



Flow injection analysis of ethyl xanthate by gas diffusion and UV detection as CS₂ for process monitoring of sulfide ore flotation

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ARTICLE INFO

Article history:

Received 5 February 2010

Received in revised form 25 May 2010

Accepted 26 May 2010

Available online 1 June 2010

Keywords:

Ethyl xanthate

Flow analysis

Gas-diffusion

Spectrophotometry

Flotation process

Mining industry

ABSTRACT

A sensitive and robust analytical method for spectrophotometric determination of ethyl xanthate, CH₃CH₂OCS₂⁻ 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, CS₂. 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 CS₂ is selectively detected by UV absorbance at 206 nm ($\epsilon = 65,000 \text{ L mol}^{-1} \text{ cm}^{-1}$). 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 $2 \times 10^{-4} \text{ mol L}^{-1}$ concentration range of ethyl xanthate in the pulp with an excellent correlation coefficient ($r = 0.999$) and a detection limit of $3.1 \times 10^{-7} \text{ mol L}^{-1}$, corresponding to $38 \mu\text{g L}^{-1}$. At flow rates of $200 \mu\text{L min}^{-1}$ of the donor stream and $100 \mu\text{L min}^{-1}$ 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 $1 \times 10^{-5} \text{ mol L}^{-1}$ 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.

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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 (C₂H₅–O–CS₂⁻K⁺ or C₂H₅–O–CS₂⁻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 $10^{-4} \text{ mol L}^{-1}$ 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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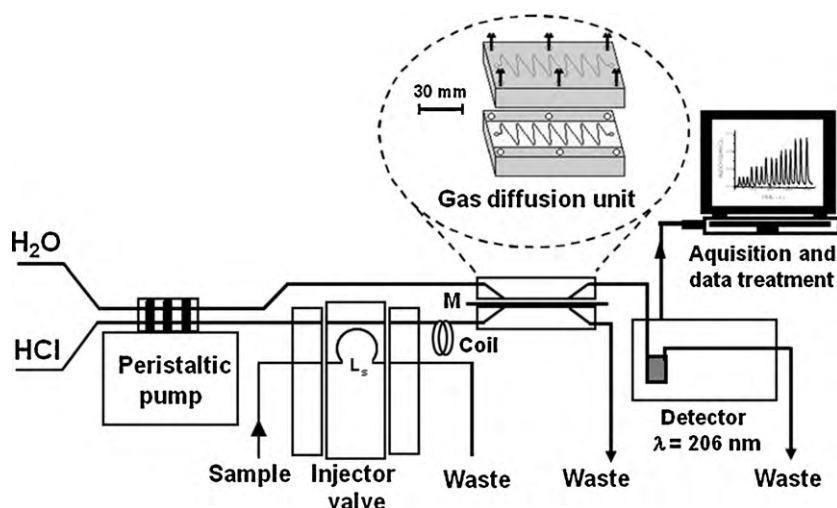


Fig. 1. Schematic diagram of the FIA system used for EtX^- determination with CS_2 spectrophotometric detection. L_s , sample loop; M, PTFE membrane.

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 $2 \mu\text{mol L}^{-1}$ 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 $> 18 \text{ M}\Omega \text{ cm}^{-1}$), obtained with a Barnsted Nanopure system. The stock solution of the potassium salt containing $1.0 \times 10^{-2} \text{ mol L}^{-1}$ 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 $100 \mu\text{m}$, 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 ($80\% \text{N}_2 + 20\% \text{O}_2$) 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 $90 \text{ mm} \times 18 \text{ mm} \times 40 \text{ mm}$ 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 ($25 \pm 2^\circ\text{C}$).

3. Result and discussion

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

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