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ANALYTICAL METHODS FOR COLLECTORS USED IN THE FLOTATION MILL AT THE KIDD CREEK CONCENTRATOR, ECSTALL MINING LIMITED, TIMMINS, ONTARIO

by

E. Rolia

EXTRACTION METALLURGY DIVISION

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SUMMARY

Analytical methods are presented for the determination of collector concentration in the mill reagent solutions and in the flotation pulp solutions from various parts of the flotation circuits in the Ecstall mill. Titration methods (by differential iodimetry) are given for the standardization of xanthate and alkyldithiophosphate (dtp^-) solutions. An extraction - spectrophotometric method for xanthate (0.1-2 ppm) and an extraction - spectrophotometric method for diethyldithiophosphate, R-208 (0.1-2 ppm), in pulp solutions are described. Analysis for sodium isobutyl xanthate (1-10 ppm) by direct spectrophotometry is discussed. The methods were tested on samples taken for the author on a visit to the mill, and the results, which are presented here, indicate that the methods would be suitable for routine analyses of the mill circuits and of tailings discharge streams.

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INTRODUCTION

Of the flotation agents, the most important are the collectors which, by attaching themselves to the mineral surfaces, so modify the surfaces that the mineral particles can adhere to air bubbles. In the flotation process, recovery and grade are controlled by increasing or decreasing the quantity of collector added. However, principally because of lack of analytical methods for collectors on the mineral surface and in flotation liquor, little is known about the relationship between the uptake of the collector by the mineral surface, its concentration in the flotation liquor, and the metallurgy obtained.

The development of analytical methods for the collectors is therefore essential to improvement in metallurgy. Also, the methods are essential for pollution control and in the reuse of the process water.

Methods of analysis for xanthate and alkyldithiophosphate (dtp^-) in flotation liquor have been developed in this laboratory. A special trip [1] was made to Ecstall Mining Company's flotation mill at Timmins to obtain filtered, flotation liquor samples to test the methods. The mill uses sodium isobutylxanthate (Z-14, 317) and sodium diethyldithiophosphate (liquid, 50% R-208) as collectors for the selective flotation of:

(1) chalcopyrite and sphalerite (circuit A),

(2) galena and sphalerite (circuit C).

This report gives the assays obtained for the two collectors in the different pulp samples and a description of the procedures used in obtaining the results. The descriptions are brief; the procedures may be modified in the light of experience. Furthermore the procedures are oriented for practical use, to permit their application to routine analysis by mill staffs.

EXPERIMENTAL

Xanthate Analysis

Apparatus and Reagents

Other than xanthate, all reagents are analytical reagent grade:

Iodine indicator (B.D.H.)

Potassium iodide

Sodium acetate, $NaC_2H_3O_2.3H_2O$

Sodium isobutyl xanthate, technical

Acetic acid, glacial

Hydrochloric acid, concentrated.

Solutions

Standard iodine solution, 0.1N

Standard iodine solution, 0.002N prepared from 0.1N solution as required

Standard sodium thiosulphate solution, 0.1N

Standard sodium thiosulphate solution, 0.002N prepared from 0.1N solution as required

Potassium iodide solution 20% w/v

Formaldehyde solution, 37% HCHO

Sodium hydroxide solution, 20% w/v

Sodium hydroxide solution, 0.1N

Buffer solution: weigh 400 grams of sodium acetate trihydrate into a one-litre beaker, add 100 ml of distilled water, stir, add 160 ml of acetic acid, and dilute with water to an 800-ml mark; stir occasionally until the salt is dissolved - this buffers at pH 4.5 and has maximum buffer capacity with the amount of acetic acid present.

Purity Determination and Standard Solution Preparation

To check the purity of a xanthate reagent or to prepare a standard solution of the reagent: dissolve 0.500 grams of the reagent in a sodium hydroxide solution (pH 11-12), transfer the solution to a 500-ml volumetric flask and make to volume with the alkaline solution. Determine the xanthate content by differential iodimetry [2] on a 5.0 ml-aliquot.

Xanthate in 10% Feed Solution

Transfer by pipette, 20.0 ml of the feed solution to a one-litre volumetric flask. Dilute to volume with water. Determine the xanthate content by differential iodimetry on a 5.0-ml aliquot of the diluted solution.

Differential Iodimetry

Duplicate sample aliquots are required for each determination. Dilute each aliquot (about 5-10 mg of reagent) in a 400-ml beaker to 200 ml with water.

The reducing power of xanthate plus impurities is determined in solution 1. Add in this order: 5 ml of formaldehyde, 20 ml of buffer solution, 5 ml of potassium iodide solution and a small scoop (about 0.2 grams) of iodine indicator. As soon as all the reagents are added, titrate with 0.002N iodine solution until a deep-blue end-point is obtained; back-titrate with 0.002N sodium thiosulphate solution to a colourless end-point. Calculate the reducing power (as ml of 0.002N iodine).

The reducing power of the impurities is determined in solution 2. Add in this order: 5 ml of hydrochloric acid, stir, and let stand 5 minutes; 20 ml of buffer solution, 5 ml of formaldehyde, 5 ml of potassium iodide solution, a small scoop of the iodine indicator. Titrate with iodine and back-titrate with thiosulphate solution. Calculate the reducing power (as ml of 0.002N iodine).

Subtract the reducing power of the impurities from the reducing power of xanthate plus impurities to obtain the volume of standard iodine solution equivalent to the xanthate content of the sample.

1 ml 0.002N I_2 = (0.002 x molecular weight) milligrams of alkali xanthate, that is, 0.3445 milligram of sodium isobutyl xanthate

Extraction - Spectrophotometric Method for Xanthate (0.1-2 ppm) in Flotation Liquor

The method is based on solvent extraction of the reaction product of formaldehyde and xanthic acid. The absorbance of the extract phase is influenced by both the pH and the volume of the aqueous phase. Consequently, extraction of the xanthate from the mill sample must be made from a solution of the same pH and volume used in the construction of the calibration curve.

Apparatus and Reagents

Spectrophotometer (UV)

Separatory funnels, Squibb, pear-shaped, 250 ml

Formaldehyde solution, 37% HCHO

Hydrochloric acid, concentrated, 37% HCl

Sodium hydroxide solution, 0.10N

Benzene (purified grade)

Sodium sulphate, anhydrous

Sodium isobutyl xanthate stock solution, 1 mg/ml, (see standard solution preparation, page 3).

Sodium isobutyl xanthate dilute solution, 10 µg/ml: transfer 5.0 ml of the stock solution to a 500-ml volumetric flask and dilute to volume with NaOH solution (pH 11-12).

Calibration Curve

Transfer 5.0 ml (50 μg of reagent) to a 250-ml Squibb pear-shaped separatory funnel and 95 ml of 0.01N NaOH solution (pH 11.5 $\pm$ 0.5 solution is suitable). Add 6 ml of formaldehyde, 10.0 ml of benzene and 4 ml of hydrochloric acid. Shake for two minutes. Rinse the stopper and the inside of the funnel with a jet of water and allow the phases to separate (about 1 minute). Discard the aqueous phase. Measure the absorbance (abs.) of the extract phase at 280 nm against pure benzene - Abs. 1.

Return the extract phase from the absorption cell to the original separatory funnel. Add 25 ml of 0.1N NaOH. Shake for 30 seconds. Rinse the stopper and the inside of the funnel with a jet of water; allow the phases to separate and discard the aqueous phase. Measure the background absorbance - Abs. 2. The difference in absorbance, Abs. 1 - Abs. 2, is due to xanthate.

Similarly treat 10.0, 15.0 and 20.0-ml aliquots of the dilute, standard xanthate solution but add 90, 85 and 80 ml respectively of NaOH solution to give 100 ml of total aqueous phase.

Procedure for Xanthate in Flotation Liquor

The procedure for mill (filtered) samples is the same as given for the construction of the calibration curve. Xanthate is extracted from the same volume of aqueous phase and at the same pH used in constructing the calibration curve. Some samples

give a turbid extract phase caused by droplets of included aqueous solution. The following remedial procedure was found adequate: add a small scoop of anhydrous sodium sulphate (about 0.5 g) to a dry, 100-ml beaker and pour in the extract phase; measure the absorbance of the clarified phase, then return it to the original separatory funnel for treatment with 0.1N NaOH.

Assay Results for Xanthate

The assay results for xanthate in the mill samples by the extraction - spectrophotometric method are given in Table 1. Xanthate in concentrations greater than 0.1 ppm was found only in "C" Pb Tails sample. The assays of spiked samples are given also.

Direct Spectrophotometry of Xanthate in Solution (1-10 ppm)

Using a 1-cm absorption cell, 1-10 ppm of xanthate can be determined in a filtered flotation liquor sample by direct spectrophotometry. The absorbance is measured at the xanthate absorption peak, which is at 299 nm for isobutyl xanthate. At pH 11-12, molar absorptivity was determined to be 17200.

Many flotation reagents, at the concentration found in flotation liquor, do not absorb light at the xanthate peak; however, usually there is a background absorbance of 0.04 to 0.11 which limits the accuracy of the determination of low xanthate concentrations. To improve the determination, background absorbance

TABLE 1

Assay for Xanthate in Mill Samples Before and After "Spiking" with Z-14

Method: Extraction - Spectrophotometric (280 nm)
Sample Size: 100 ml

Sample	Xanthate Added ppm	Sample Absorb-ance	Blank Absorb-ance	Xanthate Found µg	Xanthate Found ppm
A* Cu Primary Feed	Nil	0.18	0.06	21	0.2
	0.94	0.66	0.10	99	1.0
A Cu Scav. Feed	Nil	0.25	0.23	Nil	Nil
	0.95	0.77	0.26	90	0.9
A 1st Cu Cl Feed	Nil	0.15	0.13	Nil	Nil
	0.94	0.60	0.43	30	0.3
A 2nd Cu Cl Feed	Nil	0.06	0.04	Nil	Nil
	0.95	0.54	0.09	80	0.8
A Zn Rgh. Feed	Nil	0.14	0.08	11	0.1
	0.95	0.66	0.11	97	1.0
A Zn Regrind Feed	Nil	0.10	0.04	10	0.1
	0.94	0.67	0.09	103	1.0
A Final Tails	Nil	0.08	0.04	7	0.1
	0.95	0.63	0.08	97	1.0
C** Pb Rgh. Feed	Nil	0.04	0.02	Nil	Nil
	0.91	0.58	0.05	94	0.9
C Pb Tails	Nil	0.31	0.05	46	0.5
	0.91	0.85	0.07	141	1.4
C Zn Rgh. Feed	Nil	0.07	0.02	9	0.1
	0.91	0.60	0.05	97	1.0
C Zn Regrind Feed	Nil	0.07	0.02	9	0.1
	0.91	0.59	0.05	96	1.0
C Final Tails	Nil	0.08	0.02	10	0.1
	0.91	0.60	0.04	99	1.0

A* selective flotation of chalcopyrite and sphalerite
C** selective flotation of galena and sphalerite

is read after adding 2 drops of concentrated hydrochloric acid to the test solution in the absorbance cell. Xanthate is decomposed to alcohol and carbon disulphide, neither of which absorb at 299 nm.

The xanthate content is found by comparing the absorbance difference with a calibration curve or calculated, using the equation:

$$\text{xanthate, ppm} = \frac{1000 \times \text{Mol. Wt.} \times \text{absorbance}}{\text{molar absorptivity}}$$

which, for sodium isobutyl xanthate becomes

$$\text{xanthate, ppm} = 10.0 \times \text{absorbance.}$$

Assay Results for Xanthate by Direct Spectrophotometry

Table 2 shows the absorbance at 299 nm found in the mill solutions and the effect on the absorbance of 2 drops of hydrochloric acid. Table 3 shows the results obtained when "A" samples were spiked with 3.4 ppm of xanthate and "C" samples with 3.5 ppm of xanthate.

Diethyldithiophosphate (R-208) Analysis

Reagents and Apparatus

The same reagents and apparatus detailed for xanthate analysis are required, and also the following:

Carbon Tetrachloride, purified

2-cm quartz cells

Sodium hydroxide solution, 20% NaOH

Bismuth subcarbonate, U.S.P., powder

TABLE 2

Observed Sample Absorbance at the Xanthate Peak (299 nm) and the Effect of Acidity (2 drops of conc. HCl in absorption cell) on the Absorbance

Method: direct spectrophotometry of aqueous samples

Sample	Sample Absorbance	Absorbance of acid sample
A Cu Primary Feed	0.05	0.19
A Cu Scav. Feed	0.11	0.11
A 1st Cu Cl Feed	0.07	0.11
A 2nd Cu Cl Feed	0.12	0.12
A Zn Rgh. Feed	0.11	0.11
A Zn Regrind Feed	0.06	0.06
A Final Tails	0.06	0.06
C Pb Rgh. Feed	0.07	0.07
C Pb Tails	0.11	0.15
C Zn Rgh. Feed	0.06	0.08
C Zn Regrind Feed	0.07	0.07
C Final Tails	0.07	0.07

TABLE 3

Absorbance of Mill Samples Spiked with Z-14 Solution

The spiked samples were diluted to twice the initial volume.

Method: direct spectrophotometry (299 nm) of aqueous samples

Sample	Spiked Sample Absorbance	Absorbance of Acid Sample	Absorbance Difference	Xanthate Found ppm
Xanthate added to A samples	0.36*	0.04*	0.32	3.4
A Cu Primary Feed	0.47	0.18	0.29	3.0
A Cu Scav. Feed	0.39	0.11	0.28	2.9
A 1st Cu Cl Feed	0.36	turbid		
A 2nd Cu Cl Feed	0.44	0.12	0.32	3.4
A Zn Rgh. Feed	0.38	0.08	0.30	3.2
A Zn Regrind Feed	0.41	0.06	0.35	3.7
A Final Tails	0.39	0.06	0.33	3.5
Xanthate added to C samples	0.37*	0.04*	0.33	3.5
C Pb Rgh. Feed	0.42	0.06	0.36	3.7
C Pb Tails	0.44	0.10	0.34	3.6
C Zn Rgh. Feed	0.41	0.07	0.34	3.6
C Zn Regrind Feed	0.41	0.06	0.35	3.7
C Final Tails	0.41	0.07	0.34	3.6

*Absorbance found in an equivalent quantity of water.

Sodium diethyldithiophosphate, R-208

Bismuth reagent: dissolve 0.500 grams of bismuth subcarbonate in 100 ml of 1:1 hydrochloric acid.

Purity Determination and Standard Solution Preparation

To check the purity of the diethyldithiophosphate (dtp^-) reagent or to prepare a standard solution of the reagent: dissolve 0.500 grams of the reagent in a sodium hydroxide solution (pH 11-12), transfer the solution to a 500-ml volumetric flask and make to volume with the alkaline solution. Determine the dtp^- content by differential iodimetry described below, on a 5.0-ml aliquot.

Dtp^- in 50% Solution

Transfer by pipette, 5.0-ml aliquot of the 50% solution to a two-litre volumetric flask. Dilute to volume with water. Determine dtp^- content by differential iodimetry (described below) on a 5.0-ml aliquot of the diluted solution.

Differential Iodimetry for Diethyldithiophosphate (dtp^-) in Solution

Duplicate sample aliquots are required for each determination. Dilute each aliquot (about 5-10 mg of reagent) in a 400-ml beaker to 100 with water. Dtp^- plus impurities are titrated in one sample aliquot and impurities only in a duplicate aliquot, to which is added 10 grams of potassium iodide to prevent reaction between dtp^- and iodine.

The reducing power of dtp⁻ plus impurities is determined in solution 1. Add in this order: 5 ml of formaldehyde, 5 ml of buffer solution and a scoop (about 0.2 g) of iodine indicator. Titrate with 0.002N I_2 to the appearance of a blue color throughout the solution; back-titrate with 0.002N sodium thiosulphate solution to a colourless end-point. Calculate the reducing power (as ml of 0.002 or iodine).

The reducing power of the impurities is determined in solution 2. Add in this order: 5 ml of formaldehyde, 5 ml of buffer solution and 10 grams of KI. Stir to dissolve the KI and add a scoop of iodine indicator. Titrate with standard iodine solution to a stable purple-blue end-point; back-titrate with the standard thiosulphate solution to a colourless end-point. Calculate the reducing power (as ml of 0.002N iodine).

Subtract the reducing power of the impurities from the reducing power of dtp⁻ plus impurities to obtain the volume of standard iodine solution equivalent to the dtp⁻ reagent content of the sample.

1 ml 0.002N I_2 = (0.002 x molecular weight)
milligrams of dtp⁻ reagent, that is,
0.4162 milligram of sodium diethyldithiophosphate
(R-208)

Extraction - Spectrophotometric Method for Diethyldithiophosphate in Flotation Liquor

Add a filtered sample aliquot (10-200 μg of reagent) to a 250-ml pear-shaped Squibb separatory funnel. Add water to give 100 ml of solution and 3 drops of 20% NaOH solution, to make certain the solution is alkaline (about pH 12). Add 10 ml of CCl_4 (graduate) and shake for 2 minutes. Drain the CCl_4 phase (with any solids) into a dry 100-ml beaker, and then return the clear, solvent phase to the original separatory funnel to be certain no aqueous phase is lost. Again drain the CCl_4 phase and discard it.

To the aqueous phase, add 10.0 ml of CCl_4 (pipette), then add 1.5 ml of concentrated HCl and 1 ml of the bismuth reagent (use graduates). Shake for 2 minutes and measure the absorbance of the CCl_4 phase in a 2-cm quartz absorption cell at 329 nm. Compare with a calibration curve or use the expression:

micrograms R-208 = 210 x absorbance.

Assay Results for R-208 in Mill Samples

Assay results are given in Table 4. The assays of spiked, Final-Tails samples are given also.

DISCUSSION

"A" Cu Primary Feed

Anomalous results for xanthate were obtained in this sample (Tables 1 and 2) since no xanthate is added in this part

TABLE 4

Assay of Mill Samples for Sodium Diethyldithiophosphate, "dtp^-", (R-208)

Method: solvent extraction of bismuth diethyldithiophosphate

Sample	Sample Aliquot ml	Added dtp^- ppm	Absorbance 329 nm	Found dtp^- ppm
A Cu Primary Feed	5.0	Nil	0.55	23.4
A Cu Scav. Feed	25	Nil	0.87	7.5
A Final Tails	100	Nil	0.67	1.4
Final Tails	100	0.1	0.70	1.5
Final Tails	100	1.0	1.07	2.4
C Pb Rgh. Feed	25	Nil	0.07	0.6
Pb Rgh. Feed	100	Nil	0.24	0.5
C Pb Tails	25	Nil	0.16	1.4
Pb Tails	50	Nil	0.32	1.4
C Final Tails	100	Nil	0.06	0.1
Final Tails	100	0.2	0.13	0.3
Final Tails	100	1.0	0.45	1.0
Final Tails	100	1.6	0.70	1.5

of the circuit. At the time of the analysis, the sample pH was 3.8 and considerable brown residue settled. Tests were made on decanted portions. A more comprehensive study may reveal the cause of the anomalies. No problems were encountered in the determination of R-208 in this sample.

"A" 1st Cu Cl Feed

At the time of analysis, the sample pH was 6.8. Sodium sulphide, added to the mill sample, precipitated heavy metal sulphides which were shown by the X-ray spectrograph to contain copper, iron and zinc. The low xanthate recovery seen in Table 1 and the turbidity produced by adding acid to the spiked sample (Table 3) are results caused by the formation of metal xanthate salts.

"A" 2nd Cu Cl Feed

At the time of analysis the sample pH was 4.1. The slightly low recovery for xanthate seen in Table 1 may be attributed also to the presence of soluble heavy-metal complexes.

"C" Pb Tails

The outstanding peculiarity of this sample is that 0.5 ppm xanthate was detected by the extraction - spectrophotometric method (Table 1). The pH of the sample (pH 11.7) is sufficiently high so that xanthate could have survived complete decomposition. However, it is not certain that xanthate had been added at this part of the circuit. The remnant, 0.5 ppm, is not detected by direct spectrophotometry (Table 2).

CONCLUSIONS

(1) The two differential iodimetric procedures, one to standardize xanthate solutions and the other to standardize dithiophosphate solutions, worked satisfactorily on the mill reagent samples. Future work will consist of statistical evaluation of the methods.

(2) The extraction - spectrophotometric method for xanthate is sensitive and reproducible even at the 0.1-ppm level. However, there is danger of bias and work will be carried out to modify the procedure in order to minimize this danger, particularly in special samples, for example, Final Tails.

(3) Xanthate determination by direct spectrophotometry is rapid and accurate. The results in Table 3 show that there is some merit in obtaining the background absorbance by acid treatment of the sample solution. The method should be of value in permitting control of actual xanthate levels.

(4) The extraction - spectrophotometric method for R-208 reagent appears to have no bias, on the samples tested, even at the 0.1 ppm level. The method is satisfactory for reagent control in the circuit. Future work will consist of obtaining and evaluating data from a greater number of samples.

ACKNOWLEDGEMENTS

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