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Flow injection analysis of ethyl xanthate by gas diffusion and UV detection as CS_2 for process monitoring of sulfide ore flotation

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ABSTRACT

A sensitive and robust analytical method for spectrophotometric determination of ethyl xanthate, $CH_3CH_2OCS_2^-$ at trace concentrations in pulp solutions from froth flotation process is proposed. The analytical method is based on the decomposition of ethyl xanthate, EtX^-, with 2.0 mol L^{-1} HCl generating ethanol and carbon disulfide, CS_2. A gas diffusion cell assures that only the volatile compounds diffuse through a PTFE membrane towards an acceptor stream of deionized water, thus avoiding the interferences of non-volatile compounds and suspended particles. The CS_2 is selectively detected by UV absorbance at 206 nm ($\varepsilon = 65{,}000$ L mol^{-1} cm^{-1}). The measured absorbance is directly proportional to EtX^- concentration present in the sample solutions. The Beer's law is obeyed in a 1×10^{-6} to 2×10^{-4} mol L^{-1} concentration range of ethyl xanthate in the pulp with an excellent correlation coefficient ($r = 0.999$) and a detection limit of 3.1×10^{-7} mol L^{-1}, corresponding to 38 μg L^{-1}. At flow rates of 200 μL min^{-1} of the donor stream and 100 μL min^{-1} of the acceptor channel a sampling rate of 15 injections per hour could be achieved with RSD < 2.3% ($n = 10$, 300 μL injections of 1×10^{-5} mol L^{-1} EtX^-). Two practical applications demonstrate the versatility of the FIA method: (i) evaluation the free EtX^- concentration during a laboratory study of the EtX^- adsorption capacity on pulverized sulfide ore (pyrite) and (ii) monitoring of EtX^- at different stages (from starting load to washing effluents) of a flotation pilot plant processing a Cu–Zn sulfide ore.

1. Introduction

Flotation is an important industrial process commonly used to separate minerals from ores. The process consists in addition of the crushed ores dispersed in an aqueous solution of organic reagents known as flotation collectors that modify the surface of the ore particle, which confers a more hydrophobic character to this surface, while the gangue remains hydrophilic. Air bubbles insufflated in the flotation cell adhere preferentially to the hydrophobic particles, carrying them to the surface as froth that is skimmed off for further purification.

Potassium and sodium ethyl xanthates ($C_2H_5{-}O{-}CS_2{}^-K^+$ or $C_2H_5{-}O{-}CS_2{}^-Na^+$) are organic salts highly soluble in water and widely used in the mining industry as flotation agents for the separation of sulfide minerals The wide use of these organic salts as mineral collectors in the mining industry results from their relatively low cost and the high selectivity to metal sulfides. In order to ensure an efficient adsorption of the anionic collector on the ore surface and avoid wasting, the concentration of ethyl xanthate anion in flotation cells is typically maintained at 10^{-5} to 10^{-4} mol L^{-1} range.

From a practical point of view, the optimization of the collector concentration is usually made by laboratory scale experimental tests, which require frequent EtX^- analyses. Another parameter that requires monitoring is the residual EtX^- concentration in liquors from flotation process because EtX^- along with its decomposition products, particularly carbon disulfide, are highly toxic to aquatic fauna and flora, representing a risk to the environment if they are discharged in water streams without previous treatment. In order to check the EtX^- concentration in liquors from flotation cells, iodometric titration and spectrophotometric [1] methods have been traditionally used. Potentiometric [2], polarographic [3], voltammetric [4,5], electrophoretic and chromatographic [6–8] methods have also been proposed. Flow injection methods with amperometric EtX^- determination on carbon-paste electrodes modified with silica-gel [9] and on static mercury drop electrode [10] have been suggested to increase the analytical throughput in routine analysis. A flow injection analysis of EtX^- in NaOH 50 mmol L^{-1} with UV spectrophotometric detection at 301 nm was previously described by some authors of this work [11]. In order to remove the interference of the suspended matter in pulp sam-

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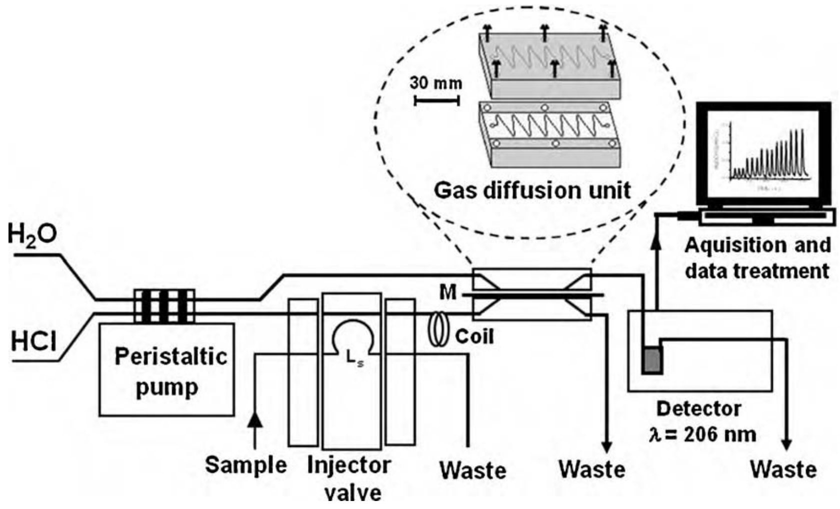

Fig. 1. Schematic diagram of the FIA system used for EtX^- determination with CS_2 spectrophotometric detection. L_s, sample loop; M, PTFE membrane.

ples from flotation plants a tangential dialysis cell was inserted between the injector valve and the spectrophotometric detector. This FIA design yielded a detection limit of 2 μmol L^{-1} and an analytical frequency of 25 determinations to be performed per hour. More recently, an online analytical system with UV detection at 301 nm was proposed for continuous xanthate determinations in laboratory flotation pulps [12]. The filter membrane overcomes interference of larger particles, but not the light dispersion effect of nanoparticles. Soluble species other than EtX^- in the dialysate or the filtrate might interfere if capable of absorbing light at 301 nm.

In this paper, a new approach to determine lower EtX^- concentration with UV spectrophotometric detection is proposed and evaluated. The FIA procedure is based on ethyl xanthate decomposition in acidic medium followed by diffusion of carbon disulfide – one of the decomposition products – across a PTFE membrane towards a receptor stream of deionized water. The dissolved CS_2 is detected at 206 nm in a flow cell. A highly sensitive and selective method was obtained, as will be shown.

2. Experimental

2.1. Reagents and solutions

The potassium salt of the ethyl xanthate was synthesized in the laboratory from ethanol and carbon disulfide, according to a method described in the literature [13]; the product was characterized by FTIR spectrophotometry and the purity was determined by iodometric titration. All reagents used were of analytical grade. The solutions were prepared with distilled, deionized water (resistivity > 18 MΩ cm^{-1}), obtained with a Barnsted Nanopure system. The stock solution of the potassium salt containing 1.0×10^{-2} mol L^{-1} of EtX^- was prepared at weekly intervals by dissolution of a required mass in deionized water. Analytical solutions of EtX^- were prepared by dilution of the EtX^- stock solution on a daily basis. Pyrite ore was obtained from mines located in Brazil's southeastern region (Espírito Santo State). Samples of the ore were milled in a mortar and sieved. The fraction with average particle size of 100 μm, determined by a particle size analyzer (Marven) was used for simulated flotation experiments.

2.2. Flotation experiments

The flotation process was simulated in the laboratory by loading a 100 mL beaker with 15 g of pyrite ore and deionized water up to 50 mL (30% ore, w/v). A 3 cm long magnetic stirring was used to vigorously stir the suspension under insufflation of synthetic air (80% N_2 + 20% O_2) at flow rate of 300 mL min^{-1}. Aliquots of an EtX^- solution were added stepwise with a micropipette in a procedure similar to titration. For each addition, after 15 min stirring, the suspension was allowed to rest for 5 min, for decantation and a sample of 2 mL of supernatant was collected for evaluation by the proposed FIA-spectrophotometric method. The original liquid volume in the flotation cell was obtained again by adding 2 mL of water.

Solid and liquid samples representative of all steps of the flotation process were obtained from a pilot plant operating with a sulfide ore rich in copper and zinc at the Universidad Nacional Mayor de San Marcos (UNMSM), Lima, Peru.

2.3. Instrumentation

A Hewlett-Packard 8452A diode-array spectrophotometer was used to obtain the absorption spectra of the potassium ethyl xanthate and of its decomposition products. Fluid propulsion was promoted with an Ismatec pump model REGLO. A 0.5 mm i.d. PTFE tubing was used throughout the FIA circuit except for the Tygon® pump tubing. Samples and reference solutions were injected in the FIA system with a manually operated, rotary injector valve provided with replaceable loops of 50–600 μL. The system was operated with an in-line gas diffusion unit, GDU made in the laboratory (Fig. 1).

The gas diffusion unit consisted of a 15 mm wide Teflon® tape inserted between two 90 mm × 18 mm × 40 mm blocks made of metacrylate polymer, held tightly together by six 3/16″ brass screws, as it can be seen in Fig. 1. The 1 mm wide and 0.2 mm deep channels engraved on each block on the surface in contact with the membrane have a triangle waveform of about 10 mm amplitude, starting and ending in orifices in the block for entrance and exit of the solutions.

The spectrophotometric detection of ethyl xanthate was made with a Femto UV–visible spectrophotometer model 700 provided with a Hellma model 178.710 micro flow-through cell of 80 μL internal volume and 10 mm light path. The absorbance signals were acquired with a PCL 711 DAQ (Advantech, USA) stored on a Pentium III 450 MHz microcomputer by using a data acquisition/processing software written in Object Pascal. All measurements were made at room temperature (25 ± 2 °C).

3. Result and discussion

The characteristic absorption bands of the ethyl xanthate anion in the UV spectral region reported [14] were experimentally

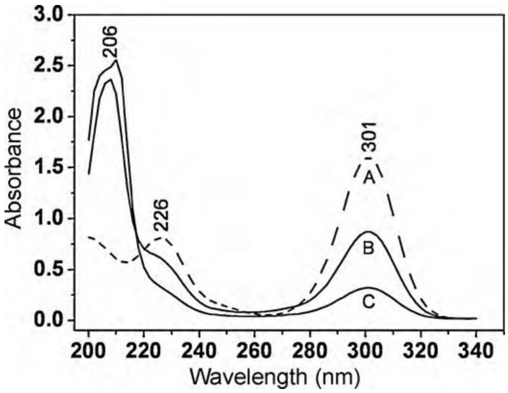

Fig. 2. UV absorption spectra of ethyl xanthate and during its decomposition after acidification. (A) Aqueous 9.0×10^{-5} mol L^{-1} EtX$^-$ solution at pH 7.0 showing the two characteristic absorption bands at 301 and 226 nm. (B) Aqueous 9.0×10^{-5} mol L^{-1} EtX$^-$ solution a few seconds after injection of acid up to pH 1.0, exhibiting decrease of the bands at 301 and 226 nm as a result of partial decomposition, and appearance of the CS_2 band at 206 nm; (C) Same as (B) after 60 s.

confirmed. In previous studies a more intense and relatively narrow absorption band at 301 nm (ε = 17,500 L mol^{-1} cm^{-1}) was employed not only to devise batch analytical methods for EtX$^-$ but also a FIA method in alkaline medium (pH 11.5) [11] and a continuous flow method without pH adjustment [12]. These methods are, however, vulnerable to interference of other species with absorption bands at the same wavelength, if present. Nanoparticles in the flotation pulp may also cross filter membranes [12] and cause some light scattering in the detector, a problem that does not arise with the use of the FIA method where there is separation by a dialysis membrane [11].

In acidic medium, the EtX$^-$K$^+$ (I) is unstable and suffers decomposition reactions with the formation of xanthic acid (II), which quickly decomposes into carbon disulfide (III) and ethanol (IV), according to (Eq. (1)):

$$\underset{\text{(I)}}{CH_3CH_2OCS_2{}^-K^+} + H^+ \rightleftarrows \underset{\text{(II)}}{CH_3CH_2OCS_2H} \rightarrow \underset{\text{(III)}}{CS_2} + \underset{\text{(IV)}}{CH_3CH_2OH} \quad (1)$$

This reaction is most effective at pH < 1.5 where HEtX predominates in the aqueous solution (HEtX $\rightleftarrows$ H$^+$+EtX$^-$, pKa = 1.6). Fig. 2 shows the absorption spectra in the range of 200–340 nm of 9.0×10^{-5} mol L^{-1} EtX$^-$ at pH 7.0 (curve A) and its decomposition recorded at pH 1.0 (curves B and C). Curve B was recorded a few seconds after the injection of 0.10 mol L^{-1} HCl and 9.0×10^{-5} mol L^{-1} EtX$^-$ solutions in a quartz cuvette while the curve C was obtained 60 s later. The absorbances measure at 301 nm show that about half of the EtX$^-$ decomposes during the acidification and mixing steps, and after a minute or so, only 20% of the EtX$^-$ remains in solution. The appearance of CS_2 in solution is unequivocally demonstrated by the band at 206 nm (ε = 65,000 L mol^{-1} cm^{-1}). The increase of the CS_2 absorbance from curve B to C was not proportional to the reduction of the EtX$^-$ concentration probably due to a combined effect of evaporation of the CS_2 and the stray radiation reaching the diode array detector at such high absorbance values (note that for $A > 2.5$, $T < 0.3\%$).

The relatively fast release of volatile CS_2 from the decomposition of EtX$^-$ in acid medium is the basis for the very selective analytical flow method developed here, where this compound is transferred to an acceptor stream in a hydrophobic membrane based gas diffusion unit. The chemical selectivity and immunity to physical interference from particulate matter in suspension is particularly important for the evaluation of low concentrations of EtX$^-$ in process monitoring in the mining industry. By using the flow system presented in Fig. 1, the effect of relevant instrumental and chemical parameters was evaluated to establish the analytical method for xanthate, as follows.

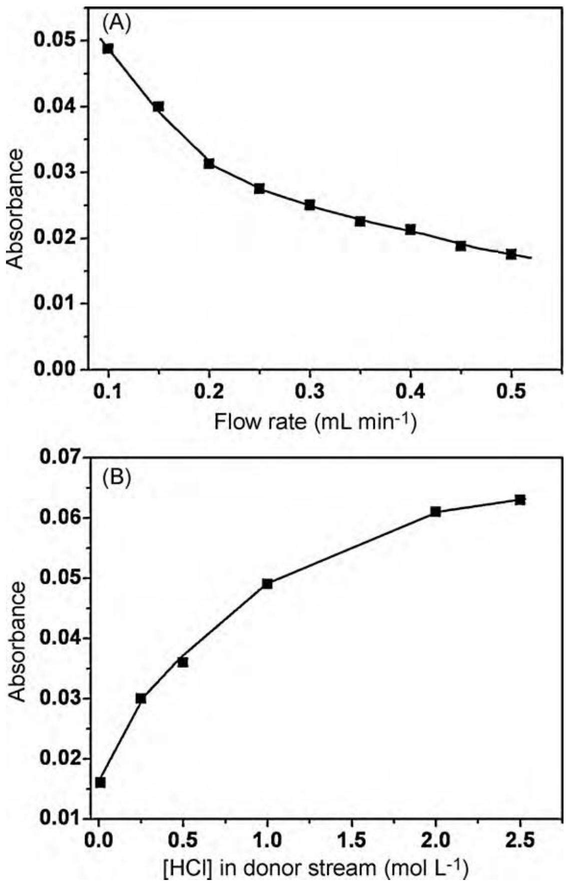

Fig. 3. (A) Effect of the flow rate on the analytical sensitivity. Sample volume: 200 μL, EtX$^-$ concentration: 1×10^{-5} mol L^{-1}; carrier sample solution: HCl 1.0 mol L^{-1}; (B) influence of HCl concentration in the donor channel. Sample volume: 300 μL. Flow rates: donor, 0.20 mL min^{-1}; acceptor, 0.10 mL min^{-1}.

3.1. FIA parameters

The carrier and the acceptor stream flow rates were evaluated in order to establish suitable working conditions. By using a fixed 200 μL sample loop volume and changing the flow rate of both the carrier and acceptor streams from 0.10 up to 0.50 mL min^{-1}, a gradual decay of the absorbance peak height was observed (Fig. 3(A)). This behavior is expected, because the increase of the flow rate in both channels shortens the residence time of the CS_2-containing donor flow in the GDU. In turn, the higher flow of the acceptor causes greater dilution of the CS_2 plug transferred through the membrane and conducted to the detector. However, the gain in sensitivity at very lower flow rate is outweighed by the reduction in the analytical frequency, so that a 0.2 mL min^{-1} of carrier stream was chosen as a compromise condition. Evaluation of the influence of the donor to acceptor ratio of flow rates showed that 0.1 mL min^{-1} is more appropriate for the acceptor because there is less dilution and the time demanded to displace the plug into de flow cell is not yet the determining factor of the analytical frequency.

The effect of the sample volume on the sensitivity was examined by changing the loop of the sample volume from 100 to 600 μL and using a 10 μmol L^{-1} EtX$^-$ standard solution. A maximum value was observed for 500 μL injections. An initial increase is expected because a broader reaction zone results in CS_2 transference through the membrane during a longer period per injection, improving the

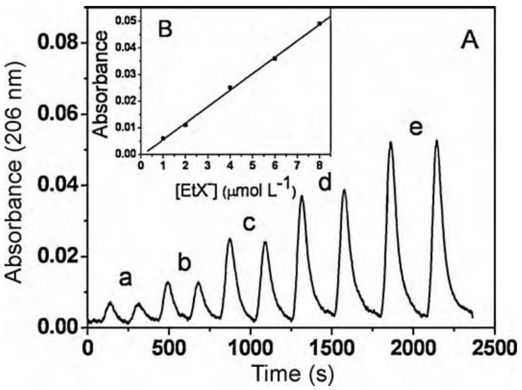

Fig. 4. (A) Absorbance signals as a function of ethyl xanthate concentration in the 1–8 × 10^{-6} mol L^{-1} range (a–e), for 300 μL injections. The peak heights correspond to the absorbance values in (B), the calibration curve, where the concentrations of the respective peaks can be readout.

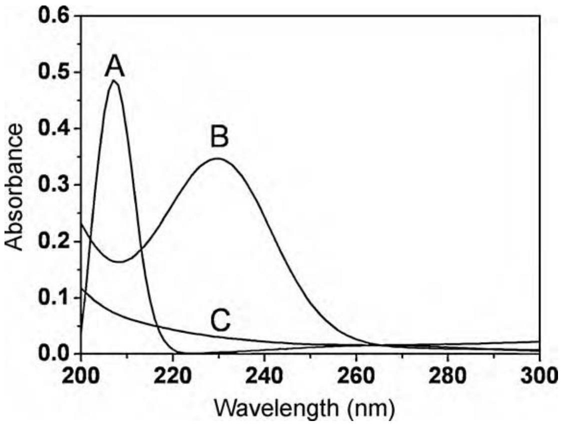

Fig. 5. UV absorption spectra of CS_2 and HS^-. (A) Aqueous 7.5 × 10^{-6} mol L^{-1} CS_2 solution; (B) aqueous 5.0 × 10^{-5} mol L^{-1} Na_2S solution, with pH adjusted to 8.3 to displace equilibrium to HS^-; (C) same as (B), pH adjusted to 5.6 with acetic acid, to simulate the pH of the acceptor stream.

sensitivity. However, for too large sample volumes, in the single flow line configuration, the central region of the plug lacks the acidity for reaction completion and the broadened peak height is reduced. The peak lowering for higher sample loops was overcome by configuring a merging zone flow circuit where the channel with continuously pumped acid merges with the sample injected in a separate channel with water as the carrier. However, the limited gain in sensitivity at sample volumes of 500 μL and higher did not pay-back for the peak broadening and lengthening of the procedure to over 8 min per determination – a disadvantage for high demand routine work. Therefore, the single line circuit with a sample injection of 300 μL was chosen as a compromise condition between sensitivity and analytical throughput.

The influence of the reaction coil length on the analytical signal was found insignificant. By shortening the coil length from 50 to 5 cm, the signal decreased by only 5%. This occurred because at the low flow rate of 0.1 mL min^{-1}, the average residence time in the GDU, of about 10 s, added to displacement time through connectors, short coil and cuvette entrance tubing, suffices for the completion of the fast reaction in the highly acidic medium.

The effect of the hydrochloric acid concentration was examined over the range of 0.1–2.5 mol L^{-1} in the donor channel for samples of 300 μL of 1.0 × 10^{-5} mol L^{-1} EtX^- standard solution at 0.2 mL min^{-1} flow rate. As it can be seen in Fig. 3(B), the absorbance signal curve grows with the acid concentration but with a slope that decreases continuously, approaching a plateau at hydrochloric acid concentrations above 2.0 mol L^{-1}, suggesting that a nearly quantitative formation of CS_2 is reached in the donor channel. For this reason, a 2.0 mol L^{-1} HCl solution was adopted in the method. This high electrolyte concentration also exerts a salting-out effect on the CS_2, improving the L/G/L transference to the H_2O acceptor stream. Addition of an extra electrolyte, like NaCl did improve the salting-out effect at the lowest examined HCl concentration (1 × 10^{-1} mol L^{-1}), but not noticeably at the already high ionic strength of the 2.0 mol L^{-1} HCl solution.

3.2. Analytical characteristics

Fig. 4 shows the UV spectrophotometric response for duplicate injections of 300 μL ethyl xanthate in the 1.0–8.0 μmol L^{-1} range. The proportionality between the absorbance and the EtX^- concentrations was confirmed from the calibration plot shown in the inset. The evaluation of this data by linear regression showed a slope of 0.0062 (s = 1.3 × 10^{-4}) L A μmoL^{-1} and a nearly null intercept of −5.4 × 10^{-4} (s = 6.6 × 10^{-4}) with a correlation coefficient of 0.999. The estimated detection limit, LOD, at the adopted conditions was 3.1 × 10^{-7} mol L^{-1} (3 s/slope criteria), and the LOQ, about 1.0 × 10^{-6} mol L^{-1}, corresponding to 36 ng of EtX^- in 300 μL the injected. The range of linear response is, however, much wider than that shown in Fig. 4, extending to 2.0 × 10^{-4} mol L^{-1}. The repeatability of the measurements was evaluated at the 8.0 × 10^{-6} mol L^{-1} EtX^- concentration, yielding a RSD of 2.3% (n = 10). For 300 μL injections at 200/100 μL min^{-1} flow rates in the donor/acceptor channels an analytical frequency of 15 injections per hour was attained. In applications where such a low LOD is not required, sample throughput can be doubled by reducing the sample loop and increasing the flow rates.

3.3. Interferences

A study of some potential interferences of the method was carried out under the above-established conditions. Particulate matter in suspension usually provides optical interferences in analytical methods with spectrophotometric detection. The suspended matter in solution scatters the incident radiation and introduces an error in the absorbance measurement. Pretreatments like decantation or filtration of the suspended particulate matter of the flotation pulp samples are time consuming and do not completely remove this interference. On line filtering of the pulp has been demonstrated in laboratory scale for speeding-up particle removal. Although no blockage was observed for 50 min periods of continuous UV spectrophotometric monitoring of xanthate [12], this approach does not remove light dispersing nanoparticles, avoidable by dialysis, as shown for ethyl xanthate determination in pulp by FIA with a tangential dialytic flow cell [11]. However, any small molecule can cross both the filter and the dialysis membrane, while the GDU with hydrophobic Teflon® semipermeable membrane used in this work guarantees that only volatile compounds in the acidified sample stream are transferred to the acceptor channel, improving the selectivity.

Suspended particles of sulfured ores in the pulp flotation process, if not completely removed (by dialysis), react with the acidic medium releasing volatile hydrogen sulfide, that can be partially transferred to the acceptor channel with the use of the proposed method. By examining the absorption spectra of CS_2, H_2S and HS^- in Fig. 5, it becomes clear that displacing the H_2S/HS^- equilibrium to the more protonated form minimizes interference [15]. The slightly acidic character of the acceptor solution (pH ∼ 5.6) caused by absorption of CO_2 from the air by the deionized water suits this purpose, while the addition of 1 mmol L^{-1} of acetic acid displaces the pH to a safer value around 3.9.

The extent of this potential interference was evaluated by adding S^{2-} to the EtX^- standard solutions. For example, addition of 1.0×10^{-4} mol L^{-1} sulfide to a 1.0×10^{-5} mol L^{-1} EtX^- solution causes a 22% increase of the absorbance peaks recorded at 206 nm. In order to perform a more realistic assessment of the matrix effect, injections of an aqueous supernatant solution from flotation pulp of pyrite ore (30%, w/v) free from EtX^- were made. These tests revealed peaks of the "blank" with absorbances of 0.003 above baseline; this would cause a positive error of only about 5.0×10^{-7} mol L^{-1} in the determined EtX^- concentration. Thus, corrections for the interference of H_2S are only recommended for determinations near the LOQ for EtX^-. For the slightly acidic acceptor (pH 5.6) where H_2S widely predominates (>96%), the molar absorptivities of the H_2S are 1500 and 600 L mol cm^{-1} at 206 and 230 nm, respectively, defining a 2.50 ratio, while for CS_2 the corresponding absorptivities are 65,000 L mol cm^{-1} and zero. Therefore, the blank correction to be applied to the EtX^- determination for a given ore being processed can be obtained by simply subtracting 2.50 times the absorbance measured at 230 nm from the total absorbance at 206 nm. When a multiwavelength spectrophotometer (e.g., diode array) is available, accurate correction can be obtained for every sample. Since little correction is required measurements at 230 nm for single wavelength photometers may occur at longer intervals of time, especially for a continuously running process with low variability of conditions.

Flotation plants use a frothing agent to control the size of the air bubbles as well as to stabilize the froth in the process. Terpenoid alcohols like methyl isobutyl carbinol (MIBC) (4-methyl-2-pentanol) are widely used, being effective in low dosage, for example, 20–53 g for a ton of ore [16]. The effect of MIBC on the analytical method was examined to evaluate possible interference on the hydrophobic properties of the PTFE membrane which could affect the diffusion of CS_2 to the acceptor channel. For this purpose, six different concentrations of MIBC ranging from 5 to 90 mg L^{-1} were mixed with an aqueous solution containing 8.0×10^{-5} mol L^{-1} of EtX^- and injected in the FI system. No noticeable difference between the absorbance peak heights was observed after twenty injections, indicating that the performance of the transference of CS_2 through the PTFE membrane is not affected by the presence of MIBC even at concentrations above the ones used in practice.

3.4. Application to the evaluation of the adsorption of EtX^- on pyrite

To evaluate the performance of the proposed FIA system, an adsorption study of EtX^- on the ore particles was carried out by experiments, which are similar to titration of the ore surface by incremental addition of EtX^-. In a 100 mL beaker, 15.0 g of pyrite powder were added to 50 mL of water containing 10 mg L^{-1} of MICB as frothing agent. Convection of the pulp was applied by a magnetic stirrer and by aeration with synthetic air under 300 mL min^{-1} flow rate. Additions of 1×10^{-6} mol of EtX^- at a time were made with the aid of a manual micropipette. After each addition, both the stirring and the aeration were activated for 15 min and turned off for 5 min, for settling of the pyrite. A 2.0 mL aliquot of the supernatant solution was filtered through a 0.45 μm pore size disposable syringe filter unit and injected into the FIA system for EtX^- determination. The flotation was restarted after addition of 2 mL of water and 1×10^{-6} mol of EtX^-.

A "titration plot" resulting from these measurements is illustrated in Fig. 6, showing that EtX^- is first detected in the solution after the addition of 10.0 μmol of EtX^- to 15 g of ore, indicating that the surface is getting saturated with adsorbate. In the present study, no sample pretreatment was required. However, for a continuously running flotation process, rather than waiting the sedimentation of the particles of the samples, it may be more advantageous to apply a filtration step with the help of disposable syringe filters. This method was found to be effective in avoiding tubing clogging and/or deposition of particles inside the donor channel of the gas diffusion unit, in the long term.

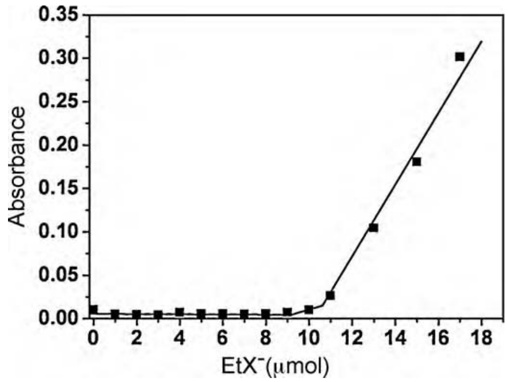

Fig. 6. Monitoring of the EtX^- adsorption capacity on powdered pyrite. Additions of EtX^- to 15.0 g of pyrite powder suspended in 50 mL of water.

Table 1
Examples of EtX^- monitoring in various stages of the flotation process of Cu–Zn sulfide ore.

Sample	EtX^- concentration (μmol L^{-1} ± SD, $n = 3$)
Ore feed liquor (before EtX^- addition)	<LOD
Flotation liquor in the cell	162.0 ± 5.0
Flotation liquor accompanying the separated tailing rock	204.0 ± 6.5
Flotation liquor accompanying the collected froth with concentrated ore	171.0 ± 2.6
Effluent (wastewater from ore washout)	1.78 ± 0.09

3.5. Monitoring EtX^- in flotation liquors of a pilot plant

The proposed FIA method was applied to samples collected at all stages of the flotation process of a pilot plant (UNMSM, Peru) running with a sulfide ore rich in copper and zinc. Some results are presented in Table 1. In the liquor of the wetted grinded starting sulfide ore before addition of flotation agent, as expected, no EtX^- was detected. The correction of the minimum interference of HS^- was evaluated for this sample (as explained in Section 3.3). It remained nearly constant throughout the monitoring and was neglectable for all but the first and last entries of Table 1, respectively, the starting liquor and the effluent water.

Table 1 shows that all liquor samples during the flotation operation present ethyl xanthate concentrations far above the region covered in Fig. 4, but still linear. For the monitoring of processes operating at higher EtX^- concentrations, instead of diluting the sample or shortening the sample loop, the most practical approach is to increase the flow rate and the HCl concentration, with gain in analytical frequency.

4. Conclusions

The new flow method for ethyl xanthate determination presented here is simple, robust, sensitive and selective, suitable for direct application to flotation liquor after filtration or some minutes of decantation, to avoid massive introduction of ore particles. The decomposition of the analyte into CS_2 and ethanol in acidic medium followed by gas diffusion through a PTFE membrane and measurement of the intense absorbance of CS_2 at 206 nm grants high selectivity to the method against colloidal matter in the flotation liquor and/or non-volatile chemicals. The only interference found stems from H_2S evolution at sulfured ore particles during the acidification step. Correction is needed only at EtX^- concentrations near the LOQ and can be easily done by direct evaluation of the HS^- concentration at 230 nm and subtraction of its corresponding absorbance at 206 nm. The quickness and wide linear dynamic response of the method, spanning from the LOQ of 97 $\mu g\,L^{-1}$ up to 24 $mg\,L^{-1}$, favors its direct application to EtX^- determination not only in samples from the flotation process itself, but to evaluate the residual EtX^- in liquid effluents as well, as demonstrated.

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