RESEARCH ARTICLE

Determination of xanthates as Cu(II) complexes by high-performance liquid chromatography – Inductively coupled plasma tandem mass spectrometry

Ronja Suvela | **Matti Niemelä** | **Paavo Perämäki**

Research Unit of Sustainable Chemistry, University of Oulu, Oulu, Finland

Correspondence
Paavo Perämäki, Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 3000, 90014, Oulu, Finland.
Email: paavo.peramaki@oulu.fi

The present study provides a novel, selective analysis method for the determination of low xanthate concentrations. The rising concern over the environmental effects of xanthates demands the development of analysis methods which this study answers. Complex formation in aqueous solution between xanthates and an excess of Co(II), Ni(II), Pb(II), Cd(II), Cu(II), and Zn(II) ions was utilized to selectively determine xanthates by high-performance liquid chromatography–inductively coupled plasma tandem mass spectrometry for the first time. The complexes that were formed were extracted to ethyl acetate using liquid–liquid extraction and separated by high-performance liquid chromatography technique before the quantitative determination of metal ions and sulfur in the xanthate complexes. Good separation and high measurement sensitivity were achieved using Cu(II) as the complex metal ion. The analysis method was optimized for the determination of sodium isopropyl xanthate and sodium isobutyl xanthate with detection limits of 24.7 and 13.3 µg/L, respectively. With a linear calibration range of 0.1–15 mg/L and a total analysis time of 4–5 min, the present method is a fast and sensitive option for selective xanthate determination.

KEYWORDS
complex formation, flotation collector, tandem mass spectrometry, xanthate

1 | INTRODUCTION

Flotation is a separation process initially developed to enrich the sulfide minerals of lead, copper, and zinc. It is based on the interactions between hydrophobic min-eral particles and air bubbled through a flotation cell [1]. Mineral surfaces can be naturally hydrophobic, but they must typically be treated with flotation reagents. A successful flotation process depends on the interactions of these reagents with metal ions on the mineral surfaces or in aqueous solutions [2].

Xanthates are organosulfur compounds that have been used in the mining industry for decades, but their environmental impact has only recently been taken into consideration. They are now listed as compounds of emerging concern, and there is a growing interest in gaining a deeper

understanding of xanthates and their derivatives [3]. The environmental concerns are mostly related to the toxic decomposition products of xanthate, such as CS_2, and the bioaccumulation of both xanthates and their heavy metal complexes [4]. For example, the accumulation of Cd^{2+} in rainbow trout gills has been found to increase in the presence of 100 μM of ethyl or isopropyl xanthate [5]. The half-life of xanthates in room temperature water is approximately 2−8 days. However, the half-life at lower temperatures has not been studied. The expected decrease in the decomposition rate at low temperatures can be a risk for the Arctic environment. Higher stability could increase the bioaccumulation of xanthates, and they could be spread further away from mining areas [4].

The decomposition rate and mechanism of xanthates depend greatly on the pH of the solution, whereby low pH values increase the decomposition rate [6]. In addition to decomposition, xanthates typically react with metal cations, such as Cu(II) and Ni(II), to form metal-xanthate complexes [7]. The general reaction for the formation of xanthate complexes with +II metal cations is shown in reaction Equation (1), where M^{2+} is a metal cation and X^- is a xanthate anion [8]:

$$n\,M^{2+}\,(aq) + m\,X^-\,(aq) \rightleftharpoons M_nX_m^{2n-m}\,(aq). \qquad (1)$$
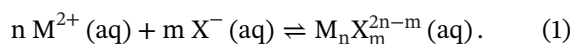
If two xanthate anions react with one metal cation, the result may be the precipitation of an insoluble MX_2 complex [8]. A typical soluble complex is MX^+, but other complexes with a higher number of either metal cations or xanthate anions can be formed [9]. Neutral or slightly acidic conditions are preferred for complex formation [8]. Highly acidic conditions increase the xanthate decomposition rate, and basic conditions could increase metal ion hydrolysis or the precipitation of metal hydroxides instead of the formation of metal xanthate complexes [8, 10].

Multiple different reactions may take place simultaneously between metal cations and xanthates. According to Sparrow et al. [11], in a solution containing Cu(II) and ethyl xanthate ions, a combination of nonionized cupric complex $Cu(EX)_2$, cuprous xanthate CuEX, and diethyl dixanthogen $(EX)_2$ will be formed. The equilibrium between these reactions depends on the molar ratio of xanthate ions to Cu(II) ions. The formation of $Cu(EX)_2$ predominates both when concentrations are very low and when they exist in near-equivalent concentrations [11].

To reliably study the behavior of xanthates, especially in the Arctic region, accurate analysis methods are needed. However, reliable quantitation of xanthates is hindered by their poor stability; decomposition in a sample continues after sampling, and the preparation of standards and reference materials is difficult. UV-visible (UV-Vis) spectrophotometry is a widely used technique for xanthate determination. It is a simple method that requires minimal sample pretreatment [12, 13]. However, it is a nonselective technique, and its detection limit is typically too high to measure xanthate concentrations such as those from environmental samples.

The complex formation reaction of xanthates presents an opportunity for selective xanthate determination. Complex formation with Cu has previously been used successfully, with Weissmahr et al. using ion-pair chromatography to detect the 1:1 complex formed between Cu(II) and ethyl xanthate by UV detection at 287 nm. The complexation and ion-pairing were done on the column using hexanesulfonate as the ion-pairing reagent [14]. Online derivatization has also been used to form 1:2 metal xanthate complexes prior reversed-phase HPLC-UV determination [15]. Few other selective methods, such as applying CE [16] and HPLC-MS/MS with SPE as a pretreatment step [17], have been developed to determine xanthates. Xanthates have also been measured by HPLC as dixanthogens after oxidation using a UV detector [15, 18] or, more recently, inductively coupled plasma MS/MS (ICP-MS/MS) [19, 20].

In this study, HPLC is coupled with ICP-MS/MS to enable the sensitive, element-selective determination of the trace levels of metals. Although the destructive nature of the ICP removes structural information, coupling it with a suitable separation technique such as HPLC enables speciation analysis. HPLC-ICP-MS/MS has been used in several different applications, such as the speciation of As and Hg in lotus seeds [21, 22] and Au speciation as hydroxyl, cyanide, and thiosulfate complexes [23]. The aim of this study is to develop a selective, sensitive analytical method for the determination of xanthates as their metal complexes. The method that is developed is based on the separation of formed complexes from the sample matrix by liquid–liquid extraction (LLE) [24]. After LLE, the organic phase is measured by HPLC-ICP-MS/MS, where the complexes are detected based on their metal and sulfur atoms. The analysis method is optimized for Cu(II) complexes of potassium ethyl xanthate (KEX), sodium isopropyl xanthate (SIPX), sodium isobutyl xanthate (SIBX), and potassium amyl xanthate (PAX), and the analytical performance is evaluated for SIPX and SIBX.

2 | MATERIALS AND METHODS

2.1 | Materials and reagents

Xanthate solutions were prepared from solid reagents. KEX (≥97.0%) was purchased from Alfa Aesar (Kandel, Germany), and SIPX (≥85%−90%), SIBX (≥60%), and PAX

(≥90%) were purchased from Algol Chemicals (Espoo, Finland). The Co(II), Ni(II), Pb(II), Cd(II), Cu(II), and Zn(II) solutions used for metal-xanthate complex formation were diluted from a stock solution (1000 mg L^{-1}, 2% HNO$_3$; VWR Chemicals). The Co, Ni, and Pb solutions consisted of dissolved metal, whereas those of Cd, Cu, and Zn were prepared from their chloride salts. pH 4 and pH 7 buffer solutions were prepared using analytical-grade sodium acetate, acetic acid, potassium dihydrogen phosphate, and sodium hydroxide.

Analytical-grade ethyl acetate (VWR Chemicals, Fontanay-sous-Bois, France), *n*-hexane (Honeywell, Seelze, Germany), dichloromethane (VWR Chemicals), and diethyl ether (Honeywell) were used as extraction solvents. HPLC-grade methanol (MeOH, Honeywell) was used for the preparation of the mobile phase for the HPLC separation. The samples were treated with analytical-grade HNO$_3$ (Honeywell) prior to total metal analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). Ultrapure water (18 MΩ cm) purified with a Millipore Gradient system was used for the preparation of all solutions.

2.2 | Instrumentation

The absorption spectra of metal xanthate samples were measured using a Shimadzu UV-1800 Series spectrophotometer at 180–500 nm using quartz cuvettes. An Agilent 1260 Infinity II HPLC system equipped with a Poroshell 120 EC-C18 (2.1 × 50 mm, 2.7 μm) column was used for the reversed-phase separation of metal-xanthate complexes. The HPLC system was coupled with an Agilent 8900 Triple-Quadrupole ICP-MS, which would enable the detection of the metal and sulfur content of the studied complexes. The ICP-MS was operated in MS/MS mode using O$_2$ as the reaction gas.

The HPLC separation of xanthates was achieved using 0.7 ml/min mobile phase flow rate, 20°C column temperature, and 6 μl injection volume. Mobile phase compositions for the separation of KEX, SIPX, SIBX, and PAX were 85:15, 90:10, 90:10, and 95:5 (MeOH:H$_2$O, %, v/v), respectively. The ICP-MS/MS operating conditions were based on a previous article [19]. The conditions were optimized for the determination of ^{32}S$^+$ as ^{32}S^{16}O$^+$, and the same conditions were used for the simultaneous detection of metal cations. The following parameters were adjusted in this study to improve the plasma stability: RF power (1600 W), nebulizer gas flow rate (0.50 L/min), O$_2$ option gas flow rate (30.0%), O$_2$ reaction gas flow rate (20%), and sampling depth (10 mm). Agilent 5110 ICP-OES was used for the determination of total Cu concentration for the aqueous samples after LLE.

2.3 | Sample preparation

In general, the sample preparation consisted of the following steps. Metal xanthate complex was formed by introducing an excess of metal ions to an aqueous xanthate solution. The aim was to quantitatively form neutral metal-xanthate complexes at a 1:2 molar ratio. Afterward, an equal volume of organic solvent was added, and the sample was shaken for 30 seconds. The LLE step would separate the complex from the excess of metal cations since the low polarity of the organic solvent would prevent the extraction of small, ionic species. An aliquot was taken from the organic phase and measured with either the UV-Vis spectrophotometer or the HPLC-ICP-MS/MS.

For the UV-Vis spectrophotometric measurements, approximately one drop of 1000 mg/L metal standard solution was added to 100 mg/L of aqueous xanthate solution (3 ml) without controlling the pH. The absorption spectrum of the samples was measured immediately after LLE. In the optimization phase of the sample pretreatment studies, xanthate concentrations from approximately 0.1 to 10 mg/L (1–60 μM) were used. The sample pH was adjusted to 4 using an acetate buffer. Metal solution (0.6–60 mg/L, 0.01–1 mM) was added immediately after pH adjustment to minimize the decomposition of xanthates.

LLE recoveries were studied using 0.06 mM KEX, SIPX, SIBX, and PAX solutions in pH 4 buffer, to which 0.1 mM of Cu(II) solution was added. All samples were prepared in triplicate. Additionally, blank samples including either xanthate or Cu(II) were prepared, then 5 ml of aqueous sample was shaken with 5 ml of ethyl acetate for 30 s in a separation funnel. After extraction, the Cu concentration of the aqueous phase was measured by ICP-OES (λ = 324 nm) after appropriate dilutions in a 2% HNO$_3$ matrix. The LLE recovery was calculated using Equation 2, where c_{added} (mmol/L) is the initial concentration of Cu(II) added to the sample and $c_{measured}$ (mmol/L) is the excess copper concentration measured by ICP-OES from the aqueous phase after LLE. The theoretical concentration, $c_{theoretical}$, (mmol L^{-1}) was calculated from the initial xanthate concentration when the formation of CuX$_2$ and quantitative extraction of the complex were assumed.

$$Q_{aq} = \frac{c_{added} - c_{measured}}{c_{theoretical}} \cdot 100\% \qquad (2)$$

The optimized sample pretreatment conditions were used when determining the analytical figures of merit. In these conditions, 0.1 mM of Cu(II) was added to samples in which the xanthate concentration range was 0.1 to 15 mg/L, and the pH was adjusted to 7. The same conditions were used when an artificial process water sample was used for studying matrix effects. The initial pH of the sample was

5.9, and its major element was calcium (511 mg/L) which originated from calcium hydroxide and sulfur (366 mg/L), which existed mainly as sulfate. The sample also included a low concentration of zinc (0.4 mg/L). Quantities of 0, 2, 5, and 10 mg/L SIPX were added to the sample prior to the sample pretreatment.

3 | RESULTS AND DISCUSSION

3.1 | Spectrophotometric measurements

UV-Vis spectrophotometry was used to preliminarily evaluate the formation and extraction of metal-xanthate complexes. Because there are no certified reference materials available for xanthates or their metal complexes, the following spectrophotometric studies were conducted to provide more experimental proof of the formation of the postulated metal-xanthate complexes.

After the complex formation, ethyl acetate, *n*-hexane, diethyl ether, and dichloromethane were studied as extraction solvents. Extraction with organic solvents was used to dissolve the water-insoluble complexes. In addition, the stability of the complexes may also be improved because it has been found that polar compounds, such as water or methanol can displace xanthate as the complexing ligand [25]. Ethyl acetate and dichloromethane resulted in significantly higher absorbance values than n-hexane and diethyl ether. The absorption spectra for metal-xanthate complexes after LLE in *n*-hexane, diethyl ether, and dichloromethane are presented in Figures S1–S3. As presented in Figure S3, diethyl ether was tested only on a few samples. This was because no significant improvement compared to other solvents was found and the use of diethyl ether would be impractical due to its high volatility.

When the same samples were later analyzed by HPLC-ICP-MS/MS, levels of metal impurities that were too high were detected in the dichloromethane. For example, a signal due to $^{63}Cu^+$ at void volume was increased 1900-fold, compared to an eluent blank sample. The tailing of this peak increased the overall background signal, decreasing the measurement sensitivity. Hence, ethyl acetate was primarily used as the extraction solvent.

The absorption spectra of pretreated samples using KEX and different metal solutions extracted in ethyl acetate are presented in Figure 1. Ethyl acetate absorbs UV radiation at wavelengths below 250 nm, so the wavelength range that was used was 250–500 nm. Distinct absorption maxima were observed for all the studied metals. Similar tests were also conducted using SIPX. All absorption maxima were detected at the same wavelength as with KEX, but the absorbance values were lower. Cu(II) and SIPX resulted in some differences in the observed spectra; for example,

an additional maximum was observed at 360 nm, and the overall absorbance values were higher than with KEX. These were probably related to the extraction efficiency of the complex that had formed. A distinct canary yellow complex was observed with Cu(II) and both KEX and SIPX. For KEX, the complex was not fully dissolved in ethyl acetate, but a fine precipitate could be seen between the aqueous and the organic phase. This phenomenon was not observed with SIPX, which may indicate a better extraction efficiency.

The measured absorption maxima of the samples are compared to the literature values in Table 1. Additionally, the absorption maxima of xanthate and its common derivatives are presented. The absorption maxima found in this study compared relatively well with those in previous studies, although only a few studies related to metal xanthate complexes have been identified. This comparison indicates that metal-xanthate complexes were formed in this study, and they were extracted from the organic solvent. For most xanthates, the absorption maxima of the metal-xanthate complexes are similar to the xanthate anion. In Nanjo and Yamasaki's study [26] of a variety of different metal xanthate complexes, it was observed that the absorption maxima of some complexes (Co(II), Ni(II), Zn(II)) shifted according to the molar ratio of xanthate to the metal cation. For example, Zn(II)-complexes should shift the maxima (301 nm) to lower wavelengths and Ni(II)-complexes to higher ones [26]. Maxima of 292 and 316 nm for Zn(II) and Ni(II), respectively, were observed in this study, indicating the formation of metal-xanthate complexes.

The aim of this study was to develop a novel method in which xanthates are quantified as their metal complexes. The spectrophotometric studies showed that a reaction occurs in a solution containing xanthate anions and metal cations. Xanthate anion was not observed to extract to the organic phase, so the observed absorbance was hypothesized to originate from the metal-xanthate complex that had formed which was a prerequisite in the method development. In addition to metal-xanthate complexes, it is probable that CS_2 and alcohols corresponding to the hydrocarbon chain of the xanthate were formed and partially extracted to the organic phase. This, however, could not be detected in our study when ethyl acetate was used as the extraction solvent.

3.2 | Identification of metal-xanthate complexes by HPLC-ICP-MS/MS

An innovative HPLC-ICP-MS/MS method was developed for identifying metal-xanthate complexes. By detecting the peaks having the same retention time for both sulfur and the metal of choice, the presence of the complexes was
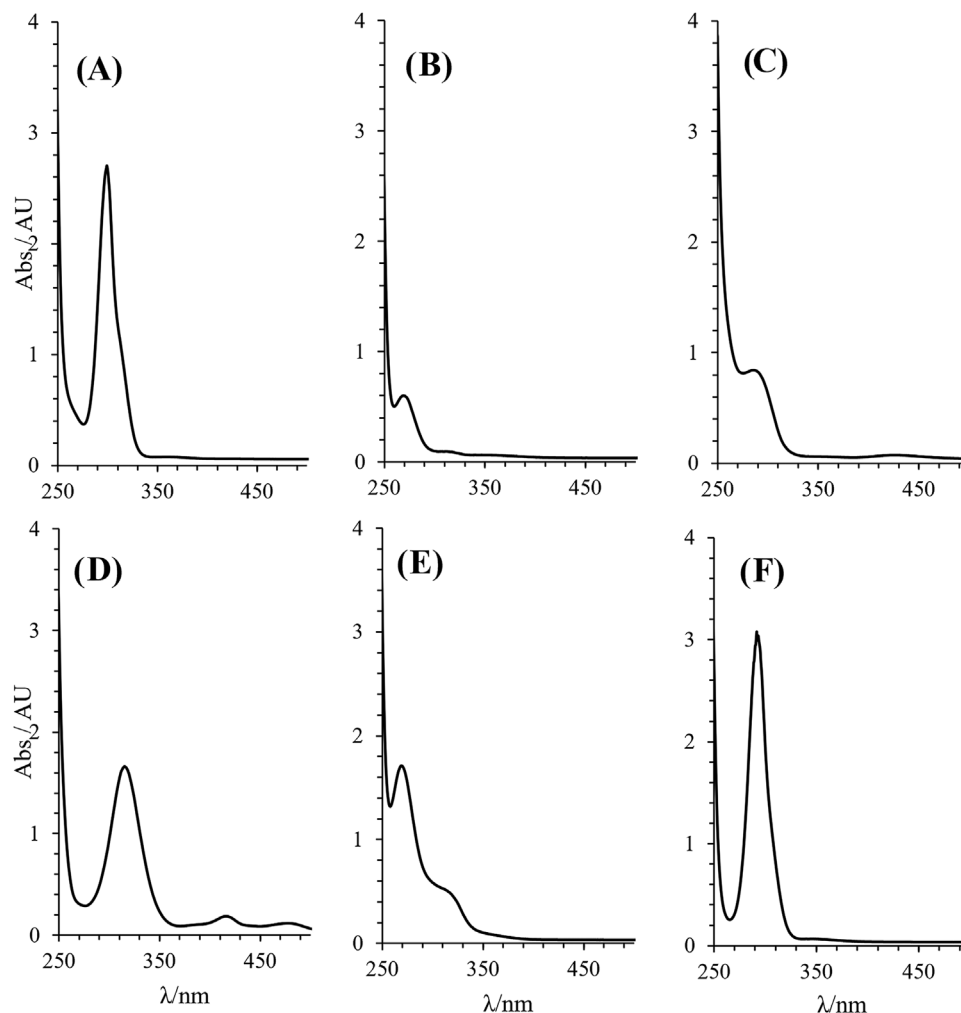
FIGURE 1 Absorption spectra ($\lambda = 250-500$ nm) of samples containing (A) Cd(II), (B) Co(II), (C) Cu(II), (D) Ni(II), (E) Pb(II), and (F) Zn(II) cations with potassium ethyl xanthate (KEX) after liquid–liquid extraction in ethyl acetate. c(KEX) = 100 mg/L.

TABLE 1 Absorption maxima of some ethyl xanthate derivatives and metal-xanthate complexes.

	Absorption maxima (nm)		
Compound	This study	Literature	Reference
Ethyl xanthate (EX)		226, 301	[27]
Carbon disulfide (CS_2)		206	[27]
Ethyl xanthic acid		274	[28]
Diethyl dixanthogen		240, 286	[29]
Ethyl perxanthate		350	[30]
$CdEX^+$	299	226, 301	[26]
$Cd(EX)_2$		306	[10]
$CoEX^+$	260	226, 300−310	[26]
$CuEX^+$, $Cu(EX)_2$	286, 360[a], 427	258, 283, 327, 383	[26]
		235. 285, 375, 410	[11]
$NiEX^+$	254[b], 316, 416, 478	226, 280, 300−320	[26]
$PbEX^+$	269, 315	250, 315	[26]
$ZnEX^+$	292	226, 280−300	[26]

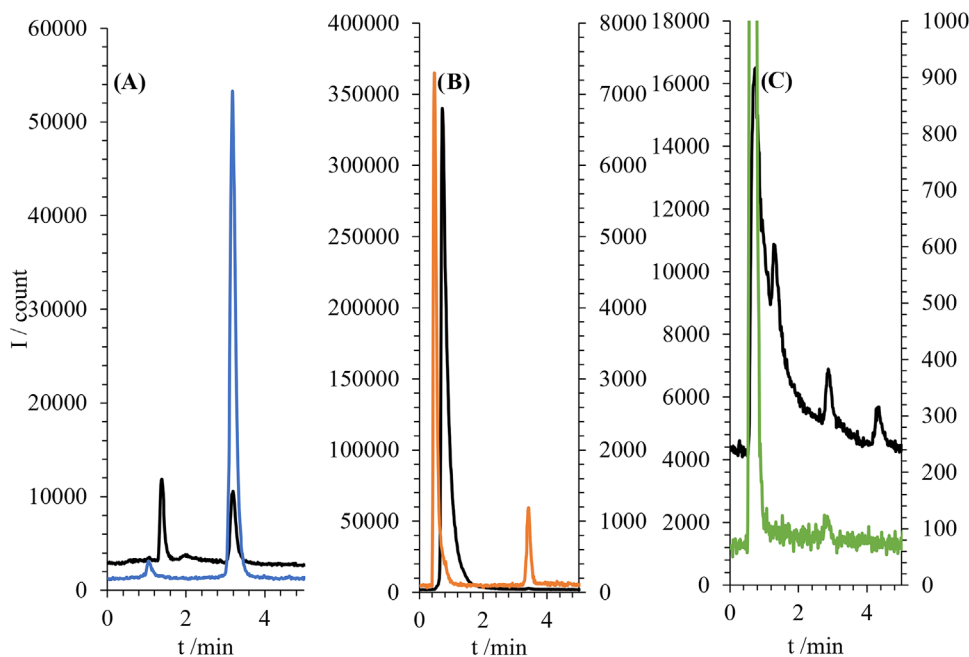[a]SIPX.

[b]Extraction with *n*-hexane.

FIGURE 2 Chromatograms obtained with HPLC-ICP-MS/MS of (A) Cu(II)-sodium isopropyl xanthate (SIPX), (B) Ni(II)-sodium isobutyl xanthate (SIBX), and (C) Cd(II)-SIPX samples by HPLC-ICP-MS/MS. Monitored masses: ▬▬ $^{32}S^+ \rightarrow {}^{32}S^{16}O^+$, ▬▬ $^{63}Cu^+$, ▬▬ $^{58}Ni^+$, and ▬▬ $^{114}Cd^+$. Signal intensities for $^{58}Ni^+$ and $^{114}Cd^+$ are presented on the secondary y-axis. c(xanthate) = 100 mg/L.

confirmed. For example, the retention time of the complex formed with Cu(II) and SIPX was 3.2 min (Figure 2A).

Xanthate samples treated with Cd(II), Cu(II), Co(II), Ni(II), Pb(II), and Zn(II) solutions were analyzed with HPLC-ICP-MS/MS after LLE extraction with ethyl acetate. In most cases, metal-xanthate complexes were detected near void volume, indicating the formation of a metal complex with xanthate at a 1:1 ratio, resulting in an unretained, charged species (MX$^+$). However, neutral complexes formed at a 1:2 ratio (MX$_2$) had better retention in the used reversed-phase column. Retained species were observed using Cu(II) and Cd(II) with SIPX and Ni(II) with SIBX. The chromatograms for SIPX with both Cd(II) and Cu(II) and SIBX with Ni(II) are presented in Figure 2. All the metals resulted in two peaks, albeit with significantly different responses. The extraction of aqueous Ni(II)-SIBX solution with ethyl acetate resulted in a signal eluted near the void volume (RT 0.6 min). Sulfur was not detected at the same retention time, which indicates that this was not a Ni-xanthate complex. Additionally, a compound with a likely formula of Ni(IPX)$_2$ was detected at 3.3 min. When Cu(II) was used, a high signal, probably due to the 1:2 complex, was detected. The Cu-compound eluted at 1.1 min was hypothesized to be CuIPX$^+$, but this could not be confirmed due to low sensitivity.

Cd(II)-xanthate complexes were found to have similar behavior to Ni(II) complexes. A high response of both Cd and S was detected for the early eluting compound. KEX, SIPX, and PAX were tested with Cd(II), and the retention

time of the first peak was slightly increased when a xanthate with a longer hydrocarbon chain was used. Retention times of 0.58-, 0.61-, and 0.73-min were observed with KEX, SIPX, and PAX, respectively. Significantly lower responses were obtained for the expected CdX$_2$ peak (RT = 2.8 min).

The improved measurement sensitivity of the metal cation, compared to sulfur, is clearly shown in Figure 2 for the Cu(II) and Ni(II) complexes. However, for Cd(II), the response of $^{114}Cd^+$ was small, compared to $^{32}S^{16}O^+$. The lowered sensitivity was found to be related to Cu(II) contamination; that is, a signal of $^{63}Cu^+$ was detected at the same retention time, indicating that Cu(IPX)$_2$ was found simultaneously, and its stability was better than that of the Cd(II) complex. This supports the use of Cu(II) as the complex metal ion.

3.3 | Optimization of the HPLC-ICP-MS/MS method for the determination of Cu(II)-xanthate complexes

Xanthate complexes of Cu(II) were separated with good resolution due to the HPLC conditions used, and the highest responses were obtained when compared to the other metal cations. The observed behavior was most likely because of the formation of neutral MX$_2$ complexes with Cu(II), whereas MX$^+$ complexes were mostly formed with other metals. Hence, the experiments were
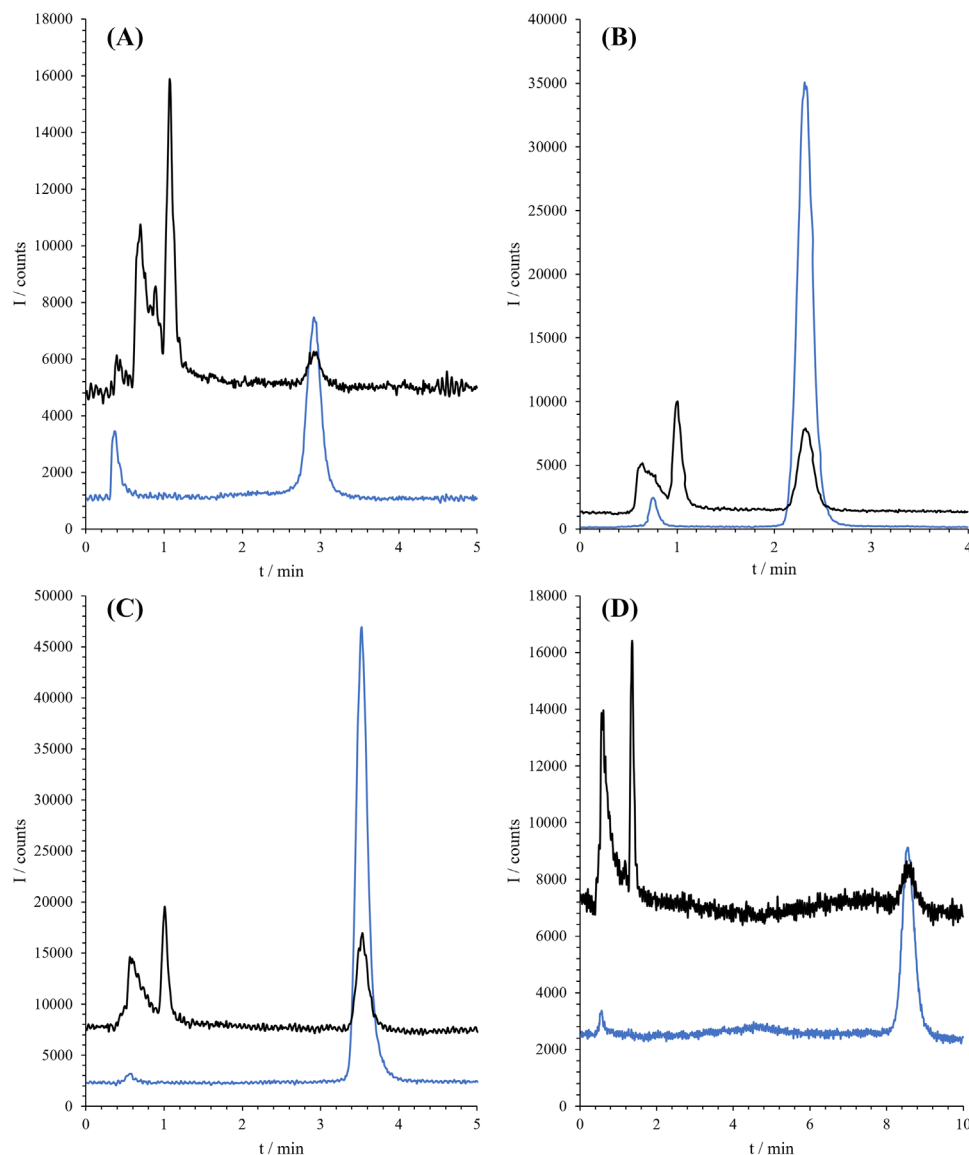
FIGURE 3 Chromatograms of (A) potassium ethyl xanthate, (B) sodium isopropyl xanthate, (C) sodium isobutyl xanthate, and (D) potassium amyl xanthate treated with Cu(II) ions in ethyl acetate extract by HPLC-ICP-MS/MS. Monitored masses: ▬▬ $^{32}S^{16}O^+$ and ▬▬ $^{63}Cu^+$. Initial concentration in aqueous phase: $c(Cu^{2+}) = 0.05$ mM, c(xanthate) $= 0.06$ mM. pH of the aqueous phase $= 4$.

continued using only Cu(II) ions. In addition to SIPX, other xanthates were also tested. Chromatographic conditions for the determination of each Cu(II)-xanthate complex were optimized separately. The chromatograms for samples with an initial xanthate concentration of 0.06 mmol L^{-1} are presented in Figure 3. All xanthates resulted in similar peak patterns, where two peaks due to Cu and at least three due to sulfur were observed. The proposed CuX$_2$ complexes were observed with the highest retention times, namely 2.9, 2.3, 3.5, and 8.5 for Cu(EX)$_2$, Cu(IPX)$_2$, Cu(IBX)$_2$, and Cu(AX)$_2$, respectively. The responses for KEX and PAX were low compared to those of SIPX and SIBX, which was mainly due to the extraction process discussed in Sections 3.4 and 3.5.

Mobile phase composition had a significant effect on the separation of the complexes. The MeOH:H$_2$O ratios used were 85:15, 90:10, 90:10, and 95:5 for KEX, SIPX, SIBX, and PAX, respectively. All other parameters were the same for all xanthates (Table 1). If isocratic elution was used, different mobile phase compositions were preferred for each xanthate. If the amount of MeOH was increased to 90% in the determination of KEX, it would result in a leading peak for Cu(EX)$_2$ (Figure S4A). Secondly, if the amount of MeOH was decreased to 85% in the determination of SIPX, it would result in a high retention time (Figure S4B). SIBX and PAX have longer hydrocarbon chains than SIPX, so their retention time would be even higher increasing the total analysis time. Especially the separation of KEX
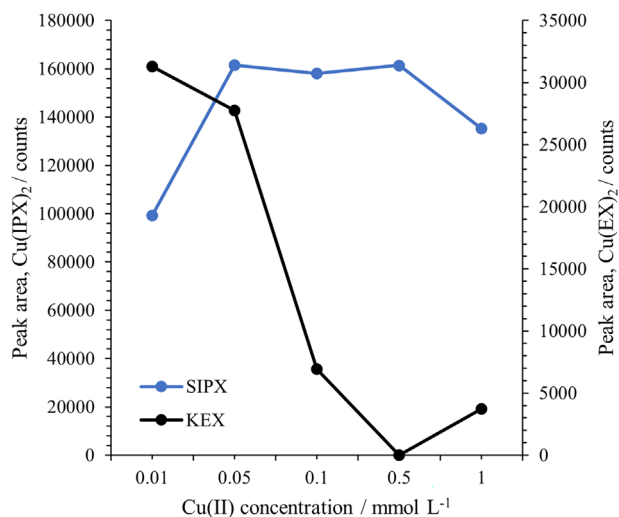
FIGURE 4 Effect of Cu(II) concentration on the response of $Cu(EX)_2$ and $Cu(IPX)_2$ complexes in ethyl acetate extract by HPLC-ICP-MS/MS ($m/z = 63$). Xanthate concentration = 0.06 mmol/L.

and PAX in the same run would require gradient elution to achieve adequate separation and reproducible peaks.

3.4 | Sample pretreatment studies

As shown in the previous section, the sensitivities of the different Cu(II)-xanthate complexes differed significantly. The sample pretreatment process was studied further to identify the critical parameters affecting the complex formation and extraction. Previous studies have indicated that the ratio of formed metal-xanthate complex to other reaction products depends on an excess of metal cations compared to the stoichiometric ratios [11]. This was studied using increasing amounts of Cu(II) with KEX and SIPX (Figure 4) in a pH 4 aqueous solution. For SIPX, the highest response was achieved within 0.05 and 0.5 mmol/L of added Cu(II) prior to LLE. For a 1:2 complex, this means approximately 1.7−17 times excess of Cu(II) to SIPX. Using 0.01 mmol/L of Cu(II) resulted in a decreased response, which was expected due to Cu(II) being the limiting reagent.

The results for $Cu(EX)_2$ were different from those for $Cu(IPX)_2$. The overall response was significantly lower, and the lowest Cu concentrations resulted in the highest responses. This was most likely related to the solubility of the formed complex since a fine yellow precipitate was observed between the two phases in the LLE step when high Cu concentrations were used. The presence of two different Cu(II) complexes was also possible. Similar behavior was observed when KEX concentrations from 0.001 to 0.06 mmol/L were treated with 0.05 mmol/L Cu(II). The

TABLE 2 Extraction recoveries of Cu(II)-xanthate complexes from aqueous solution to ethyl acetate. The initial xanthate concentration was 0.06 mM, and the initial Cu(II) concentration was 6.5 mg/L (0.1023 mM).

Xanthate	$c(Cu(II))_{aq} \pm sd$, $\mu mol/L$[a]	Extraction recovery, %[b]
KEX	65.3 ± 0.04	123.3 ± 1.2
SIPX	76.3 ± 1.18	86.7 ± 9.8
SIBX	73.3 ± 0.42	96.5 ± 3.4
PAX	66.0 ± 0.90	120.8 ± 7.4

[a]Measured Cu concentration in the aqueous phase after extraction.
[b]95% confidence level (n = 3).

response of $Cu(EX)_2$ increased in a somewhat linear trend up to 0.03 mmol/L, but in higher concentrations, the response decreased significantly.

3.5 | Extraction recovery

The efficiency of the LLE was evaluated by measuring the total Cu concentration in the aqueous phase after the extraction step by ICP-OES. The raw data of these measurements are presented in Tables S1 and S2. As shown in the raw data, no significant extraction of Cu was found in the blank samples containing only Cu(II) ions. Hence, it was assumed that Cu(II) could be extracted to the organic phase after reaction with xanthates only as xanthate complexes. The extraction recoveries of approximately 87%–97% (Table 2) for SIPX and SIBX indicate that almost quantitative recovery is achieved. The obtained recoveries show that ethyl acetate is a suitable solvent for the extraction of Cu(II) complexes of SIPX and SIBX.

However, as stated earlier, KEX and PAX were not fully dissolved in either of the phases, but a cloudy precipitate was found between the two phases. Combining the visual observation with the extraction recoveries of over 100% they indicate that the precipitation removed the complex from the aqueous phase. Additionally, some copper was coextracted with the precipitate. The low signal intensities of the detected KEX and PAX complexes (Figure 3) in the organic phase also suggest that the complex mainly existed as a solid precipitate.

3.6 | Analytical figures of merit

Analytical figures of merit, including linear equations and their correlation coefficients, LODs, and RSDs at two concentration levels were determined for SIPX and SIBX, and they are presented in Table 3. First, the figures of merit were studied in pH 4 samples using SIPX, as

TABLE 3 Linear calibration equation, LOD, and RSD for the determination of sodium isopropyl xanthate (SIPX) as Cu(IPX)$_2$ complex and sodium isobutyl xanthate (SIBX) as Cu(IBX)$_2$ complex by HPLC-ICP-MS/MS. In LOD determination, $n = 4$ for SIPX pH 4 and SIBX, and $n = 6$ for SIPX pH 7.

Xanthate	Sample pH	Monitored mass	Linear equation	R^2	LOD[a] (μg/L)		RSD% ($n = 3$)	
						c	1 mg L^{-1}	15 mg L^{-1}
SIPX	4	^{63}Cu$^+$	y = 22073x−10552	0.9962	30.6		13.4	16.7
		^{32}S^{16}O$^+$	y = 3678x−3223	0.9821	320[b]		43.7	15.5
SIPX	7	^{63}Cu$^+$	y = 41337x−17492	0.9985	24.7		12.5	2.3
		^{32}S^{16}O$^+$	y = 7147x−3549	0.9967	249		25.6	3.8
SIBX	7	^{63}Cu$^+$	y = 52281x−9420	0.9993	13.3[c]		9.4	3.9
		^{32}S^{16}O$^+$	y = 10283x−4082	0.9985	137		22.7	2.2

σ for a 0.5 mg/L sample[a], 1 mg/L sample[b], and 0.1 mg/L sample[c].

in the previous experiments. It should be noted that in the validation experiments, a higher number and volume of samples were prepared, requiring more preparation time. These differences in sample pretreatment increased the time between pH adjustment and the Cu(II) addition and decreased the sensitivity by half at the low pH value. This was because the acidic conditions increased the xanthate decomposition rate. Therefore, the amount of xanthate available for complex formation was decreased. The RSD values were also increased from 12.5% to 13.4% and 2.3% to 16.7% for 1 and 15 mg/L samples (m/z 63), respectively. To reduce the decomposition of xanthates, the measurements were made at pH 7. For SIBX, only pH 7 was used. No differences in the retention time of Cu(IPX)$_2$ or Cu(IBX)$_2$ between the pH 4 and 7 samples were observed.

The linear calibration equations, method LODs, and RSDs at two concentration levels for the determination of SIPX and SIBX are presented in Table 3. The linear calibration ranges for SIPX and SIBX were 0.5–15 and 0.1–15 mg/L ($n = 3$), respectively. The LOD of the method was calculated using the equation 3σ/S, where S is the slope of the calibration curve and the standard deviation σ ($n = 4–6$) was calculated from the peak area of a low concentration standard. The LODs for the methods were improved by one order of magnitude when ^{63}Cu$^+$ was used instead of ^{32}S^{16}O$^+$. The lower sensitivity of sulfur also affected the RSD, especially at low concentration levels.

The obtained method's detection limits of 13.3 and 24.7 μg/L for the determination of SIBX and SIPX, respectively, are comparable to other selective methods for the determination of xanthates. The previous method of applying triiodide oxidation and HPLC-ICP-MS/MS determination resulted in an instrumental detection limit [19] of 20 μg/L and a method detection limit [20] of 0.29 mg/L. Similar detection limits have been achieved with other selective methods, namely CE (10 μg/L) [16], anion interaction chromatography (30 μg/L) [31], SPE-

HPLC-MS/MS (0.06−0.24 μg/L) [17] and ion-pair chromatography (4 μg/L) [14].

The sample pretreatment of the developed method is straightforward, requiring minimal waiting time, and the HPLC-ICP-MS/MS analysis time of 4–5 min (Figure 3, SIPX and SIBX) is very fast compared to previous studies, where the analysis times have ranged from 8 to 12 min [15–17]. To our knowledge, this is the only reported method in which different metal-xanthate complexes have been detected element-selectively. This provides an opportunity to develop methods for the speciation analysis of different metal-xanthate complexes.

The SIPX method was applied to an artificial tailings sample to evaluate the existence of matrix effects. The linear calibration equations obtained with the method of standard additions and an external calibration curve were compared. The slopes of the linear equations and their confidence intervals ($\alpha = 0.05$) for standard additions and external calibration were (39 624 $\pm$ 9204) counts L/mg and (45 208 $\pm$ 2855) counts L/mg, respectively. There were no statistically significant differences between the slopes, indicating no significant matrix effects [32].

4 | CONCLUDING REMARKS

In this work, the complex formation of Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) with KEX, SIPX, SIBX, and PAX was studied. The formation and extraction of the different complexes were observed first using UV-Vis spectrophotometry. Next, the samples were analyzed by reversed-phase HPLC-ICP-MS/MS. It was hypothesized that if metal xanthate complexes formed at a molar ratio of 1:2 (metal:xanthate), they would be retained in the reversed-phase column and could be separated with reasonable resolution. The complexes were identified by ICP-MS/MS using overlapping signals of ^{32}S$^+$ as ^{32}S^{16}O$^+$ and the used metal. With a higher sensitivity than ^{32}S^{16}O$^+$,

the metal ion isotope was then used for quantitative measurements.

Xanthate complexes formed with Cu(II), Ni(II), and Cd(II) were observed using HPLC-ICP-MS/MS. Signals for Pb(II), Zn(II), and Co(II) were also detected, but their complexes were not retained in the column used. Cu(II)-xanthates resulted in the highest sensitivity, and the analysis method was then optimized for KEX, SIPX, SIBX, and PAX. It was found that the extraction performed well with $Cu(IPX)_2$ and $Cu(IBX)_2$, whereas $Cu(EX)_2$ and $Cu(AX)_2$ were poorly extracted from the used solvents.

The HPLC-ICP-MS/MS methods were validated for the determination of SIPX and SIBX, and the obtained method detection limits were 24.7 and 13.3 µg/L, providing a sensitive option for selective xanthate analysis. This method presents an improvement in the HPLC-ICP-MS/MS analysis of xanthates by utilizing the higher measurement sensitivity of copper compared to sulfur. The developed method was also applied to an artificial process water sample, and no significant matrix effect was observed.

The present method is limited to the quantitative analysis of SIPX and SIBX. Further studies on the extraction process are needed to fully utilize the method for other xanthates. It would also be beneficial to study the extraction process in more detail to see if the stability of the complexes is improved in an organic solvent. This would ease the storage of the samples. The method also shows potential to study the speciation of xanthates in the flotation process of water and the environment. This will require profound experiments on the complex formation reactions between xanthates and different metal cations.

ACKNOWLEDGMENTS

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

ORCID

Ronja Suvela https://orcid.org/0000-0003-4775-980X
Paavo Perämäki https://orcid.org/0000-0001-7106-5678

REFERENCES

1. Wills BA, Finch JA. Wills' mineral processing technology. Oxford: Elsevier Science; 2015.
2. Chen J. The interaction of flotation reagents with metal ions in mineral surfaces: a perspective from coordination chemistry. Miner Eng. 2021;171:107067.
3. Ryskie S, Neculita CM, Rosa E, Coudert L, Couture P. Active treatment of contaminants of emerging concern in cold mine water using advanced oxidation and membrane-related processes: a review. Minerals 2021;11:1–23.
4. Bach L, Dyrmose Nørregaard R, Hansen V, Gustavson K. Scientific report from DCE-Danish Centre for Environment and Energy No. 203. Review on environmental risk assessment of mining chemicals used for mineral separation in the mineral resources industry and recommendations for Greenland. 2016.
5. Block M, Pärt P. Increased availability of cadmium to perfused rainbow trout (Salmo Gairdneri, Rich.) Gills in the presence of the complexing agents diethyl dithiocarbamate, ethyl xanthate and isopropyl xanthate. Aqua Toxicol. 1986;8:295–302.
6. Shen Y, Nagaraj DR, Farinato R, Somasundaran P. Study of xanthate decomposition in aqueous solutions. Miner Eng. 2016;93:10–5.
7. Bulatovic SM. Handbook of flotation reagents: chemistry, theory and practice. Oxford: Elsevier Science and Technology Books; 2007.
8. Zhang YH, Wu LM, Huang PP, Shen Q, Sun ZX. Determination and application of the solubility product of metal xanthate in mineral flotation and heavy metal removal in wastewater treatment. Miner Eng. 2018;127:67–73.
9. Yamasaki T, Nanjo M. Studies of xanthate complexes by solubility method. Sci Rep Res Inst Tohoku Univ Ser A. 1969;45–62.
10. Sasaki Y. Chloroform extraction of cadmium and zinc with methyl, ethyl, propyl and butyl xanthates. Bunseki Kagaku. 1983;32:17–23.
11. Sparrow G, Pomianowski A, Leja J. Soluble Copper Xanthate Complexes. Sep Sci Technol. 1977;12:87–102.
12. Fu P, Wang L, Ma Y, Hou Z. A comparative study on the degradation of ethyl xanthate collector by O3, UV254nm, UV185+254 nm, O3/UV254nm and O3/UV185+254 nm processes. J Environ Chem Eng. 2020;8:103628.
13. García-Leiva B, Teixeira LAC, Torem ML. Degradation of xanthate in waters by hydrogen peroxide, Fenton and simulated solar photo-Fenton processes. J Mater Res Technol. 2019;8:5698–706.
14. Weissmahr KW, Houghton CL, Sedlak DL. Analysis of the dithiocarbamate fungicides ziram, maneb, and zineb and the flotation agent ethylxanthogenate by ion-pair reversed-phase HPLC. Anal Chem. 1998;70:4800–4.
15. Zhou C, Bahr A, Schwedt G. Studies on the HPLC determination of xanthates via copper(I) xanthates and dixanthogens. Fresenius Z Anal Chem. 1989;334:527–33.
16. Sihvonen T, Aaltonen A, Leppinen J, Hiltunen S, Sirén H. A novel capillary electrophoresis method with pressure assisted field amplified sample injection in determination of thiol collectors in flotation process waters. J Chromatogr A. 2014;1325:234–40.
17. Qiao YT, Lu YX, Yu PF, Feng NX, Li YW, Zhao HM, et al. A novel method based on solid phase extraction and liquid chromatography-tandem mass spectrometry warrants occurrence of trace xanthates in water. Chemosphere 2023;310:136770.

18. Zhou C, Bahr A, Schwedt G. Separation and determination of xanthates in mixtures as dixanthogens by normal-phase HPLC on a diol-phase. J Fresenius J Anal Chem. 1990;338:908–11.

19. Suvela R, Niemelä M, Perämäki P. Determination of ethyl xanthate in aqueous solution by high performance liquid chromatography–inductively coupled plasma–tandem mass spectrometry and spectrophotometry. Anal Lett. 2022;55:1857–71.

20. Suvela R, Genevrais S, Niemelä M, Perämäki P. The effect of experimental conditions on the formation of dixanthogen by triiodide oxidation in the determination of ethyl xanthate by HPLC–ICP-MS/MS. Anal Sci. 2022;38:1221–31.

21. Zhang D, Yang S, Ma Q, Sun J, Cheng H, Wang Y, et al. Simultaneous multi-elemental speciation of As, Hg and Pb by inductively coupled plasma mass spectrometry interfaced with high-performance liquid chromatography. Food Chem. 2020;313:126119.

22. Zhang D, Yang S, Cheng H, Wang Y, Liu J. Speciation of inorganic and organic species of mercury and arsenic in lotus root using high performance liquid chromatography with inductively coupled plasma mass spectrometric detection in one run. Talanta 2019;199:620–7.

23. Ta C, Reith F, Brugger J, Pring A, Lenehan CE. Analysis of gold(I/III)-complexes by HPLC-ICP-MS demonstrates gold(III) stability in surface waters. Environ Sci Technol. 2014;48:5737–44.

24. Donaldson EM. Solvent extraction of metal xanthates. Talanta 1975;23:417–26.

25. Eggers H, Russel HA. Liquid Chromatography of Xanthate Complexes. Chromatographia 1983;17:486–90.

26. Nanjo M, Yamasaki T. Spectrophotometric studies of EX complexes in aqueous solutions. Bull Chem Soc Jpn. 1969;42:968–72.

27. Cordeiro TG, Hidalgo P, Gutz IGR, Pedrotti JJ. Flow injection analysis of ethyl xanthate by gas diffusion and UV detection as CS2 for process monitoring of sulfide ore flotation. Talanta. 2010;82:790–5.

28. Fontenele RS, Hidalgo P, Gutz IGR, Pedrotti JJ. Flow injection analysis of ethyl xanthate by in-line dialysis and UV spectrophotometric detection. Talanta 2007;72:1017–22.

29. Jones MH, Woodcock JT. Dixanthogen determination in flotation liquors by solvent extraction and ultraviolet spectrometry. Anal Chem. 1986;58:588–91.

30. Montalti M, Fornasiero D, Ralston J. Ultraviolet-visible spectroscopic study of the kinetics of adsorption of ethyl xanthate on pyrite. J Colloid Interface Sci. 1991;143:440–50.

31. Hao FP, Silvester E, Senior GD. Spectroscopic characterization of ethyl xanthate oxidation products and analysis by ion interaction chromatography. Anal Chem. 2000;72:4836–45.

32. Miller JN, Miller JC. Statistics and chemometrics for analytical chemistry. Hoboken, NJ: Prentice Hall; 2010.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.