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Short communication

Determination of flotation reagents used in tin-mining by capillary electrophoresis

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Abstract

Alkyl xanthates (*O*-alkyl dithiocarbonates) and phosphonates are important organic collectors for the flotation of metals from crude ore. Leaching from waste dumps into river and ground water, these substances can cause environmental pollution.

A capillary electrophoretic method for the routine determination of ethyl, isopropyl, hexyl xanthate, and styrene phosphonate has been developed. Separation within 12 min could be achieved in borate pH 8.8 performing UV detection at 254 and 300 nm simultaneously. To improve the limits of detection obtained with hydrodynamic injection (0.4–1.5 ppm), field amplified sample injection (FASI) and stacking were investigated. An increase in sensitivity up to 4–8 fold could be achieved by pressure assisted FASI. Applying a stacking method to enrich the analytes by filling the capillary with sample solution to one third of its length, the limits of detection could be decreased to 10–40 ppb.

Water samples from a former tin ore mining area have been analyzed using the optimized stacking technique. Quantitation was performed by standard addition. Good precision and accuracy were obtained, making this robust capillary electrophoretic method well-suited for routine analysis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Alkyl xanthates [*O*-alkyl dithiocarbonates, ROC(S)S⁻] and styrene phosphonate (CH₂=CHC₆H₅-PO₃H²⁻) are important organic collectors for the flotation of metals from crude ore [1]. In the flotation process small mineral grains (produced by crushing and grinding) are rendered hydrophobic in aqueous solution by the addition of organic molecules (collectors). The coated grains attach themselves to air bubbles that float to the solution surface where they are removed. Alkyl xanthates are

especially suited for the flotation of mineral sulfides. They are selectively adsorbed onto the metal sulfide surface because there is either no adsorption at the non-sulfide mineral–water interface or if adsorption occurs, the short alkyl chain can not impart a hydrophobic character to the grain. Over a billion tons of ore are processed by flotation each year worldwide. After use waste material including large amounts of the organic collectors is deposited on slag heaps (“tailings”). Leaching into river and ground water, flotation reagents can cause environmental pollution. Therefore, monitoring the tailings outlets is important to prevent a negative impact on the environment.

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Analytical methods for the determination of flotation reagents include spectroscopic techniques [2–5], normal-phase HPLC [6], and ion chromatography [7–9]. The disadvantage of liquid chromatography is that direct injection of real sample matrices onto the column can cause problems (column pressure build-up, retention time shift, deterioration of separation efficiency) or even irreversibly destruction the column. Capillary electrophoresis (CE) has not been applied for the separation of xanthates, although it has a great potential due to its power of rapid method development, fast separations, high separation efficiency, and robustness of capillaries. The high detection limits of CE have been the bottleneck in environmental analysis where low concentrations need to be determined. For that reason, several techniques to enhance sensitivity in CE have been developed, including derivatization, modifications of the capillary in the detection region, on-line solid-phase, and immunoaffinity extraction, as well as optimized sample introduction such as stacking [10].

In our work capillary zone electrophoresis has been studied for the determination of alkyl xanthates and phosphonates. A method was developed with regard to separating and detecting the relevant species of ethyl, isopropyl, hexyl xanthate, and styrene phosphonate simultaneously; decreasing the limits of detection; and determining flotation reagents in water samples from the former tin ore mining area of Altenberg (Germany).

2. Experimental

2.1. Chemicals

Styrene phosphonate (SP), ethyl xanthate (EX), isopropyl xanthate (IX), and hexyl xanthate (HX) were purchased from Sigma (Deisenhofen, Germany). Boric acid and borax (analytical grade) were obtained from Merck (Darmstadt, Germany). All solutions were prepared with laboratory-distilled water (Millipore).

2.2. Capillary electrophoretic conditions

The experiments were carried out on a Beckman MDQ electrophoresis system (Fullerton, CA, USA)

with diode array detector using a fused-silica capillary, 30 cm×75 μm I.D. (Beckman). The electrophoretic buffer consisted of 65 mM boric acid and 16 mM borax in aqueous solution, pH 8. Separation was performed at +25 kV with 13 min data acquisition time. The capillary was rinsed with 0.1 M sodium hydroxide solution at the beginning of the analysis of a sample set, between separations with water for 1 min and buffer solution for 1 min. The UV detection wavelengths were set at 254 nm for SP and 300 nm for HX, IX, and EX after optimization in diode array mode. Data analysis was carried out using SQS quality assurance software (Perkin-Elmer, Überlingen, Germany).

2.3. Injection modes

Hydrodynamic injection was carried out for 10 s at 3.57 kPa. For electrokinetic injection pressure assisted field amplified sample injection (PA-FASI) was used at –5 kV and 5 kPa or –10 kV and 7.14 kPa for 12 s.

The stacking procedure consisted of 2 steps: first the hydrodynamic injection was performed for 51 s at 14.28 kPa (this corresponds to 10 cm capillary filling), then –15 kV was applied for 85 s while monitoring the current. The stacking was interrupted at 95% of maximum current.

2.4. Water samples

Samples were taken from the outlet of the tin ore tailings into the river Biela and collected in 2 l glass bottles. Transport was carried out in an ice box. The samples were stored in the refrigerator for one day before analysis. Further pretreatment of the samples was not necessary.

3. Results and discussion

3.1. Development of a separation method

Xanthates and phosphonates are anions with low electrophoretic mobility. For that reason, separation was carried out in a borate buffer at pH 8 under positive voltage polarity (detection at the cathode). Under these conditions the strong electroosmotic

flow (EOF) transported the anionic compounds to the detection side of the capillary. Separation of all four analytes, migrating in the order of low to high mobility, was achieved within 13 min (7.3–11.2 min migration times, R.S.D. 1–2.2%). The determination could be performed in a shorter time, but with decreased peak resolution. That can be a problem for complex sample matrices where interferences might be present.

The detection wavelengths were optimized for each compound using diode array detection. Maximum absorption was observed at lower wavelengths in the 200 nm range. However, many compounds absorb in this region, and interferences are more likely. For that reason, the second maxima at 254 nm for phosphonate and 300 nm for xanthates were used. In the further experiments detection was carried out simultaneously at these two wavelengths.

Fig. 1 shows the electropherograms of aqueous standards at 100 ppb using the stacking technique. The optimization of the sample introduction methods is described in the next section.

3.2. Optimization of an injection method

The concentrations of flotation reagents expected in environmental samples are in the middle to lower $\mu\text{g/l}$ range. Prior to the analysis of real samples, the injection conditions were optimized to improve the limits of detection obtained by hydrodynamic injection (see Table 1). To simply increase the injection volume is only possible to a certain degree because a deterioration of the separation efficiency or even current break down can occur if the electric field strength is not consistent throughout the capillary.

A possibility to enhance the amount of analytes injected is electrokinetic injection. This method has the advantage of selective introduction of charged species, whereas sample bias and nonlinear calibration functions are disadvantages. If the sample solution has a lower ionic strength than the buffer solution, analytes migrate rapidly into the capillary. When they reach the higher ionic strength region, migration slows down and the compounds are enriched at the sample/buffer interface. This process is called field amplified sample injection (FASI) because a higher field strength is generated in a

solution of lower ionic strength leading to faster migration. Electrokinetic injection of xanthates and phosphonates was performed using a negative voltage polarity at the injection side. The application of pressure during the injection was necessary to compensate the strong electroosmotic flow generated in the opposite direction (PA-FASI). The use of a higher injection voltage required also a higher compensation pressure to avoid the transport of the analytes with the EOF. The pressure settings were optimized accordingly to obtain a high intensity for the analyte peaks and weak intensity for the EOF marker peak. Fig. 2 presents a comparison of signal intensities obtained with different injection methods. A significant improvement in sensitivity of four to eight fold (depending on injection voltage and analyte), compared with hydrodynamic injection, was achieved by PA-FASI. The best enhancements were observed for the compounds with higher electrophoretic mobilities, such as ethyl xanthate and styrene phosphonate. However, this technique is not well-suited for routine analysis because it can not be automated with the used CE apparatus.

Therefore, a stacking technique was developed leading to a further increase in sensitivity (see Fig. 2). The capillary was filled to one third of its length with sample solution by hydrodynamic injection. After that, a negative voltage was applied leading to the removal of aqueous matrix by the EOF, while the anionic analytes migrated in the anodic direction and enriched in a narrow zone. Monitoring the current during the procedure was important to obtain maximum enrichment and to avoid transport of analytes out of the capillary. The stacking process was stopped as the current reached 95% of its maximum value. Good reproducibility was obtained while reducing the limits of detection up to 10-fold (Table 1). The species with the lowest electrophoretic mobility (hexyl xanthate) showed a higher increase in sensitivity than using PA-FASI. This compound migrated less against the EOF creating a very sharp, concentrated zone. In contrast to PA-FASI, calibration curves using the stacking technique are linear and the process could be easily automated with the CE apparatus. Both hydrodynamic and stacking injection techniques were validated according to DIN using the SQS quality assurance software. Calibration was performed at seven concentration levels

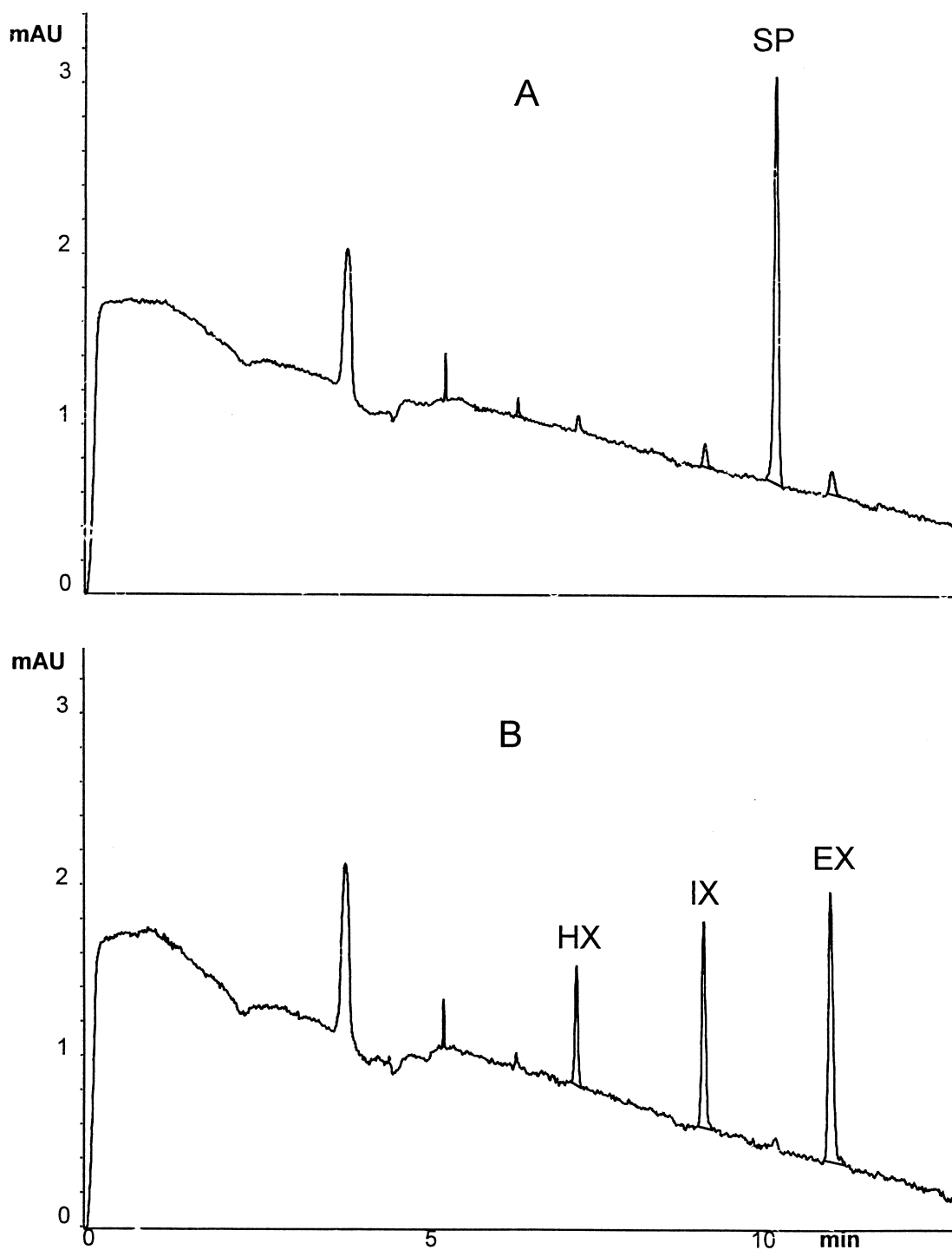


Fig. 1. Separation of 100 ppb alkyl xanthate (A) and styrene phosphonate (B) standards using the stacking procedure. For sample injection and separation conditions, see Section 2.

Table 1
Comparison of hydrodynamic injection and stacking

Component	Hydrodynamic injection			Stacking		
	LOD (ppb)	RSD (%)	R^2	LOD (ppb)	RSD (%)	R^2
SP	200	2.11	0.9996	21	2.28	0.9995
HX	360	3.88	0.9996	49	5.29	0.9996
IX	70	0.75	0.9999	10	1.09	0.9999
EX	200	2.12	0.9986	20	2.15	0.9974

(0.5–15.0 mg/l for hydrodynamic injection, 50–1500 $\mu\text{g/l}$ for stacking). Every concentration was analyzed three times by CE. For the lowest and highest concentration ten replicates were carried out. For calibration curves the F-test for linearity (Mandel adaptation test) was performed. The test for homogeneity of variances of the lowest and highest concentration level met the required criteria for DIN 38402. The calculation of the limits of detection corresponds to DIN 32645.

3.3. Analysis of a seepage water sample

Because the CE capillary could tolerate the raw

water samples without performance loss, no requirement of sample preparation arose. The stacking technique was applied to obtain optimum sensitivity. The identification of styrene phosphonate was achieved by diode array detection, comparison of migration times, and standard spikes. This compound was exclusively used throughout the recent years for the extraction of tin ore. No interferences from matrix components were observed. Quantitation was performed by the standard addition technique to consider impacts of the sample matrix on the stacking procedure. Spiking known concentrations of analyte into the same sample keeps the matrix influences constant during the calibration process.

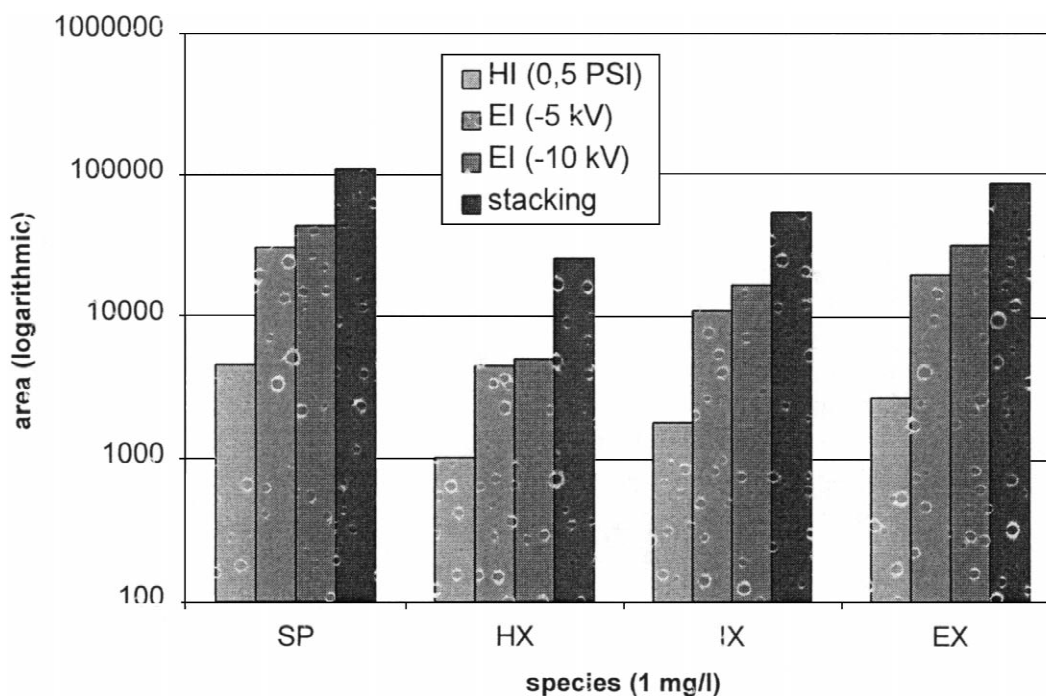


Fig. 2. Comparison of signal intensity using different injection methods.

Four times 0.5 mg/l was added to the sample to create the calibration function $y=4108.8x+2840$, $R^2=0.998$. A content of 0.69 mg/l styrene phosphonate was determined in the water sample. This concentration is below the authorized limit.

Xanthates were no longer used for flotation during the last few years. Due degradation processes occurring, the concentration of the xanthates in the water samples was below the limits of detection. It can be assumed that the traces of xanthates that possibly exist do not have a negative impact on the environment.

Capillary zone electrophoresis is well suited to the determination of flotation reagents used in tin ore mining because of its robustness, fast separations, and low limits of detection. It has been used routinely to monitor the concentration of styrene phosphonate in environmental samples with a throughput of 30 samples/7.5 h. The method might also be applied to commercial flotation reagent formulations or in pre-studies of new collectors.

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