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POLAROGRAPHIC AND AMPEROMETRIC METHODS
APPLIED TO METALLURGICAL ANALYSIS

by

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ABSTRACT

A general outline is given for the determination of copper, nickel, cobalt, zinc, lead, cadmium, bismuth, manganese, uranium, molybdenum, vanadium, sulphate and fluoride by polarographic or amperometric methods in a variety of ores or metallurgical products. The detection of oxygen in gas mixtures by an amperometric method used as a safety device is also discussed.

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MÉTHODES POLAROGRAPHIQUES ET AMPÉROMÉTRIQUES
APPLIQUÉES À L'ANALYSE MÉTALLURGIQUE

par

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RÉSUMÉ

L'auteur expose à grand traits les méthodes employées (polarographiques ou ampérométriques) pour doser le cuivre, le nickel, le cobalt, le zinc, le plomb, le cadmium, le bismuth, le manganèse, l'uranium, le molybdène, le vanadium, le sulfate et la fluorure dans une gamme étendue de minerais ou de produits métallurgiques. Il explique également la méthode ampérométrique employée comme mesure de sécurité pour détecter l'oxygène dans divers mélanges de gaz.

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INTRODUCTION

In this paper a general outline will be given of the polarographic and amperometric methods used for the chemical analysis of various ores and metallurgical products in the Chemical Analysis Section of the Extraction Metallurgy Division of the Mines Branch. The methods to be discussed will be confined to those based on the use of normal d-c polarography and will not include those methods which utilize a cathode-ray, square wave, pulse or a-c type of polarograph.

For the sake of convenience the polarographic methods will be discussed according to the type of supporting electrolyte employed, since the same electrolyte may serve to determine more than one element in more than one type of ore. Amperometric methods will be discussed according to the element to be determined rather than the supporting electrolyte, because--unlike polarography--generally only one element is being determined, regardless of the type of ore.

The usual analytical methods for the dissolution of the ores and for the elimination of interferences can be applied to polarographic procedures and these will not be discussed here except where the application of the method is unusual or if there is need for clarification.

For polarography the optimum concentration of the elements to be determined is between 2 and 20 milligrams per 100 ml of final solution, i.e., 10^{-3} molar. The lower limit of detection is of the order of 0.5 milligram per 100 ml of final solution, i.e., 10^{-5} molar. An H-type of polarographic cell, one arm of which contains a saturated calomel electrode (SCE), is usually used. The portion of solution taken for analysis is 20 to 25 ml. By means of special cells, 1 to 2 ml may be analyzed. Dissolved oxygen is purged from the solution by nitrogen, or sometimes with sodium sulphite if alkaline solutions are employed.

Amperometric titrations are commonly carried out in beakers of suitable size. The reference electrode may be a mercury pool, a saturated calomel electrode, or a silver-silver chloride electrode. The indicator electrode may be either a dropping mercury electrode (DME) or a rotating platinum electrode. Dissolved oxygen may be removed by purging the solution with nitrogen but often this step is unnecessary.

POLAROGRAPHIC METHODS

The following electrolytes are the ones most commonly used in the Chemical Analysis Section of the Extraction Metallurgy Division:

1. 5% Pyridine + 2% Hydrochloric Acid.
2. (a) 1M Ammonium Hydroxide + 1M Ammonium Chloride.
(b) 1M Ammonium Hydroxide + 0.5 Ammonium Chloride + 0.5M Lithium Chloride.
3. 2M Ammonium Acetate + 2M Acetic Acid.
4. 0.5M Ammonium Acetate + 0.1M Acetic Acid + 0.1M Sodium Ethylenediaminetetraacetic Acid (EDTA).

1. Pyridine + Hydrochloric Acid

This electrolyte, which consists of 5% pyridine and 2% concentrated hydrochloric acid by volume, is used for the determination of copper, nickel, and zinc or cobalt, either singly or in combination (1,2). In this solution the half wave potentials for copper, nickel, zinc and cobalt are, respectively, -0.25, -0.78, -1.05 and -1.07 volts versus the SCE. Zinc and cobalt are reduced at essentially the same potential and no distinction can be made between the two elements. It is, therefore, necessary to make a separation of the two prior to polarography.

In this electrolyte, which has a final pH of 5.0 to 5.5, the copper, nickel, and zinc or cobalt form soluble complexes that are not appreciably coprecipitated with iron or aluminum. Most other common elements, with the exception of vanadium (V), chromium (III), chromium (VI), uranium (VI), molybdenum (VI), lead and cadmium, do not interfere. Arsenic, antimony and tin could cause interference but can easily be removed by volatilization with hydrobromic and hydrochloric acids. A list of these elements with their half wave potentials and characteristics is given in Table 1.

This table shows that several elements would interfere to a greater or lesser degree with the determination of copper, nickel, zinc or cobalt. Fortunately, if sufficient iron (and/or aluminum) is present these elements are adsorbed and removed by the hydrous oxide precipitate.

TABLE 1
Polarographic Characteristics of Metal Ions in
5% Pyridine + 2% Hydrochloric Acid

| Element | $E_{1/2}$ vs SCE | Characteristic |
|----------|---------------------|----------------|
| As (III) | -0.9, -1.05 | Drawn out, P |
| As (V) | -- | NW |
| Cd (II) | -0.6 | W |
| Co (II) | -1.07 | W |
| Cr (III) | -0.6 to -1.1 | Drawn out, P |
| Cr (VI) | -0.05, -1.1 | P |
| Cu (II) | -0.25 | W |
| Mo (VI) | -0.67 | W |
| | -1.0 | Small, P |
| Ni (II) | -0.78 | W |
| Pb (II) | -0.45 | W |
| Sb (V) | -0.4 to -0.7 | P* |
| Sn (II) | -1.1 ? | NW |
| Sn (IV) | -0.25, -0.5 | P |
| U (VI) | -0.15, -0.55, -0.72 | P |
| V (V) | 0.0, -0.87 | P |
| Zn (II) | -1.05 | W |

NW - no wave, P - poorly defined wave, W - well defined wave.

*Two waves merging together.

The electrolyte is used mostly for the analysis of samples containing 0.02 to 20% of the desired element under favourable conditions, i.e., $\text{Cu} \rightleftharpoons \text{Ni} \rightleftharpoons \text{Zn}$ or Co. In some cases, however, concentrations up to 60 or 80% may be determined if the accuracy of the method is sufficient. The accuracy and precision of the method are about 1 to 2% of the amount present in the range 1 to 20%, and 5 to 20% in the range 0.02% or less.

This medium is used to determine copper and nickel in copper-nickel ores and solutions, for zinc in zinc ores, for copper, nickel, and cobalt in cobalt concentrates, and for copper, nickel, and cobalt in uranium ores and leach solutions. It is used also to determine copper, nickel, and zinc in cyanide solutions obtained from the treatment of gold ores, and in the ores themselves.

This electrolyte has been used to determine copper, nickel, and cobalt in geological rock samples from the International Upper Mantle project in the Coppermine River area of the Northwest Territories. Some of these samples presented a difficult problem because they contained chromite, which rendered them difficult to dissolve, and also because of the large and widely varying amount of silica, sulphur and iron present. The copper content was between 0.01 and 5%, nickel between 0.02 and 2%, cobalt between 0.002 and 0.2%, in the presence of 2 to 50% iron and 0.2 to 36% sulphur, as well as unknown but significant amounts of silica.

The samples were decomposed by a sodium peroxide sinter. After a water leach, and acidification with hydrochloric acid, silica was dehydrated and removed in the usual way. The filtrate was treated with sodium tartrate, made ammoniacal, and the copper, nickel, and cobalt extracted with sodium diethyldithiocarbamate and chloroform. The extract was evaporated with nitric acid and a little perchloric acid, to destroy organic material. The residue was dissolved in a little water and the copper, nickel, and cobalt were determined in the pyridine-hydrochloric acid electrolyte.

This medium has also been used to determine copper, nickel, zinc, and cobalt after these elements have been separated from one another by ion exchange or solvent extraction procedures.

2. Ammonium Hydroxide + Ammonium Chloride

This solution, which usually consists of a mixture of 1M ammonium hydroxide + 1M ammonium chloride, is used for the determination of copper, nickel, zinc, cadmium, and cobalt (3,4). The half wave potentials of these elements in this electrolyte are -0.51, -1.10, -1.35, -0.81 and -1.29 volts vs the SCE respectively. This medium has the disadvantage, however, that the elements tend to be coprecipitated with iron to a greater extent than in the pyridine-hydrochloric acid electrolyte. In addition, the nickel and zinc or cobalt waves are not as well separated as they are in the pyridine medium. It is useful if the iron content is low or if relatively few other elements are present.

A list of some elements that give waves in this electrolyte, together with their half wave potentials, is given in Table 2. Most of the data are taken from the compilation by Meites (5). For a more complete list his work should be consulted.

TABLE 2
Polarographic Characteristics of Metal Ions in
1 M Ammonium Hydroxide + 1 M Ammonium Chloride

| Element | $E_{1/2}$ vs SCE | Characteristic |
|----------|------------------|----------------|
| As (III) | -1.71 * | -- |
| Cd (II) | -0.81 | W |
| Cr (II) | (-0.85) ** | Drawn out wave |
| Cr (III) | -1.43, -1.71 | -- |
| Cr (VI) | -0.2, -0.6 | -- |
| Co (II) | -1.29 | W |
| Cu (II) | -0.24, -0.51 | W |
| Fe (II) | (-0.34), -1.49 | -- |
| Pb (II) | -0.45 | W |
| Mn (II) | -1.66 | W |
| Ni (II) | -1.10 | W |
| U (VI) | -0.8, -1.4 | -- |
| V (IV) | (-0.32), -1.28 | -- |
| V (V) | -0.96, -1.26 | -- |
| Zn (II) | -1.35 | W |

* In 0.1 M NH_3 + 0.1 M NH_4Cl

** In 0.1 M NH_3 + 5M NH_4Cl

W - well defined wave.

This list shows that several elements may cause mutual interferences which would require them to be separated.

This electrolyte is frequently used for the determination of zinc in zinc-lead ores and in tin ores, and for cadmium in zinc ores. It is used for the determination of copper and cadmium in concentrated, i.e., 2 molar, zinc sulphate solutions if a dilution is required; otherwise, the zinc sulphate solution can be used as the supporting electrolyte without preparation or treatment.

The ammonia electrolyte is used for the determination of cadmium in uranium concentrates (6). Ten to twenty or more grams of the concentrate is dissolved in hydrochloric or sulphuric acid and some arsenic is added as a carrier. Cadmium and arsenic are precipitated by hydrogen sulphide and after filtration the arsenic is removed by volatilization with hydrobromic and hydrochloric acids. The residue containing the cadmium is dissolved in a little dilute hydrochloric acid, made up to volume with the ammonium hydroxide-ammonium chloride electrolyte, and the polarographic wave recorded. Copper, or lead, if present in significant amounts, can be determined simultaneously with the cadmium. Unfortunately, the lead wave coincides with the copper wave at -0.5 volt vs the SCE and to distinguish between these elements a different electrolyte would have to be employed.

The solution can be used for the determination of manganese in steels or in manganese ores such as pyrolusite. The half wave potential of manganese is -1.66 volts vs the SCE. For the determination of manganese, the solution is modified by the substitution of 0.5M lithium chloride for one-half of the ammonium chloride. The resulting mixture gives a wave step that has a longer and flatter plateau than with ammonium hydroxide-ammonium chloride alone. Ascorbic acid is added to prevent air oxidation of the manganese.

3. Ammonium Acetate + Acetic Acid

This electrolyte is primarily used for the determination of lead, although a number of other elements may also be determined (7). The concentration employed is 2 molar with respect to both ammonium acetate and acetic acid. In most cases the lead in the sample is first separated from the other elements as lead sulphate. The lead sulphate is filtered off, dissolved in the ammonium acetate electrolyte, and the polarographic wave recorded. The half wave potential for lead in this medium is -0.45 volt vs the SCE. There are few interferences if the lead is first separated as lead sulphate.

The lead may be separated as lead sulphide, in which case copper, bismuth, cadmium, arsenic, etc., will accompany the lead. Copper, bismuth, and cadmium also give well defined waves in this medium and can be determined simultaneously. Their half wave potentials are -0.07, -0.25, and -0.65 volt vs the SCE, respectively. A list of some elements which give waves in this electrolyte, together with their half wave potentials, is given in Table 3.

Several of the elements listed in Table 3 would interfere to a greater or lesser extent with the determination of copper, bismuth, lead, and cadmium. Arsenic, tin, and antimony can be removed by volatilization with hydrobromic and hydrochloric acids after the sulphide separation. Molybdenum (VI), which gives a wave at -0.6 volt, may affect the lead wave if it is present in large amounts, and it would also interfere directly with cadmium. Uranium (VI) gives a wave at -0.45 volt, which coincides with that

TABLE 3

Polarographic Characteristics of Metal Ions in
2M Ammonium Acetate + 2M Acetic Acid

| Element | $E_{1/2}$ vs SCE | Characteristic |
|----------|------------------|----------------|
| As (III) | -0.8 to -1.3 | P |
| As (V) | -- | NW |
| Bi (III) | -0.25 | W |
| Cd (II) | -0.65 | W |
| Cu (II) | -0.07 | W |
| Mo (VI) | -0.6 | W |
| Pb (II) | -0.5 | W |
| Sb (V) | -0.5 | W |
| Sn (II) | (-0.25), -0.65 | 2nd wave W |
| Sn (IV) | -0.9 to -1.2 | P |
| U (VI) | -0.45 | W |
| Zn (II) | -1.1 | W |

P - poorly defined wave, W - well defined wave, NW - no wave.

of lead. Fortunately, molybdenum and uranium do not occur to any great extent in the usual lead, zinc or copper ores.

If it is desired to determine only lead, it may be extracted from an ammoniacal tartrate-cyanide solution with sodium diethyldithiocarbamate and chloroform. The lead, after removal of the chloroform and the destruction of the organic material, is dissolved in the ammonium acetate electrolyte and the polarographic wave is recorded. This procedure is almost a specific one for lead.

Bismuth and tin are extracted, along with the lead, by the diethyldithiocarbamate. The bismuth gives rise to a wave before lead but is sufficiently well separated from it so as not to interfere. Tin interferes with the lead wave and must be removed by treatment with hydrobromic and hydrochloric acids. Antimony and arsenic are not extracted by the diethyldithiocarbamate under the conditions used.

Copper, bismuth, and lead are determined in molybdenite ores by extracting them from an ammoniacal tartrate solution with diethyldithiocarbamate and chloroform. Cyanide is omitted in this procedure, but otherwise the method is the same as described above for lead only.

4. Ammonium Acetate + Acetic Acid + EDTA

This electrolyte is used for the determination of molybdenum in binary alloys of molybdenum and uranium. Its composition is 0.5M with respect to ammonium acetate and 0.1M each in acetic acid and EDTA. The half wave potential of molybdenum in this medium is -0.83 volt vs the SCE.

Uranium gives a single well-defined wave at -0.43 volt, which is well in advance of that due to molybdenum. This does not interfere with the estimation of molybdenum, however, providing the molybdenum content is greater than 2% and not more than 100 to 150 milligrams of uranium is present per 100 ml. of the final solution taken for polarography. The method is suitable for the determination of 2 to 20% molybdenum in uranium-molybdenum binary alloys. The accuracy and precision are greatly improved if the molybdenum is extracted with α -benzoinoxime and chloroform in order to eliminate the uranium. This also enables much smaller amounts of molybdenum to be determined.

AMPEROMETRIC TITRATIONS

The Determination of Sulphate with the DME

The determination of sulphate is carried out by titration with a standard solution of lead nitrate at a potential of -0.7 to -0.8 volt vs the SCE (8). The current remains constant until an excess of lead is present, at which point a sudden increase in current is observed. A plot of current versus the volume of lead solution added enables the end-point to be determined. The graph is of the reversed L shape type.

Before titration the solution, containing 5 to 15 milligrams S, is made just acid to methyl red and then made 20 to 25% in ethanol. Dissolved oxygen and carbon dioxide are removed by bubbling with nitrogen. Interferences are few and consist of those substances, in addition to sulphate, which would be precipitated by lead ion, i. e., carbonate, bicarbonate, sulphite, chromate, and sulphide. Lead chloride is much more soluble than lead sulphate, and not enough lead chloride will be produced to cause its precipitation until after all the sulphate has been precipitated. Carbonate, bicarbonate, sulphite, and sulphide may be removed by boiling an acidic solution of the sample. There is some danger of oxidizing some of the sulphite and sulphide to sulphate in this way, but the error should be small. Certain metals--such as copper; iron, and uranium, for instance--are reduced at potentials less than -0.8 volt; hence, while not interfering directly with the precipitation of lead sulphate, they give rise to a large residual current, which would increase the amplitude of the galvanometer oscillations and hamper the reading of the galvanometer.

Copper and iron may be reduced by treatment with metallic aluminum, or if iron alone is present ascorbic acid may be used. The effect of uranium would depend on the amount present and its ratio to that of sulphate. If a large amount of uranium is present, it is best removed by ammonium hydroxide precipitation in the absence of carbonate.

The method has been used for carbonate-sulphate leach solutions or for determining sulphate in samples from which sulphate can be extracted with sodium carbonate. The method is suitable for determining sulphate in solutions having a concentration of 0.2 g S/l or more. For solutions which contain less than 0.2 g S/l, a suitable aliquot may be concentrated by evaporation. The accuracy of the method compares favourably with the gravimetric BaSO_4 method.

Amperometric Determination of Fluoride with the DME

Fluoride is determined with a DME by titration with a standard thorium nitrate solution at a potential of -1.7 volts vs a mercury pool in an electrolyte of 0.1N potassium chloride (9). The graph is of the reversed L shape type.

Prior to the titration, the fluoride is separated from interferences by distillation from sulphuric or perchloric acid. The distillate is made up to a known volume after adding sufficient potassium chloride to make its final concentration 0.1N. Suitable aliquots are taken to give about 5 to 10 milligrams of fluoride. The acidity of the solution is adjusted to pH 7 to 8 and the dissolved oxygen is purged with nitrogen before titration with the standard thorium solution. The smallest amount of fluoride that can be easily determined is 0.5 to 1 milligram.

Amperometric Determination of Manganese with a Rotating Platinum Electrode

Manganese is determined, using a rotating platinum electrode, by titration at zero applied potential vs the SCE with a standard potassium permanganate solution (10). The electrolyte consists of a solution of sodium pyrophosphate at a pH of 6 to 7.

The sample of manganese ore is dissolved in sulphuric acid with the aid of hydrogen peroxide. Any residue is fused with potassium pyrosulphate or sodium carbonate. An aliquot of the sample, containing 50 to 100 milligrams of manganese, is then added to 50 ml of the sodium pyrophosphate solution (120 g $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ /l), diluted to 100 to 150 ml, and the pH adjusted to between 6 and 7.

The solution is titrated with standard 0.02M potassium permanganate solution until the end-point is reached. The graph is of the reversed L shape type. The end-point is indicated with extreme sensitivity; 0.2 to 0.3 ml of the 0.02M permanganate is sufficient to cause full-scale deflection at a sensitivity of 200 on a Sargent manual polarograph.

Smaller amounts of manganese can be determined by use of a more dilute permanganate solution.

Amperometric Monitoring of Oxygen in Hydrogen Gas Used for the Reduction of Iron Oxides

A rotating platinum electrode has been used as a safety device to detect the presence or absence of oxygen in hydrogen gas used for the reduction of iron oxides at elevated temperatures (11).

The gas is bubbled through a solution of potassium chloride in which are immersed a rotating platinum electrode and a silver-silver chloride reference electrode. The platinum electrode is maintained at -0.7 volt vs the Ag-AgCl electrode, by means of a battery and a rheostat. A microammeter is used to measure the current directly. Oxygen, if present, is reduced and the current is a measure of the concentration of oxygen in the solution. The latter is determined by the partial pressure of the oxygen in the gas being bubbled through the solution.

No attempt was made to make this a quantitative determination of oxygen, since it was merely desired to use it as a safety device to ensure the absence of oxygen from hydrogen and thus prevent explosions.

Amperometric Determination of Vanadium, Using the Rotating Platinum Electrode

Vanadium is determined by titration with standard ferrous ammonium sulphate solution at a potential of +1.0 volt vs SCE, using a platinum rotating electrode (12). The electrolyte consists of either 5% perchloric acid or 5% sulphuric acid volume/volume. Prior to titration the vanadium is oxidized to vanadate by treatment with perchloric acid and permanganate.

The presence of As, Sb, and W leads to low recoveries of vanadium, and they must be removed if present. Chromate interferes, but the interference may be overcome by the addition of ferrous iron to reduce both the chromate and the vanadate, followed by the selective oxidation of the vanadate with permanganate. After treatment with sodium nitrite and urea the vanadate is titrated with the standard ferrous solution. Amounts of vanadium from 10 micrograms to 50 milligrams can be conveniently titrated. The method is simple, rapid, and accurate to within 1% of the amount of vanadium present.

The method is used to determine vanadium in uranium ores; in petroleum coke ash, and in leach liquors associated with these materials. It can be applied to a large variety of products since it is subject to few interferences and is simple to perform.

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