



Xanthate degradation occurring in flotation process waters of a gold concentrator plant



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ABSTRACT

Xanthates enhance the separation of valuable metals from minerals in hydrometallurgical processes. They degrade to structurally related decomposition products under the chemical and physical conditions in flotation processes, which minimizes the extraction recovery of metals. To monitor low quantities of the decomposition products, the flotation process requires sensitive, qualitative, or even quantitative controlling.

The goal of the present research was to develop a sensitive separation method for on-line monitoring of the degradation of collector chemicals in the waters of a gold concentrator plant. To that end, an on-line coupling of capillary electrophoresis with a pressure-assisted field-amplified sample injection (PA-FASI) was developed. The purpose of the overall system set-up was to fortify concentrations during sample introduction in order to study xanthates and thiocarbonate directly in flotation waters during the process. The system developed from these methods was reliable and reproducible, enabling detection of below 10 mg L⁻¹ quantities for ethyl and isobutyl xanthates as well as for isobutyl thiocarbonate.

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1. Introduction

Froth flotation improves the extractability of minerals. In aqueous processes, thiol collectors in particular are important flotation chemicals. They are additives, which improve metal extraction from, for example, sulfide minerals. In process waters, thiol collectors are the chemicals used for selectively separating hydrophobic minerals from hydrophilic ones. Xanthates, dithiophosphates, and dithiocarbamates are different classes of thiol collectors, each compound forming different surface products on different minerals (Hangone et al., 2005). For gold extraction, the most effective thiol collectors are xanthates. Benefits of their use are lower dosage requirements, improved selectivity, fast metal isolation, and high recovery, including enhancement of the recovery of coarse particles.

However, in mineral processing systems, xanthates tend to decompose and to produce different types of degradation products, which may in turn decrease the xanthate concentration. The degradation thus decreases the recovery of metal extraction and disturbs the process productivity (Bulatovic, 2007; Yekeler and Yekeler,

2004). Usually, froth flotation occurs in the pH range 6–12 (Bulatovic, 2007), where xanthates may actively produce side-products such as dixanthogen (Eliseev, 2012), thiocarbonate (Eliseev, 2012), perxanthate (Sun and Forsling, 1997; Hao et al., 2000), and xanthyl thiosulfate (Hao et al., 2000).

According to the literature, the most popular technique used in the determination of xanthates has been ultraviolet/visible/infrared spectrophotometry (UV/VIS) Hao et al., 2000, even though with this method, the metal species and degradation products cannot be differentiated, and the determination is a sum result. In general, lack of separation is the main problem in the monitoring of xanthate processes, as the degradation of the process chemicals cannot be avoided. In such cases, to obtain reliable information, Hao et al. (2000) isolated the xanthates from the process waters using a liquid–liquid extraction containing organic solvents before quantification. However, the method was time consuming, and it could not easily be coupled to the main industrial processes. Hao et al. (2000, 2008) have also previously studied ethyl xanthate, ethyl dixanthogen, ethyl thiocarbonate, ethyl perxanthate, and ethyl xanthyl thiosulfate with Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. Conversely, Trudgett (2005) separated the species using high-performance liquid chromatography (HPLC), and examined the kinetics of the decomposition of xanthate. In particular, the determination of compounds in sample mixtures should be made

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Nomenclature

Symbols

BGE	background electrolyte solution	KEX	potassium ethyl xanthate
CE	capillary electrophoresis	KETC	ethyl thiocarbonate
LOD	limit of detection (ng mL^{-1})	NH ₄ EPX	ammonium ethyl perxanthate
LOQ	limit of quantification (ng mL^{-1})	TBAEXT	tetrabutylammonium ethyl xanthyl thiosulfate
PA-FASI	pressure-assisted field amplified sample injection	Dana	Danafloat™ 507
UV	ultraviolet	CAPS	3-(cyclohexylamino)propane-1-sulfonic acid
UV/VIS	ultraviolet–visible spectrophotometry	PDA	photodiode array detector
FTIR	Fourier transfer infrared spectroscopy	UK 1–3	unknown compounds
NMR	nuclear magnetic resonance spectroscopy	L_{det}	length of separation in capillary (m)
HPLC	high performance liquid chromatography	L_{tot}	total length of capillary (m)
DTP	diisobutyldithiophosphate	μ_{ep}	electrophoretic mobility of the species ion ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
DTPI	diisobutyldithiophosphate	μ_{app}	apparent mobility of the species ion ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
EPX	ethyl perxanthate	μ_{eof}	electroosmotic mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
EXT	ethyl xanthyl thiosulfate	t_{m}	detection time of the species ion (min)
EX	ethyl xanthates	t_{eo}	detection time of the electroosmosis (min)
IBX	isobutyl xanthates	U	applied electric voltage (V)
IBPX	isobutyl perxanthate		
IBTC	isobutyl (mono)thiocarbonate		

using a separation technique to ensure reliability of the identification of the by-products in the process waters (Trudgett, 2005).

In previous years, capillary electrophoresis (CE) was used for various purposes, such as for the determination of metals without complex formation and for the quantification of inorganic compounds in environmental waters and food (Sprung et al., 2008; Soomro et al., 2012; Pimrote et al., 2012; Timerbaev, 2013; Rovio et al., 2010; Sirén et al., 2015). Generally speaking, CE is well suited to even broader scientific fields, particularly in pharmaceutical, clinical, and bioprocess applications (Jones and Woodcock, 1986; Amundsen et al., 2007; Turkia et al., 2013; Marina et al., 2005). The idea of the technique is based on an electro-aided separation of ionic compounds in narrow-bore fused silica capillaries (with a volume below $1 \mu\text{L}$) under an applied electric field ($100\text{--}800 \text{ V cm}^{-1}$). Electrical separation of the side-products of thiois is possible due to the ionization of compounds in industrial process waters and the flotation chemicals in water (Kokkonen et al., 2004; Hissner et al., 1999; Sihvonen et al., 2014; Sihvonen, 2012). In the present project, CE was used because it is applicable to on-line measurements due to the low eluent and sample consumption and to the reusability of the separation capillaries (Kokkonen et al., 2004). In addition, the electrolyte-filled capillaries are more robust for withstanding the extremes of the pH than are the sorbent-filled columns in HPLC. Furthermore, CE has a higher separation efficiency due to electro-aided movement than that obtained from HPLC, which uses pressure-driven separation. However, because of the low capillary volumes in CE, the injection volumes are only tens of nanoliters, which leads to lower detection quantities of the compounds with CE than with HPLC. On-line methods for concentrating real samples require a high sensitivity of detection, since detection is generally made with an in-line UV spectrophotometer with CE.

Only two articles have been published which describe the use of CE in analyses of flotation chemicals; Hissner et al. (1999) authored one of them. They developed methodologies for various kinds of flotation reagents and also tested various injection methods. They concluded that on-line concentration by stacking yields the best sensitivity. However, Sihvonen et al. (2014) have recently found that pressure-assisted field-amplified sample injection (PA-FASI) is even more effective than stacking when the sample matrices contain high ionic strengths, as is the case for waters of flotation processes. Their research aimed at finding an optimized

method for quantification of diisobutyl dithiophosphate (DTP), diisobutyl dithiophosphate (DTPI), ethyl xanthates (EX) and isobutyl xanthates (IBX), which are all used as thiol collectors in froth flotation.

In the present study, we focused our research on the monitoring of the decomposition products of ethyl xanthate – especially ethyl thiocarbonate, ethyl perxanthate, and ethyl xanthyl thiosulfate – by using CE coupled with an UV/VIS spectrophotometer. The method was thereby optimized and implemented without any sample preparation for the various types of process waters generated at a concentrator plant. Then, the monitoring system required a new sample introduction technique, which was based on PA-FASI. The optimized method was applied to the flotation water monitoring of a gold concentrator plant.

2. Materials and methods

2.1. Chemicals

Potassium ethyl xanthate (KEX, purity 85%, $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$, MW $160.30 \text{ g mol}^{-1}$) was purchased from Alkemin (85%, Michoacan, Mexico). The degradation chemicals were potassium ethyl thiocarbonate (KETC), ammonium ethyl perxanthate (NH₄EPX), and tetrabutylammonium ethyl xanthyl thiosulfate (TBAEXT). They were synthesized according to the technique described by Hao et al. (2000) in the laboratory of organic chemistry at Lappeenranta

Table 1
Chemicals used in the method development.

Compound name	Molecular formula	Abbreviation
Potassium ethyl xanthate	$\text{C}_3\text{H}_5\text{S}_2\text{OK}$	KEX (Alkemin)
Potassium ethyl thiocarbonate	$\text{C}_3\text{H}_5\text{SO}_2\text{K}$	KETC (in-house synthesis)
Ammonium ethyl perxanthate	$\text{C}_3\text{H}_5\text{S}_2\text{O}_2\text{NH}_4$	NH ₄ EPX (in-house synthesis)
Tetrabutylammonium ethyl xanthyl thiosulfate	$\text{C}_3\text{H}_5\text{S}_4\text{O}_4(\text{NC}_4\text{H}_9)_4$	TBAEXT (in-house synthesis)
Isobutyl xanthate	$\text{C}_5\text{H}_8\text{S}_2\text{O}$	IBX
Isobutyl thiocarbonate	$\text{C}_5\text{H}_9\text{S}_3$	IBTC
Isobutyl perxanthate	$\text{CS}_2\text{O}_2(\text{C}_4\text{H}_9)$	IBPX

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