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SHORT COMMUNICATION

Highly Sensitive Determination of Butyl Xanthate in Surface and Drinking Water by Headspace Gas Chromatography with Electron Capture Detector

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Abstract A highly sensitive and convenient method for the determination of butyl xanthate in surface water and drinking water was developed by headspace gas chromatography with electron capture detector (HS–GC–ECD). The analytical method was based on the decomposition of butyl xanthate under an acidic condition, generating carbon disulfide, which could be sensitively detected by gas chromatography with electron capture detector. The signal of CS_2 from the decomposition of potassium butyl xanthate was directly proportional to the concentration of potassium butyl xanthate over the range 0.7–100 ng/mL. The detection limit at a signal-to-noise ratio of three ($S/N = 3$) for potassium butyl xanthate was 0.3 ng/mL (~1.6×10^{-9} mol/L), which was more than two orders of magnitude lower than the popular UV methods and close to one order of magnitude lower than the similar headspace gas chromatography–mass spectroscopy method. The relative standard deviation (R.S.D.) within a day and in 3 days for potassium butyl xanthate at both 5 and 50 ng/mL was less than 4.7 %, suggesting good analytical performance of the present method. Good recoveries from 93.3 to 104.7 % were obtained from spiked surface and drinking water samples, indicating that the proposed HS–GC–ECD method was applicable for the quantification of butyl xanthate in surface and drinking water. Compared with other reported methods, the present method is highly sensitive, without sample preparation, and easily extended to the analysis of other xanthates.

Keywords Butyl xanthate · Headspace · Gas chromatography · Water quality control

Introduction

Xanthates refer to organosulfur salts with the formula $ROCS_2^-M^+$ (R = alkyl; M = Na, K), which are widely used as selective collectors in flotation processes due to their relatively low cost and high selectivity to metal sulfides. In flotation process, approximately half of xanthates are consumed, while the remaining half are discharged in mill-tailings waste. Therefore, xanthate-containing wastewater generated by ore flotation process has become a considerable environmental challenge. Generally, more than five tons water is utilized to process one ton raw ore, and then comparable large quantities of wastewater are generated resulting from the flotation process. Throughout the world, it was estimated that more than one billion cube meter ore processing effluents with large quantities of xanthate residues were produced per year, and most of them were charged into natural water body without any treatments, representing a risk to water supplies and natural water resources.

From the environmental point of view, xanthates are generally poisonous to biota, and some of their decomposition products (like carbon disulfide) are highly toxic to the aquatic flora and fauna. As an example, rainbow trout had lethal concentrations of sodium ethyl xanthate ranging from 1 to 50 μg/mL depending on test conditions [1]. Other

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fishes had lethal concentrations of sodium ethyl xanthate ranging from 0.01 to 10 μg/mL (emerald shiner) and 0.32 to 3.2 μg/mL (fathead minnow) [2]. Daphnia magna, which is an aquatic invertebrate, also exhibited a median effective concentration (EC50) of 0.35 μg/mL [3]. An assessment by Environment Australia presented a predicted no effect concentration of sodium ethyl xanthate as low as 1 ng/mL [4]. Moreover, the toxicity of xanthates to mammalian and human has been investigated. It was reported that xanthates were potent inhibitors and selective mechanism-based inactivators of some mammalian cytochrome CYP isoforms, namely rat CYP2B1 and human CYP2B6 [5]. It has been found that after binding to the enzyme (inhibition of the enzyme), the xanthates would undergo catalytic conversion to reactive intermediates that covalently bind to the enzyme molecule and cause its inactivation [5]. Quantitative structure–activity relationship analysis results have concluded that the inactivation potency of the xanthates is related to their chemical structures and xanthates with longer alkyl chains or more branched chains exhibit the more efficient inactivation potency [6]. As a consequence, zero level of exposure is recommended for humans, especially for the xanthates with long alkyl chains or the xanthates with many branched chains, such as butyl xanthate, amyl xanthate, etc.

Governments worldwide have issued stringent regulations to limit xanthate levels in surface and drinking water. Australia and New Zealand have established a trigger value of 0.05 ng/mL for sodium ethyl xanthate to protect aquatic life [7]. Ministry of Environmental Protection of the P. R. China has mandated that the maximum potassium butyl xanthate content is 5 ng/mL in surface water source for domestic and drinking water [8].

Many methods for the monitor of xanthates in flotation process or wastewaters have been reported, such as ultraviolet–visible spectrophotometry [9, 10], fourier transfer infrared spectrometry [11], and electrochemical analysis [12, 13]. As residues of xanthates, in most tailings effluents, were generally found at concentrations in the range of 0.2–1.2 μg/mL, the detection limit of these methods for the determination of xanthates in flotation process or wastewaters was in the range of 10^{-6} to 10^{-7} g/mL. Suffered from the high detection limits, these analytical methods could not be utilized for the monitoring of xanthates below 100 ng/mL in water body without additional sample concentrations.

As a result, a number of approaches have been involved to enhance the sensitivity of the analytical methods for the analysis of xanthates in water body, including capillary electrophoresis [14], high-performance liquid chromatography [15], ultra-performance liquid chromatography [16], mass spectrometry [17], etc. Among them, ultra-performance liquid chromatography with mass spectrometry was the most sensitive method. However, in order to prevent the decomposition of xanthates, the pH of the mobile phase was 9.5, which is too high to shorten the life of C_{18} analysis column.

In fact, most analytical methods for the determination of xanthates have designed to prevent the decomposition of xanthates. Alternatively, based on the decomposition of xanthates under acidic medium to produce CS_2, a delicate approach to determine xanthates with UV detection was proposed [18]. Moreover, the similar approach was utilized in infrared spectrometry for the monitor of xanthates in ore surface [19]. Unfortunately, these delicate methods have not been successfully applied to monitor the xanthates in water quality control because the detection limits of these methods (e.g., 38 ng/mL) have not reached the extremely low trigger value of xanthates in governmental regulations (e.g., 5 or 0.05 ng/mL).

Headspace gas chromatography methods, which are widely accepted as an efficient tool to analyze the concentration of CS_2 in water for their sensitivity and convenience [20]. Subsequently, utilizing the decomposition of xanthate to yield CS_2 under acidic conditions, the headspace gas chromatography method may be a promising technique to monitor trace amount of xanthates in water body. In 2012, headspace gas chromatography–mass spectrometry (HS-GC–MS) was tried to monitor butyl xanthate in surface water [21]. Comparing with the tradition methods, the HS-GC–MS method was not only simple (without sample pretreatment) but also sensitive. The limit of linear range for potassium butyl xanthate using the HS-GC–MS method was 10 ng/mL, which was close to the maximum xanthate levels in regulations of Environmental Protection of the P. R. China (5 ng/mL). In the present work, more sensitive and more convenient headspace gas chromatography–electron capture detector (HS-GC–ECD) approach is proposed to determine butyl xanthate in surface and drinking water. The analytical method was based on the decomposition of butyl xanthate under an acidic condition to generate carbon disulfide, which was sensitively detected by gas chromatography with electron capture detector. Headspace analytical conditions, including headspace operating time, headspace operating temperature, and the pH of the decomposition reaction, were optimized. A high sensitivity was obtained. The applicability of the highly sensitive method for the determination of butyl xanthate in real samples was explored.

Materials and Methods

Chemicals and Solutions

Potassium butyl xanthate was purchased from Tokyo Chemical Industry Shanghai (Shanghai, China); the stock

solution (0.1 mg/mL) of potassium butyl xanthate was prepared freshly in sodium hydroxide solution (1 mmol/L) and was stored in dark at 4 °C. For headspace gas chromatography analysis, the working solutions of potassium butyl xanthate were obtained by diluting the stock solutions with appropriate amount of ultra-pure water. HCl, H_3PO_4, NaOH, and CS_2 were obtained from Sinopharm Chemical Reagent Co. Ltd (Chengdu, China). All reagents were of analytical grade and ultra-pure water prepared by a direct-Q 3 UV water purification system (Millipore, USA) was used throughout.

Apparatus and Operations

A GC system (Agilent, USA) with an automatic headspace sample (Dani, Italy) was used for the headspace GC measurement. The headspace operating conditions were as follows: shaking for sample equilibration at the temperature of interest; vial pressurization time: 0.2 min; and sample loop fill time: 0.2 min. The volume of the headspace sample vials was 20 mL. The volume of the sample loop was 1 mL. The GC system was equipped with an electron capture detector and a DB-5 capillary column (30 m × 0.25 mm, 0.25 μm) (Agilent, USA) operating at a temperature of 45 °C with nitrogen carrier gas (flow rate = 2 mL/min). The injection temperature was 230 °C. The oven temperature program was started at an initial temperature of 45 °C (hold for 2.0 min), then ramped at 20 °C/min to 80 °C, and then again ramped at 40 °C/min to 230 °C (hold time 0.5 min), resulting in a total run time of 8 min. The detector temperature was 300 °C.

Water Samples

The first surface water sample was collected from Baihuatan Park (No. 175 Sec. 1 Western First circle Street at Chengdu City, Qingyang District, Chengdu 610072, China), which was located in an area with strong urban influences. The second surface water sample was collected from Jiang'an river at 30°46′37″N, 103°47′55″E, which was located in suburban district with little anthropogenic influence. The drinking water sample was obtained from bottles of drinking water from Wahaha Group Co. Ltd. (Hangzhou, China).

Surface water samples were collected by directly inserting one liter plastic bottles to a depth of 30 cm, and performed according to clear technique protocols to avoid contamination of the samples from the time of collection. Samples were stored in a freezer (at −4 °C) not more than 72 h and analyzed by GC as soon as possible. For the determination with GC, the samples were stabilized at ambient temperature (from 20 to 26 °C) before small volume (10 mL) of the samples was taken with the addition of acidic solutions (100 μL).

Results and Discussion

HS–GC Chromatogram of Butyl Xanthate Under Acidic Medium

When a 20 ng/mL potassium butyl xanthate solution (10 mL) with 100 μL 5 wt%. hydrochloric acid was added into the headspace cell, a reproducible peak at 3.680 min in chromatograms was observed (Supplementary Material). Control solution without butyl xanthate was investigated under the same condition and no significant peak at 3.680 min was observed (Supplementary Material). As a result, the chromatographic peak at 3.680 min rationally derived from butyl xanthate.

Under acidic conditions, xanthates are unstable and suffer from the decomposition reactions with the formation of xanthic acids, which quickly decomposes into carbon disulfide and alcohols, according to (Eq. 1):

$$H^+ + X^- \overset{\text{yields}}{\rightarrow} HX \overset{\text{yields}}{\rightarrow} ROH + CS_2, \quad (1)$$

where X^- are xanthate ions; HX are xanthic acids; and ROH are alcohols.

The compound with the retention time at 3.680 min must be one of the products of the decomposition of butyl xanthate under acidic conditions. To validate the hypothesis, a control solution of CS_2 standard sample was evaluated with the same method. The retention time of CS_2 is 3.680 min (Supplementary Material), which indicated that the compound with the retention time at 3.680 min is the CS_2 derived from the decomposition of butyl xanthate under acidic conditions.

Optimization of Headspace Conditions

Based on the decomposing of butyl xanthate under acidic conditions, a HS–GC–ECD method for the determination of butyl xanthate was proposed. The headspace operating conditions including temperature, the pH value of the decomposition reactions, and shake time were studied.

Considering the boiling point of CS_2 (43.5 °C), the effect of the temperature of headspace cell was tested over the range 50–80 °C. The signal of CS_2 from the decomposition of butyl xanthate increased with the increase of the headspace temperature. However, at higher temperature, more water vapor would be induced into the capillary column and increase the risk of damaging the solid phase of the analytical column. Therefore, 80 °C was chosen as an appropriate temperature in further headspace experiments.

The effect of the pH of the decomposition reactions of butyl xanthate on analytical method was also examined. Samples of different pH were prepared by the addition of

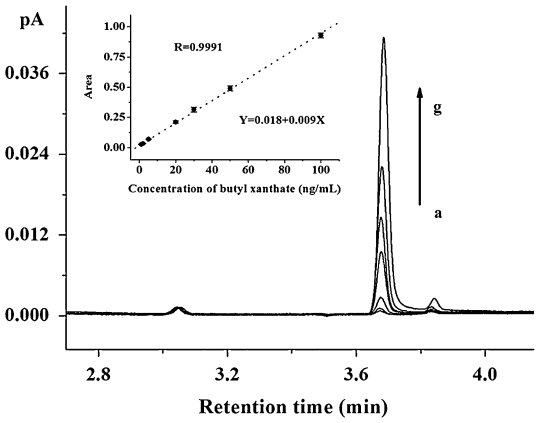

Fig. 1 Chromatographic signals as a function of the concentration of potassium butyl xanthate in the 0.07–100 ng/mL range. The *inset* shows the respective calibration plot

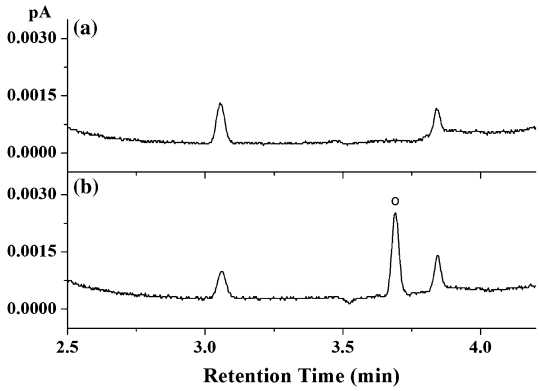

Fig. 2 Gas chromatograms of the surface water sample from Baihuatan Park (**a**) and the sample spiked with 7 ng/mL of potassium butyl xanthate (**b**)

NaOH (0.1 mol/L) in H_3PO_4 (1×10^{-2} mol/L) solution to yield phosphate buffer solutions. The signal of CS_2 from the decomposition of butyl xanthate significantly decreased when the pH was increased from 2.0 to 7.0, indicating that the higher pH could help the production of CS_2 from the decomposition of butyl xanthate. It was reported that ethyl xanthate quickly decomposed in the pH range from 0.1 to 3.0, but the decomposition reactions in a solution with the pH more than 4.0 needed a quite long time. For example, when the pH was less than 3.0, 98 % ethyl xanthate decomposed in 16 min; when the pH was more than 4.0, 70 % ethyl xanthate decomposed more than 1 h. For the sake of the analytical time, an appropriate value of pH was 2.0.

Subsequently, the shake time of the headspace condition was studied. The signal of CS_2 from the decomposition of butyl xanthate increases obviously with the shake time over 5–15 min, but it stabilizes when shake time is longer than 15 min. Therefore, the recommended headspace shake time was 15 min.

Determination of Xanthate by Headspace Gas Chromatography

Under the optimal headspace conditions, a typical chromatogram of CS_2 derived from the decomposition of butyl xanthate is shown in Fig. 1. The retention time of butyl xanthate (CS_2) was 3.680 min. The chromatographic peak area was linear with the concentration of potassium butyl xanthate in the range from 0.7 to 100 ng/mL. The regression equations were $A = 0.018 + 0.009\ C$ with a regression coefficient of 0.9991. The limit of detection (LOD) and the limit of quantitation (LOQ) at a signal-to-noise ratio of three and ten ($S/N = 3$ and 10) for potassium butyl xanthate are 0.3 and 0.9 ng/mL, respectively. The reproducibility of the signal was evaluated by detecting butyl xanthate

Table 1 Analytical methods utilized for the analysis of xanthates

Methods	Limit of detection	References
UV detection		
Capillary electrophoresis method–UV	60 ng/mL	[14]
UPLC–UV	0.8 ng/mL	[16]
UPLC–MS	0.2 ng/mL	[17]
FIA	38 ng/mL (3.1×10^{-7} mol/L)	[18]
UV	3×10^{-7} mol/L	[9, 10]
Electrochemical detection		
ED–CSV	1.8×10^{-5} mol/L	[13]
DC–AM	2×10^{-6} mol/L	[12]
HAGIS	–	[11, 19]
HS–GC–MS	2 ng/mL	[21]
HS–GC–ECD	0.3 ng/mL (1.6×10^{-9} mol/L)	The present work

Table 2 Results for the determination of butyl xanthate in surface and drinking water using the HS–GC–ECD method

	Matrix blank (ng/mL)	Spiked conc. (ng/mL)	Found (ng/mL)	Recovery (%)
Surface water sample 1 (Baihuatan Park)	ND	3.00	2.80 ± 0.08	93.3
		7.00	6.68 ± 0.27	95.4
Surface water sample 2 (Jiang'an river)	ND	3.00	2.82 ± 0.17	94.1
		7.00	7.33 ± 0.43	104.7
Drinking water sample 3 (Wahaha)	ND	3.00	2.96 ± 0.18	98.7
		7.00	6.76 ± 0.27	96.6

with different concentrations 7 times. The relative standard deviation (R.S.D.) within a day (intra-day precision, $n = 7$) for 5 and 50 ng/mL potassium butyl xanthate was 4.0 and 1.5 %, respectively; the R.S.D. in 3 days (inter-day precision, $n = 21$) for 5 and 50 ng/mL potassium butyl xanthate was 4.7 and 4.6 %, respectively, indicating good analytical performance of the present method.

A comparison of the proposed protocol with other reported methods for the determination of xanthates was made, as shown in Table 1. Compared with the reported method, the proposed method exhibited the extremely high sensitivity. Specially, the lower limits of linear ranges for potassium butyl xanthate using the HS–GC–ECD method (0.7 ng/mL) are one order of magnitude lower than the HS-GC–MS method (10 ng/mL), and the detection limit of the HS–GC–ECD method (0.3 ng/mL) is closed to one order of magnitude lower than the HS–GC–MS method (2 ng/mL).

Determination of Butyl Xanthate in Surface and Drinking Water

In order to validate the applicability of the proposed method in real samples, surface and drinking water spiked with potassium butyl xanthate at two different concentrations were analyzed by the HS–GC–ECD method. The typical chromatograms of the first surface sample and the sample spiked with 7 ng/mL potassium butyl xanthate are shown in Fig. 2. The peaks at 3.680 min were identified as CS_2 derived from the decomposition of potassium butyl xanthate. The analytical results for the sample and the other two samples are presented in Table 2. Good recoveries from 93.3 to 104.7 % were obtained, indicating that the proposed HS–GC–ECD method was applicable for the quantification of potassium butyl xanthate in surface and drinking water. Therefore, the present method provided a highly sensitive method for the monitoring trace amount of butyl xanthate in water quality control.

Conclusions

Based on the decomposition of butyl xanthate to generate carbon disulfide under acidic conditions, a novel headspace gas chromatography method with electron capture detection was proposed for the determination of trace amount of butyl xanthate in surface and drinking water. Headspace conditions including the temperature, pH, and shaking time, which obviously affected the signal of CS_2 derived from the decomposition of xanthate, were optimized. Under the optimal conditions, the proposed method was applicable for the monitor of butyl xanthate in surface and drinking water. The proposed method has several advantages: a highly sensitivity was obtained by the proposed method, and the detection limit of potassium butyl xanthate using the proposed HS–GC–ECD method was closed to one order of magnitude lower than the HS–GC–MS method. Moreover, butyl xanthate is unstable and undergoes decomposition. In the present work, it was converted to a relative stable CS_2 and was detected. This method is also easily extended to analyze other xanthates such as ethyl xanthate, propyl xanthate, amyl xanthate, etc., and may be a promising method for the monitor of xanthates in water quality control.

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