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Disposable Electrochemical Sensor for Rapid Determination of Ethyl Xanthate in the Mining Industry

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Abstract: Xanthate is a widely used reagent in sulfide mineral flotation. A simple and reliable method is presented for the direct monitoring of xanthate in flotation baths and their effluents, as a tool for their reconditioning, and reducing their environmental impact. For this purpose, screen-printed graphite electrodes (SPE) were modified with a polyelectrolyte-surfactant matrix which was able to adsorb the xanthate, whose concen-

tration is determined by electrochemical impedance spectroscopy (EIS) following the change in the electron transfer resistance of ferrocyanide after a pre-oxidation treatment. Linear ranges from 0.25 to 1 μM and 15 to 100 μM were determined for effluents and flotation baths, respectively. A mechanism for the electron transfer process is proposed based on Quartz crystal microbalance, IR and cyclic voltammetry studies.

Keywords: Effluents • electrochemical impedance spectroscopy • flotation • mineral samples • xanthate

1 Introduction

Mining is an activity of critical importance in human society. The raw materials provided by mining sustain cutting edge industries such as pharmaceuticals and electronics. However, mining can cause numerous impacts, including soil and/or water contamination. Particularly, modern mining demands high volumes of water for extraction, processing, and waste disposal. These processes can pollute nearby water sources and deplete freshwater supplies in the region surrounding the mine [1–3]. Xanthates are salts of alkyl dithiocarbonic acid commonly used in the mining industry as collectors in the flotation of sulfide minerals, metallic elements (e.g., copper, nickel, silver, gold) and some oxidized minerals of lead and copper, from ore slurries. It is estimated that over 2×10^9 tons of ores are processed by flotation each year worldwide, a significant fraction of which are the mentioned ores. The importance of the low priced xanthate salts can be inferred by knowing that, in general, 50 to 300 g of xanthate are required per ton of ore [4,5]. Beyond the focus of this work, it is important to note that xanthates are also used in the production of insecticides, and for the fumigation of soils [6–8].

Xanthates are unstable compounds and decompose in the presence of water, generating, in some cases, more dangerous products [3]. Xanthate salts can undergo a number of reactions. In acidic medium, xanthates are protonated to yield the corresponding xanthic acid, which in turn decomposes into carbon disulfide. They can also be oxidized to dioxanthogen (ROCS-S-S-COR). In neutral or basic media, hydrolytic decompositions producing carbonate and trithiocarbonate (CS_3^{2-}) salts, carbon disulfide and alcohol have been observed [9].

Xanthate salts may pose a risk of adverse health and environmental effects during manufacturing, transportation and final disposal [9,10]. The toxicity of xanthates

and of some of their decomposition products are subject of regulation in some labor environments, due to their extended use in the mining industry and their potential for occupational and environmental exposure [11,12]. Although very little is published on the toxicity of xanthates, it is known that it is high and due mainly to the formation of carbon disulfide and its ability to inhibit certain enzymes (e.g. cytochrome C oxidase, ascorbate oxidase). Since xanthate and CS_2 are highly toxic to the aquatic flora and fauna [13], it is important to measure xanthate concentrations in the flotation facility, in the processed ore and in the effluents [5,6,10].

In order to obtain the maximum floatability, the bath should contain the mineral in a concentration of around 10% w/v, a foaming agent and the xanthate between 10 and 100 μM [13,14] depending on the type of mineral. Since the flotation is carried out in a continuous flow, fairly frequent monitoring of the concentration is necessary for efficient process control [14]. It is known that xanthates can cause toxicity to aquatic fauna at levels of 0.06 to 0.6 μM potassium ethyl xanthate for *N. atherinoides* or greater than 0.6 μM for *D. magna* and *P. promelas* [9]. Predicted $\text{LC}_{50\text{s}}$ for aquatic fauna are about 12 μM , and chronic end-points are around 1.2 μM . Effects on algal growth are predicted at concentrations below 6 μM [9]. In this work, the value 0.6 μM was chosen as an

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acceptable concentration in effluents. Despite having been used in the flotation process for many years, and given its industrial as well as its environmental importance, sensitive, robust and rapid techniques of xanthate determination, preferably compatible with field operation, are still required for closer monitoring of this compound during the continuous flotation process and its effluents [13]. Various analytical techniques and methods have been proposed for the determination of xanthates. Iodometric titration is one of the oldest methods for determining xanthate but it is time consuming and non-specific [13]. A method for determining xanthate recommended by Australian authorities [9] is based in a spectrophotometric determination (UV, $\lambda=301$ nm) with a limit of detection of $1 \mu\text{M}$ [15,16]. However, the interference of other species absorbing in the UV region present in real samples (i.e. containing mineral, see Section 2.5), prevents its practical use [5]. In [13] a flow injection method with in-line dialysis coupled with filtration was proposed to eliminate the residual interference of suspended material prior to spectrophotometric detection. The dialysis step makes the method more expensive and complex. A polarographic procedure for the determination of ethyl xanthate making use of the static mercury drop electrode, was presented [5]. The same method could be applied for the simultaneous determination of sulfide, a possible pollutant in real samples. However, a method that would avoid the use of mercury would be desirable.

Comparing to other methods, electrochemical techniques have some advantages such as simplicity, rapidity and high selectivity and sensitivity [17]. In this work, an electrochemical impedance spectroscopy-based sensor is presented for monitoring ethyl xanthate in mineral processing (flotation) baths and in their effluents as a tool for adjusting the xanthate concentration in the former and reducing the environmental impact of the latter, thus contributing to a rational use of water resources.

We were able to implement the proposed method in mineral samples after a simple clean-up procedure.

The method is based on the use of a polymeric matrix deposited on screen-printed graphite electrodes as a retention medium, avoiding the use of mercury electrodes. The polymeric matrix is prepared from the interaction between a polyelectrolyte (polyallylamine) and a surfactant (sodium dodecylsulfate) [18–21], and cast on the electrodes, which can be stored and easily transported. The accuracy of the method was evaluated by preparing and measuring the analyte in a mineral matrix. These samples were measured using the proposed method and UV as the reference method [9,13,15,16], and the results were compared. The monitoring of xanthate in flotation baths in a suitable concentration range is demonstrated, which in turn optimizes its use and the rational use of water and reduces the environmental impact of effluents, while measurements in effluents allow the control of discharges to the environment.

In order to elucidate the mechanism of the sensor, electrochemical (Cyclic Voltammetry, CV), infrared (At-

tenuated Total Reflectance, ATR) and acoustic (Quartz Crystal Microbalance, QCM) measurements were performed.

2 Experimental

2.1 Reagents and Solutions

Potassium ethyl xanthate (Sigma Aldrich), polyallylamine (PAA, Sigma Aldrich), H_2SO_4 (Carlo Erba), sodium dodecyl sulphate (SDS, Wiener Lab), boric acid (Anedra), sodium hydroxide (Merck), potassium ferrocyanide (Biopack) and petroleum ether (Carlo Erba) were analytical grade reagents and were used as received.

Xanthate stock solutions (0.1 M) were prepared daily. Borate buffer solutions (1 M) of pH 9.4 and containing potassium ferrocyanide were prepared daily by dissolving H_3BO_3 and NaOH in water and adding $\text{K}_4[\text{Fe}(\text{CN})_6]$ in a final concentration of 100 mM.

Solutions were prepared with deionized water (resistivity $> 18 \text{ M}\Omega \text{ cm}$) obtained from a Millipore® system.

2.2 UV Measurements

Calibration standards in the range of 0 to $200 \mu\text{M}$ xanthate were prepared and their absorption spectra between 250 and 350 nm were measured using a 1 cm light path quartz cell and a modular OceanOptics DT-Mini-2 spectrophotometer with a diode array detector connected to a PC and operated through SpectraSuite software. Real samples prepared and treated as indicated in Section 2.5 were measured in the same way.

2.3 Construction of the Electrochemical Sensors

Electrochemical measurements were carried out using graphite screen printed electrodes [22] modified as indicated below. The electrodes were provided by Donflex Saja S.R.L. (Buenos Aires, Argentina) with the working, counter and reference electrodes integrated in one array designed to be connected to a USB terminal (See Supplementary information, SI 1). The working electrode had an area of 0.64 cm^2 and the counterelectrode, 1.13 cm^2 . The reference electrode was a silver surface which was treated with sodium hypochlorite in basic medium (55 g L^{-1} active chlorine) for 10 minutes and then rinsed with $18 \text{ M}\Omega \text{ cm}$ resistivity water. The reproducibility and stability of these electrodes were studied and they resulted suitable as pseudo reference electrodes. The potential of these pseudo reference electrodes was measured against a commercial Ag/AgCl electrode, and all potentials reported in this paper were corrected in order to express them vs. Ag/AgCl.

The working electrodes were modified as follows: $250 \mu\text{L}$ of a 0.26% solution of PAA adjusted with H_2SO_4 to a final pH of 7 with a negligible change in volume were added to $500 \mu\text{L}$ of a 1% SDS solution and $8 \mu\text{L}$ of the resulting dispersion were cast on the working electrode.

Afterwards, the sensors were dried at 50 °C for 30 minutes and stored in the dark at room temperature (approximately 25 °C). It was found that under these conditions, they can be employed at least a month after their preparation with acceptable performance.

2.4 Electrochemical Measurements

The used electrochemical device was a μ AUTOLAB type III system and was run on a PC using FRA[®] (Frequency Response Analyser) software.

The sensors were connected to the potentiostat using an adapted USB terminal and the measurements were carried out as follows: 0.1 mL buffer solution (1 M borate, pH 9.4, containing 100 mM $K_4Fe(CN)_6$) was added to 1 mL aliquots of each calibration standard or sample treated as outlined in Section 2.5, after which 0.3 mL of these mixtures was cast on the electrode. An oxidizing potential (1.15 V vs. Ag/AgCl) was applied to the working electrode for 150 or 300 seconds, and the impedance spectrum was measured by superimposing a sinusoidal potential modulation of 10 mV amplitude onto the formal potential of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox probe (0.356 V vs. Ag/AgCl) in the 1 Hz to 10 kHz frequency range (spaced logarithmically, 9 per decade). It was observed that the range of 1 to 40 Hz was the sensitive region to xanthate concentration.

The EIS results were analyzed by fitting the experimental impedance data to a modified Randles electrical equivalent circuit lacking the Warburg element (Figure 1).

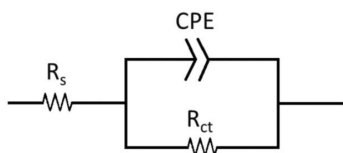


Fig. 1. Modified Randles electrical circuit used to analyze the impedance spectra.

This circuit was chosen because no mass transport process was observed in the range of frequencies evaluated. The circuit parameters were calculated by fitting the impedance function to the measured spectra with a nonlinear least-squares program, using Frequency Response Analyser (FRA[®]) software. The criterion used to accept the fitting was that chi-square value be lower than 0.05. At least two independent measurements were carried out for each reported concentration of xanthate since good agreement was usually observed between two replicates. Then, the values for each electrical component were calculated by averaging the fitted values and the errors were estimated by their standard deviation.

In order to test the performance of the sensor in conditions closer to industrial samples, xanthate concentration was measured in solutions prepared and treated as

outlined in Section 2.5 using the UV and the electrochemical methods.

2.5 Mineral Matrix and Clean-up

A mineral sample from Bajo La Alumbreira Mine (27°19'7"S, 66°36'31"W, Catamarca Province, Argentina), containing approximately 0.7% Cu and 0.7 g Au per ton, was crushed in a mortar and sieved through a 90 μ m particle size sieve (ASTM No 170) [13].

Aliquots of 1.5 g of the powder were suspended in 10 mL water and the resulting suspension was used as a matrix. Then standards with different amounts of xanthate were prepared. A picture of the resulting suspension is shown in Supplementary information, SI2. Afterwards, air was bubbled for two minutes and samples were taken three minutes after finishing the bubbling. Between xanthate addition and sample collection, orbital agitation was applied at 135 rpm.

The samples were treated in two different ways to eliminate suspended solids: one aliquot was filtered through a 0.1 μ m pore diameter membrane (See picture in Supplementary information, SI 2). Another aliquot was centrifuged at 8000 g for 10 minutes (Hermle Z 326 K centrifuge), the supernatant was removed and centrifuged again in the same conditions. The supernatant obtained from the second centrifugation was used for the measurements. After these clean-up procedures, samples were measured as described in Sections 2.2 and 2.4.

2.6 Cyclic Voltammetry

Cyclic voltammograms were acquired using the same potentiostat employed for impedance measurements, although General Purpose Electrochemical System (GPES[®]) software was used for its operation. Modified electrodes were studied using CV in a solution containing 0.1 mM ferrocyanide, 0.01 M borate buffer (pH 9.4) and increasing concentrations of xanthate (0 to 150 μ M). The potential was swept at 5 mV/s between -0.35 and 1.2 V vs. Ag/AgCl.

2.7 Attenuated Total Reflectance (ATR) Measurements

ATR spectra were measured for electrodes before and after electrochemical treatment in the presence of varying concentrations of xanthate with the oxidizing potential described previously. Such spectra were taken with an IR Thermo Nicolet 8700 instrument equipped with an ATR Smart Orbit accessory with diamond prism and a DTGC detector. Typically, 64 spectra acquired with a resolution of 4 cm^{-1} were averaged. To operate the infrared instrument, Omnic[®] software was employed.

2.8 Quartz Crystal Microbalance

A Q-Sense quartz crystal microbalance (QCM-D) instrument (Biolin Scientific, Finland) was used and operated

with software Q-Soft 401. The gold layer on the 5 MHz crystal (Gold (Ti Adhesion)) was modified with 4 μL of the PAA-SDS polymeric matrix mentioned in Section 2.3 and was left to dry in air (unassisted air dry).

On the QCM instrument one of the crystals was stabilized in 0.1 M borate buffer (pH 9.4) containing 500 μM xanthate and 5 mM ferrocyanide. On the other hand, another crystal was stabilized in a similar solution, but without ferrocyanide. All solutions were filtered with a 0.1 μm pore diameter membrane and carried to the QCM cell at a flow rate of 60 $\mu\text{L}/\text{min}$. Once the baseline was stable, an oxidizing potential (1.1 V vs. Ag/AgCl) was applied for 100 s. The frequency in the third overtone was monitored, because it was the parameter showing the largest response to the potential pulses.

3 Results and Discussion

3.1 Reference Method

A method for quantitative analysis of aqueous xanthate solutions recommended by regulatory agencies utilizes ultraviolet spectrophotometry at 301 nm wavelength [9, 13]. Here, we use it as reference method to assess the quality of our results.

Calibration standards in the range of xanthate concentration ($[\text{EtX}^-]$) of 0 to 200 μM were measured, giving a linear response up to 100 μM . The equation of the corresponding calibration curve was $A_{301\text{nm}} = (1.31 \times 10^{-2} \pm 6 \times 10^{-4}) \mu\text{M}^{-1} [\text{EtX}^-] + (4 \times 10^{-2} \pm 3 \times 10^{-2})$, $R^2 = 0.9944$, and the limit of detection obtained from our measurements, calculated as indicated in [23], was 9 μM .

This calibration behaviour was used to measure treated mineral samples using both clean-up procedures proposed in this work (centrifugation and filtration). With the goal of evaluating its applicability to measuring xanthate in flotation samples, the performances of both methods were compared by plotting the results obtained for centrifuged vs. filtered samples using the reference method (Supplementary information, SI 3). It is expected for such a plot to yield a calibration line near the identity ($y = x$) [24]. A linear fit of our data (Figure 4) yields the following calibration curve: $y = (0.97 \pm 0.1) x + (2.9 \pm 5.5)$, $R^2 = 0.9088$, indicating that both sample preparation methods yielded comparable results.

3.2 Electrochemical Method in Flotation Baths

Disposable graphite screen printed electrodes were modified with a polyelectrolyte-surfactant complex (PAA-SDS). Aliquots of 300 μL of xanthate standards (i.e. prepared in distilled water) and treated mineral samples (both containing buffer solution and ferrocyanide ion) were placed on the sensors. After that, an oxidizing potential was applied for 150 seconds and the impedance spectra were measured (see Section 2.4). The impedance spectra corresponding to standards in the range of 0 to 75 μM xanthate are shown in Figure 2.

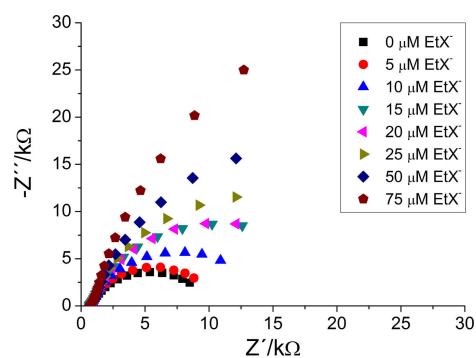


Fig. 2. Impedance spectra for electrodes measured after the oxidative treatment in the presence of varying xanthate concentrations.

Fitting the spectra shown in Figure 2 using the equivalent circuit presented in Figure 1 yielded the results presented in Supplementary information, Table 1. In this circuit R_s represents the resistance of the solution and R_{ct} , the charge transfer resistance. The constant phase element (CPE), is related to the non-ideal behavior of the double layer capacity.

From Table 1 (Supplementary information), R_{ct} is the only element that has a dependence on xanthate concentration. A plot of R_{ct} vs. $[\text{EtX}^-]$ is shown in Figure 3. It is noteworthy that graphite electrodes without modification were measured but no significant variation in the R_{ct} values was found. Therefore, we conclude that the polymeric matrix is important for the sensor to be sensitive to xanthate.

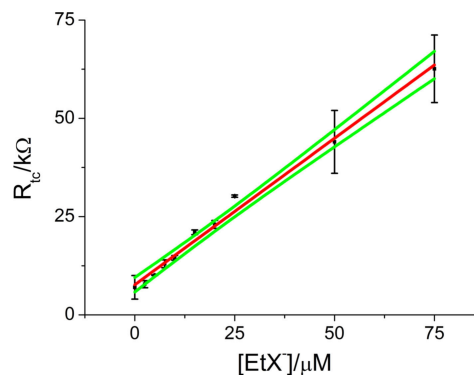


Fig. 3. Plot of R_{ct} vs. $[\text{EtX}^-]$ in the range of 0 to 75 μM and the corresponding linear fit. Oxidation time prior to measurement: 150 s. Calibration line: $R_{ct} = (0.73 \pm 0.03) \text{ k}\Omega \mu\text{M}^{-1} [\text{EtX}^-] + (8.1 \pm 0.8) \text{ k}\Omega$; $R^2 = 0.9882$, LOD = 15 μM .

Regarding the analysis of real samples, this method was used to estimate the remaining xanthate concentration in the baths after exposure to the mineral. At the pH of the samples and considering the solubility of copper sulphide, the expected $[\text{Cu}^{2+}]$ in solution was approx-

imately 10^{-15} M. Therefore, it is expected that copper ions did not interfere in the xanthate determination.

Considering UV absorption as the reference method, we constructed a plot of measured xanthate concentration using the electrochemical vs. UV method. Such a plot is shown in Figure 4 for both sample preparation methods, and in Table 2 (supplementary information), the parameters of the corresponding linear fits are reported.

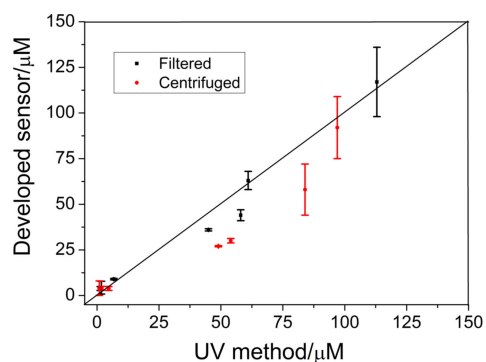


Fig. 4. Comparison of the concentration values measured by the UV and the electrochemical method for both clarification methods. The calibration lines are outlined in Table 2. The line $y=x$ is included to facilitate the comparison.

The data in Table 2 (supplementary information), and a visual inspection of the data in Figure 4, show that centrifugation yields smaller values than UV, while for the filtered samples, the agreement between both methods is better. This could be explained by the presence of colloids in the samples, which are better removed by filtration than by centrifugation. These colloids would affect the UV measurement, but not the impedance spectra. Therefore, it can be claimed that filtration has a better analytical performance than centrifugation in regard to the electrochemical measurements.

3.3 Electrochemical Method in Effluents

Xanthate is toxic for aquatic life at levels higher than $0.6 \mu\text{M}$. Given that the reported UV method has a detection limit of $1 \mu\text{M}$, this technique could not be applicable to determine if such effluents can be released to the environment or not [14,25]. Bearing this in mind the electrochemical method was applied to construct a calibration curve in aqueous xanthate solutions up to $1 \mu\text{M}$. For this purpose, the time for the previous oxidation was doubled (from 150 to 300 s) and the Nyquist graphs were adjusted between 1 and 630 Hz. The impedance spectra and the corresponding calibration curve are shown in Supplementary information, SI 4, while in Table 3 (supplementary information) we present the parameters of the equivalent circuit, which is the same as the one previously used. Determinations were made in duplicate because the reproducibility was good enough and the LOD was $0.25 \mu\text{M}$.

3.4 Underlying Mechanism

Measurements using cyclic voltammetry (CV), IR spectroscopy (ATR) and quartz crystal microbalance (QCM) were carried out to characterize the surface-adsorbate interactions at a molecular level and shed light on the signal generation mechanism.

It is known that xanthate reacts with ferricyanide giving a greenish-yellow precipitate but presents no reaction with ferrocyanide. Therefore, we propose that the oxidation of ferrocyanide to ferricyanide and the consequent formation of a precipitate would be responsible for the changes in R_{ct} . This hypothesis is supported by the measurements using cyclic voltammetry and QCM, as we explain below.

3.4.1 Cyclic Voltammetry Measurements

The Obtained Results are Shown in Figure 5.

In Figure 5a, voltammograms for buffer solutions containing only xanthate are shown. Xanthate oxidation is irreversible and occurs at approximately 0.5 V vs. Ag/AgCl. In Figure 5b) (black line), the oxidation of

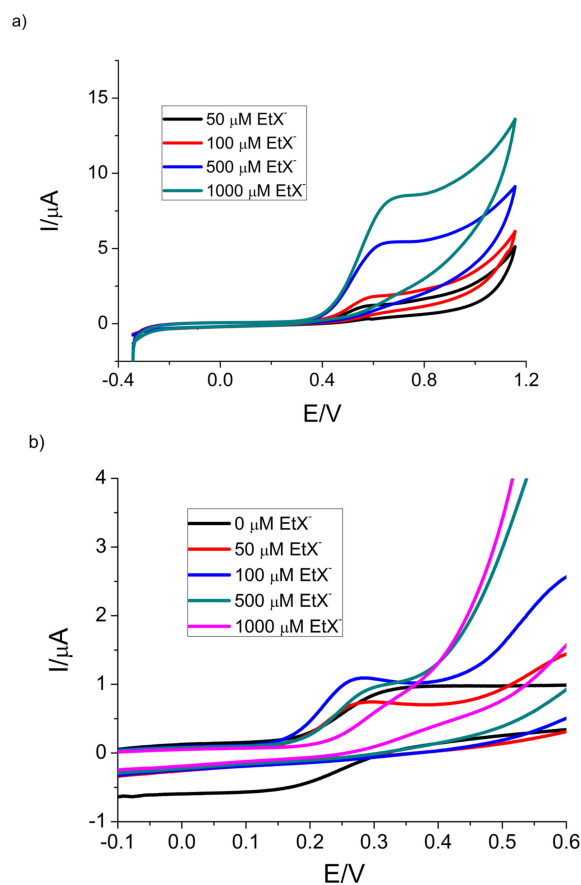


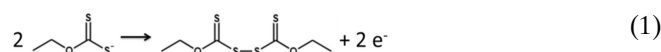
Fig. 5. Voltammograms at 5 mV/s for a) 50 to 1000 μM potassium ethyl xanthate in 0.01 M borate buffer pH 9.4 (absence of ferrocyanide); b) 50 to 1000 μM ethyl xanthate in 0.01 M borate buffer pH 9.4 (0.1 mM ferrocyanide). Potentials vs. Ag/AgCl.

ferrocyanide at 0.3 V vs. Ag/AgCl is observed. By studying solutions containing both xanthate and ferrocyanide, no reduction peak is observed for ferricyanide, indicating that after the oxidation, this compound is not electrochemically available under the conditions of this experiment. The full scale graph, corresponding to Figure 5b, can be found in Supplementary information, SI 5.

The possibility that ferrocyanide was acting as a catalyst in the oxidation of xanthate to dixanthogen was considered. However, in supplementary information (SI 6), voltammograms are presented for a fixed xanthate concentration (500 μM), in which ferrocyanide concentration was varied between 0 and 0.25 mM. As the ferrocyanide concentration increased, the oxidation peak for xanthate was increased in the same amount as the signal corresponding to ferrocyanide (i.e. the same xanthate peak is superimposed on the ferrocyanide signal). This indicates that ferrocyanide does not present a relevant catalytic activity in the oxidation of xanthate to dixanthogen under the conditions of this experiment.

3.4.2 ATR Measurements

We used ATR to identify possible oxidation products of the xanthate. It has been reported that ethyl xanthate can be oxidized to diethyl dixanthogen in surfaces such as Hg [26,27], Pt, Au, Cu and galena [28,29] according to:



In this work, we used this technique to detect the oxidation product of xanthate, diethyl dixanthogen, in the surface of the sensors treated with the oxidizing potential for 150 s.

ATR spectra of electrodes modified with polymeric matrix and treated with the oxidizing potential in the presence of varying concentrations of xanthate were measured using a graphite surface as a blank. The obtained spectra show the characteristic peaks corresponding to dixanthogen (Figure 6) [30]. A dixanthogen

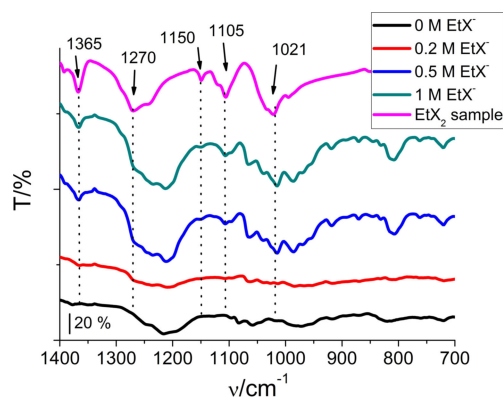


Fig. 6. ATR spectra for electrodes treated with the oxidizing potential (1.1 V vs. Ag/AgCl for 150 s) in the presence of varying concentrations of xanthate.

sample was synthesized and purified as reported in [31] and the corresponding IR spectrum was measured (Figure 6).

3.4.3 Quartz Crystal Microbalance Measurements

Figure 7 shows the results corresponding to QCM technique. Potential pulses of 1.1 or 0.5 V vs. Ag/AgCl are indicated.

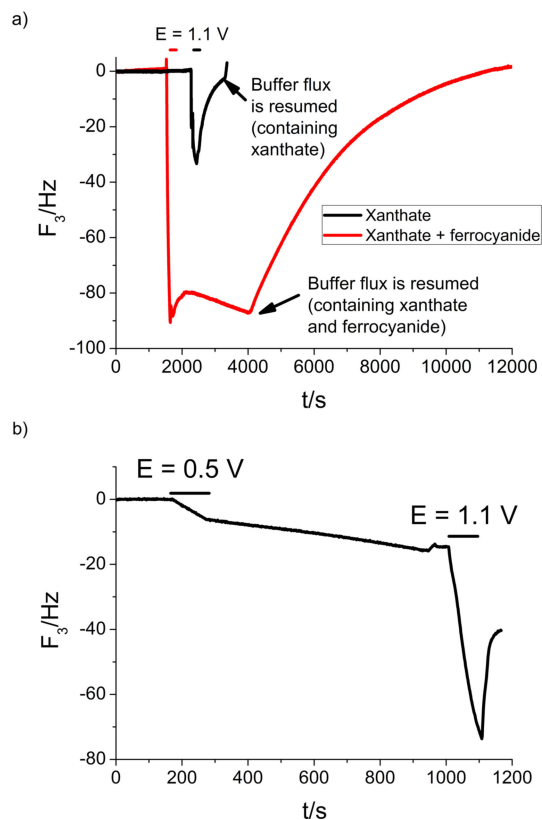


Fig. 7. Measurements by quartz crystal microbalance. a) Frequency in the third overtone vs. time for a quartz crystal stabilized with 0.1 M boric/borate buffer solution (pH=9.4) containing xanthate (500 μM) or xanthate and ferrocyanide (5 mM), to which an oxidizing potential (1.1 V vs. Ag/AgCl) was applied during 100 s, b) Frequency in the third overtone corresponding to the crystal in Figure a). To this crystal two 100 s potential pulses were applied: 0.5 V and 1.1 V vs. Ag/AgCl.

From Figure 7a, for the crystal stabilized with xanthate alone, when a potential pulse is applied, a decay in the resonance frequency of about 35 Hz is observed. However, the crystal stabilized with both xanthate and ferrocyanide gave a resonance frequency drop of 90 Hz. This indicates that in both cases mass is incorporated to the polymer, but in the presence of ferrocyanide, such incorporation is greater. Furthermore the material incorporated to the polymer is easily leached out by diffusion or by passage of a solution. In Figure 7b, the frequency of the third overtone is shown

for a crystal to which two potential pulses were applied (0.5 or 1.1 V vs. Ag/AgCl). To have an appreciable change in frequency, both ferrocyanide and xanthate need to be oxidized.

The increase in R_{ct} is not observed if the solution contains ferricyanide, which must be generated in-situ during the oxidative treatment. This step must be carried out at a potential at which both xanthate and ferrocyanide are oxidized. To evaluate the effect of xanthate oxidation in on R_{ct} values, impedance measurements were made using the modified electrodes, adding the ferrocyanide after the oxidation step. The observed differences in R_{ct} were very small (data not shown).

Thus, we conclude that the generation of the dimer in the polyelectrolyte matrix by itself is insufficient to explain the analytical response of the sensor, and that the oxidation of the ferrocyanide at the electrode surface is necessary for a useful signal generation.

4 Conclusions

An electrochemical sensor was developed using impedance spectroscopy to quantify xanthate in flotation baths and in effluents of such activity. The method was applied to real samples containing mineral and the obtained results were compared to the current standard method. Regarding sample pretreatment, centrifugation and filtration through membrane yielded comparable results. Considering this, and the fact that filtration is simpler and faster than centrifugation (< 1 min vs. 20 min), the former is considered to be the optimal method for sample clarification.

The developed method is based on the measurement of charge transfer resistance for graphite electrodes modified with a polymeric matrix (PAA-SDS). The method is useful in the range of concentrations found in flotation baths after a simple pretreatment (filtration through membrane). It was also adapted to be used in effluents of such activity. The method allows 6 to 10 samples per hour, which is compatible with its application to mining samples. Due to the oxidation pretreatment, interferences are expected to play a minor role in the determination.

For the sensor to show an appropriate response to xanthate concentration, it was necessary to apply an oxidizing potential prior to EIS measurement. This is explained by the oxidation of ferro- to ferricyanide and xanthate to dixanthogen, preventing the electron exchange of the redox probe, which results in an increase in the R_{ct} . This hypothesis is supported by CV, IR spectroscopy and QCM techniques.

5 Associated Content

SI 1. Screen printed graphite electrodes used for the sensors.

SI 2. Mineral sample and removal of suspended material through membrane filtration.

SI 3. Comparison of concentrations measured by the UV method using centrifugation and filtration as clarification methods.

SI 4. Impedance spectra and calibration line for the measurements in the range applicable to effluents.

SI 5. Voltammograms for potassium ethyl xanthate in buffer containing 0.1 mM ferrocyanide.

SI 6. Voltammograms for xanthate in the presence of increasing concentrations of ferrocyanide ion.

Table 1. Fitting of the impedance spectra shown in Figure 5.

Table 2. Linear regressions resulting from comparing the electrochemical to the UV method.

Table 3. Fitting of the EIS spectra corresponding to effluents.

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