



A novel capillary electrophoresis method with pressure assisted field amplified sample injection in determination of thiol collectors in flotation process waters



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ABSTRACT

A new capillary electrophoresis method was developed for the quantification of diisobutylidithiophosphate (DTP), diisobutylidithiophosphinate (DTPI) and ethyl and isobutyl xanthates (EX, IBX) all of which are used as thiol collectors in froth flotation. This method uses pressure assisted field amplified sample injection (PA-FASI) to concentrate the analytes at the capillary inlet. The background electrolyte in electrophoretic separation was 60 millimolar (mM) from 3-(cyclohexylamino)propane-1-sulfonic acid (CAPS) in 40 mM NaOH solution. The similar CAPS electrolyte solution has earlier been used for screening for diuretics that contained sulphonamide and/or carboxylic groups. In this study, the functional groups are xanthate, phosphate and phosphinate. The method was developed using actual flotation process waters. The results showed that the water delivered from the plant did not contain significant amount of collectors; therefore, method development was accomplished by spiking analytes in these waters. Separation of analytes was achieved in 15 min. The range of quantification was 0.27–66.6 mg/L (R^2 0.9991–0.9999) for all analytes other than ethyl xanthate, for which the range was 0.09–66.6 mg/L (R^2 0.9999). LOD ($S/N=3$) and LOQ ($S/N=10$) values for DTP, DTPI, IBX and EX were 0.05, 0.07, 0.06 and 0.01 mg/L and 0.16, 0.25, 0.21 and 0.04 mg/L, respectively. No interference from the matrices was observed, when the method was tested at a gold concentrator plant.

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1. Introduction

Froth flotation is a process for separating valuable minerals from ore. First, the ore is crushed, ground and mixed with water. Secondly, the resulting slurry is treated with flotation chemicals, and air bubbles generated by a flotation machine, to remove minerals from slurry for further processing. Surface active collector chemicals play a key role in the flotation process, as they are required for isolating minerals and metal species from multicomponent process mixtures. In the flotation process, their role is to bind specific minerals to air bubbles and to move them into the froth phase [1–3].

Generally, mixtures of collectors result in an effective process performance for metal complex formation. In particular, thiol collector mixtures are commonly used in the flotation of metal sulphides and platinum-bearing ores. The collector chemicals most

utilized in the flotation of sulfide minerals and gold are xanthates, dialkyl dithiophosphinates and dialkyl dithiophosphates [4,2,1].

Adsorption mechanisms of thiol collectors are based on coupled electrochemical and chemical reactions (EC-mechanism, [5]), catalytic oxidation, metathetical substitution reaction, chemisorption, physisorption, or a combination of the last two. In the procedures, mechanisms occur below the thermodynamic potentials for metal–thiol complex formation. When the minerals are sufficiently oxidized, they form metal-xanthates. On the other hand, when thiophosphates and thiophosphinates complexes are formed, without exception, the metal complexes have low pK values. During the flotation process, thiol ends of the collectors adsorb onto mineral surfaces, while the carbon structure of the chemical creates the necessary hydrophobicity for bubble–particle attachment. [1–3]

In manufacturing processes, water should be circulated not only to minimize water waste, but also to reduce water purification costs. During production, collectors, their complexes or decomposition species may accumulate to such concentrations that they start to decrease the recovery of metals in the process. Furthermore, in a flotation process, in which different minerals are floated in succession, they are exposed repetitively to collectors. In this case, the collectors that have decomposed on the surfaces may affect the

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Table 1
Collectors used in this study.

Collector	CAS no.	Structure
Sodium ethyl xanthate (SEX)	140-90-9	
Isobutyl xanthate (IBX)	25306-75-6	
Sodium diisobutylidithiophosphate (DTPI)	13360-78-6	
Sodium diisobutylidithiophosphate (DTP)	53378-51-1	

minerals' floatability [4,6]. Techniques to control and adjust the processes on-line are needed. Thus far, many methods have only been used either to determine the bulk amount of collectors in process waters, or to determine the amounts of different collectors in isolation of metals in waters. Earlier, Hao et al. [7] have studied xanthate decomposition and analyzed degradation species in process waters. As far as we know it is the only article yet published on the process monitoring of flotation chemicals.

There are a number of different methods for analyzing xanthates and other thiol collectors. Studies have been conducted by means of ultraviolet–visible (UV–vis) spectrophotometry [7,8], titration [9], and Fourier transform infrared (FTIR) spectrometry [10]. Unfortunately, these methods usually yield information only on the overall concentrations of those collectors present in the waters. However, high performance liquid chromatographic (HPLC) methods may be used for obtaining separation and determining individual thiol collectors [11–15]. To use analysis methods for separation of multicomponent, derivatization of the compounds before the various analyses is needed. It is noteworthy that the literature also includes a couple of articles about the use of capillary electrophoresis (CE) for the determination of collector compounds [16,17]. Despite the good results of Hissner et al., there are no other articles to be found from the last 10 years.

One of the main issues with UV–vis spectrophotometry in analyzing industrial samples is interferences from the matrices. Even when only xanthates are present, UV–vis spectrophotometry merely provides the combined absorbance of all xanthates [7]. In spite of that, UV–vis spectrophotometry is still used to check the purity of industrial grade collectors [15].

Leppinen and Vahtila [18] have studied thiol collectors in waters using differential pulse polarography, their aim being to analyze xanthates and dithiophosphates in the presence of sulphides in the flotation of sulfide minerals. Selective electrodes have also been used in studies of collectors in research and development; Bugajski and Gamsjäger [19] have developed an electrode for xanthate chemicals. It was concluded that their electrode could be used in process conditions as long as only one kind of xanthate is present.

Regardless of a few drawbacks, high-performance liquid chromatography (HPLC) is still one of the most used and studied chromatographic methods for separation of xanthates that may be determined either without complex formation or with metal complexes. However, in the monitoring of processes, capillary electrophoresis (CE) has several advantages over HPLC. The ionization of compounds is high enough for separation by CE, rendering unnecessary the use of counter ions in the separation solutions, as would be necessary in HPLC. In particular, the possibility of

real-time monitoring with high-throughput determination may be a process scale set-up at mills [20]. Its advantage is better separation efficiency than that obtained from HPLC. Therefore, CE is capable of use for follow-up and control of processes. The main disadvantage of CE coupled with UV absorbance detection is the high detection limits, as the path length through the capillary is very narrow. In flotation process the collectors are added in small doses. Most of the collectors also adsorb to the mineral surface, as they should, and so only small concentrations of collectors are present in the process waters. To overcome this, some kind of sample concentration must be done, before analysis with CE.

In this work, a capillary electrophoresis method was developed for the monitoring of process waters containing metal collectors. CE provides higher separation efficiency and lower eluent consumption; therefore, the technique is suitable and economical enough for routine and high-throughput analyses of anions in the process waters. In the paper, we introduce a new electrolyte system for studying collectors in flotation process waters of high ionic strength.

2. Materials and methods

2.1. Chemicals

Industrial grade collector chemicals were used for the preparation of the standards and sample mixtures. Potassium ethyl xanthate (PEX, 160.30 g/mol) and sodium isobutyl xanthate (SIBX, 158.2 g/mol) were purchased from Alkemin (Michoacan, Mexico); sodium diisobutylidithiophosphate (DTP, 264.32 g/mol) from Cheminova (Lemvig, Denmark), and sodium diisobutylidithiophosphinate (DTPI, 232.32 g/mol) from Cytec (West Paterson, NJ, USA). The molecular structures of the collectors are listed in Table 1. For the background electrolyte analytical grade chemicals were used. N-cyclohexyl-3-aminopropanesulfonic acid (CAPS, 221.317 g/mol) was obtained from Sigma–Aldrich (St. Louis, MO, USA) and sodium hydroxide was purchased from Merck (Darmstadt, Germany). Pure water was prepared by Elga Centra-R 60/120 (Elga Veolia Water Solutions, Marlow, UK).

2.2. Instrumentation

The separation and quantification method was developed using a Beckman Coulter P/ACE MDQ capillary electrophoresis instrument with a photodiode array detector (PDA) (Fullerton, CA, USA). Fused silica capillaries used in separation were obtained from Polymicro Technologies (Phoenix, AZ, USA). The dimensions of the

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