

Application of redox titration techniques for analysis of hydrometallurgical solutions

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Regular analysis of different streams is important for the control of hydrometallurgical processes. Various physical and physical-chemical methods are applied for this purpose. Many modern methods require costly equipment and are subject to interferences. Therefore, redox titration methods remain of interest. The use of different types of oxidizing and reducing agents as well as redox indicators enables many cations and anions to be rapidly and accurately analysed. Sometimes redox titrations require the prior preparation and addition of masking agents. Selective, sensitive and low-cost methods of redox titration of copper and SO₂ in plant conditions are described.

Introduction

Hydrometallurgical processes involve the removal of metals from different types of ores, concentrates, and waste products by aqueous solutions containing different chemical reagents. Processes include a number of sequential steps such as ore preparation, leaching, precipitation, extraction, ion exchange, cementation and electrodeposition. Successful realization of metal recovery requires accurate analyses of feedstock composition, intermediate and auxiliary solutions, and final products. Effective analytical methods provide the opportunity to manage and improve a process.

The main problems of analysis in hydrometallurgical processes are associated with the complicated compositions of solutions. Raw materials usually contain many components and can include base metals such as Fe, Co, Ni, Cu, Cr, Mn, Al, Pt and U groups of metals, and rare-earth metals. These metals as a rule are in the form of different salts or oxides. After the leaching process the solutions also contain an excess of leaching reagent. The most commonly used leaching agents are sulphuric acid (Cu, Zn), sodium carbonate (U, V, Mo, W), sodium hydroxide (W), ammonia (Cu, Ni), cyanide and thiosulphate (Au, Ag), sulphite (Sb, Hg), chlorine and chloride (platinum group metals and rare-earth metals).

Selection of an appropriate method of analysis is based on criteria such as accuracy, precision, sensitivity, urgency for results, costs per analysis, number of samples to be analysed, amount of sample available, and avoidance of chemical and physical interferences¹.

This paper summarizes methods used to analyse hydrometallurgical solutions, with titration methods receiving particular attention.

Physical and physical-chemical methods

At present different physical and physical-chemical analytical methods are widely applied in hydrometallurgy. These include various spectral techniques based on the absorption, emission, or scattering of electromagnetic radiation. Atomic absorption spectroscopy (AAS) with flame and atomization, atomic emission spectroscopy (AES), inductively coupled plasma-mass spectroscopy (ICP-MS), and X-ray fluorescence analysis (XRF) can be considered the most sensitive detection methods for about 30 elements. Important characteristics of spectral techniques are the short time of analytical signal registration, low detection limit, and wide calibration ranges, which give the advantage of minimal sample preparation². Along with these complicated methods, photometry and spectrophotometry are effectively and widely used by analysts. There are many selective organic and inorganic reagents that form the coloured substances that absorb light in visible or ultraviolet regions and provide the opportunity to determine almost all elements of the Periodic system.³⁻⁸ Electrochemical methods such as voltamperometry, coulometry, and potentiometry are also used in hydrometallurgy for analysis, but generally for single-component samples.⁹⁻¹¹

Titration methods

In spite of intensive development of physical-chemical methods, titration has not lost its importance for chemical analysis. This method of analysis is easy to use and fast. Titration does not require complicated and expensive devices or equipment and is based on selective reactions. It is usually used to determine medium and high concentrations of elements. Furthermore, titration gives reliable results even in field conditions.

One of the titration methods used in hydrometallurgy is an oxidation-reduction (redox) titration. Redox titrimetry is used to analyse a wide range of inorganic analytes. Although many of these methods have been replaced by newer ones, a few of them continue to be listed as standard methods of analysis.

Redox titrimetry is based on a redox reaction between the analyte and titrant. The oxidizing and reducing agents most commonly used in hydrometallurgy^{12, 13} are shown in Table I.

In some cases samples require preparation before the titration. Sometimes substances analysed by titration with an oxidizing agent must be converted into a reduced state with auxiliary reducing agents. There are several ways to prereduce an analyte quantitatively. Reductors could be used: a Jones reductor is a column filled with granular Zn coated with a Zn(Hg) amalgam^{14, 15}, and a Valden reductor contains spongy, granular Ag coated with HCl. In other cases preoxidation is necessary. For ferric reduction to ferrous, the treatment with stannous chloride, and the addition of HgCl₂ to destroy any excess of SnCl₂ are often used. To transform a substance into an oxidized state, auxiliary oxidizing agents are used, for example, ammonium peroxydisulfate and hydrogen peroxide. These reagents are capable of oxidizing Mn²⁺ to MnO₄⁻, Cr³⁺ to Cr₂O₇²⁻, and Ce³⁺ to Ce⁴⁺. Any excess of auxiliary oxidizing agents is easily destroyed by a short boiling of the solution.

There are several methods to find the end point in redox titrimetry. A few titrants, such as permanganate, have oxidized and reduced forms whose colours in solution are significantly different, and it is not necessary to use any indicator. Specific indicators are substances that indicate the presence of oxidized or reduced species. For example, starch forms a dark blue complex with iodide; thiocyanate forms a red complex with ferric. The most important class of redox indicators are substances that may be reversibly oxidized and reduced, and change the colour upon oxidation or reduction. Redox indicators impart a colour that depends on the solution's electrochemical potential. A list of general redox indicators^{16, 17} is shown in Table II.

Table I
Common oxidizing and reducing agents

Agent	Redox half-reaction	Standard reduction potential (v)	Ions that can be determined
<i>Oxidizing agents</i>			
Cerium IV Ce ⁴⁺ IV	$\text{Ce}(\text{ClO}_4)_6^{2-} + e^- = \text{Ce}^{3+} + 6 \text{ClO}_4^-$	+ 1.7	As (III), Cu (I), Fe (II), V (IV), Mo (V), Ti (III), U (IV)
Permanganate MnO ₄ ⁻	$\text{MnO}_4^- + 8 \text{H}^+ + 5 e^- = \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	+1.49	Fe (II), Sb (III), Mn (II), V (IV), W (V), U (IV), Tl (I), Cr (III), H ₂ O ₂ , (indirect determination Cr (II), V (II), Ti (III), Nb (III), Mo (III), Cu (I), Sn (II), Ca (II), Cd (II), Zn (II), Pb (II), (II), Ni (II))
Bromate BrO ₃ ⁻	$\text{BrO}_3^- + 6 \text{H}^+ + 6 e^- = \text{Br}^- + 3 \text{H}_2\text{O}$	+ 1.42	As (III), Sb (III), Fe (II)
Dichromate Cr ₂ O ₇ ²⁻	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 e^- = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	+ 1.33	Fe (II), As (III), Cu (I), U (IV), Sn (II), Te (IV), W (III), Mo (III), Ti (III), V (IV), SO ₃ ²⁻ , Ag (I), Ba (II), Pb(II)
Vanadate VO ₃ ⁻	$\text{VO}_2^+ + 2 \text{H}^+ + e^- = \text{VO}^{2+} + \text{H}_2\text{O}$	+ 0.994	Fe (II), As (III), Hg (I), Tl (I), Sn (II), Sb (III), Ti (III), V (III), Mo (III, V), W (V), U (IV), SO ₃ ²⁻
Ferric Fe ³⁺	$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+ 0.771	Cu (I), U (IV), Sn (II), U (IV)
Iodine I ₂	$\text{I}_2 + 2 e^- = 2 \text{I}^-$	+ 0.521	As (III), Sn (II), SO ₃ ²⁻ , Sb (III)
<i>Reducing agents</i>			
Ferrous Fe ²⁺	$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+ 0.771	VO ₃ ⁻ , Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , MnO ₂
Iodide I ⁻	$\text{I}_2 + 2 e^- = 2 \text{I}^-$	+0.521	Fe (III), Cu (II)), Cr ₂ O ₇ ²⁻
Ascorbic acid C ₆ H ₆ O ₆	$3 \text{C}_6\text{H}_6\text{O}_6 + 6 \text{H}^+ + 6e^- = 3 \text{C}_6\text{H}_8\text{O}_8$	+ 0.185	VO ₃ ⁻ , CrO ₄ ²⁻ , MnO ₄ ⁻ , AsO ₄ ³⁻ , Ce (IV), Sn (IV), Ag (I), Hg (II), PbO ₂ , MnO ₂
Stannous Sn ²⁺	$\text{Sn}^{4+} + 2 e^- = \text{Sn}^{2+}$	+ 0.15	Cu (II), Fe (III), VO ₃ ⁻ , Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻
Titanium III Ti ³⁺	$\text{TiO}^{2+} + 2 \text{H}^+ + e^- = \text{Ti}^{3+} + \text{H}_2\text{O}$	+ 0.1	Cu (II), Fe (III), Sb (V), Cr ₂ O ₇ ²⁻ , MoO ₄ ⁻
Thiosulphate S ₂ O ₃ ²⁻	$\text{S}_4\text{O}_6^{2-} + 2 e^- = 2 \text{S}_2\text{O}_3^{2-}$	+ 0.09	Cu (II), Fe (III), VO ₃ ⁻ , Sb (V), Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , MnO ₂

Another method for locating the end point of a redox titration is the potentiometric method. It is based on the use of an appropriate electrode to monitor the change in electrochemical potential as titrant is added to a solution of analyte. The end point can then be found from a visual inspection of the titration curve.¹

While selecting the method for analysis it is necessary to estimate the composition of analytes and possible chemical interferences that can cause erroneous analytical results. Unfortunately, analytical methods are rarely selective toward a single species. Different separation techniques such as precipitation, extraction, or chromatography can be used to remove either the analyte or the interferent from the sample matrix. A simpler variant that analytical chemists use to reduce matrix effects to either a negligible or a minimal magnitude

Table II
Redox indicators

Indicator	Transition potential (v)	Colour of Ox form	Colour of red form
<i>pH independent indicators</i>			
N-phenylantranilic acid (2-carboxy-diphenylamine)	+ 1.08	purple	colorless
Ferroin (tris-(1,10-phenanthroline) iron (II) sulphate)	+ 1.06	cyan	red
o-Dianizidine (5,3'-dimethoxybenzidine)	+ 0.85	red	colourless
Sodium diphenylamine sulfonate	+ 0.84	red-violet	colourless
Diphenylamine	+ 0.76	violet	colourless
Diphenylbenzidine	+ 0.76	violet	colourless
3,3'-Dimethylnaphthidine (3,3'-(dimethyl-4,4'-diamino-1,1'-dinaphthyl))	+ 0.7	purple red	colourless
Variamine blue (4-amino-4'-methoxy-diphenylamine)	+ 0.575	violet blue	colourless
Nitroferroin (tris(5-nitro-1,10-phenanthroline) iron (II) sulphate)	+ 1.25	cyan	red
5,6-Dimethylferroin (tris-(5,6-dimethyl-1,10-phenanthroline) iron(II) sulphate)	+ 0.97	yellow-green	red
<i>pH dependent indicators</i>			
Sodium o-Cresol indophenol	+ 0.62 (pH =0) + 0.19 (pH =7)	blue	colourless
Methylene blue (Bis-3,9-dimethylamino phenazothionium chloride)	+ 0.53 (pH =0) + 0.01 (pH =7)	blue	colourless
Thionine (diaminophenathiozine)	+ 0.56 (pH =0) + 0.06 (pH =7)	violet	colourless
Indigocarmine (indigodisulfonic acid)	+ 0.29 (pH =0) - 0.13 (pH =7)	blue	colourless
Phenosafranin	+ 0.28 (pH =0) - 0.25 (pH =7)	red	colourless
Safranin T	+ 0.24 (pH =0) - 0.29 (pH =7)	red-violet	colourless
Neutral red	+ 0.24 (pH =0) - 0.33 (pH =7)	red	colourless

is masking. Masking is technically not a separation technique because the analyte and interferent are never physically separated from each other. The masking agent binds the interferent as a soluble complex or changes the oxidation number of the interferent, preventing it from affecting determination of the analyte. A wide variety of ions and molecules are used as masking agents (Table III).

Titration methods of Cu and SO₂ in hydrometallurgical solutions

One of the most important applications of redox titration in hydrometallurgy is a determination for copper. Various redox titration methods have been developed for copper analysis including iodometry, chromatometry, cerimetry, mercurimetry, or permanganometry.¹⁸ For analysis of copper electrowinning solutions an iodometric titration of copper is used.

Table III
Masking agents

Masking agent	Ions that can be masked
Cyanide CN ⁻	Fe (II), Fe (III), Co (II), Ni (II), Cd (II), Zn (II), Hg (II), Ag (I), Au (III), Pt (II), Pd (II)
Fluoride F ⁻	Al (III), Fe (III), Mg (II), Ca (II), Sr (II), Ba (II), Ti (IV), Cr (III)
Phosphate PO ₄ ³⁻	Fe (III), UO ₂ ²⁺
Thiosulphate S ₂ O ₃ ²⁻	Ag (I), Fe (III), Pb (II), Cu (II), Au (III), Pt (II), Pd (II), Hg (II), Cd (II)
Hydroxylamine NH ₂ OH	Fe (III), Co (II), As (V), Sb (V)
Thiourea CS(NH ₂) ₂	Fe (III), Hg (II), Cd (II), Ag (I), Sb (III)
EDTA (CH ₂ N) ₂ (COOH) ₂ (COO) ₂ ²⁻	Fe (III), Cu (II), Co (II), Ni (II), Cd (II), Zn (II), Mg (II), Mn (II)
Citrate (CH ₂) ₂ C(OH)(COO) ₃ ²⁻	Ag (I), Fe (III), Sb (III), Cu (II), Hg (II), Cd (II)
Tartrate (CHOH) ₂ (COO) ₂ ²⁻	Fe (III), Al (III), Cu (II), Hg (II), Cd (II), Pb (II), Zn (II)
Ascorbic acid C ₆ H ₆ O ₆	Fe (III), Sn (IV)

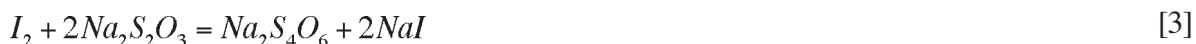
The iodometric determination of copper is a type of displacement redox titration. Cu²⁺ reacts with an excess of potassium iodide in an acid medium:



The reaction is accompanied by the liberation of a stoichiometric amount of iodine. A large excess of potassium iodide is also necessary to minimize the losses of iodine by evaporation from the solution. Free iodine is not lost in the presence of excess KI, due to the formation of I₃⁻ ion:



Once the reaction is complete the iodine produced is titrated with sodium thiosulfate:



The end point of the iodine titration with thiosulfate is indicated by the colour change of the starch indicator. The amount of standard sodium thiosulphate solution required to titrate the liberated iodine is equivalent to the amount of copper.

Ions that reduce iodide such as Fe³⁺, As (V), and Sb (V), or oxidize iodine such as Cr₂O₇²⁻, As (III), and Sb (III) can exert an influence on the copper determination. Pb and Bi form coloured substances with iodide and create difficulty for titration; they must be masked or removed. Since iron forms stable fluoride complexes, Fe³⁺ can be masked by sodium, ammonium or potassium fluoride. As (V) and Sb (V) react with iodide only in strong acid media.

The samples that are usually analysed at Mintek originate from hydrometallurgical processes and contain not only Cu but Fe (II), Fe (III), Co (II), Ni (II), Zn, (II), Mn (II), and Cr (III). Thus, addition of fluoride only is sufficient for accurate copper determination. The procedure for analysis includes the following steps:

- NaF is added for ferric masking
- an excess of KI is added and the mixture is shaken. After about 10 minutes the solution becomes deep-brown and contains solids
- the mixture is titrated with the standard thiosulfate solution until the slurry has a light yellow tint. At this step, 1 ml of starch indicator is added and titration must be continued until the mixture in the flask turns white.

The use of this method for real solutions provided good results. Moreover, titrations were performed on plant samples, quickly, without additional capital inputs for equipment.

Sulphur dioxide and sulphites are often used in hydrometallurgy as reducing agents for metal recoveries.^{19, 20} Their concentrations can be determined by oxidizing titrations, but if the analyte contains other reducing agents interferences occur. Our objective was to analyse samples that contained both sulphite and ferrous ions. In this case we determined sulphite by indirect titration.

In the first step the amount of Fe^{2+} and SO_2 (SO_3^{2-}) can be determined by a dichromatometric method, which is based on reactions:



The titration is performed in an acid medium (the addition of sulphuric acid). Phosphoric acid is added to mask ferric ions. Diphenylamine is used as a reversible oxidation-reduction indicator.

In the second step the amount of iron (III) is determined by titration with EDTA. Iron (III) forms with EDTA stable complex at pH value of 2 or lower. Other base metals do not react with ADTA at low pH. Sulphosalicylic acid is used as indicator for titration of iron (III).

And in the third step the amount of iron (II) and iron (III) is determined by titration with EDTA after oxidizing Fe^{2+} with hydrogen peroxide and decomposing of peroxide excess by heating. The concentration of sulphite ions is calculated by subtracting the results of the second and third steps from the result of the first titration.

This method of redox titration was applied successfully for analysis of the solution after the SO_2 leaching of an ore.

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