Spectroscopic Characterization of Ethyl Xanthate Oxidation Products and Analysis by Ion Interaction Chromatography

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An ion interaction chromatographic separation method, coupled with UV spectroscopic detection, has been developed for the analysis of ethyl xanthate (O-ethyl dithiocarbonate) and its oxidative decomposition products in mineral flotation systems. The effects of the ion-pairing agent (tetrabutylammonium ion), pH modifier (phosphoric acid), and organic modifier (acetonitrile) in the eluant upon the retention characteristics of the ethyl xanthate oxidation products have been determined. The optimized separation procedure has been successfully applied to the analysis of ethyl xanthate and its oxidation products in a nickel-iron sulfide mineral suspension containing a number of other anionic species, including cyanide complexes of nickel and iron, as well as sulfur-oxy anions. The ethyl xanthate oxidation products investigated in this study have been isolated as pure compounds and characterized by UV-visible, FT-IR, and NMR spectroscopies. The UV-visible and FT-IR spectroscopic properties of these species are discussed in terms of the chemical modifications of the thiocarbonate group.

Froth flotation is extensively used in the processing of mineral ore deposits as a method of enriching the concentrations of valuable minerals. Using this technique, very low grade ores, containing as little as 1% of the desired mineral component, can be processed economically. Central to the success of mineral flotation is the selective surface adsorption of collector (surfactant) molecules which convert mineral surfaces from hydrophilic to hydrophobic character. The hydrophobic mineral particles accumulate at the air–water interface of dispersed air bubbles which, in turn, form a froth layer from where the valuable mineral is collected. The measurement of collector concentrations in the aqueous phase of flotation pulps is important in both laboratory research and the industrial application of flotation, in determining the effect of differing treatment strategies upon collector adsorption.

Xanthates (*O*-alkyl dithiocarbonates, **I** (Scheme 1)) are widely used as collectors in the processing of sulfide minerals. The interaction of xanthates with sulfide mineral suspensions leads to a number of surface-mediated electron-transfer processes, all

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of which involve oxygen. One of these processes leads to the formation of bis[alkoxy(thiocarbonyl)] disulfide (V), which has been suggested to be the hydrophobic entity responsible for flotation.1 Other processes lead to the oxidative decomposition of the xanthate molecule. A number of metastable oxidation products are known, including (Scheme 1) O-alkyl S-peroxido dithiocarbonate (III),^{2,3} *O*-alkyl thiocarbonate (III),^{4,5} and *O*-alkyl S-thiosulfonato dithiocarbonate (IV).⁶ The importance of xanthate oxidation products in mineral flotation systems and in the subsequent environmental fate of xanthates in mineral tailings is largely unknown due to the lack of suitable analytical techniques. The work presented in this paper was carried out as a first step toward rectifying this situation. Xanthate oxidation products are generally known by trivial names. These names are listed in Table 1, along with the acronym abbreviations that have been used in this paper, for the ethyl xanthate series of oxidation products.

The usual method by which xanthates are measured in solution is direct spectroscopic detection in the UV region.⁷ More recently, HPLC-based methods have been reported for the analysis of mixtures of different alkyl xanthates,^{8–10} as well as the separation

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Table 1. IUPAC Names, Trivial Names, Chemical Compositions, and Abbreviations for Ethyl Xanthate and Associated Oxidation Products

IUPAC name	trivial name	chem comp (neutral salt)	abbrevs used in this work ^a	no. in decomp Scheme 1
O-ethyl dithiocarbonate	ethyl xanthate	$C_2H_5OCS_2^-$ (K+•C_2H_5OCS_2^-)	EX ⁻ (KEX)	Ι
<i>O</i> -ethyl <i>S</i> -peroxido dithiocarbonate (or <i>O</i> -ethyl carbonothio(thioperoxoate))	ethyl perxanthate	$C_2H_5OCS_2O^-$ (NH ₄ +·C ₂ H ₅ OCS ₂ O ⁻)	EPX ⁻ (NH ₄ +•EPX ⁻)	II
O-ethyl thiocarbonate	ethyl (mono)thiocarbonate	$C_2H_5OCOS^-$ (K ⁺ ·C ₂ H ₅ OCOS ⁻)	ETC ⁻ (KETC)	III
<i>O</i> -alkyl <i>S</i> -thiosulfonato dithiocarbonate (or ethoxythioxomethyl sulfo disulfide)	ethyl xanthyl thiosulfate	$C_2H_5OCS_2 \cdot S_2O_3^-$ (TBA+ $\cdot C_2H_5OCS_2 \cdot S_2O_3^-$)	EXT ⁻ (TBA ⁺ •EXT ⁻)	IV
bis[ethoxy(thiocarbonyl)] disulfide (or <i>O</i> , <i>O</i> -diethyl dithiobis(thioformate))	diethyl dixanthogen	$(C_2H_5OCS_2)_2$	(EX) ₂	v
^a Abbreviation of neutral salts prepared in	n this study given in parenthese	s. TBA ⁺ = tetrabutylammoniu	m.	

of EX⁻ from dithiocarbamates.¹¹ The measurement of xanthate oxidation products has been attempted using a spectral deconvolution procedure,¹² which in principle should provide reliable results due to the distinctive UV spectra of these species. In practice, the aqueous phase of a sulfide flotation pulp is particularly complex and analysis in this way is unreliable. To our knowledge, there has been only one previous report of an HPLC-based procedure for the analysis of an alkyl xanthate and its associated oxidative decomposition products.¹³ In this previous study, the reaction products of the EX- and hydrogen peroxide were analyzed using an anion chromatographic procedure. While the separation and analysis of EX⁻ and EPX⁻ was achieved using this method, the identification of ETC- was ambiguous and the determination of EXT⁻ not considered at all. It appears that there is no general analytical procedure, HPLC based or otherwise, that allows accurate quantitative determination of ethyl xanthate oxidation products in complex mixtures.

In this paper, we describe an anion interaction chromatographic method coupled with UV spectroscopic detection which allows the determination of solution concentrations of EX⁻ and the oxidation products EPX⁻, ETC⁻, and EXT⁻, which for convenience we have termed the "ethyl xanthate decomposition species". In sulfide flotation systems, significant oxidation of the sulfide mineral surface occurs, releasing sulfur–oxy anions into solution. Thiosulfate is of particular importance with regard to UV-based detection methods due to its absorbance at wavelengths shorter than 230 nm. The behavior of thiosulfate in the anion interaction chromatography method developed is also described in this paper. The application for which this method was originally developed was for the flotation of a fine-grained nickel–iron sulfide ore. As part of the standard metallurgical procedure for the flotation of this particular ore, cyanide in the form of NaCN was

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added. The formation of metal cyanide species can occur in this system as a result of the reaction of free cyanide with sulfide mineral surfaces, with the possible metal cyanide species being $[Ni(CN)_4]^{2-}$, $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$. The separation of metal cyanide complexes by anion interaction chromatography has been extensively studied,^{14–16} and it is not our intention to repeat this work here. We do however discuss the general chromatographic behavior of the metal cyanide complexes of iron and nickel under the optimized chromatographic conditions developed for the separation and analysis of the ethyl xanthate decomposition species.

During the course of this work, we have recorded new FT-IR and UV spectroscopic data for EPX⁻ and EXT⁻, which are also presented here, in the belief that these data will be useful in surface spectroscopic studies of xanthate adsorption at sulfide mineral surfaces.

EXPERIMENTAL SECTION

Materials. All chemicals were analytical grade and used without any further purification. All solutions were prepared using Milli-Q water (18 M Ω). The preparation of potassium ethyl xanthate and the intermediate oxidation products of ethyl xanthate are described in the following sections.

Potassium Ethyl Xanthate (KEX). KEX was prepared following the method described by Foster.¹⁷ A potassium ethoxide solution was prepared by dissolving 13 g of pulverized potassium hydroxide in 100 g of ethanol. An 18-g sample of redistilled carbon disulfide was added slowly with continuous stirring of the ethoxide solution. The yellow KEX product was chilled at 5 °C, filtered, and recrystallized twice from warm ethanol. The purity of the product was determined by chemical microanalysis (Calcd for C₃H₅OS₂K: C, 22.48; H, 3.15; O, 9.98; S, 40.01; K, 24.39. Found: C, 22.57; H, 3.04; S, 39.91; K, 25.45.). ¹H and ¹³C NMR analysis: $\delta_{\rm H}$ (D₂O, 250 MHz) 1.35 (3H), 4.45 (2H); $\delta_{\rm C}$ (D₂O, 62.9 MHz) 16.3 (*C*H₃), 72.9 (*C*H₂), 235.4 (*C*(=S)S⁻). Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) yielded a

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Figure 1. FT-IR spectra of potassium *O*-ethyl dithiocarbonate (KEX), ammonium *O*-ethyl *S*-peroxido dithiocarbonate (NH₄⁺·EPX⁻), potassium *O*-ethyl thiocarbonate (KETC), tetrabutylammonium *O*-ethyl *S*-thiosulfonato dithiocarbonate (TBA⁺·EXT⁻), and bis[alkoxy(thiocarbonyl)] ((EX)₂). The solid bar shows the position of the $-CS_2$ -asymmetric stretch and the dashed bar shows the position of the -C-O-C- asymmetric stretch.

negative ion parent peak at m/e 121.1 which compares well with the calculated value of m/e 121 for the isotopically dominant ion. The KEX product was further characterized by FT-IR (Figure 1) and UV-visible (Figure 2) spectroscopies.

Ammonium Ethyl Perxanthate (NH₄+·EPX⁻). NH₄+·EPX⁻ was prepared from KEX by a method similar to that described by Jones and Woodcock³ for the preparation of a longer chain (*sec*-butyl) perxanthate. A 0.5-g sample of KEX and 0.5 g of sodium carbonate were dissolved in 50 cm³ of water. A H₂O₂ solution (3.5 cm³ of 1 mol dm⁻³) was then added. After 20 min, the pH of the solution was lowered (with HNO₃) to between 1.5 and 1.75 and maintained in this range for 30 min to destroy any remaining



Figure 2. UV-visible spectra of the xanthate decomposition species. Solid lines show the spectra of *O*-ethyl dithiocarbonate (EX⁻), *O*-ethyl *S*-peroxido dithiocarbonate (EPX⁻), *O*-ethyl thiocarbonate (ETC⁻), and *O*-ethyl *S*-thiosulfonato dithiocarbonate (EXT⁻). All spectra relate to the scales shown on the left-hand side except for the expanded low-energy peaks shown for EX⁻ and EXT⁻, which relate to the scales shown on the right-hand side. Also shown is the spectrum of protonated *O*-ethyl S-peroxido dithiocarbonate (H⁺•EPX⁻) (dashed line). All spectra were recorded in aqueous solution at 8 < pH < 11 and at 25 °C.

EX⁻.18 The protonated EPX⁻ (H⁺·EPX⁻) was extracted into 50 cm³ of petroleum spirits (100-120 °C); the solvent was dried with Na₂-SO₄ and filtered. Ammonia gas was passed through the filtered solvent, precipitating NH₄⁺·EPX⁻, which was filtered off and dried. The solid product was purified by dissolving it in 30 cm³ of water, lowering the pH to \sim 2 for 30 min, and reextracting the H⁺·EPX⁻ into 50 cm³ of chloroform. The H⁺·EPX⁻ was again converted to NH₄⁺·EPX⁻ by passing ammonia gas through the chloroform solution and the solid product collected by filtration. Despite this purification procedure, aqueous solutions prepared from the NH_4^+ ·EPX⁻ salt were always found to contain trace levels (<1%) of EX⁻, as determined by the ion interaction chromatographic method developed in this study. The purity of the product was determined by chemical microanalysis (Calcd for C3H9O2NS2: C, 23.21; H, 5.84; O, 20.6; N, 9.02; S, 41.30. Found: C, 23.36; H, 6.02; N, 8.88; S, 41.61.). ¹H and ¹³C NMR analysis: $\delta_{\rm H}$ (D₂O, 250 MHz) 1.39 (3H), 4.69 (2H); δ_C (D₂O, 62.9 MHz) 16.4 (CH₃), 71.1 (CH₂), 227.7 ($C(=S)SO^{-}$). APCI-MS examination of the NH₄+·EPX⁻ product yielded a negative ion parent peak at m/e 137.0 which is equal to the value calculated for the dominant ion. The FT-IR

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spectrum of NH_4^+ ·EPX⁻ and the UV-visible spectrum of EPX⁻ are shown in Figures 1 and 2, respectively.

Potassium Ethyl (Mono)thiocarbonate (KETC). KETC was prepared by the reaction of carbonyl sulfide gas with a potassium ethoxide solution.^{17,19} Carbonyl sulfide gas was generated by reacting ammonium thiocyanate with sulfuric acid. Ammonium thiocyanate, 12 g in 20 cm3 of water, was added to 150 cm3 of 40% (v/v) sulfuric acid solution. Liberation of the COS gas was facilitated by heating the solution to between 40 and 50 °C and using high-purity nitrogen as a carrier gas. HCN impurities were removed by passing the COS gas through two solutions of 1 mol dm⁻³ potassium hydroxide. The COS gas was then passed into a potassium ethoxide solution prepared by dissolving 7.8 g of pulverized potassium hydroxide in 160 cm3 of ethanol. At the completion of the reaction, the white KETC product was chilled at 5 °C and filtered. The crude KETC product was recrystallized twice from warm ethanol. Product purity was determined by chemical microanalysis (Calcd for C₃H₅O₂SK: C, 24.98; H, 3.49; O, 22.18; S, 22.23; K, 27.10. Found: C, 24.68; H, 3.38; S, 22.25; K, 28.6.). ¹H and ¹³C NMR analysis: $\delta_{\rm H}$ (D₂O, 250 MHz) 1.25 (3H), 4.1 (2H); δ_C (D₂O, 62.9 MHz) 16.4 (CH₃), 65.4 (CH₂), 188.1 $(C = O)S^{-}$). APCI-MS examination of the KETC product yielded negative ion parent peak at m/e 105.2, compared to the expected value of *m*/*e*.105. The FT-IR spectrum of KETC is shown in Figure 1, and the UV-visible spectra of the ETC- anion is shown in Figure 2.

Tetrabutylammonium Ethyl Xanthyl Thiosulfate (TBA+· **EXT**⁻). TBA⁺·EXT⁻ was prepared using a method adapted from Jones and Woodcock.⁶ A 1.2-g sample of KEX and 1.92 g of sodium thiosulfate pentahydrate were dissolved in 20 cm³ of water. Iodine, 2.08 g dissolved in 25 g of ethanol, was added to the ethyl xanthate/thiosulfate mixture until a slight excess of iodine was observed. As reported by Jones and Woodcock,⁶ the reaction products include EXT⁻, (EX)₂, and tetrathionate $(S_4O_6^{2-})$, as well as excess iodine. The (EX)₂ and iodine were removed by washing three times with 30 cm³ of chloroform and three times with 30 cm³ of diethyl ether. The EXT⁻ remaining in the aqueous phase was then precipitated as a partially water insoluble material by the addition of tetrabutylammonium bromide (TBA⁺·Br⁻). The quantity of TBA+ required was determined by measurement of the solution concentration of EXT⁻, using the extinction coefficient of the 289-nm absorption band determined in this work (see Figure 2 and Table 3). The TBA+•EXT- was extracted with two portions of 60 cm³ of diethyl ether, with the $S_4O_6^{2-}$ remaining in the aqueous phase. The two diethyl ether extracts were combined and washed with 25 cm3 of 0.1 mol dm-3 potassium iodide in order to convert any remaining iodine into I_3^- , which would be transferred to the aqueous phase. The diethyl ether fraction was dried with Na₂SO₄ and evaporated, yielding a crude TBA⁺•EXT⁻ oil-like product. The crude TBA+•EXT- was dissolved in 5-10 cm³ of ethanol and added dropwise to 50 cm³ of rapidly stirred water. The redispersed TBA+·EXT- was extracted into 30 cm3 of chloroform; the chloroform phase was dried (Na₂SO₄) and evaporated to yield a more pure TBA+•EXT- oily product. Aqueous solutions of the sparingly soluable TBA+•EXT- product were shown by ion interaction chromatography to be free of UV-visibleabsorbing impurities, in particular, iodine, $S_4O_6^{2-}$, and $(EX)_2$. The

Table 2. Schedule of Events for the Optimized Chromatographic Method^a

time (min)	E1 (%)	E2 (%)	E3 (%)	E4 (%)	function
0.0	0	50	20	30	column equilibration
0.1	0	50	20	30	injection
1.0	2	50	20	28	addition of NaOH
3.9	2	50	20	28	start acetonitrile gradient
4.0	0	50	20	30	stop NaOH addition
6.5	0	50	50	0	complete acetonitrile gradient
12.9	0	50	50	0	end isocratic run
13.0	0	50	20	30	stop chromatogram
^a E1,	100 mr	nol dm	ı−3 Na(DH; E2	, 10 mmol dm ⁻³ TBA+•OH [−] , 10

^a E1, 100 mmol dm⁻³ NaOH; E2, 10 mmol dm⁻³ IBA^{+,}OH⁻, 10 mmol dm⁻³ phosphoric acid, in 20% (v/v) acetonitrile-water solution (pH 8.0); E3, 50% (v/v) acetonitrile-water solution; E4, Milli-Q water.

purity of the TBA+•EXT- product was determined by chemical microanalysis (Calcd for C₁₉H₄₁O₄NS₄: C, 47.96; H, 8.69; O, 13.45; N, 2.94; S, 26.96. Found: C, 48.36; H, 8.89; N, 3.07; S, 26.49.). Traces of CHCl₃ (\sim 3%) were detected in the TBA⁺·EXT⁻ product (via analysis of Cl), and the experimental microanalysis results listed for the TBA+·EXT- product have been corrected for the carbon and hydrogen contributions from CHCl₃. Attempts to remove all traces of CHCl₃ from the product resulted in decomposition of the EXT-, as revealed by HPLC analysis. ¹H and ¹³C NMR analysis yielded the following results: $\delta_{\rm H}$ (CDCl₃, 250 MHz) 1.41 (3H), 4.64 (2H); δ_C (CDCl₃, 62.9 MHz) 13.3 (CH₃), 71.0 (CH₂), 211.0 (C(=S)S). Analysis of the product by APCI-MS yielded a negative ion parent peak at m/e 233.0, which is equal to that expected for the dominant ion. The FT-IR spectrum of TBA+•EXTis shown in Figure 1, and the UV-visible spectrum of the EXT anion is shown in Figure 2.

Instrumentation. A Dionex DX300 chromatography system was used in this study, consisting of a model AGP-I gradient pump (Dionex) and a multiport valve injector fitted with a $50 \cdot \mu L$ sample loop. The column eluant was monitored with a multiwavelength (rapid-scanning) UV-visible detector (Linear PHD 206) which was configured to record full spectra over the wavelength range 200–360 nm in 5-nm steps. In addition, the specific wavelengths of 221, 289, 301, and 348 nm were monitored. The analytical column used was a Waters (Milford, MA) Nova-Pak C-18 column (150 mm by 3.9 mm i.d.) fitted with a C-18 guard column, held in a Guard-Pak module. The chromatographic data were collected and processed with a Dionex AI-450 program.

The eluant flow rate was fixed at 2.0 cm³ min⁻¹ for all eluant compositions described in this paper. Whenever the composition of the eluant was changed, the column was reequilibrated with the new mobile phase for at least 20 min prior to injecting the sample. Each species was loaded onto the column using a 25% acetonitrile–water eluant containing 2.5 mM TBA⁺ and 2.0 mM phosphoric acid. All data points were obtained in at least duplicate. All the experiments were conducted at 21 ± 1 °C.

The high-field ¹H and ¹³C NMR spectra were recorded on a Bruker AC250 NMR spectrometer at 250.13 and 62.90 MHz, respectively. All chemical shifts are reported in ppm relative to tetramethylsilane (TMS). FT-IR spectra shown in Figure 1 were recorded using a Perkin-Elmer 2000 FT-IR spectrometer. UV– visible spectra shown in Figure 2 were recorded using a Cary 500 UV–visible–NIR spectrophotometer.

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	Table 3.	Proton	Dissoci	ation	Constan	ts and l	JV S	Spectr	oscopi	сD	ata f	or t	he l	Etř	nyl	Xant	hat	еĽ	Decomp	osit	lion	Spec	ies
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		band 1^a (n	$\rightarrow \pi^*$)	band 3^a (7	$\tau \rightarrow \pi^*$)	band 4 ^a (unassigned)		
species	pKa	$\overline{\lambda_{\max}}$ (nm)	ϵ	$\overline{\lambda_{\max}}$ (nm)	E	$\lambda_{\rm max}$ (nm)	ϵ	
$\mathbf{E}\mathbf{X}^{-}$	1.6 ³⁷	380	${\sim}50$	301	17600	226	8750	
EPX ^{- b}	5.1 ²	347	10400	285	$\sim \! 1300$	215	$\sim \! 10900$	
$H^+ \cdot EPX^-$	(as for EPX ⁻)	${\sim}350$	${\sim}100$	297	${\sim}7000$	225	${\sim}14000$	
ETC ⁻	<7 5			222	12400			
EXT^{-}	<2 6	${\sim}350^c$	${\sim}100$	289	${\sim}6000$	230	${\sim}12000$	
$(EX)_{2}^{1}$				283	8600	238	17800	

^{*a*} Bands 1, 3, and 4 as defined by Timons and Kreze.³² All extinction coefficients are given in the units of mol⁻¹ dm³ cm⁻¹. ^{*b*} Band assignments uncertain for reasons described in text. ^{*c*} Shoulder on band 3.

HPLC Reagents. The mobile phase was prepared using tetrabutylammonium hydroxide (TBA⁺OH⁻), HPLC grade acetonitrile, and phosphoric acid. The final optimized eluant contained 5.0 mmol dm⁻³ TBA⁺ and 5.0 mmol dm⁻³ phosphate in 20% acetonitrile, adjusted to pH 8.0 with sodium hydroxide. The percentage of acetonitrile was increased over the course of the chromatogram, to a final value of 35%. The pH of the eluant was increased for a short period during the chromatogram in order to achieve an optimum peak shape for the EX⁻ species, for reasons discussed later in this paper. The gradient timetable for the optimized method is listed in Table 2.

RESULTS AND DISCUSSION

Infrared Spectroscopic Characterization. FT-IR spectra of KEX, NH₄⁺·EPX⁻, KETC, TBA⁺·EXT⁻, and (EX)₂ are shown in Figure 1. The IR spectra of KEX, KETC, and (EX)₂ have been published previously²⁰ and are included here for comparison purposes only. We are unaware of any published FT-IR spectra of salts of EPX- or EXT-. Comparative studies of the infrared spectra of O-alkyl dithiocarbonates have been conducted by Little et al.²⁰ and Poling.²¹ The IR spectra of xanthates have been treated more recently by Woods and Hope²² and at a theoretical level by Mattes and Pauleickhoff,23 Colthup and Powell,24 and Tossell and Vaughan.²⁵ The IR spectrum of KEX is characterized by strong absorption bands at 1050 $\rm cm^{-1},$ arising from the asymmetric stretching mode of the CS₂ group and, at \sim 1150 cm⁻¹, arising from the asymmetric stretching mode of the C–O–C group. These bands are indicated in the KEX spectrum shown in Figure 1. Between these two bands are strong absorption bands corresponding to rocking and twisting modes of -CH₂- and -CH₃. On the low-energy side of the 1050-cm⁻¹ band, at 1007 cm⁻¹, there is a medium-intensity absorption band related to a CCOC stretching mode.²⁴ The two sets of absorption bands between 1360 and 1390 cm⁻¹ as well as between 1420 cm⁻¹ and 1480 cm⁻¹ are due to C-H bending modes and appear in a similar position, to a greater or lesser extent, in all of the FT-IR spectra shown in Figure 1.

The band assignments for $NH_4^+ \cdot EPX^-$ can be deduced by analogy with the spectra of KEX and (EX)₂. The strong band at

1050 cm⁻¹ most likely corresponds to the CS₂ asymmetric stretching mode. Both this band and the weaker CCOC stretching band are in positions in NH4+•EPX- similar to that observed for KEX. The strong band at 1208 cm⁻¹ is probably due to the C-O-C asymmetric stretching mode, shifted to higher energy compared to KEX. This shift in the C–O–C stretching frequency is typical of O-alkyl dithiocarbonates in which a substituant is covalently bonded to the dithiolate sulfur.²⁰ An example of this effect is the IR spectrum of $(EX)_2$ in which the C–O–C asymmetric stretching band appears at 1240 cm^{-1} (Figure 1). The medium-intensity bands between the CS₂ asymmetric band and the C-O-C asymmetric band most likely correspond to the -CH₃ and -CH₂- rocking and twisting modes identified for KEX. A quite distinctive difference in the IR spectra of NH4++EPXcompared to that for KEX is the presence of two strong bands between 850 and 890 cm⁻¹. The origin of these bands is not clear, although on the basis that the principal difference between these two molecules is the presence of a covalently bonded oxygen on the dithiolate sulfur, these bands may be due to a vibrational mode involving the $C-S-O^{-}$ group.

The FT-IR spectrum of KETC is distinctly different from that of KEX and NH₄⁺·EPX⁻, with a strong band at 1585 cm⁻¹ indicative of a carbonyl group. This band occurs at the lower frequency limit of the C=O stretching mode, which is probably the result of some electron reasonance with the monothiolate sulfur.¹⁹ Consistent with this interpretation, for the dimeric form of ETC⁻, bis-(ethoxycarbonyl) disulfide, in which this electron sharing is not possible, the C=O stretch occurs at 1750 cm^{-1,19,26} The strong presence of the carbonyl band indicates that KETC is dominantly in the form of a thiol (C(=O)S⁻). As expected, the CS₂ asymmetric stretching band is absent in the IR spectrum of KETC. The strong band at 1107 cm⁻¹ and shoulder at 1085 cm⁻¹ are most likely associated with the C-O-C asymmetric stretching mode as well as the $-CH_2$ - and $-CH_3$ rocking and twisting modes.

The spectrum of TBA⁺·EXT⁻ has a number of peaks that originate from the TBA⁺ cation. Absorption bands that can be unambiguously assigned to EXT⁻ are at 1240, 1018, and 605 cm⁻¹. In addition, there are clearly a number of unresolved peaks in the band centered about 1018 cm⁻¹. The 1240-cm⁻¹ band is most likely associated with the C–O–C asymmetric stretching mode while the 1018-cm⁻¹ band is probably due to the CS₂ asymmetric stretching mode. Support for these assignments comes from a comparison with the IR spectrum of (EX)₂ (Figure 1), which has a close structural similarity (Scheme 1). In the IR spectrum of

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(EX)₂, the C-O-C stretch occurs at 1240 cm⁻¹ and the CS₂ asymmetric stretch occurs at 1020 cm⁻¹, values very similar to that observed for TBA+•EXT-. Sulfur-oxy anionic species exhibit bands arising from the symmetric and asymmetric stretching of the $-SO_2$ - group. The symmetric stretching frequency is typically in the range 950–1050 cm⁻¹ while asymmetric stretching bands may appear over the range 930 (SO₃^{2–}) to 1100 cm⁻¹ (SO₄^{2–} and $S_2O_3{}^{2-}).{}^{27}$ These bands are in a region similar to that expected for the CS₂ asymmetric stretching mode, so it is possible that absorption bands corresponding to the thiosulfate group are present in the cluster of bands around the asymmetric CS₂ stretching mode peak at 1018 cm⁻¹. The band at 605 cm⁻¹ is in a typical position for a -SO₂- bending mode, and the absence of this band in all other IR spectra shown in Figure 1 would support the assignment of this band to a mode involving the thiosulfate group.

UV Spectroscopic Characterization. In Table 3 are shown pK_a values for the protonated forms of EX⁻, EPX⁻, ETC⁻, and EXT⁻. In Figure 2 are shown the UV spectra for these species in water at 8 < pH < 11, conditions under which all species are almost exclusively (>99%) in anionic forms. The solvatochromic behavior of dithiocarbonates were investigated by Janssen^{28,29} as well as by Shankaranarayana and Patel, 30,31 and the band assignments were summarized by Timmons and Kresze.32 This class of molecules exhibits three distinct absorption bands in the UV and near-UV region arising from the C(=S)S group. For an uncharged chromophore these bands are as follows: (i) a weak (log $\epsilon \approx 1$) $n \rightarrow \pi^*$ transition at ~360 nm, (ii) a strong (log $\epsilon \approx 4$) $\pi \rightarrow \pi^*$ transition at \sim 280 nm, and (iii) a strong (log $\epsilon \approx$ 4) unassigned transition at ~220 nm.³² The n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ assignments have been largely confirmed by the molecular orbital calculations carried out by Tossell and Vaughan.²⁵ The UV spectra of EX-, EPX⁻, and EXT⁻ (as well as (EX)₂) can be understood in terms of the chemical modifications of the dithiocarbonate chromophore in these molecules. Monothiocarbonates exhibit two bands in the UV region, of which only the $\pi \rightarrow \pi^*$ transition at ~230 nm has appreciable intensity (log $\epsilon \approx 4$).³² The absorption band positions and intensities for EX⁻, EPX⁻, ETC⁻, and EXT⁻ are summarized in Table 3. The band assignments given in Table 3 are in accordance with the classifications developed by Timmons and Kresze.32

In the UV spectrum of EX⁻, the $n \rightarrow \pi^*$ (380 nm) and $\pi \rightarrow \pi^*$ (301 nm) transitions are shifted to longer wavelengths relative to the uncharged dithiocarbonate chromophore due to the negative charge centered on the dithiolate sulfur atoms.²⁹ The $n \rightarrow \pi^*$ transition is particularly weak, although it is clearly evident on the expanded scale shown in Figure 2. The $\pi \rightarrow \pi^*$ transition is intense and is the usual basis by which EX⁻ concentrations are determined in solution.⁷

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Scheme 2



For EPX⁻, the assignment of the absorption bands is less obvious. The strong band at 348 nm has been attributed to the π $\rightarrow \pi^*$ transition³³ although it would be surprising if the position of this band could be shifted by \sim 70 nm compared to the uncharged dithiocarbonate chromophore. In fact, this band is closer in position to that expected for the $n \rightarrow \pi^*$ transition, although the intensity is orders of magnitude higher than expected. It is interesting to note that the UV spectrum for the protonated form of EPX⁻ (H⁺·EPX⁻) (shown in Figure 2) is much closer to that expected for a dithiocarbonate species. This result would suggest that the protonated and deprotonated forms of the EPX⁻ species have distinctly different structures in solution. In the synthesis of NH₄⁺•EPX⁻, the EPX⁻ anion is formed from EX⁻ by the action of hydrogen peroxide. It has been suggested that the oxidation of xanthates by peroxide-type oxidants leads to the formation of "sulfines" (IIb) which subsequently decompose via an oxathiirane (IIc) intermediate,³⁴ as shown in Scheme 2. It is possible that H⁺·EPX⁻ is present in the form of a dithiocarbonate (IIa), while the deprotonated form is in the form of a sulfine (IIb), the spectroscopic characteristics of which are probably quite different from that of IIa. A comprehensive analysis of the spectroscopic characteristics of the perxanthate species is beyond the scope of this study, although it is would seem that the resolution of the solution structure of EPX- will assist in understanding the solution and surface adsorption reactions of this species.

The UV spectrum of ETC⁻ is characterized by an absence of absorption bands in the 250–400-nm region. The band at 221 nm with $\epsilon = 12 400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ is similar in position and intensity to that observed for both thiol (C(=O)S⁻) and thiono (C(=S)O⁻) chromophores.³² For this reason, it is not possible to determine from the UV data alone the dominant configuration of the COS⁻ chromophore in aqueous solution. ¹³C NMR measurements were performed on KETC solutions prepared in D₂O in order to provide additional information. ¹³C NMR peaks were observed at chemical shifts of 16.4, 65.4, and 188.1 ppm, which can be readily assigned to *C*H₃, *C*H₂, and *C*OS⁻ carbons, respectively. The chemical shift for the COS⁻ carbon is in a position similar to that observed for carboxylate anions (175–195 ppm).³⁵ It appears therefore that the charge on the COS⁻ headgroup is localized on sulfur and that the ETC⁻ anion is in a thiol form in aqueous solution. The high

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intensity of the absorption band observed for ETC⁻ would indicate that that it is due to a $\pi \rightarrow \pi^*$ transition.

EXT⁻ exhibits electronic transition energies that are typical for dithiocarbonates, with the $\pi \rightarrow \pi^*$ transition at 289 nm and short-wavelength band at 229 nm. As expected, both of these bands are quite intense ($\epsilon_{289} \approx 6000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and $\epsilon_{229} \approx 12\ 000\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$, respectively). The n $\rightarrow \pi^*$ transition appears only as a weak shoulder at ~350 nm on the $\pi \rightarrow \pi^*$ band. It would appear that localization of the negative charge on the thiosulfate group results in transition energies that are essentially unaffected by the charged nature of this species. As was the case for the IR characteristics of TBA⁺·EXT⁻, the UV characteristics of EXT⁻ are very similar to that for (EX)₂ (Table 3).

Anion Interaction Chromatography. Figure 2 shows that all of the ethyl xanthate decomposition species have distinctive UVvisible spectra, allowing straightforward detection in HPLC-based methods. Since all of the species are in anionic forms at pH > 7, it was considered possible that separation and analysis could be achieved using an anion exchange-based HPLC method, similar to that achieved by Palsson for the separation of EX⁻ and EPX⁻.¹³ This was attempted using a Dionex Pax-100 anion exchange column with a sodium hydroxide eluant. It was found that while a good separation of EX⁻, EPX⁻, and ETC⁻ could be achieved with this configuration, EXT⁻ could not be eluted from the column, even at high eluant strengths with the inclusion of acetonitrile. Further, the anion exchange method was found to be unsuitable for the analysis of the cyanide complexes of nickel and iron, which as noted previously were also of interest in the final application of this method. For this reason, a reversed-phase anion interactionbased HPLC method was developed for the analysis of the xanthate species.

The anion interaction chromatography system that was constructed consisted of a C-18 column, dynamically coated in tetrabutylammonium ion (TBA⁺). Acetonitrile and phosphoric acid were included in the mobile phase as the organic modifier and pH buffer, respectively. This HPLC configuration is typical of that used in the analysis of metal cyanide species,^{14–16} and initially the procedure used in our laboratory for the analysis of Ni(II) and Fe(II/III) cyanide complexes was used for the analysis of xanthate species. In general, it was found that ETC⁻, S₂O₃²⁻, EPX⁻, and EX⁻ (in this order) eluted before the metal cyanide species, while EXT⁻ eluted after the metal cyanide species. This general order of elution was unchanged throughout the range of eluant conditions studied. While the standard method employed gave a poor separation of the xanthate species, it was considered likely that optimization of the eluant conditions would lead to a method enabling the analysis of xanthate species as well as the metal cyanide complexes of interest. The ethyl xanthate decomposition species are effectively short-chain surfactants, with polar headgroups and nonpolar tails. This mixed character allows for both hydrophobic interactions with the C-18 column and anion exchange interactions with dynamically adsorbed TBA+.

The dependence of retention times of the ethyl xanthate decomposition species upon the eluant parameters is discussed in the following sections. The effect of each parameter is considered in terms of the retention factor, defined by eq 1,

$$k' = (t_{\rm R} - t_0) / t_0 \tag{1}$$

Table 4. Effect of TBA⁺ Concentration on the Retention Factor (*k*') of Thiosulfate and the Ethyl Xanthate Decomposition Species^a

TBA^+		retention factor k'									
(mmol dm^{-3})	ETC-	$S_2O_3{}^{2-}$	EPX-	$\mathbf{E}\mathbf{X}^{-}$	EXT-						
1.0	0.587	0.683	1.571	1.714	5.90						
2.0	0.841	1.095	2.429	2.825	8.43						
3.0	1.032	1.476	3.016	3.635	12.04						
4.0	1.222	1.937	4.238	4.921	13.60						
5.0	1.540	2.302	5.048	5.937	15.63						

 a Eluants contained TBA+ at the values listed and were prepared in 5.0 mmol dm^-3 phosphate and 20% (v/v) (30% (v/v) for EXT-) acetonitrile-water, adjusted to pH 8.0.

where t_R is the retention time of the species and t_0 is the dead volume time. From these results we have established the optimum conditions for the separation and analysis of the ethyl xanthate decomposition species and applied it in a sulfide flotation system containing metal cyanide complexes.

Effect of TBA⁺ Concentration in Anion Interaction Chromatography. The effect of the concentration of TBA⁺ upon the retention factors of the species under consideration was investigated at an acetonitrile level of 20% (v/v) with 5.0 mmol dm⁻³ phosphoric acid, adjusted to pH 8.0, except in the case of EXT⁻. EXT⁻ exhibited an extremely high retention factor (*k*) compared to the other xanthate species, so in this case, the dependence upon TBA⁺ concentration was investigated at 30% (v/v) acetonitrile. The effect of TBA⁺ concentration upon the retention factors for the ethyl xanthate decomposition species and thiosulfate is shown in Table 4. It was found that the retention factors for all species increased with increasing TBA⁺ concentration over the range 1.0-5.0 mmol dm⁻³. This dependence is consistent with a retention mechanism on the C-18 column based on a typical ion interaction mechanism. Of particular interest is that both ETCand S₂O_{3²⁻} as well as EPX⁻ and EX⁻ elute as closely spaced "pairs", a property that considerably limits the range of eluant conditions which can be used in obtaining an adequate separation for analysis. The data shown in Table 4 reveal that in order to achieve a good separation of these pairs, it is necessary to use the maximum level of TBA+ possible. Balanced against this is that while the separation improves with increasing TBA⁺ concentration, the retention factor of EXT⁻ becomes unreasonably high at the higher TBA⁺ concentrations investigated, even at an acetonitrile level of 30% (v/v).

Effect of Phosphate Concentration in Anion Interaction Chromatography. The effect of phosphate concentration was investigated for a constant TBA⁺ concentration of 5.0 mmol dm⁻³ and 20% (v/v) (30% (v/v) for EXT⁻) acetonitrile, adjusted to pH 8.0. The dependence of the retention factors of thiosulfate and the ethyl xanthate decomposition species upon the phosphate concentration, over the range 5.0-15.0 mmol dm⁻³, are shown Figure 3a. The primary function of phosphate in the mobile phase is to neutralize the hydroxide added with TBA⁺, lowering the pH to an acceptable value for the silica-based C-18 column. The minimum concentration of phosphoric acid that can be added is therefore an equivalence of the TBA⁺ concentration, 5.0 mmol dm⁻³ in this instance. In addition, phosphate acts as a competing anion, with the result that increasing the phosphate concentration



Figure 3. (a) Dependence of the retention factor of thiosulfate and the ethyl xanthate decomposition species upon the concentration of phosphate (added as phosphoric acid) in the mobile phase. Singlecomponent solutions (50 μ L) were loaded onto a C-18 column and eluted with a mobile phase containing 5 mmol $dm^{-3}\ TBA^+$ and phosphate in the range 5-15 mmol dm-3 in 20% (v/v) acetonitrilewater (30% for EXT⁻), adjusted to pH 8.0. The left-hand scale corresponds to ETC⁻, S₂O₃²⁻, EPX⁻, and EX⁻ while the right-hand scale corresponds to EXT⁻. (b) Dependence of the retention factor of thiosulfate and the ethyl xanthate decomposition species upon the percentage of organic modifier (acetonitrile) in the mobile phase. Single-component solutions (50 µL) were loaded onto a C-18 column and eluted with a mobile phase containing 5 mmol dm⁻³ TBA⁺ and 5 mmol dm⁻³ phosphoric acid in acetonitrile-water, with the acetonitrile in the range 10-35% (v/v) (25-45% (v/v) for EXT⁻), adjusted to pH 8.0.

decreases the retention time of other anions in the system, as can be observed in Figure 3a.

It is interesting to note that while ETC^- elutes before $S_2O_3^{2^-}$ at low phosphate concentrations, the order switches at phosphate concentrations greater than 10.0 mmol dm⁻³. As noted previously, the mechanism of retention of the ethyl xanthate decomposition species may involve some hydrophobic interactions with the C-18 column, interactions that will be largely unaffected by increasing the phosphate concentration. Thiosulfate on the other hand can only be retained by an anion exchange-based mechanism, so the retention factor would be expected to decrease more strongly with increasing phosphate concentration. An additional factor that may lead to a greater dependence upon phosphate concentration in the case of thiosulfate is the doubly charged nature of this species, giving rise to a much stronger dependence upon competing anions.

In general, only a weak dependence of the retention factors upon the phosphate concentration was observed across the range of phosphate concentrations studied. Consequently, apart from the poorer separation of ETC^- and $\text{S}_2\text{O}_3^{2-}$ at higher phosphate concentrations, the separation between the other species shown in Figure 3a is largely unaffected by the phosphate concentration. In addition, the retention factors of nickel and iron cyanide complexes were found to have stronger dependence upon phosphate concentration, such that considerable peak overlap between these cyanide complexes and xanthate species was observed at phosphate concentrations above 10.0 mmol dm⁻³. For these reasons, in the final optimized method, the phosphate concentration was maintained at a constant concentration of 5.0 mmol dm⁻³.

Effect of Organic Modifier in Anion Interation Chromatography. The dependence of the retention factor of thiosulfate and the ethyl xanthate decomposition species upon the proportion of acetonitrile in the eluant was investigated at a TBA⁺ concentration of 5.0 mmol dm⁻³ and a phosphoric acid concentration of 5.0 mmol dm⁻³, adjusted to pH 8.0. Figure 3b shows how the retention factor of these species varies with percentage of acetonitrile in the eluant. In the case of EXT⁻, the dependence upon the proportion of acetonitrile was investigated over a higher range due to the strong retention of this species. A decreased retention factor was observed for all of the ethyl xanthate decomposition species as well as thiosulfate with increasing acetonitrile percentage from 10 to 35% (25 to 45% for EXT). This effect can largely be attributed to the influence of the acetonitrile upon the partitioning of TBA⁺ between the stationary and mobile phases.

An additional mechanism by which the proportion of acetonitrile in the mobile phase may modify the retention characteristics of the ethyl xanthate decomposition species is as a result of any hydrophobic interactions between the alkyl chains and the hydrophobic character of the C-18 column. While it is difficult to resolve the contributions of these two mechanisms to the retention factor, it is interesting to note that while ETC⁻ and S₂O₃²⁻ retention factors decrease by a factor of ~10 in changing the acetonitrile percentage from 10 to 35% (v/v), EPX⁻ and EX⁻ retention factors change by a factor of ~30 over the same acetonitrile range. While this may be interpreted as evidence for hydrophobic interactions in the case of EX⁻ and EPX⁻, it should be kept in mind that ETC⁻ would reasonably be expected to exhibit a similar hydrophobic affinity for the C-18 column.

The results shown in Figure 3b demonstrate that the elution of ETC⁻ and $S_2O_3^{2-}$, as well as EX⁻ and EPX⁻, as pairs remains unchanged across the range of acetonitrile levels studied, with the pairs ultimately converging at the highest acetonitrile concentrations investigated. Accordingly, to obtain an acceptable separation of these two pairs of species it is necessary to use a low percentage of acetonitrile. Balanced against this is the observation that EXT⁻ is very strongly retained and can only be eluted in a reasonable time (k' < 10) when an acetonitrile content of greater than 30% (v/v) is used. In the optimized method, these conflicting requirements are solved by a gradient increase in the acetonitrile level, following the elution of ETC⁻, S₂O₃²⁻, EPX⁻, and EX⁻ (Table 2).

Effect of Eluant pH in Anion Interaction Chromatography. The operation of silica-based C-18 columns is essentially limited



Figure 4. Effect of eluant pH upon the peak shape of ethyl xanthate. To obtain these chromatograms, 50 μ L of a 10 ppm EX⁻ solution was injected onto the C-18 column and then eluted using a mobile phase consisting of 5 mmol dm⁻³ TBA⁺ and 5 mmol dm⁻³ phosphoric acid in 20% (v/v) acetonitrile, adjusted to pH 8.0, 8.5, and 9.2.

to the pH range 2–8. Continuous operation at higher pH eventually leads to dissolution of the silica substrate and loss of capacity. Below pH 7, complete ionization of all of the ethyl xanthate decomposition species is not assured, so the operational pH range for this anion interaction-based separation method is essentially limited to the narrow pH range of 7–8. An additional reason for maintaining the eluant pH above 7 is that below this value both ETC[–] and EX[–] rapidly decompose via acid-mediated pathways.^{5,18} For these reasons, the dependence of the retention factors upon eluant pH was not investigated.

A curious pH effect was observed in the case of EX⁻, which displayed an anomalous peak shape, dependent upon the eluant pH, over a narrow range of eluant pH conditions. The dependence of EX⁻ peak shape upon eluant pH was investigated using a mobile phase with 5.0 mmol dm⁻³ TBA⁺, 5.0 mmol dm⁻³ phosphate, and 20% (v/v) acetonitrile in water, adjusted to pH 8.0, 8.5, and 9.2. In Figure 4 are shown EX⁻ peak shapes obtained for each of these pH conditions. At both pH 8.0 and 8.5, EX⁻ elutes as an ill-formed (split) peak while at pH 9.2 a single peak of typical shape is observed. UV spectral analysis of the EX⁻ peak at each of the pH conditions studied revealed that the UV spectrum was unchanged throughout the peak profile, regardless of the peak shape. It would appear that at pH <9.2 EX⁻ is present as both a free anion and a complexed or ion-paired form. The p K_a of EX⁻ is ~1.7, and while the pK_a can be modified in the presence of organic solvents due to a modified solvent polarity, it is unlikely that the protonated form of EX⁻ could be present in appreciable amounts. Previous studies have shown that acetonitrile at the levels of interest in this study (20–35% (v/v)) may change the pK_a of carboxylic acids by 1 unit at the most.³⁶ It is likely that the dependence of the pK_a of dithiocarbonic acids upon the acetonitrile volume fraction is quite similar. At the present time, the origin of this pH effect upon the EX⁻ peak shape is unknown. In the optimized chromatographic method developed for the ethyl xanthate decomposition

Table 5. Calibration Range, Detection Limit, and
Precision for S ₂ O ₃ ²⁻ and the Ethyl Xanthate
Decomposition Species

	ETC-	$S_2O_3{}^{2-}$	EPX-	$\mathbf{E}\mathbf{X}^{-}$	EXT-
calibration (ppm)	60	200	140	100	100
detection limit (ppm)	0.03	0.2	0.1	0.03	0.2
precision (RSD %)	2.0	0.5	0.5	1.0	0.7

species, the pH of the eluant is increased for a short period prior to and during the elution of EX^- in order to obtain an optimal peak shape for this anion.

Optimized Procedure for Anion Interaction Chromatography. An optimized procedure based on the studies presented in the previous sections was developed for the separation and analysis of thiosulfate and the ethyl xanthate decomposition species in the presence of nickel and iron cyanide complexes. The optimized eluant contained 5.0 mmol dm⁻³ TBA⁺ and 5.0 mmol dm⁻³ phosphate in 20% (v/v) acetonitrile-water. A linear gradient increase in the acetonitrile level from 20 to 35% (v/v) is applied over the period 3.9-6.5 min in order to allow the elution of EXT⁻. In addition, the pH is temporarily raised from 8.0 to 9.2 over the period 1.0-4.0 min to improve the peak shape of EX⁻. The details of the gradient method are given in Table 2. Figure 5 shows a spectrally resolved chromatogram for a mixture of thiosulfate, EX⁻, EPX⁻, ETC⁻, and EXT⁻ using the optimized method developed in this study and demonstrates that the xanthate species are well separated and identified by this procedure. The calibration range, precision (10 injections), and detection limits achieved using this method are listed in Table 5.

Application of the Anion Interaction Method to the Analysis of Flotation Pulps. The optimized method was tested for solution samples collected from a nickel-iron sulfide mineral (pentlandite, (Ni,Fe)₉S₈) suspension to which both EX⁻ and NaCN were added. In this experiment, the solution pH was maintained at 9.2 (1 mmol dm⁻³ Borax buffer) and air was passed through the suspension to promote the adsorption of xanthate onto the mineral surface. An aqueous sample was collected from the suspension by filtration of a 1-cm³ suspension sample through a 0.22-µm membrane and injected directly into the HPLC sample loop. Figure 6 shows the chromatogram obtained for this solution using the specific detection wavelengths of 269 ($[Ni(CN)_4]^{2-}$) and 221 nm (all other species). This figure demonstrates that, even under these simplified detection conditions, all species of interest in this study can be adequately determined. In this particular experiment, neither [Fe^{III}(CN)₆]³⁻ nor [Fe^{II}(CN)₆]⁴⁻ was observed; however, the positions of these species under the optimized conditions are shown in Figure 6, indicating that if these species were to be present, determination would be possible.

Although determination of all of the ethyl xanthate decomposition species is possible using single-wavelength detection (221 nm), a more robust analytical method is achieved via the use of a multiwavelength or diode array detector. Due to the distinctive UV spectra of ethyl xanthate and the associated decomposition products, this type of configuration provides a more reliable method of species identification. In pure mineral sulfide suspensions, this level of detection is not required; however, we have found multiwavelength detection to be invaluable in the analysis

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Figure 5. Spectrally resolved chromatogram for a mixture of thiosulfate and ethyl xanthate decomposition species. A $50-\mu$ L aliquot of solution containing 3 ppm ETC⁻, 20 ppm S₂O₃²⁻, 10 ppm EPX⁻, 10 ppm EX⁻, and 50 ppm EXT⁻ was loaded onto the column, with the components eluted using the chromatographic conditions described for the optimized procedure developed in this study. Comparison with Figure 2 demonstrates that the xanthate decomposition species can be separated and uniquely identified using this ion interaction-based HPLC method.



Figure 6. UV chromatogram showing the simultaneous determination of the ethyl xanthate decomposition species and the tetracyanonickelate(II) complex. The solution sample was generated by the reaction of ethyl xanthate and sodium cyanide with the nickel–iron sulfide mineral pentlandite ($(Ni,Fe)_9S_8$) at pH 9.2 in the presence of air. The ethyl xanthate decomposition species were detected at 221 nm while tetracyanonickelate(II) was detected at 269 nm. Also shown are the positions of the iron cyanide complexes hexacyanoferrate(II) and hexacyanoferrate(III). These complexes were not observed as reaction products in this system, although their separation under these conditions is clearly possible. Chromatographic conditions are as described for the optimized procedure developed in this study.

of flotation pulps containing several different mineral species as well as a range of flotation reagents.

CONCLUSIONS

The anion interaction-based HPLC method developed in this study provides, for the first time, a convenient and robust way of

analyzing xanthate species and associated oxidation products present in flotation pulps, in both laboratory- and industrial-scale systems. The application of this method in studies in which the dependence of mineral recovery upon pulp solution conditions is investigated may lead to more rapid optimization of process conditions. The analytical method described in this paper will also have application in understanding the environmental fate of xanthate collectors in tailings dams and surrounding groundwater systems. We envisage that both the spectroscopic information presented here and the HPLC-based solution analytical method will be a valuable resource in future studies of xanthate interactions with mineral surfaces.

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