical manipulation are not very significant.

The greatest error is generally 0.3 mgrm. in 5 mgrms. and the usual 0.1 - 0.2 mgrm. in 5 mgrms.

When placing indiferous ores in categories of varying indium content, it will seldom be necessary to demand high accuracy than this.

With richly indiferous ores, say about 0.1% indium, a final ash of 0.06 gram indium oxide will be weighed, starting with 50 grams of ore and estimating each lot separately without uniting pairs.

In this case, an absolute error of 0.3 mgrm. represents a relative error of only 0.5%, which is negligible in this type of analysis.

It is ofcourse feasible, that there might be an increase in the absolute error with increase in indium, but this is not so likely when one considers that the indium, in 5 groups out of 8 in the presence of bismuth and 6 groups out of 8 in the absence of bismuth, is in the precipitate and not in the filtrate.

Moreover, when the indium is in the filtrate, the accompanying precipitate is not highly adsorbent (mainly $PbCl_2$ in Group 1 and $PbSO_4$ in Group 5)

This leads to a minimum of loss of indium through adsorption in discarded precipitates.

This will probably minimise the increase in absolute error with increase in indium.

In the method detailed above, the indium is determined gravimetrically as oxide.

There are ofcourse other methods of estimating the indium.

The final hydroxide precipitate from Stage 8 may be dissolved in the most suitable acid, correctly treated and then the indium estimated in one of the following ways:-

(1) Gravimetrically as sulphide (21), (27).

(2) Gravimetrically as 8-Hydroxyquinolate (68).

(3) Volumetrically with bromate (68).

(4) Volumetrically with ferrocyanide (69).

(5) Electrolytically (10), (70), (71), (72), (73).

(6) Potentiometrically (71).

Spectroscopic and microscopic methods have not been included, as these are more adaptable to very small weights of indium, resulting from the treatment of moderate to large amounts of ore containing very small traces of indium or of comparatively small amounts of ore containing moderate to large proportions of indium.

(For details of the spectroscopic methods, see (74), (75), (76), (77), and of the microscopic method, see (78).The last is strictly a qualitative method).

With experience, the gravimetric method as described above, can be carried out in approximately 14 working hours.

This time excludes the period necessary for dissolving the ore in acid.

The time necessary for solution varies considerably from ore to ore.

More than 14 working hours will ofcourse be necessary in cases where more than two hydrogen sulphide separations (in Stage 3) are made.

The best scheme of organising the analysis, is to dissolve the ore throughout the first day and filter off the solution and possibly complete Stage 2 as well.

By the end of the second day, the analysis should have reached Stage 5 and the lead sulphate (if present) allowed to stand overnight.

The analysis is completed on the third day.

Quadruplicate analysis can be done in this way and in this time.

SECTION 9.

ESTIMATION OF THE INDIUM CONTENT OF CERTAIN SOUTHERN AFRICAN SPHALERITES, BY MEANS OF THE ANALYTICAL METHOD DESCRIBED IN SECTION 8.

The following specimens of sphalerite were analysed:-

(a) Sphalerite from Witkop, Marico, Western Transvaal, South Africa.

(b) Sphalerite from Buffelshoek, Zeerust, Western Transvaal, South Africa.

(c) Sphalerite from Stinkhoutboom, Ottoshoop, Western Transvaal, South Africa.

(d) Sphalerite from Kaalplaats, Marico, Western Transvaal, South Africa.

(e) Sphalerite from Grootfontein, South West Africa.

(f) Sphalerite from Lonely Mine, Bulawayo, Southern Rhodesia.

(g) Sphalerite from Broken Hill, Northern Rhodesia.

(h) Sphalerite from Broken Hill, Northern Rhodesia.

Besides these eight specimens from Southern Africa, a specimen of sphalerite from the richly indiferous deposits of America (forwarded by the Indium Corporation of America) was analysed.

The actual district was not disclosed by the consignor, but the specimen was taken from deposits, which are being worked for indium.

ANALYTICAL DETAILS.

SPECIMEN (a).

Locality: Witkop, Marico, Western Transvaal, South Africa.

Physical and Mineralogical Nature:

Massive, coarse-grained, yellowish-brown, sphalerite. Mineralogically, very pure.

Iron Content: 1.6% (as Fe).

Weight taken for analysis.

Four lots of 40 grams each were taken for analysis.

Group Treatment (Refer to Section 3).

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

Results of Analysis.

TABLE 39.

Anal.	Wt. of Sphal.	Wt. of final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grms.	0.0022 grams.	0.2 mgrm.	0.0020 grm.	0.0041
2.	" "	0.0022 "	0.2 "	0.0020 "	0.0041
3.	" "	0.0024 "	0.4 "	0.0020 "	0.0041
4.	" "	0.0023 "	0.2 "	0.0021 "	0.0043

Average - 0.0042%.

In this analysis, each of the four lots, was taken through the complete separation process; duplicates were not combined in Group 6.

After the completion of the analysis, the four lots of indium chloride (aliquots of which were used for the colorimetric estimation of iron) were combined and concentrated down to about 30 ml.

This acid solution was neutralised with ammonia (after adding 0.5 gram of tartaric acid), acetic acid added to 1.5N and then hydrogen sulphide bubbled in.

The characteristic bright yellow indium sulphide was precipitated almost immediately.

Specimen (b).

Locality. Buffelshoek, Zeerust, Western Transvaal, South Africa.

Physical and Mineralogical Nature.

Massive, Coarse-grained, yellowish-brown sphalerite. Mineralogically, very pure.

Iron Content. 2.0% (as Fe).

Weight taken for Analysis.

Eight lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once.

In Group 6, the eight precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

This was done because Group 6 showed a very light precipitate of hydroxide.

Results of Analyses.

TABLE 40.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grms.	0.0020 grm.	0.7 mgrm.	0.0013 grm.	0.0007%
2.	" "				
3.	" "				
4.	" "				
5.	" "	0.0017 grm.	0.6 mgrm.	0.0011 grm.	0.0006%
6.	" "				
7.	" "				
8.	" "				

Average - 0.0006%

Specimen (c).

Locality. Stinkhoutboom, Ottoshoop, Western Transvaal, South Africa.

Physical & Mineralogical Nature.

Massive, fairly fine-grained, brown Sphalerite. Mineralogically, fairly pure, with slight indications of galena.

Iron Content 2.2% (as Fe).

Weight taken for Analysis.

Four lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

In Group 6, the four precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

Quadruplicates were concentrated to duplicates.

Results of Analyses.

TABLE 41.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grams.	0.0025 grm.	0.4mgrm.	0.0021grm.	0.0022%
2.	" "				
3.	" "	0.0024 grm.	0.3mgrm.	0.0021grm.	0.0022%
4.	" "				

Average - 0.0022%

Specimen (d).

Locality. Kaalplaats, Marico, Western Transvaal, South Africa.

Physical & Mineralogical Nature.

Massive, fairly fine-grained, dark brown, Sphalerite.

Iron Content. 2.6% (as Fe)

Weight taken for Analysis.

Four lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Three times
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

In Group 6, the four precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

Quadruplicates were concentrated to duplicates.

Results of Analyses.

TABLE 42.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grams	0.0016 grm.	0.5 mgrm.	0.0011 grm.	0.0011%
2.	" "				
3.	" "	0.0016 grm.	0.5 mgrm.	0.0013 grm.	0.0013%
4.	" "				

Average - 0.0012%

Specimen (e).

Locality. Grootfontein, South West Africa.

Physical & Mineralogical Nature.

Massive, fine-grained Sphalerite with quartz and silicate m veins. Generally, Arenaceous. Colour, brown.

Iron Content. 0.49% (as Fe).

Free and Combined Silica. 6.8%.

Weight taken for Analysis.

Eight lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

Ferric Chloride was introduced just prior to adding Sodium Hydroxide in Group 2, in order to bring up the weight of iron in each lot to approximately 0.5 gram. (See page 55).

In Group 6, the eight precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

This was done because Group 6 showed a very light precipitate of hydroxide.

Results of Analyses.

TABLE 45.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 Grams.	0.0015 grm.	0.8 mgrm.	0.0009 grm.	0.0004%
2.	" "				
3.	" "				
4.	" "				
5.	" "	0.0018 grm.	0.7 mgrm.	0.0011 grm.	0.0006%
6.	" "				
7.	" "				
8.	" "				

Average - 0.0005%

Specimen (f).

Locality. Lonely Mine, Bulawayo, Southern Rhodesia.

Physical & Mineralogical Nature.

Massive, Fairly Fine-grained Sphalerite with very fine veins of siliceous material. Colour, brown.

Iron Content 3.4% (as Fe).

Free and Combined Silica. 4.0%.

Weight taken for Analysis. Eight lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Three Times
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

In Group 6, the eight precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

This was done because of the very light hydroxide precipitate in Group 6.

On filtering off the insoluble matter from the Group 1 treatment, a fair volume of gelatinous silicic acid was found on the filter.

Owing to its gelatinous and adsorptive nature, this silicic acid was treated according to the method described on page 64 in order to remove traces of indium adsorbed in the precipitate.

Results of Analyses.

TABLE 44.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grams				
2.	" "	0.0026 grm.	1.1 mgrm.	0.0015 grm.	0.0008%
3.	" "				
4.	" "				
5.	" "				
6.	" "	0.0017 "	0.4 "	0.0013 "	0.0007%
7.	" "				
8.	" "				

Average - 0.0007(5)%

Specimen (g).

Locality. Broken Hill, Northern Rhodesia.

Physical & Mineralogical Nature.

Massive, fine-grained, dark brown Sphalerite.
Mineralogically fairly pure.

Iron Content. 1.6% (as Fe).

Weight taken for Analysis. Eight lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

In Group 6, the eight precipitates were dissolved in hydrochloric acid and the solutions combined so as to obtain two lots.

Results of Analyses.

TABLE 45.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grms.				
2.	" "	0.0020 grm.	0.8 mgrm.	0.0012 grm.	0.0006%
3.	" "				
4.	" "				
5.	" "				
6.	" "	0.0016 grm.	0.4 mgrm.	0.0012 grm.	0.0006%
7.	" "				
8.	" "				

Average - 0.0006%

Specimen (h).

Locality. Broken Hill, Northern Rhodesia.

Physical & Mineralogical Nature.

Massive, coarse-grained, yellowish-brown Sphalerite.
The lustre of this specimen was almost adamantine.
Mineralogically, very pure.

Iron Content. 0.81%(as Fe).

Weight taken for Analysis. Eight lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Twice
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

In Group 6, the eight precipitates were dissolved in hydrochloric acid and the solutions combined, so as to obtain two lots.

Results of Analyses.

TABLE 46.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grams.				
2.	" "	0.0027 grm.	0.9 mgrm.	0.0018 grm.	0.0009%
3.	" "				
4.	" "				
5.	" "	0.0022 "	0.4 "	0.0018 "	0.0009%
6.	" "				
7.	" "				
8.	" "				

Average - 0.0009%

Sphalerite from America.

Physical & Mineralogical Nature.

Massive, fine-grained, dark-brown Sphalerite.
There was a fair admixture of Galena, Pyrite and Chalcopyrite.
Some Quartz veining was observed.

Iron Content. 5.7% (as Fe).

Weight taken for Analysis. Four lots of 40 grams each.

Group Treatment.

Group 2 - Once
Group 3 - Three times
Group 4 - Once
Group 5 - Once
Group 6 - Once
Group 7 - Once
Group 8 - Once

Results of Analyses.

TABLE 47.

Anal.	Wt. of Sphal.	Wt. of Final Oxides.	Wt. of Fe_2O_3	Wt. of In_2O_3	Percentage of Indium.
1.	40 grams.	0.0110 grm.	0.3 mgrm.	0.0107 grm.	0.0220%
2.	" "	0.0108 "	0.8 "	0.0100 "	0.0205%
3.	" "	0.0133 "	3.3 "	0.0100 "	0.0205%
4.	" "	0.0113 "	1.0 "	0.0103 "	0.0215%

The percentages here are ± 0.0005%.

Average - 0.0210% (±.0005%)

Degree of Accuracy of above data.

(a) "Wt. of Sphalerite" Column.

The ore was weighed ± 0.2 gram.

(b) "Wt. of Final Oxides" Column.

These weights are ± 0.1 mgrm.

(c) "Weight of Fe_2O_3 Column.

The Fe_2O_3 was estimated colorimetrically to an accuracy of ± 0.05 mgrm., although it has invariably been reported ± 0.1 mgrm.

(d) "Weight of In_2O_3 " Column.

As a result of (b) and (c) above, the weights here are ± 0.1 mgrm.

(e) "Percentage of Indium" Column.

From the point of view of gravimetric and colorimetric accuracy the percentages recorded in these columns are ± 0.00005% in the cases of analyses b, e, f, g and h, ± 0.0001% in the cases of c and d and ± 0.0002% in the case of a.

Owing to the relatively high percentage of indium in the American specimen, the final results have been reported ± 0.0005%.

Summary of Analyses.

TABLE 48.

Specimen.	Locality.	Indium Percentage
a	Witkop, Western Transvaal, South Africa.	0.0042%
b	Buffelshoek, Zeerust, Western Transvaal, South Africa.	0.0006%
c	Stinkhoutboom, Ottoshoop, Western Transvaal, South Africa.	0.0032%
d	Koolplaats, Marico, Western Transvaal, South Africa.	0.0012%
e	Grootfontein, South West Africa.	0.0005%
f	Lonely Mine, Bulawayo, Southern Rhodesia.	0.0007%
g	Broken Hill, Northern Rhodesia.	0.0006%
h	Broken Hill, Northern Rhodesia.	0.0009%
American	Exact Locality not Known.	0.0210%

SECTION 10.

SUMMARY OF THESIS.

(a) An Analytical Scheme is described in outline and later in detail, for the estimation of Indium in Zinc Ores.

The method is a chemical one and is presented in Group Form.

(b) Other methods are described and commented upon.

(c) The qualitative and quantitative significance of the Group Separation Scheme is dealt with in detail.

(d) The efficacy of the analytical method is confirmed by the estimation of Indium in comprehensive Synthetic Mixtures.

(e) The isolation of Indium and the elimination of other elements, by means of this method, are presented diagrammatically.

(f) The Analytical Scheme developed and described in this work, is used for the estimation of Indium in certain sphalerites from Western Transvaal, South Africa and also from Rhodesia and South West Africa and the results recorded.

For purposes of comparison a richly indiferous American Sphalerite was analysed and the results are recorded.

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