

# THE SEPARATION AND DETERMINATION OF XANTHATES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY<sup>①</sup>

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## ABSTRACT

Three HPLC methods for the separation and determination of xanthate mixtures are described. The chromatographic behaviours, advantages and application ranges of various methods have been discussed in detail. A calculation method for determining the results of individual xanthates from the complicated chromatographic peaks of xanthate mixtures is presented. The limits of detection are 0.15—2.0 ng.

**Key words:** xanthate, dioxanthogen, collector, liquid chromatography

## 1 INTRODUCTION

Xanthates are generally prepared by the reaction of a sodium or potassium alkoxide solution with carbon disulfide<sup>[1]</sup>. Since the introduction of alkyl xanthates in mineral flotation in 1925 by Keller<sup>[2]</sup> they have been widely used for the flotation of sulfide minerals<sup>[3]</sup>. Recently, the xanthates and related compounds have also been used in such fields as cellulose synthesis, pesticide manufacturing, engine oil additives, production of fireproofing agents and corrosion inhibitors<sup>[4]</sup>.

Because of the widespread application of xanthates, their separation and determination in mixtures are of great importance. Numerous methods, including gravimetric<sup>[5]</sup>, titrimetric<sup>[6,7]</sup>, conductometric<sup>[8]</sup>, potentiometric<sup>[9]</sup>, polarographic<sup>[10]</sup> and spectrometric<sup>[11]</sup> procedures have been proposed. These methods are

suited for the determination of the sum of xanthates, but not for the identification and determination of individual xanthates in mixtures, because they are all based on the functional group of dithiocarbonates, without considering the difference of alkyl groups. Hasty<sup>[12,13]</sup> first applied HPLC to the determination of xanthates. The xanthates are first oxidized to dioxanthogens and then injected into the chromatographic system. With this method, the xanthates of various alkyl chains can be identified. However, the preparation of the dioxanthogens from xanthate mixtures is complicated and a suitable method for calculating analytical results has not been found yet. Additionally, the extension of this method is limited by the low solubility of dioxanthogens and by the excess injection of oxidizing agents that shorten the life of the chromatographic column.

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Three HPLC methods which are suitable for the identification and determination of individual xanthates in mixtures are described in this paper. They are:

A. Reversed-phase chromatography by oxidation before the column:

B. Reversed-phase chromatography by complexation before the column:

C. Normal-phase chromatography by oxidation before the column. Some of these methods are developed on the basis of our previous work<sup>[14]</sup>.

## 2 EXPERIMENTAL

**Instrumentation:** Following apparatus were used: LC pump, Series 400; UV spectrophotometer, LC—85B; Integrator, LC—100 Laboratory; Column for methods A, B, HS—5, C18(5 $\mu$ m), 4.6 $\times$ 150mm; Column for method C, LiChrosorb-Diol (5 $\mu$ m), 4.6 $\times$ 250mm.

**Reagents:** Standard-reagents of xanthates were prepared from raw xanthates (industrial-reagent grade) by the method described in the reference<sup>[15]</sup>. The other reagents were of analytical grade. The solvents used as mobile phase were of HPLC grade and degassed before use.

**Procedure:** Method A: Xanthates were dissolved in water, and then oxidized by 0.01 mol/l iodine solution in 0.20 mol/l potassium iodide. Dixanthogens formed were extracted by n-hexane. Six  $\mu$ l of this extraction solution was injected into the HPLC-system (stationary phase RP18). A solution of methanol and water (90:10) was used as mobile phase. The determination was accomplished at a wavelength of 240 nm by the UV detector.

**Method B:** Xanthates were dissolved in a methanol-water solution (80:20), into which an excess of copper subchloride powder was

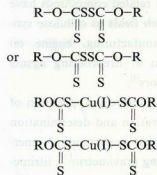
added. The solution was fully stirred until completion of the complex reaction of Cu(I)—xanthates. The solutions of these compounds were filtered (0.45 $\mu$ m millipore filter) before use. A 6 $\mu$ l-solution sample was injected into the chromatographic system (stationary phase RP 18). The mobile phase was a methanol-water (90:10)solution which contained 0.1% hydroxylammomium chloride. The wavelength of UV detector was set permanently at 301nm.

**Method C:** The stationary phase was LiChrosorb-Diol and n-hexane was used as mobile phase. The rest procedure followed method A.

## 3 RESULTS AND DISCUSSION

### 3.1 Derivation before the Column and Selection of Chromatographic System

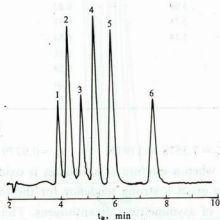
Since the xanthates have strong polarity, their adsorption and separation in the HPLC system become difficult, and a direct chromatographic determination has not been reported thus far. In this work, xanthates were oxidized to dixanthogens (methods A,C)and made into metal complexes (method B), respectively.



In these molecules, the xanthate charge is screened partially, the polarity weakened, and the hydrophobicity increased. So, these molecules have a moderate adsorption at some common stationary phases, e. g. RP 18 and

Diol. Furthermore, the difference of carbon atom numbers between the molecules increases owing to the increment of molecule groups, so chromatographic separation becomes easier.

An oxidation of iodine was applied in method A. Dixanthogens were extracted with *n*-hexane. A higher chromatographic sensitivity and a better distination were both obtained (Fig. 1).



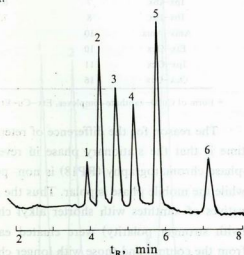
**Fig.1** Chromatogram of a xanthate mixture by method A

determining conditions; UV, 240 nm; column HS-5 C18,  $150 \times 4.6$  mm (5 $\mu$ m); mobile phase, methanol; water 90; 10; flow rate 1.0ml / min; concentration of xanthates before oxidation in  $10^{-5}$ mol / l. Na-Etx (sodium ethyl xanthate) 0.6, Na-Ipx(sodium isopropyl xanthate) 0.7, K-Ibx(potassium isobutyl xanthate) 0.8

1—(Etx)<sub>2</sub>; 2—Etx-Ipx; 3—(Ipx)<sub>2</sub>;  
4—Etx-Ibx; 5—Ipx-Ibx; 6—(Ibx)<sub>2</sub>

Since the xanthate radical forms very stable complexes with the elements which have an affinity for sulfur, e.g. ions of heavy metals ( $\text{Cu}^{2+}$ ), both dixanthogens and complexes of metal-xanthates formed while the flotation solutions of heavy metals minerals (e. g. copper sulfide ore) were determined by method A. Consequently, the chromatographic separation and determination can not be carried out owing to the formation of complicated peaks. To overcome this difficulty, a procedure of com-

plex Cu(I)—xanthates (method B) was developed. After derivation only one kind of complex Cu(I)—xanthates was formed. In addition to the Cu(I)—complexes, other metal complexes have been also investigated. The experiments showed that Cu(I)—complexes are better. Fig.2 describes a chromatogram of six complexes from three xanthates and Cu(I). Thus it can be seen that method B has shorter retention time and maintains better distinction.



**Fig.2** Chromatogram of a xanthate mixture by method B

wavelength 301 nm, conditions as method A; Concentration of xanthates before complexation( $10^{-5}$ mol / l); Na-Etx 0.50, Na-Ipx 0.70, K-Ibx 0.60

1—(Etx)<sub>2</sub>Cu; 2—Etx-Cu-Ipx; 3—(Ipx)<sub>2</sub>Cu;  
4—Etx-Cu-Ibx; 5—Ipx-Cu-Ibx; 6—(Ibx)<sub>2</sub>Cu

Usually, a detection limit of 2 ng was attained by methods A and B, but in some cases, e.g. in the study of the mechanism of mineral flotation and in environmental analysis a lower detection limit is desirable. Besides, the retention times of xanthates with more than six alkyl carbon atoms are usually over 30 min. It is evident that the period is too long. These two problems can be resolved if the chromatographic system of method C is applied (Fig.3).

### 3.2 Chromatographic Behaviour

The retention time sequences of xanthate derivatives in both systems are the opposite

(Table 1). The flow rate of reversed-phase chromatography is 1.0 ml/min, and the flow rate of normal phase chromatography is 0.6 ml/min.

Table 1 Chromatographic system and retention time

Form of derivative *	Number of C atoms	Retention time $t_R$ (min)		
		Method A	Method B	Method C
EtX-EtX	4	4.00	3.81	7.20
EtX-Ipx	5	4.42	4.16	6.86
Ipx-Ipx	6	4.91	4.60	6.52
EtX-Ibx	6	5.41	5.09	6.62
Ipx-Ibx	7	6.09	5.71	6.31
Ibx-Ibx	8	7.72	7.14	6.14
AmX-AmX	10			6.18
EtX-OcX	10			6.24
Ipx-OcX	11			6.00
OcX-OcX	16			5.57

\* Form of Cu(I)-xanthate-complexes: EtX-Cu-EtX, EtX-Cu-Ipx...

The reason for the difference of retention time is that the stationary phase in reversed-phase chromatography (RP18) is non-polar, while the mobile phase is polar. Thus the derivatives of xanthates with shorter alkyl chains (with stronger polarity) were eluted earlier from the column and those with longer chains (with weaker polarity) were eluted later. In normal-phase chromatography the stationary phase is polar (Diol) and the mobile phase is non-polar solvent (n-hexane). According to the principle of "like dissolve like" the derivatives of longer alkyl chains carbon atoms (with weaker polarity) are eluted earlier but those with shorter chains are eluted later.

Therefore, the retention times of xanthate derivatives can be regarded as a function of the number of carbon atoms. The following three lineal regression formulas and their correlation coefficient were obtained from the data in Table 1:

$$Y_A = -0.0410 + 0.9110X \quad r_A = 0.9595$$

$$Y_B = 0.1590 + 0.8210X \quad r_B = 0.9589$$

$$Y_C = 7.3578 - 0.1197X \quad r_C = 0.9279$$

when a mixture of xanthates is oxidized, there exists a strong tendency for the formation of asymmetrical dioxanthogens. Thus the acquired chromatograms are not only chromatographic peaks with symmetrical chains of carbon atoms, but also those with asymmetrical chains formed from different xanthates. The peaks 2, 4, 5 in Fig. 1 and 2, 3, 5 in Fig. 3 belong to the chromatographic peaks with asymmetrical chains. When a few symmetrical dioxanthogens or symmetrical complexes of Cu(I)-xanthates were immediately injected into the HPLC-system after mixing, a chromatogram with only symmetrical peaks, as shown in Fig. 4, can be observed first, but a few hours later part of these symmetrical derivatives would be automatically transformed into asymmetrical ones (Fig. 1-3). This is because xanthate groups with shorter chains of carbon atoms form easily asymmetrical dioxanthogens or Cu-complexes with longer chains of xanthate groups. These asymmetrical derivatives

dissolve with more difficulty in water and is stabler than the symmetrical derivatives with shorter chains.

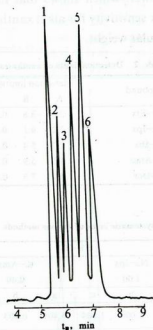


Fig.3 Chromatogram of a xanthate mixture by method C

Conditions; Column, LiChrosorb-Diol, 250 × 4.6mm (5μm); mobile phase, n-hexane; 0.6ml / min; 254 nm. concentration of xanthates (10<sup>-5</sup>mol / l); K-Oex (potassium octyl xanthate)0.30; Na-Etx 0.30.

- |                        |            |                      |
|------------------------|------------|----------------------|
| 1 (Ocx) <sub>2</sub> ; | 2 Ipx-Ocx; | 3 Etx-Ocx;           |
| 4 (Ipx) <sub>2</sub> ; | 5 Etx-Ipx; | 6 (Etx) <sub>2</sub> |

### 3.3 Calculation of Analytical Results

The chromatograms of either dixanthogens or metal complexes would be complicated because of the formation of asymmetrical compounds. Furthermore, the heights (area) of peaks in the determination of the same mixture were changed by the undulation of determination condition. It is quite evident that the analytical results calculated on only symmetrical or asymmetrical compounds are not accurate.

In our study, a weighted addition for the

calibration and calculation was proposed. The calibration curves of symmetrical peaks were plotted as in common analysis, and asymmetrical peaks were calibrated by "subtraction". The calibration formula of various peaks is as follows:

$$h = a + bc$$

where h, a, b and c represent the peak height, intersection, slope and the concentration of substances to be determined.

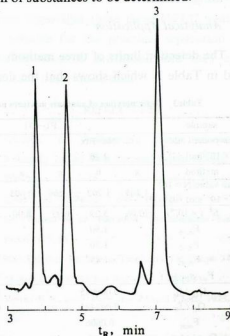


Fig.4 Chromatogram of symmetric dialkyl dixanthogens

Method and conditions as method A, concentration of xanthates (10<sup>-5</sup>mol / l);

Na-Etx 0.40, Na-Ipx 0.40, K-Ibx 0.50

- |                        |                        |                      |
|------------------------|------------------------|----------------------|
| 1 (Etx) <sub>2</sub> ; | 2 (Ipx) <sub>2</sub> ; | 3 (Ibx) <sub>2</sub> |
|------------------------|------------------------|----------------------|

Fig. 3 describes the chromatogram of a mixture consisting of three xanthates, and indicates that each xanthate involves three peaks. The concentration calculations are as follows;

$$C_{Opx} = 2 / b_1(h_1 - a_1) + 1 / b_2(h_2 - a_2) + 1 / b_3(h_3 - a_3)$$

$$C_{Ipx} = 2 / b_4(h_4 - a_4) + 1 / b_2(h_2 - a_2) + 1 / b_5(h_5 - a_5)$$

$$C_{\text{Ext}} = 2 / b_6(h_6 - a_6) + 1 / b_3(h_3 - a_3) + 1 / b_5(h_5 - a_5)$$

where the numbers at angles correspond to the numbers of chromatographic peaks.

In all three chromatographic methods the calibration curves of symmetrical and asymmetrical compounds were linear in the concentration range from  $1.5 \times 10^{-8}$  to  $1.0 \times 10^{-4}$  mol/l (correlation coefficients  $r = 0.9900$  to  $0.9951$ )

### 3.4 Analytical Application

The detection limits of three methods are listed in Table 2, which shows that the detec-

tion limits of methods A and B are very close but that of method C is ten times lower. The detection limit of xanthates with long alkyl chains is lower, which shows that method C has a higher sensitivity for alkyl xanthates with large molecular weight.

Table 2 Detection limits of xanthates

compound	detection limits(ng)		
	A	B	C
Na-Etx	2.0	3.8	0.25
Na-Ipx	2.2	4.1	0.22
K-Ibx	2.7	5.4	0.22
K-Amc	3.1	5.9	0.21
K-Ocx	4.0	7.5	0.15

Table3 Determination of xanthate mixtures and test of the identity and systematic error of various methods.

sample		F1-031						F1-037					
component add. ( $\times 10^{-5}$ mol/l)		Na-Etx			K-Ibx			Na-Ipx			K-Amx		
		1.20			0.60			1.00			0.40		
method		a	b	c	a	b	c	a	b	c	a	b	c
mean value( $N=10$ ) ( $\times 10^{-5}$ mol/l)		1.205	1.202	1.206	0.603	0.602	0.610	1.007	1.009	1.004	0.404	0.403	0.401
$S^2$ ( $\times 10^{-4}$ )		10.06	5.29	6.93	8.90	5.73	6.67	4.90	6.77	8.27	4.49	4.68	5.87
I	$F_{A-B}$		1.90			1.55			1.38			1.04	
	$F_{B-C}$		1.30			1.16			1.22			1.25	
	$F_{A-C}$		1.45			1.33			1.69			1.31	
	$F_{\alpha/2} (n, n)$						3.18						
II	$Q_G / f_G$	0.000045			0.00019			0.000065			0.000025		
	$Q_E / f_E$	0.007425			0.00071			0.0006644			0.0005014		
	$F_{\text{exp}}$	0.0606			0.268			0.0978			0.0499		
	$F_{0.05} (n, n)$						3.32						

I: test of identity; II: test of systematic error

Because there is as yet no practically feasible HPLC method for determining xanthates, it is impossible to test these new developed methods with a known method. In order to confirm their reliability, these three methods have been examined by the analysis of synthetic mixtures and statistical tests. Part of the results are compiled in Table 3. F-test was used as the identity test of various methods ( $\alpha = 0.10$ ).  $E_{A-B}$ ,  $E_{B-C}$  and  $E_{A-C}$  represent the F-values calculated from experimental results of

methods A and B, B and C as well as A and C. The test of the systematic errors between various methods were also performed by F-test.  $Q_G / f_G$  in Table3 represents the estimated values of the variance between methods, while  $Q_E / f_E$  represents that of the experimental effect,  $f_G$  and  $f_E$  are the corresponding degree of freedom. It is obvious that F-values from the experiments are less than the corresponding critical F-values. Therefore, the methods A, B and C can be regarded as the identity for



Table4 Determination of xanthates in solution of mineral flotation

sample components method	solu. of Cu sulfide ore						solu. of Pb, Zn sulfide ore					
	Na-Etx			K-Amx			Na-Etx			K-Ibx		
	a	b	c	a	b	c	a	b	c	a	b	c
results ( $\times 10^{-6}$ mol/l)	1.21	1.17	1.23	0.83	0.81	0.85	1.53	1.51	1.54	1.48	1.49	1.50
	1.01	1.03	1.04	0.49	0.48	0.49	1.19	1.23	1.24	1.21	1.21	1.24
	0.59	0.63	0.64	0.31	0.30	0.31	0.71	0.73	0.75	0.68	0.71	0.75
	0.31	0.30	0.31	0.14	0.14	0.14	0.41	0.45	0.41	0.38	0.37	0.39
	0.28	0.29	0.28	0.15	0.14	0.13	0.40	0.38	0.37	0.34	0.35	0.37

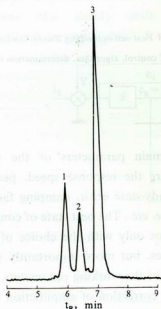


Fig.5 Determination of Na-Etx and K-Amx in flotation solution of lead-zinc sulfide ore

Method and conditions as method C results: Na-Etx  $0.23 \times 10^{-6}$  mol/l, K-Amx  $0.39 \times 10^{-6}$  mol/l  
1—(Etx)<sub>2</sub>, 2—Etx-Amx, 3—(Amx)<sub>2</sub>

the determination of xanthates, but the systematic errors between them do not exist.

These methods were developed for the study of adsorption mechanism of mineral processing and the optimization of processing technology. Consequently, the three methods mentioned above were examined using a large number of real samples Fig. 5. is chromatogram of the flotation solution for lead-zinc

sulfide ore by method C. Part of the results are given in Table 4. The chromatogram and datum show that these three HPLC methods are suitable for the practical separation and determination of xanthates, and they agree with each other quite well.

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