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A RAPID METHOD FOR ESTIMATING NICKEL AND COBALT IN ORES AND ALLOYS.—PART I.

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(Read at the Meeting, May 2, 1917.)

THE present investigation, referred to in the reply to the discussion on the authors' previous paper (*Analyst*, 1916, **41**, 124), is an endeavour to elaborate a quick method for assaying materials containing nickel and cobalt. Though the experimental work on the new method is not yet concluded, we consider the encouraging results so far obtained justify the publication of this paper, as the information may be of use to analysts dealing with the metals in question. An account of the complete investigation will be given later.

We do not lay claim to having discovered the reaction on which the process is based, it having been shown some years ago that potassium iodide precipitates

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nickel in ammoniacal solution; this reaction was stated to afford a means of separating nickel from zinc. The idea occurred to us that nickel, and cobalt also, might be separated from other metals by this method. Apart from a patent claiming the separation of nickel from zinc, copper, etc., by means of an excess of alkali chloride and ammonia added to a solution of the mixed chlorides (*J. Chem. Soc.*, 1904, **85**, ii., 128), nothing could be found in the technical literature concerning such separation. Qualitative tests proved that nickel solutions treated with excess of strong ammonia and potassium chloride, bromide, or iodide, gave pale mauve crystalline precipitates; cobalt solutions under the same conditions yielded similar, flesh-coloured precipitates. By their mode of formation, these precipitates were presumably compounds of the metallic halides with two, four, or six molecules of ammonia, the description of which may be found in Gmelin-Kraut's "Handbuch der anorganischen Chemie" (7th ed., vol. v., part 1, 95, 265). We have adopted Werner's nomenclature (Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie") in referring to these substances, the composition of which was ascertained (in the case of the iodides) by dissolving the precipitate, obtained from a known weight of metal and washed free from ammonia with alcohol, in excess of $\frac{\pi}{3}$ acid, and titrating back with $\frac{\pi}{3}$ alkali.

Ratio NH_3 : Ni found : 6.04 : 1.
 „ NH_3 : Co „ : 5.94 : 1.

These figures prove the precipitates to consist of hexamminenickelous iodide, $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$, and hexamminecobaltous iodide, $[\text{Co}(\text{NH}_3)_6]\text{I}_2$.

An endeavour was made to substitute the cheaper alkali chlorides for the iodide, but the attempt had to be abandoned, as the precipitation was very incomplete. Potassium bromide in sufficient quantity gave a more complete precipitation, but the best results were obtained with iodide. This is shown in Table I., in which the figures indicate the quantities of nickel and cobalt that passed into the filtrate after adding varying amounts of halide to 0.1 gram. of metal in 100 c.c. of solution containing 80 c.c. of strong ammonia.

TABLE I.

| Halide added. | Nickel Solution. | | Cobalt Solution. | |
|---------------|------------------|--------------|------------------|---------------|
| | + KI. | + KBr. | + KI. | + KBr. |
| 1 gram. | 0.0153 gram. | 0.0406 gram. | Considerable. | Considerable. |
| 2 grms. | 0.0028 „ | 0.0076 „ | 0.0066 gram. | „ |
| 3 „ | 0.0007 „ | 0.0053 „ | 0.0026 „ | 0.0155 gram |
| 4 „ | 0.0005 „ | 0.0047 „ | trace | 0.0115 „ |
| 5 „ | 0.0002 „ | 0.0040 „ | „ | 0.0086 „ |

The figures show that, in presence of excess of iodide, the precipitates are sufficiently insoluble to be utilised for quantitative purposes. This excess of iodide

required was not recognised for some time, and much delay occurred before the cause of our low results was discovered. Sufficient iodide must be added over and above the quantity required for precipitation (0.6 gm. KI per 0.1 gm. Ni + Co) to yield a solution containing 4 per cent. of the precipitant. Table II. gives the minimum amount of potassium iodide required for complete precipitation. It is added to the assay in cold saturated solution immediately after the ammonia, to avoid oxidation of the cobalt.

TABLE II.

| <i>Volume of Ammoniacal Solution.</i> | <i>Grms. Ni + Co in Solution.</i> | | | | |
|---------------------------------------|-----------------------------------|------|------|------|------|
| | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 |
| 60 c.c. | 2.7 | 3.0 | 3.3 | 3.6 | 3.9 |
| 80 ,, | 3.5 | 3.8 | 4.1 | 4.4 | 4.7 |
| 100 ,, | 4.3 | 4.6 | 4.9 | 5.2 | 5.5 |

Other experiments proved that the concentration of the ammonia need not be regulated so strictly as that of the iodide; but the volume of strong ammonia (sp. gr. 0.88) should be at least two-thirds of the total. The authors always aim at four-fifths. The bulk of solution should be kept as low as possible, and not greatly exceed 80 c.c. Under these conditions the loss of metal in the filtrate is inappreciable.

With quantities of nickel or cobalt exceeding a few mgrms., the precipitation appears to be almost instantaneous; in all the test assays the solutions were never left to stand for more than ten to fifteen minutes before filtering. Though very small quantities (*e.g.*, less than 2 mgrms.) fail to precipitate within that time, precipitation may be induced by adding a small quantity of strong sodium sulphate solution, which, by double decomposition with the potassium iodide, causes a precipitate of potassium sulphate, more or less insoluble in strong ammonia. This precipitate will carry down the metallic iodide. Working in this manner, 0.00066 gm. of cobalt was recovered from 75 c.c. of solution containing 60 c.c. of ammonia, 4 grms. of potassium iodide, and 0.00088 gm. of cobalt; from a similar solution containing 0.00103 gm. of nickel, 0.00086 gm. was obtained. The method is therefore not suitable for detecting or estimating traces of nickel or cobalt.

In filtering the iodide precipitate, the use of a filter pump would be of advantage, but we purposely carried out all filtrations at ordinary pressure, using a very loose filter-paper (Whatman No. 4) and carefully selected funnels. In spite of the high filtering speed thus attained, the precipitate, being crystalline, never ran through the filter. Water decomposes the precipitate with formation of basic salts; hence washing must be effected with a cold solution containing 800 c.c. of strong ammonia

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and 40 grms. of potassium iodide per litre. A filtering flask fitted with a Bunsen valve is suitable as a wash-bottle, the side-tube being closed with the finger whilst blowing.

For the separation and estimation of nickel and cobalt, the washed precipitate is rinsed back with water, without removing the filter-paper from the funnel, through a short-stemmed funnel into the precipitation flask; the filter is washed with dilute hydrochloric acid and a small quantity of sulphurous acid to bleach the filter coloured by iodine, the washings being allowed to run into the flask containing the precipitate. The latter is now dissolved in a small excess of hydrochloric acid, more sulphite being added if required. The solution is then filtered through the same filter into a 300 c.c. beaker to remove any gangue or other insoluble material; it is now ready for the precipitation of cobalt ammonium phosphate, which may be titrated according to the authors' alkalimetric method (*cf.* our previous paper, *loc. cit.*). The ammoniacal filtrate containing the nickel is titrated with cyanide, no indicator being required, as the liquor already contains iodide; the small amount of sulphite, if not previously destroyed in the boiling, has not been found to interfere with the nickel titration.

The property of forming complex iodides insoluble under the conditions here described is not confined to nickel and cobalt, being common to several bivalent metals. The behaviour of the latter and of the commoner elements, when present in an assay based on this method, will now be considered.

Iron.—In presence of sufficient tartaric acid to prevent precipitation of the hydroxide (*i.e.*, ten times the amount of iron present), ammoniacal solutions of ferrous salts yield a white precipitate of hexammineferrous iodide, $[\text{Fe}(\text{NH}_3)_6]\text{I}_2$; the ratio $\text{NH}_3 : \text{Fe}$ found in duplicate titrations was 5.78 and 5.59 : 1. The figures are low because the white precipitate cannot be washed with alcohol without decomposition and oxidation, the colour gradually changing to rust-brown. Ferric salts in ammoniacal tartrate solution are not precipitated by iodide; and, provided the necessary excess of tartaric acid has been added (as shown by the pale green colour of the ammoniacal solution), a quantitative separation from cobalt and nickel by a single precipitation can be effected in this manner (see Ore A).

Manganese.—Manganous salts are precipitated in ammoniacal tartrate solution in the form of white pentamminemanganous iodide, $[\text{Mn}(\text{NH}_3)_5]\text{I}_2$; the estimation of the ratio $\text{NH}_3 : \text{Mn}$ gave 5.00 and 5.13 : 1. The precipitate is more stable than the ferrous salt, but begins to decompose, with separation of manganic hydroxide, on removing the excess of iodide and ammonia by washing with alcohol.*

Manganese is not precipitated so readily as nickel or cobalt, hence a small quantity (*e.g.*, 5 mgrms. or less) by itself fails to precipitate within the time allowed before filtration (ten to fifteen minutes); but in presence of nickel or cobalt much smaller quantities of manganese are carried down by the iodide precipitate. The problem of overcoming the interference of manganese is still under investigation;

* As far as the authors are aware, the ferrous and manganous iodides described above have not before been obtained by precipitation. Hexammineferrous iodide (Moissan, "Chimie minérale," tome iv., 339) and hexamminemanganous iodide (Abegg, "Handbuch der anorganischen Chemie," vol. iv., part 2, 711) have been prepared by the interaction of the anhydrous iodides and gaseous ammonia. Most polyamine iodides decompose on drying or by contact with water.

for the present the simplest procedure seems to be solution of the mixed iodide precipitate in a small excess of dilute acid, addition of excess of sodium acetate, and precipitation of nickel and cobalt by hydrogen sulphide.

Copper is not precipitated under the conditions of the assay (*i.e.*, in ammoniacal 4 per cent. iodide solution), though with a much higher concentration of iodide (about 10 per cent.) blue crystalline tetramminecupric iodide, $[\text{Cu}(\text{NH}_3)_4]\text{I}_2 \cdot \text{H}_2\text{O}$, is precipitated (Gmelin-Kraut, *loc. cit.*, vol. v., part 1, 953). In presence of nickel or cobalt, however, co-precipitation of copper takes place, and this is indicated by the blue colour of the precipitate; the precipitation of the copper is incomplete, as the filtrate always exhibits the familiar deep blue colour. Unlike manganese, very small amounts of copper (about 0.01 grm.) are not co-precipitated.

On dissolving a cupriferous cobalt-nickel iodide precipitate in dilute hydrochloric acid, cuprous iodide is precipitated with liberation of iodine. In presence of a slight excess of sulphur dioxide or a sulphite, quantitative precipitation of the copper ensues (Crookes, "Select Methods," 4th ed., 1905, 324). The filtering properties of cuprous iodide are much improved by boiling the liquid containing it; but, as the hot solution has a solvent effect upon cuprous iodide, due to soluble iodides and chlorides, it should be cooled to room temperature before filtration. The washing is carried out with cold water. This separation of copper from cobalt and nickel has been found very satisfactory. If it is preferred to remove copper as cuprous thiocyanate previous to the precipitation of cobalt and nickel, the filtrate from the thiocyanate is oxidised with nitric acid, boiled down almost to dryness, and treated with tartaric acid, ammonia, and iodide, as prescribed (Ore D). Copper, if not removed, would cause high results in the nickel titration.

Cadmium.—This metal is precipitated as white, crystalline tetramminecadmium iodide, $[\text{Cd}(\text{NH}_3)_4]\text{I}_2$; titration gave an $\text{NH}_3:\text{Cd}$ ratio of 3.74:1. This low result is probably due to loss of ammonia in washing; the identity of the precipitate can hardly be in doubt, as a compound answering the above formula has been obtained by the action of strong ammonia on cadmium iodide solution (Gmelin-Kraut, *loc. cit.*, vol. iv., part 1, 878).

Like manganese, cadmium is co-precipitated even if present in small quantity, and interferes with the subsequent estimation of cobalt as phosphate; however, the rare occurrence of cadmium except in zinc ores, from which cobalt and nickel are almost invariably absent, makes the possibility of its interference a remote one. If present, cadmium could be readily eliminated by passing hydrogen sulphide through the solution of the iodide precipitate faintly acidified with sulphuric acid.

Zinc has not been found to give any insoluble compounds with ammonia and potassium iodide, nor has co-precipitation been observed to take place in presence of nickel or cobalt.

Alkaline Earth Metals.—Barium occurs most commonly as, or can be converted into, sulphate, and in this form is eliminated at the same time as the insoluble gangue. —Soluble lime salts do not interfere, strictly speaking, but if in large quantities they slowly crystallise out as a complex tartrate, with attendant risk of contaminating the cobalt precipitate in the phosphate separation. It is therefore advisable, in such a case, to evaporate the solution of the ore with 1 c.c. of strong sulphuric acid

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to fumes, and take up with a little water followed by an equal volume of methylated spirit. The anhydrous calcium sulphate is filtered off and washed with 50 per cent. spirit; the alcoholic filtrate is boiled down until about 5 c.c. remain (see Ore B). Smaller quantities of lime need not be thus removed (Ore C).—Magnesium is without influence on the assay (Ore B).

Lead, Mercury, Silver.—Lead iodide is soluble in ammoniacal tartrate solution, and appears to be harmless. In dealing with large quantities of lead, recourse can always be had to the separation as sulphate, avoiding the use of an excess of sulphuric acid (as for lime).—Mercuric salts yield a complex iodide (probably $[\text{Hg}(\text{NH}_3)_2]\text{I}_2$; Gmelin-Kraut, *loc. cit.*, vol. v., part 2, 796) which slowly crystallises out in long glistening needles decomposed by water and acids, leaving insoluble mercuric iodide.—Silver is thrown down as a curdy white precipitate, the composition of which is uncertain; it is converted by dilute acids or water into the normal iodide, in which form it is removed by filtration.

Trivalent Metals.—The non-interference of ferric salts has already been mentioned. Nor is the presence of aluminium, chromium, antimony, or bismuth, objectionable, provided sufficient tartaric acid has been added.

Arsenic is a very common constituent of cobalt and nickel ores; nitric acid converts it into arsenic acid, which, under the conditions attained by the ordinary procedure, is without influence (Ore A). The simultaneous presence in an ore of large amounts of arsenic and magnesium (*e.g.*, as dolomite)—an unusual case—would necessitate a preliminary reducing roast, or fusion with soda-sulphur or soda-nitre mixture; otherwise the addition of tartaric acid and ammonia would cause precipitation of magnesium ammonium arsenate, which, by remaining with the iodide precipitate, would interfere with the separation of cobalt as phosphate.

Sulphur.—Sulphides (unless capable of being decomposed by hydrochloric acid) are oxidised by nitric acid to sulphates. Though the presence of the latter presents no real objection, the addition of the strong ammonia to a solution containing much copper and an excess of sulphuric acid may produce a blue precipitate of tetramminecupric sulphate, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, while addition of potassium iodide to the ammoniacal liquor causes precipitation of potassium sulphate. The bulk of precipitate to be washed out is thus increased, while potassium sulphate is apt to slowly crystallise out in the filtrate, which might be mistaken for incomplete precipitation. On treating the mixed iodide precipitate with hydrochloric acid, any tetramminecupric sulphate is converted into cuprous iodide, provided enough nickel or cobalt iodide is present; if not, sufficient potassium iodide must be added to complete the precipitation of the copper. If an ore is treated with sulphuric acid, as little as possible should be used, or the excess almost completely expelled (see under lime). If sodium iodide be used instead of the potassium salt, no precipitation of sodium sulphate takes place.

Chlorine.—Ammonium chloride, in quantities exceeding 0.5 grm., has a slight but distinct solvent effect upon the iodide precipitates, especially that of nickel. Hence, if hydrochloric acid has been used for opening up an ore, the excess should be expelled by boiling, and the chlorides formed destroyed by one evaporation with nitric acid to small bulk, carefully avoiding separation of basic salts. The required

amount of tartaric acid is then added, together with a minimum of hot water necessary to dissolve it; the assay is cooled and treated with ammonia and iodide.

Citric Acid should not be used instead of tartaric, because it leads to low results; it probably exerts a retarding effect on the precipitation.

Several examples will now be given of the application of the method to some ores and metallurgical products of known composition, together with a brief description of the procedure followed in each case. A complete analysis of each sample was made, disregarding elements present in minute quantities. The separation and estimation of the nickel and cobalt in the complete analyses was carried out by various standard methods other than electrolytic. In order to obtain an additional and independent check on their results by the new process, we secured the co-operation, with the courteous permission of Messrs. D. C. Griffith and Co., Assayers to the Bank of England, of their chief chemist, Mr. Charles E. Barrs, who estimated the sum of nickel and cobalt by electrolysis. The errors in the test assays of samples A to D are calculated on the figures supplied by Mr. Barrs.

A.—SPEISS (TABLE III.).

One gram. was treated with nitric acid in a 200 c.c. flask and the excess of acid boiled off. Five grms. of tartaric acid and 65 c.c. ammonia (sp. gr. 0.88) were added, the solution being kept cool, and 4 grms. potassium iodide added in saturated solution. Filtered after ten minutes, washed with ammoniacal iodide solution till free from iron; dissolved the precipitate in dilute hydrochloric acid, adding a little sodium sulphite; filtered off insoluble matter through the same filter into a beaker. The filtrate was then ready for nickel-cobalt separation. The time required for complete assay in duplicate was two to two and a half hours.

TABLE III.

Ni + Co (C. E. Barrs): 12.31%.

Composition (per Cent.): Ni, 4.53; Co, 7.75; Fe, 54.03; As, 20.33; S, 8.57; Insol., 4.06; Total, 99.27.

| <i>Exp.</i> | <i>Ni %.</i> | <i>Co %.</i> | <i>Sum %.</i> | <i>Error %.</i> |
|-------------|--------------|--------------|---------------|-----------------|
| 46a | 4.53 | 7.68 | 12.21 | - 0.10 |
| 46b | 4.61 | 7.80 | 12.41 | + 0.10 |
| 46c | 4.58 | 7.33 | 11.91 | - 0.40 |
| 50a | 4.56 | 7.51 | 12.07 | - 0.24 |
| 51a | 4.56 | 7.74 | 12.30 | - 0.01 |
| 51b | 4.61 | 7.68 | 12.29 | - 0.02 |

B.—BASIC ORE (TABLE IV.).

One grm. was dissolved in nitric acid in a porcelain basin, evaporated with 1 c.c. of strong sulphuric acid until fumes were given off, and taken up with 20 c.c. of water and 25 c.c. of methylated spirit. Filtered after half an hour, and washed with 50 per cent. spirit; the filtrate was boiled down to 5 c.c., adding 2 grms. of tartaric acid; cooled, and added 60 c.c. of strong ammonia and 4 grms. of iodide (saturated solution). Filtered after ten minutes, and washed with ammoniacal iodide solution. The precipitate was rinsed back and dissolved in dilute hydrochloric acid, and cuprous iodide filtered off as described under copper; the filtrate was then ready for cobalt-nickel separation. The time required was about four hours.

TABLE IV.

Ni + Co (C. E. Barrs): 9.07%.

Composition (per Cent.): Ni, 6.66; Co, 2.40; Cu, 9.40; Fe, 3.00; Zn, 0.05; S, 13.72; SO₄, 4.54; CaCO₃, 32.36; MgCO₃, 26.80; Insol., 0.92; Total, 99.85.

| <i>Exp.</i> | <i>Ni %.</i> | <i>Co %.</i> | <i>Sum %.</i> | <i>Error %.</i> |
|-------------|--------------|--------------|---------------|-----------------|
| 77h | 6.61 | 2.41 | 9.02 | -0.05 |
| 78d | 6.53 | 2.44 | 8.97 | -0.10 |
| 78e | 6.43 | 2.50 | 8.93 | -0.14 |
| 78f | 6.47 | 2.65 | 9.12 | +0.05 |
| 78g | 6.59 | 2.50 | 9.09 | +0.02 |
| 80c | 6.72 | 2.43 | 9.15 | +0.08 |
| 80d | 6.72 | 2.47 | 9.19 | +0.12 |

C.—SULPHIDE CONCENTRATE (TABLE V.).

0.5 grm. was dissolved in nitric acid, the excess of acid removed by boiling, and 2 grms. tartaric acid, 60 c.c. strong ammonia, and 4 grms. of iodide were added. The subsequent treatment was similar to that described under B. The time required was about three hours.

Examples of low results due to insufficiency of potassium iodide are shown in Tables V. and VI.

TABLE V.

Ni + Co (C. E. Barrs): 21.12%.

Composition (per Cent.): Ni, 15.50; Co, 5.01; Cu, 21.03; Fe, 8.41; Zn, 0.48;
S, 44.52; CaCO₃, 2.86; MgCO₃, 0.97; Insol., 0.72; Total, 100.16.

| <i>Exp.</i> | <i>Grms. KI added.</i> | <i>Ni %.</i> | <i>Co %.</i> | <i>Sum %.</i> | <i>Error %.</i> |
|-------------|------------------------|--------------|--------------|---------------|-----------------|
| 57a | 3 | 15.25 | 5.28 | 20.53 | -0.59 |
| 57b | 3 | 15.25 | 5.10 | 20.35 | -0.77 |
| 83a | 4 | 15.50 | 5.49 | 20.99 | -0.13 |
| 83b | 4 | 15.50 | 5.65 | 21.15 | +0.03 |
| 83c | 4 | 15.47 | 5.65 | 21.12 | 0.00 |
| 83d | 4 | 15.41 | 5.65 | 21.06 | -0.06 |

D.—MATTE (TABLE VI.).

0.4 gram. was dissolved in nitric acid, and the copper precipitated with thiocyanate and sulphur dioxide. The excess of thiocyanate in the filtrate was destroyed by nitric acid; after boiling down to a very small bulk, 1 gram. tartaric acid, 60 c.c. strong ammonia, and 4 grms. iodide, were added. The precipitate was filtered off and washed with ammoniacal iodide solution, dissolved in hydrochloric acid, and titrated with cyanide without separating the minute quantity of cobalt, the brown colour of which was very conspicuous in all the titrations.

TABLE VI.

Ni + Co (C. E. Barrs): 41.74%.

Composition (per Cent.): Ni, 41.55; Co, 0.22; Cu, 37.50; Fe, 0.45;
S, 16.80; Insol., 2.91; Total, 99.43.

| <i>Exp.</i> | <i>Grms. KI added.</i> | <i>Ni + Co %.</i> | <i>Error %.</i> |
|-------------|------------------------|-------------------|-----------------|
| 66a | 3 | 41.36 | -0.38 |
| 66b | 3 | 41.18 | -0.56 |
| 66c | 4 | 41.78 | +0.04 |
| 66d | 4 | 41.75 | +0.01 |
| 68a | 4 | 41.82 | +0.08 |
| 68b | 4 | 41.78 | +0.04 |

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The method was further tested on three nickel-silicate ores, with the following results:

| % Ni by— | <i>Iodide Method.</i> | <i>Other Method.</i> |
|----------|-----------------------|----------------------|
| Ore E | 1.46 | 1.44 |
| „ F | 1.85 | 1.85 |
| „ G | 1.89 | 1.90 |

The experimental evidence proves that the new method is applicable to ores containing iron, copper, lime, magnesia, arsenic, or sulphur, and that it results in a considerable saving of time as compared with any other process. We trust in due course to be able to publish another paper dealing with the assay of manganiferous, lead-zinc, and argentiferous ores from Cobalt (Ont.), etc., as well as cobalt-steel and non-ferrous alloys; we are also working out a process for recovering the iodide from the ammoniacal filtrates and washings.

The greater part of the experimental work, which so far has necessitated over 300 estimations of cobalt and nickel, was carried out at the Sir John Cass Technical Institute.

APPENDIX.

Since the above paper was written, we were informed by Mr. J. H. Wells, who formerly assisted Mr. L. Parry, that the latter was the originator of the separation of nickel and zinc by potassium iodide and ammonia, the method having been published in the *Mining Journal*. The following is an abstract of the two brief communications by Parry dealing with the process (*Min. J.*, 1909, **85**, 728, 805):

In the course of a general analysis, the metals of the first two groups are precipitated by hydrogen sulphide; the filtrate is oxidised and precipitated with bromine, ammonia, and ammonium carbonate. The acidified filtrate is boiled down to 30 c.c., cooled and neutralised with ammonia; an excess of 10 c.c. is added, followed by 10 grms. of potassium iodide in 20 c.c. of water. The nickel precipitate is redissolved and the solution titrated with cyanide. In the filtrate from the nickel zinc is titrated with ferrocyanide.

Parry merely mentions that cobalt is also precipitated, and remarks that this separation of nickel and zinc affords a means of estimating them, in solutions free from metals of the preceding groups and from cobalt, which, for quickness and accuracy, cannot be surpassed. He also states that copper is co-precipitated, in which case the precipitate is blue instead of violet.

We submit that the method elaborated by us represents a considerable advance on that given by Parry, inasmuch as we separate both nickel and cobalt at the outset as hexamine iodides without a preliminary treatment by hydrogen sulphide or bromine and ammonia, the latter procedure for removing iron and manganese being quite unsatisfactory, as it gives low results, especially for cobalt. We have

also ascertained the best conditions for the quantitative precipitation of nickel and cobalt and the behaviour of the commoner elements in the assay, and have converted the original nickel-zinc separation into a method of general applicability for the estimation of nickel and cobalt.

DISCUSSION.

Mr. G. N. HUNTLY said the fact that the presence of iron did not interfere with the process was important, as the estimation of nickel and cobalt in the presence of iron was admittedly difficult, and although dimethyl-glyoxime gave a satisfactory separation of the nickel the reagent was expensive. With regard to the errors shown in the tables, perhaps the authors would say what was the unavoidable experimental error in the phosphate titration corresponding to one drop of the standard solution.

Dr. SCHOELLER said that the differences mainly arose in the separation of the nickel and cobalt from one another by the phosphate method, this being really more difficult than the iodide separation of nickel and cobalt from other metals; but in the phosphate method any cobalt that might be lost in the filtrate would count as nickel, while any nickel co-precipitated with the cobalt would count as cobalt. Although they preferred the phosphate separation as being much the quickest, the glyoxime and other methods might also be used, provided that a satisfactory separation of nickel and cobalt from other metals was obtained in the first place.

Mr. C. E. BARRS said that in estimating nickel and cobalt in the presence of iron he had usually resorted to the ether separation, which was fairly well known and satisfactory. In order to make sure of obtaining all the nickel and cobalt, a little iron might be allowed to go through also, as that did not interfere with the satisfactory carrying out of the electrolytic process. With regard to the phosphate method, the separation of the cobalt required practice, and even in experienced hands small errors were likely to occur, unless the addition of ammonia was carefully regulated. But, as the authors worked, nickel and cobalt replaced one another, so that the sum of the two could be taken, and confirmation of the separate amounts obtained in another way. The dimethyl-glyoxime precipitation also had its difficulties. Indeed, on one occasion he had failed to get a satisfactory separation, and had since been told that this was probably due to the fact that he was using an isomer of dimethyl-glyoxime which did not effect a separation.

Dr. SCHOELLER said that, as Mr. Huntly had remarked, the most satisfactory result of their work was the separation of iron from nickel and cobalt. In fact, provided sufficient tartaric acid was used, any trivalent metal would without difficulty be obtained in the filtrate, leaving the precipitate quite free.

