UREAP Summer 2017 Report

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Determination of Xanthate Compounds in Mining Process Waters by Capillary Electrophoresis

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Table of Contents

Experimental

Results and Discussion

Acknowledgements

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Abstract

An analytical capillary electrophoresis method was developed for the identification and quantification of the xanthate family of organosulfur compounds, all of which are used in froth floatation during the milling process of mined ore. Using this previously optimized novel method, bulk samples of unknown composition were characterized by their concentration of each xanthate, as well as the concentration of unknown compounds arising from contaminants on the manufacturing side or degradation products. Calibration curves were prepared for the four different organic-chain xanthates: amyl, ethyl, isopropyl, and isobutyl.

Introduction

Xanthates; a family of chemical compounds used to aid froth flotation in the mining industry, are used every day by mining companies across the globe. Potassium amyl xanthate (PAX) (Figure 1.) is the most commonly used floatation agent, but the market for xanthates is not tightly regulated. Many purchased floatation agents will be mixtures of xanthates, giving rise to a large variation in individual bag composition and inconsistencies in the amount needed per volume of water. Since there are eight different xanthate compounds found in industry, all of which have different masses, it is important to know the exact make-up of each bag of PAX.

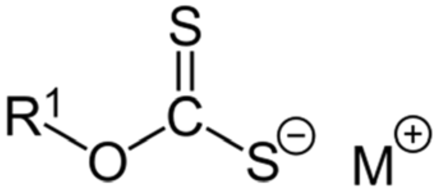


Figure 1. General structure of xanthate molecules

In the mining industry today, a very large volume of water is used for flushing and slurry formation during the milling process. Water is introduced at the start of the milling process and acts as a medium with which the flurry can be carried through the mill to prevent buildup or blockage. This water often contains substantial amounts of copper or gold particulate that will be lost if sent directly to tailings ponds.[3-5,9] To prevent this loss of product, a process called froth flotation is implemented. PAX is currently the most commonly used xanthate, but industry professionals have been bringing to light the issue of mislabeled products. Mining companies can order a bag of xanthates that claims to be 90% PAX, but what they receive is a mixture of different xanthates in inconsistent quantities. This becomes an issue when trying to standardize the addition of PAX to froth floatation. The different molecular masses give rise to varying amounts of available xanthates, which in turn means variation in the required mass of product that needs to be added. If too much PAX is added it is wasted and leads to an increase in operation costs, but if not enough is added metal product will be lost to tailings ponds. This has quickly become a major concern among industry professionals.

The use of xanthates in metal recovery was first proposed by Cornelius H. Keller in 1925, and has remained a core component of the milling process to this day. [4] The mechanism of reaction occurs when the two polar sulfur "heads" of the xanthate molecule attach to the ore particles in a bidentate chelating manor, and the non-polar hydrocarbon "tail" forms a hydrophobic layer. This forms a pocket that can then be carried to the surface by air bubbles with the ore remaining trapped inside. [3,4,7] Upon reaching the surface, the froth is collected and the ore is extracted to be added to the rest of the final product.

Preliminary literature research has shown that xanthates have mainly been studied regarding their aqueous degradation products. Extensive research has been done on identification of these degradation products, as well as their removal from water systems. [2,5,9,10] Xanthates and their by-products tend to bioaccumulate in bodies of water, demonstrating very toxic affects to the central nervous system, liver, and spleen in biological systems at relatively low concentrations. [9] Therefore, much focus has been put on identification and removal of these compounds from tailings ponds being used by mines. Although industry professionals have complaints of the uncertainty within each order of xanthates, little to no research appears to have been previously done on developing a method to reliably identify their composition.

Experimental

Instrumentation

A Beckman P/ACE capillary electrophoresis (Figure 2.) instrument was used, utilizing an ultraviolet (UV) detector. Direct detection was employed, and after trying multiple wavelengths of light it was optimized at 254 nm. Due to instrument failure, a different detector was used for sample analysis that did not have a 254 nm lamp, so 214 nm was used instead with comparable results. The capillary used was a 50 μm diameter uncoated, fused-silica capillary, and temperature was kept at 25^{o} C (± 0.1^{o} C) by having a constant flow of liquid fluorocarbon coolant through the capillary cartridge during analysis.

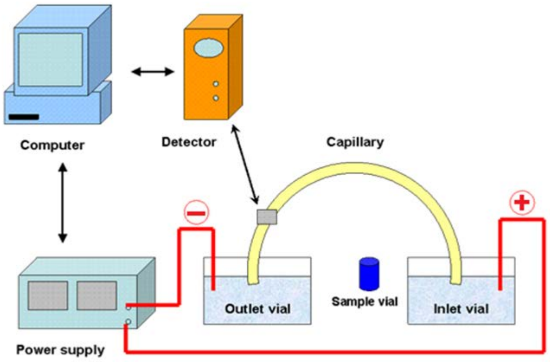


Figure 2. General schematic of Capillary Electrophoresis (CE) Instrumentation

Xanthate samples were injected by pressure (1.0 psi) for 5 seconds before analysis. Using normal polarity, an applied voltage of 20 kV was found to produce the quickest and most clearly separated electropherograms. Trials were done with buffer pH's ranging from 7 – 11, and a pH meter was used to adjust the buffer pH to the optimized 9.1 (± 0.1).

Every time a new capillary was prepared, it was first conditioned by flushing with 1.0 M NaOH for 60 minutes, 0.1 M NaOH for 30 minutes, 18 MΩ water for 10 minutes, and finally buffer solution for 30 minutes. Prior to each individual run the capillary was flushed with 1.0 M

NaOH for eight minutes, 0.1 M NaOH for four minutes, 18 MΩ water for four minutes, and borate buffer for five minutes.

Materials and Reagents

All xanthate samples and standards were obtained from the New Afton Gold Mine in an aqueous medium and stored at 4^{o} C in a dark fridge. Sodium tetraborate decahydrate was used for the buffer preparation, and was obtained from Sigma Aldrich. All reagents were of analytical grade and used without any additional purification. Deionized 18 MΩ water was used to prepare and dilute all standard and buffer solutions, which were filtered through a 0.45 µm Nylon filter and stored in dark plastic bottles in the fridge.

Sample Preparation

Sodium borate decahydrate was analytically weighed out to make a 60 mM buffer solution. The pH of the buffer was then adjusted by adding 1.0 M NaOH dropwise until it reached the desired 9.1 pH. After pH modification was complete, the solution was added to a 100 mL volumetric flask and diluted to volume. The buffer was filtered and stored in a dark cupboard prior to use.

All standards were received in an aqueous medium at approximately 20,000 ppm concentration. These standards were used to prepare 5,000 ppm stock solutions of each standard, which were then filtered through 0.45 µm nylon filters and used to prepare calibration curves for quantification.

Batch samples of unknown composition were analyzed and their compositions were reported as percent mass of each xanthate, as well as the percent of sample remaining as unknown or degradation compounds.

Solid-Phase Extraction (SPE)

Two different polymeric solid phase columns were explored to remove positively interfering compounds. A Strata-X column selective for neutral compounds was found to remove interfering compounds without significant loss of analyte. A Strata-X-C column selective for ion-exchange was also tested, but results suggested that some xanthate compounds were lost during extraction

Each column was conditioned with 4 mL 18 MΩ water and 4 mL acetone prior to extraction. Extraction was performed under gentle vacuum on 10 mL aqueous samples, and the filtrates were collected for analysis. Once completely dry, elution was performed by gravity using 10 mL of acetone and the eluent was collected for analysis. All solid phases were discarded after elution.

Results and Discussion

Summary of Utilized Conditions

Table 1. CE analysis conditions

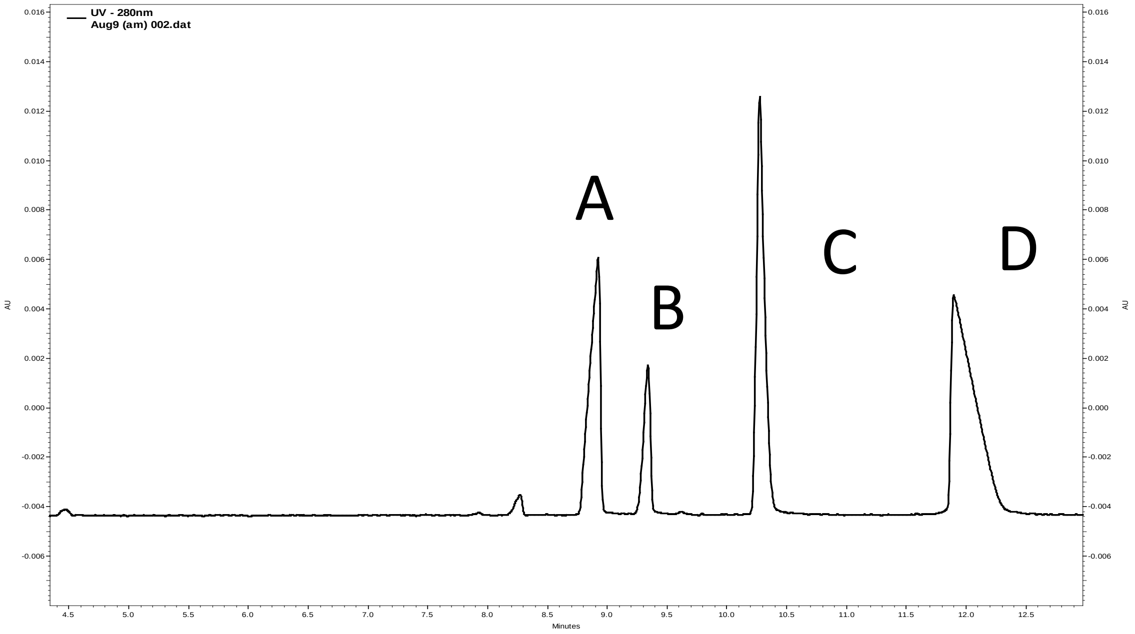
UV Detector Absorbance	214 nm
Capillary Inner Diameter	50 µm
Borate Buffer Concentration	60 mM
Borate Buffer pH	9.1
Temperature	25° C
Voltage	20 kV
Limit of Quantification (LOQ)	10 ppm
Analysis Time	12 minutes

Table 1 outlines the experimental and instrumental conditions that were optimized and implemented for analysis of both known standards and batch samples. All conditions were validated and optimized prior to batch sample analysis, and provided highly reproducible results.

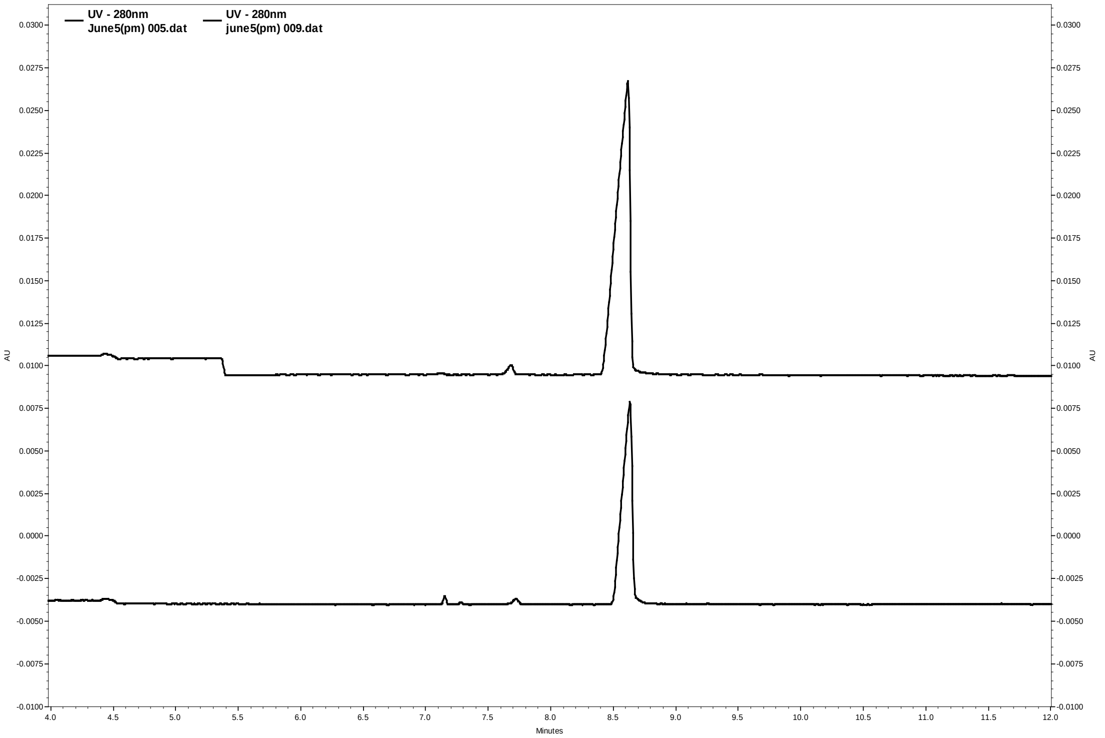
Table 2. Approximate migration times of each xanthate

Xanthate	**~ Migration Time (min)**
PAX/SAX	8.2
PIBX/SIBX	9.1
PIPX/SIPX	9.6
PEX/SEX	10.9

Separation of Four Xanthate Hydrocarbon Variations

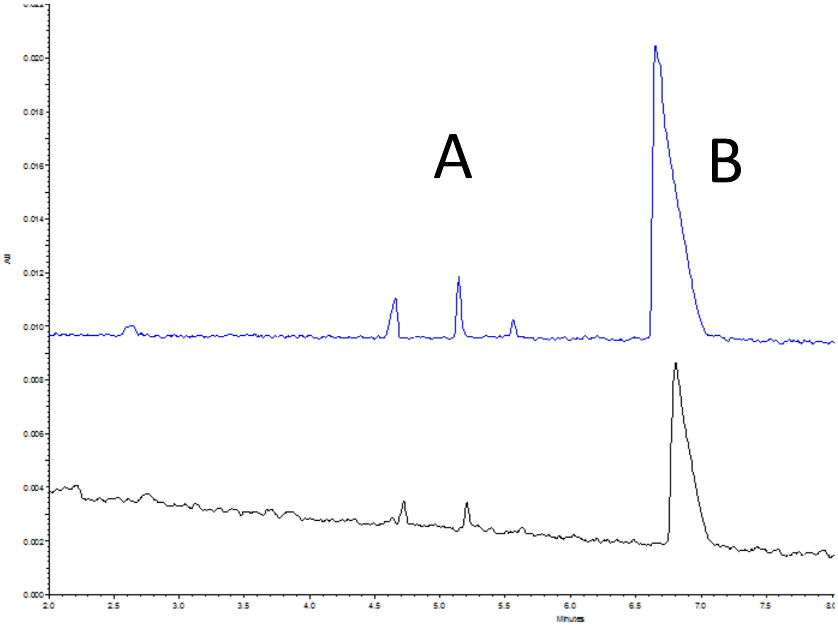


Electropherogram 1: Separation of 500 ppm PAX (A), PIBX (B), PIPX (C), and PEX (D) standards

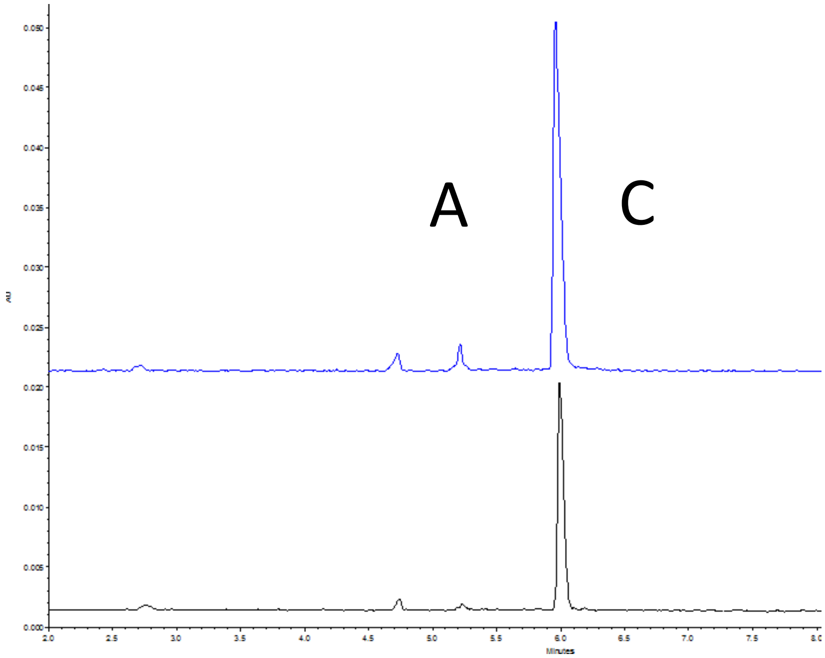


Electropherogram 2: PAX peak isolated at 500 ppm (bottom) and 1000 ppm (top)

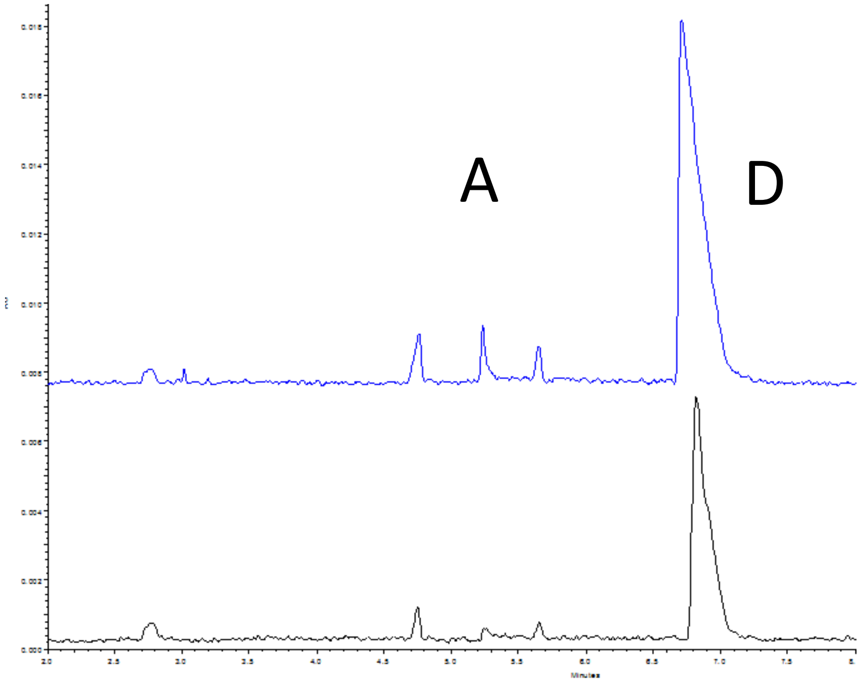
Pairings Results



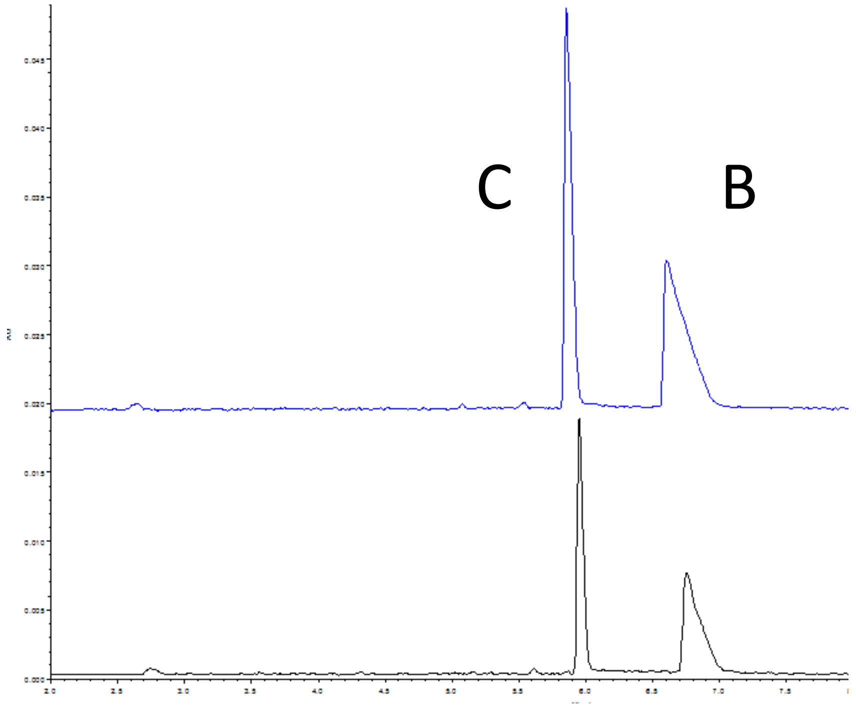
Electropherogram 3: Pairing of PAX (A) and PEX (B) at 500 ppm and 1000 ppm



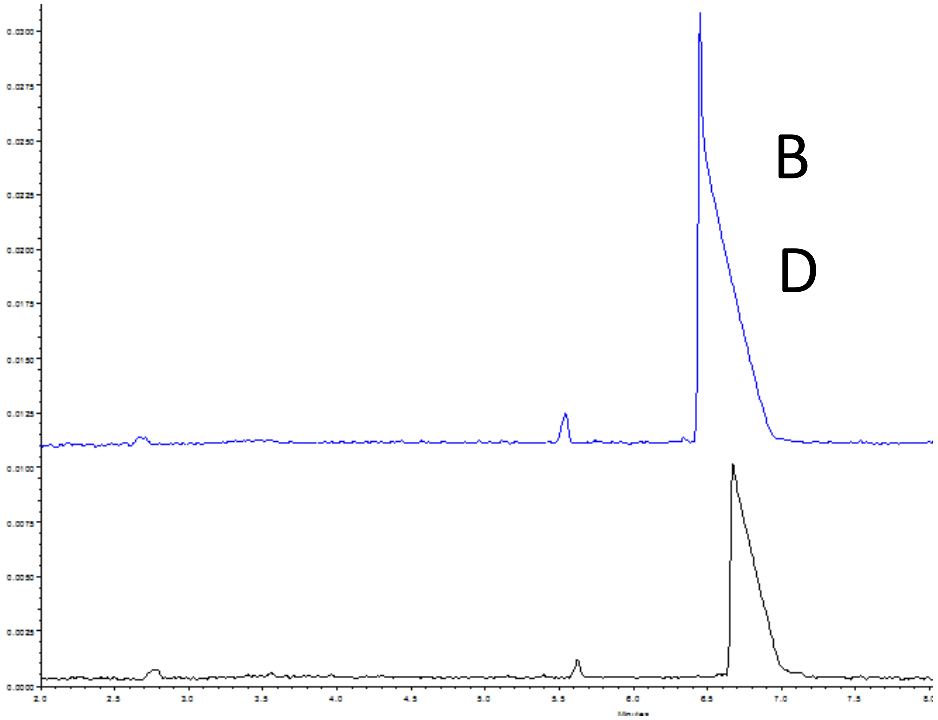
Electropherogram 4: Pairing of PAX (A) and PIPX (C) at 500 ppm and 1000 ppm



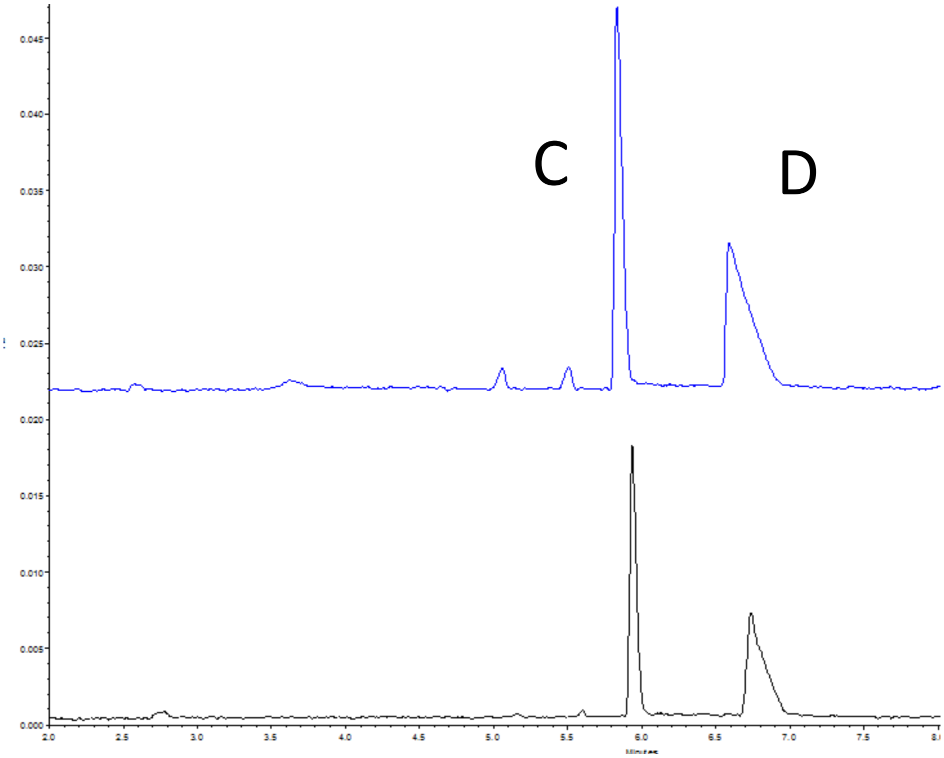
Electropherogram 5: Pairing of PAX (A) and SEX (D) at 500 ppm and 1000 ppm



Electropherogram 6: Pairing of PIPX (C) and PEX (B) at 500 ppm and 1000 ppm



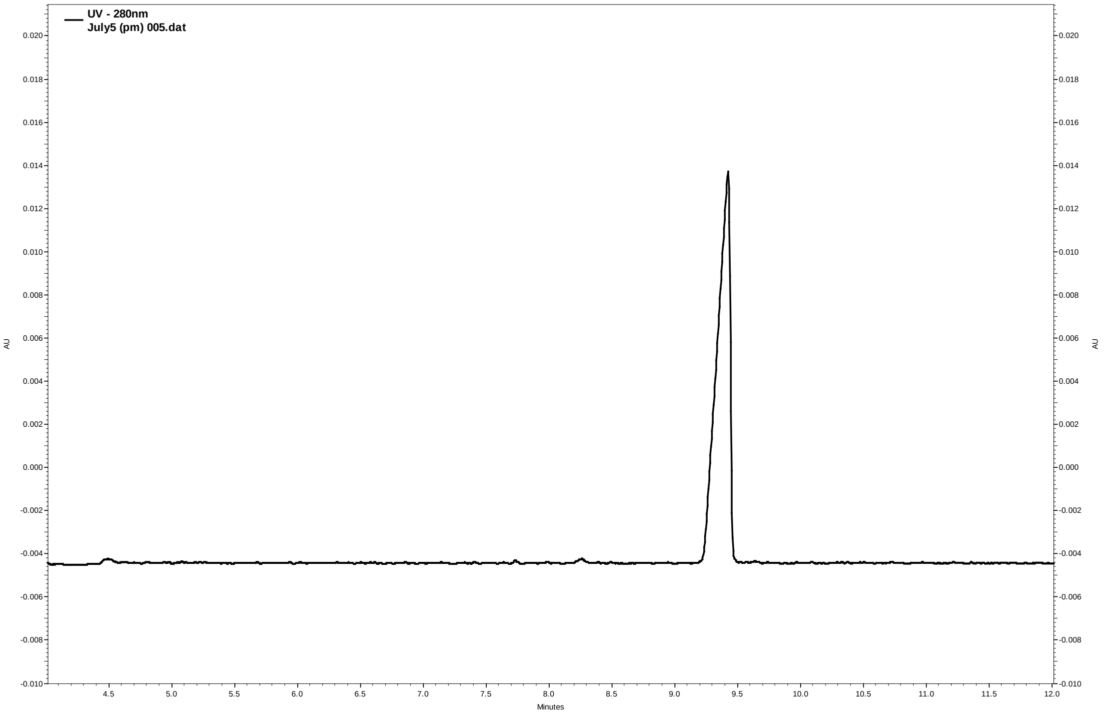
Electropherogram 7: Pairing of PEX (B) and SEX (D) at 500ppm and 1000 ppm



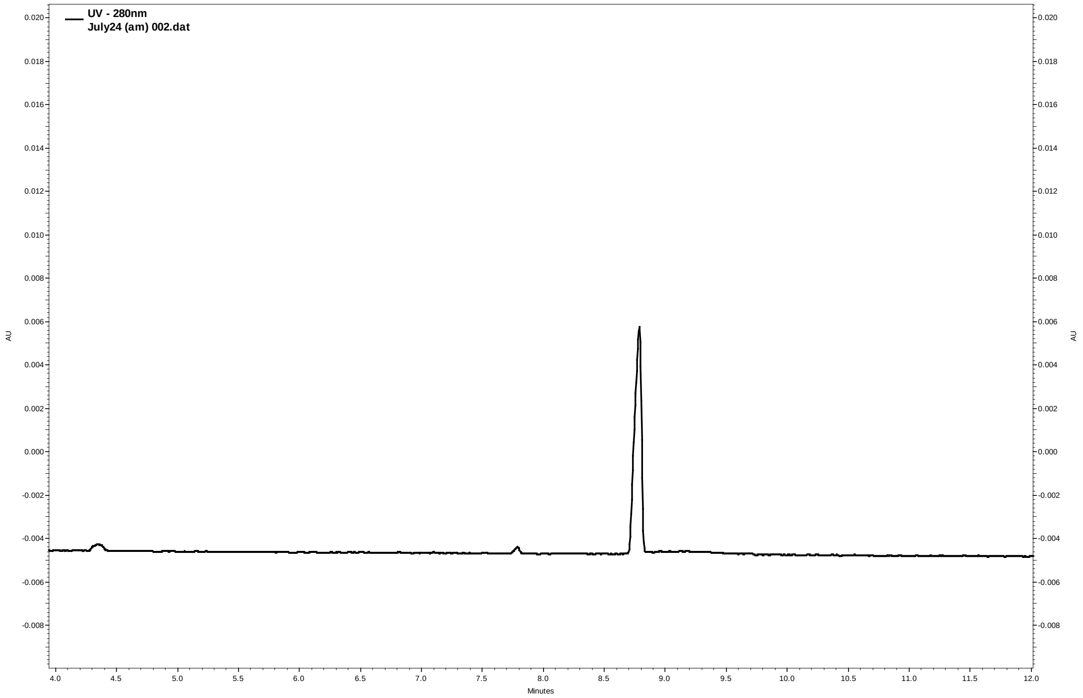
Electropherogram 8: Pairing of PIPX (C) and SEX (D) at 500 ppm and 1000 ppm

Electropherograms 3 through 8 show the results of pairing each individual xanthate with the others. This was done to validate that no interactions were occurring during analysis, as well as identify any possible overlapping peaks. Since all xanthates placed in the CE buffer will be ionized, only the anionic portion of the molecules will be separated. Electropherogram 7 demonstrates this problem, showing that when the xanthates vary by only the cationic metal portion (Sodium versus Potassium) the peaks will overlap, preventing their separation. Because of this instrumental limitation, all xanthate compositions had to be reported as a possibility of either sodium xanthates or potassium xanthates (ie. 80% PAX or SAX). It is also worth noting that at the time of xanthate pairing studies, the PAX and PIPX standards had undergone degradation, PAX more extensively. This is why the PAX peak appears as three separate small peaks, and the main PIPX peak is accompanied by two small peaks with shorter migration times.

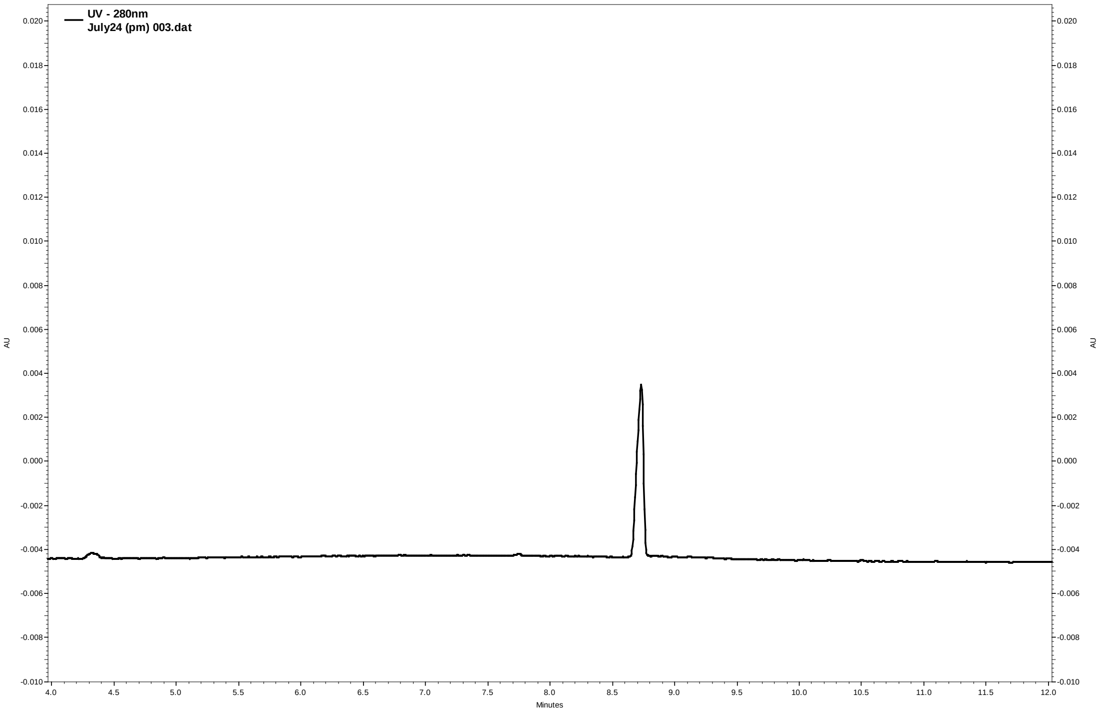
SPE Results



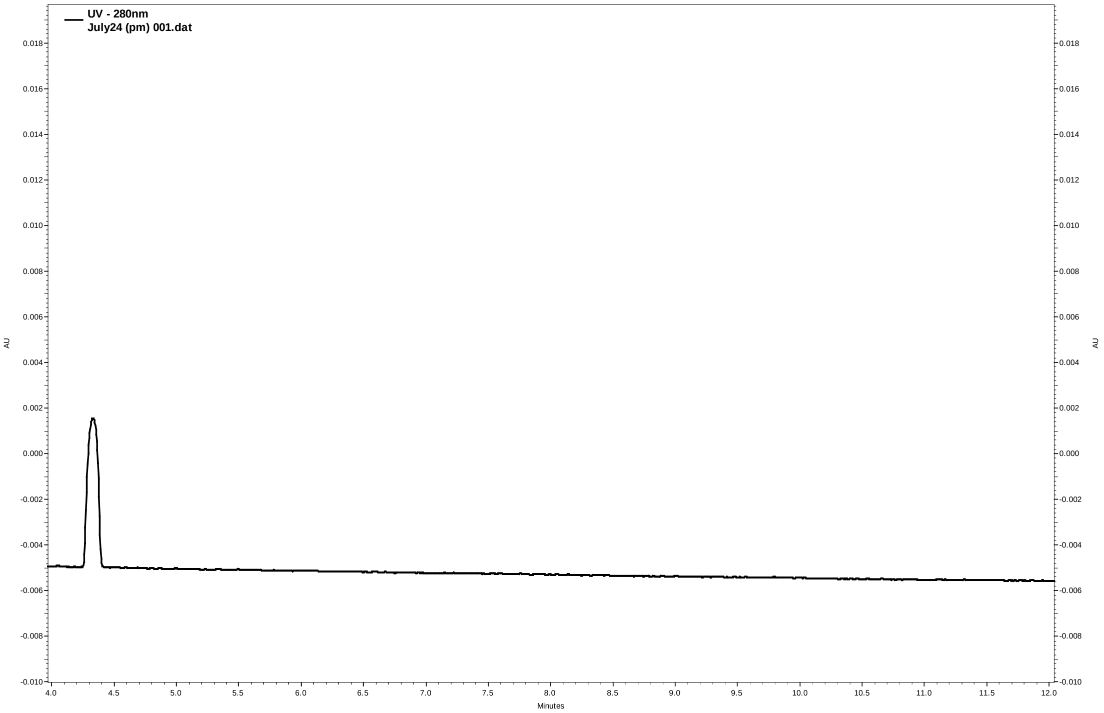
Electropherogram 9: Quadra PIBX (no SPE)



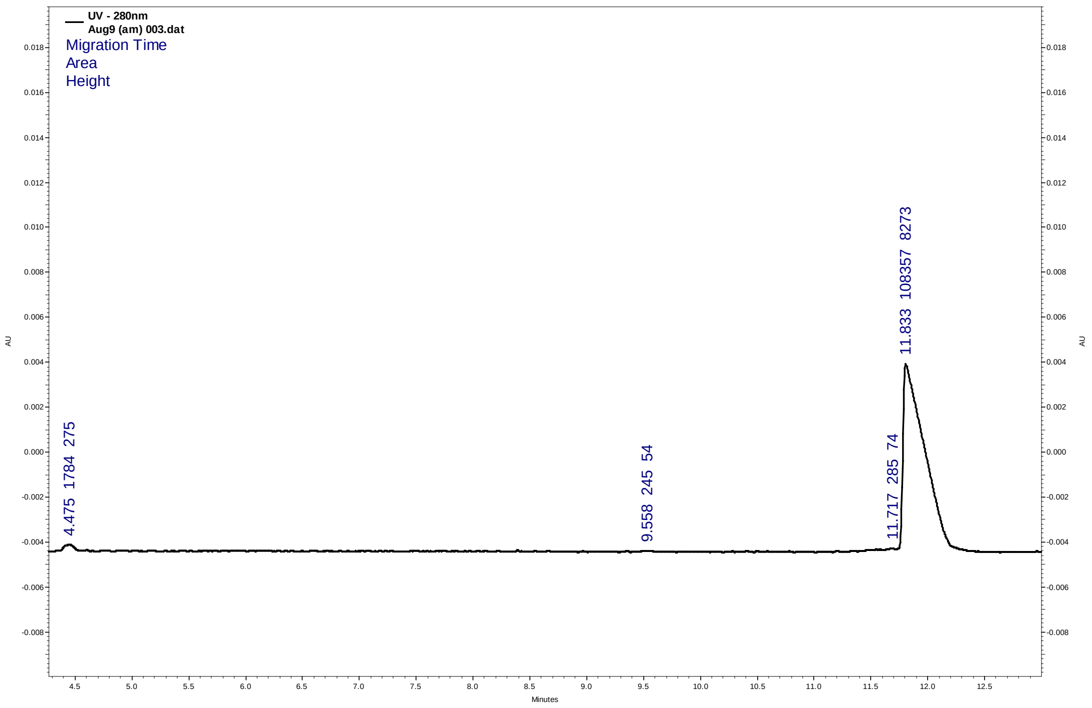
Electropherogram 10: Quadra PIBX (Strata-X Filtrate)



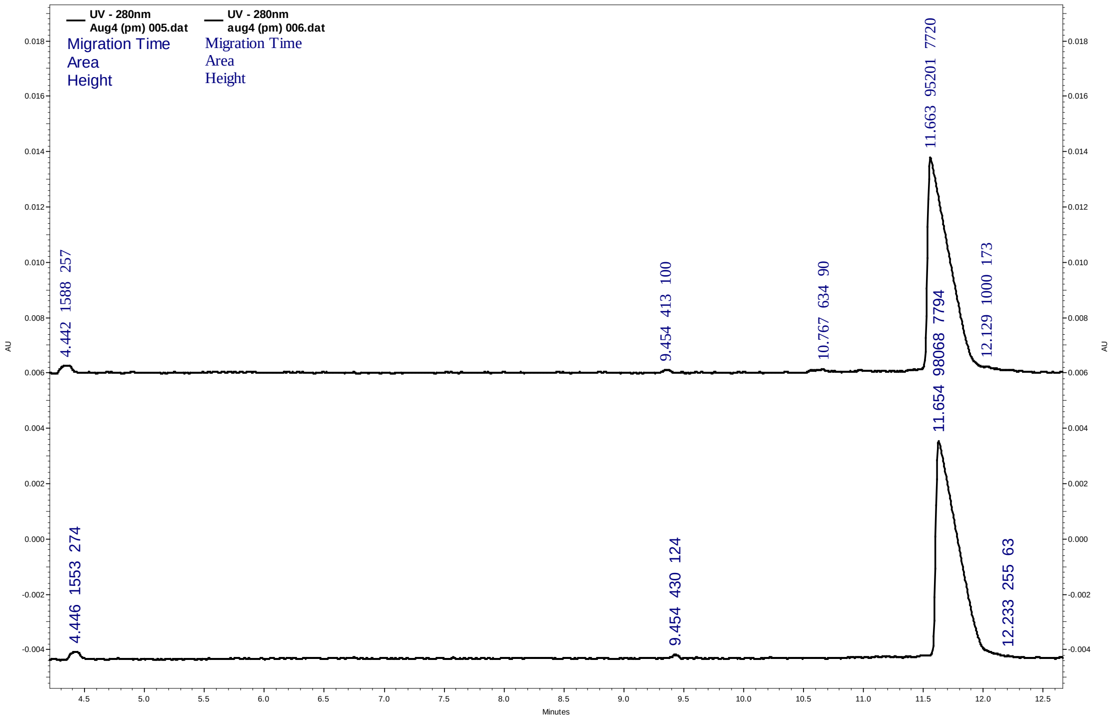
Electropherogram 11: Quadra PIBX (Strata-X-C Filtrate)



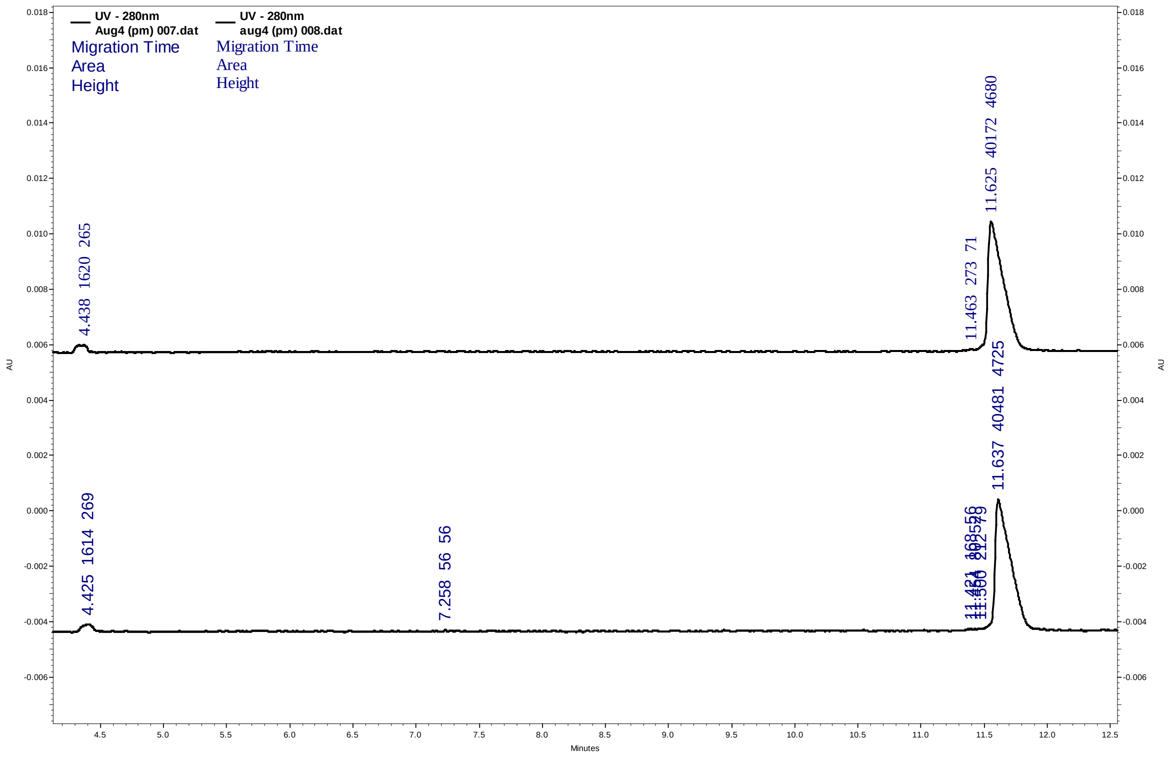
Electropherogram 12: Quadra PIBX (Strata-X Elution)



Electropherogram 13: Alfa Aesar PEX Standard (no SPE)



Electropherogram 14: Alfa Aesar PEX Standard (Strata-X Filtrate)



Electropherogram 15: Alfa Aesar PEX Standard (Strata-X-C Filtrate)

Electropherograms 9 through 12 show the success of SPE in removing positively interfering compounds. Before SPE, the peak is broad with an apparent overlapping peak on the shoulder. After SPE was performed, the peak became a narrow band with no shouldering at all. This lead to a decrease in peak area, indicating a removal of contaminants. The acetone elution was analyzed to validate that no xanthate molecules were retained in the solid phase, which are highly soluble in acetone and would be eluted if present. A clear peak at 4.3 minutes belongs to the acetone solvent itself, and the complete absence of the PIBX peak at 8.8 minutes shows that no xanthates were retained and the positively interfering molecules were removed.

Electropherograms 13 through 15 demonstrate that minimal xanthate loss occurs through SPE with the Strata-X solid phase, and that the Strata-X-C solid phase removes a substantial amount of the analyte. Only 2.34% of the PEX standard was lost during extraction, so it was deemed successful and will be utilized going forward.

Batch-Sample Analysis

Table 3. Xanthate characterization data of batch-samples

Manufacturer	Reported Xanthate	PAX/SAX (%)	PEX/SEX (%)	PIPX/SIPX (%)	PIBX/SIBX (%)	Degredation/Unknown (%)
Qixia	PAX	10.63	0.00	0.00	15.54	73.83
old 2012	PAX	29.95	37.67	0.00	0.00	32.37
Quadra	PAX	86.79	0.00	0.00	17.31	trace
Quadra	PEX	0.00	99.81	0.00	0.00	0.19
Quadra	SEX	0.00	115.69	0.00	trace	trace
Quadra	SAX	63.03	0.00	0.00	trace	36.97
Quadra*	SIBX	0.00	trace	0.00	112.48	trace
Quadra*	SIPX	0.00	11.09	124.04	0.00	trace
Quadra*	PIBX	0.00	0.00	0.00	112.53	trace
Flowmin C3535	PAX	97.31	0.00	0.00	0.00	2.69
G&T*	SIBX	0.00	0.00	0.00	115.16	trace
G&T	SEX	0.00	84.77	0.00	trace	15.23
G&T	PAX	21.13	trace	trace	21.12	trace
G&T*	PIPX	0.00	0.00	7.78	125.51	trace
Flottec	PAX	78.89	0.00	trace	0.00	11.11
Prospec Chem KAX-51	PAX	51.64	17.60	0	27.81	2.95

* - Reported xanthate composition over 100%, suggesting positive interference. These batches were chosen for SPE

Table 4. Results of batch-sample analysis for main xanthate before and after SPE

Sample	Before SPE (%)	Strata-X (%)	Strata-X-C (%)
Alfa Aesar PEX (standard)	100.00	97.66	45.16
Quadra SIBX	112.48	102.40	20.33
Quadra SIPX	124.04	93.70	64.71
Quadra PIBX	112.53	65.27	53.59
G&T SIBX	115.16	83.79	54.82
G&T PIPX	125.51	58.57	32.49

Table 3 shows the collection of data acquired for batch-samples acquired from the New Gold mine for analysis. It is reported in percent-mass of each xanthate, which was then compared to the composition claimed by the manufacturer. After compiling results, it was noticed that some specific samples reported a xanthate composition over 100%. This indicated the presence of positive interference and those samples were chosen for SPE experimentation. The results before SPE and after each of the implemented solid-phases are reported in Table 4.

Conclusions

A novel method was developed for determination of xanthate composition of purchased floatation agents used in the mining industry by capillary zone electrophoresis (CZE). Capillary electrophoresis offers high resolving power, while also requiring very small sample volumes and short analysis times. The method was optimized by running the same standards through varying buffer or instrument conditions, and was validated by analyzing mixtures of all four hydrocarbon variations of xanthates and efficiently separating them. Ambiguously labelled packages of xanthate floatation agents were successfully characterized, and a method for purification by solid-phase extraction (SPE) was explored for the removal of positively interfering compounds.

Future Work

Moving forward, more bulk samples will be characterized as they are purchased by the New Afton Gold Mine. Different concentrating methods will be examined to lower the LOQ, allowing for analysis of tailings pond water samples. A mass spectrometry (MS) detector will be utilized in order to identify all degradation products and positively interfering compounds. A solid phase column specific for anionic exchange will be used to improve SPE selectivity and minimize analyte loss. Finally, a comprehensive summary of all available batch sample data will be compared to analysis done by New Afton using different instrumentation to further validate the developed method.

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