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İzopropil Ksantat ile Cloud Point Extraction Metodu

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Anahtar Kelimeler: Cloud point ekstraksiyonu, İzopropil ksantat, Su örnekleri, Alevli atomik absorpsiyon spectrometresi

ÖZET

İzoproil ksantat sentezlenerek çeşitli su örneklerinde alevli atomic absorpsiyon spektroskobisinde (FAAS) Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) ve Ni(II) iyonlarının cloud point metoduyla tayini için kullanıldı. Bu çalışmanın amacı izopropil ksantat gibi bir yüzey aktif madde vasıtasıyla analit metal iyonlarının cloud point ekstraksiyon yöntemiyle tayinine dayanmaktadır. İzopropil ksantat metalleri tututarak kompleks halinde miseller oluşturdu. Daha sonra da FAAS de metal iyonlarının analizleri yapıldı. Çalışmada farklı pH seviyeleri, yüzey aktif madde derişimi, sıcaklık, bekleme süresi gibi parametreler tarandı. Standart sapma değeri % 2.10 ve tayin sınırı 0.3-0.7 arasında bulundu.

Cloud Point Extraction Method with Isopropyl Xanthate

Key Words: Cloud point extraction, Isopropyl xanthate, Water samples, Flame atomic absorption spectrometry.

ABSTRACT

Isopropyl xanthate is synthesized and used in various water samples with Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) and Ni(II) ions with flame atomic absorption spectrometry (FAAS) using cloud point extraction (CPE) method. Metal complexes containing isopropyl xanthate are subsequently entrapped in the surfactant micelles. The proposed method is based on cloud point extraction of analyte metal ions without ligand using isopropyl xanthate as surfactant. In this paper, the effects of pH degree, concentration of chelating agent, surfactants, equilibration temperature and time on CPE are examined. Standard deviation was 2.10% between the detection ranges of 0.3-1.7.

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1. Introduction

During last century, many studies about xanthate have been carried out. They have been originated for the utilization of flotation in mine industry, for cancer treatment in medicine in the form of liquid crystals. Since they have good surface activity, they are seen in many fields of chemistry. Nowadays, the utilization of surface active materials is very common on cloud point extraction method in analytical chemistry [1-18].

Although there are many methods that are directly used in trace elements analysis, enrichment and separation methods are still needed, especially due to matrix effect and low concentration of trace elements. Besides simultaneous collapsing and solid phase extraction, cloud point extraction method is quite good as a method of enrichment. Even though the analytical performance of CPE is controversial, it is quite advantageous due to its applicability, low cost and large application areas. Even in different matrices, it can be successfully applied for enriching trace elements. Additionally, it is successfully used in analytical chemistry for enriching purposes [19-28]. Cloud point extraction method (1) can be used for creating metal ion complexes with a suitable ligand; or (2) can be directly applied as a surface active material.

Xanthates can also be used to enrich some trace elements without needing any ligand, just like the second method that has been discussed above. As per the literature analysis, isopropyl xanthates have not been used on cloud point method in analytical chemistry up to now. Thus, this study is defined as cloud point extraction method with xanthates and its purpose is enriching isopropyl xanthate with some trace level metal ions in different matrices.

1. Materyal ve metot

1.1. Experimental

1.2. Instrumentation

For the determination of metal ions, PerkinElmer Model 3110 atomic absorption spectrometer equipped with PerkinElmer single-element hollow cathode lamps and a 10-cm air–acetylene burner was used. All instrumental settings were done as recommended in manufacturer's manual, given in Table 1. For measuring pH values in the aqueous phase, a pH meter with Sartorius PT-10 Model glass-electrode was used. ALC PK 120 model centrifuge was used in the centrifuge of the solutions. The water was purified in a Human model RO 180, resulting in a conductivity of 1 µS cm^{-1} whereas samples were heated by Nüve ST 402.

Table 1 Analytical parameters for Perkin Elmer 3110 AAS.

Element current	Wavelength (nm)	Slit width (mm)	Lamb (mA)
Pb	283.3	0.7	15.0
Fe	248,3	0.2	20.0
Cu	324,8	0.7	25.0
Ni	232,0	0.2	25.0
Cd	228,8	0.7	15.0
Mn	279,5	0.2	15.0

1.3. Synthesis of isopropyl xanthate

Isopropyl xanthate was synthesized as per the literature. 3.74 g KOH (0.067 mol), 4,5 ml CS_2, 6 ml isopropyl alcohol and 9 ml benzene were heated under a reverse cooler. The blend was mixed 20 minutes at 35 ^{0}C and then 45 minutes at 45 ^{0}C. Subsequently, it was mixed 1 hour at 60 ^{0}C. At the end of this process, approximately 9 grams of product was formed and purified by drying in the oven for 48 hours with acetone [1-18].

1.4. Reagents

High purity reagents were used for all standard and sample solutions' preparations. Stock metal solution with a concentration of 1000 mgL-1 was daily diluted to be used as reference and working solutions.

Stock solutions of diverse elements were prepared using high purity compounds (99.9%, E. Merck, Darmstadt). All plastic and glassware equipments were cleaned by soaking into dilute HNO_3 and rinsed with deionised water prior to use. Phosphate buffers (0.1mol L^{-1}) and ammonium chloride buffer solutions (0.1mol L^{-1}) were used for obtaining pH 7–8.5 and pH 9–10 solutions utilized during experiments.

1.5. Procedure for cloud point extraction

Proposed procedure for cloud point extraction was tested by using the model solution prepared by adding 10 µg of Cr(III), Pb(II) and 5 µg of Cu(II), Ni(II), Mn(II) and Cd(II) to approximately 5–10 mL deionised water in a polyethylene centrifuged tube (max. capacity 25 mL). Then, pH level of this model solution was adjusted to 9.5 by adding 5 mL of ammonium chloride buffer. Subsequently, 3 mL of isopropyl xanthate (4%, w/w) solution was added to the model solution, which was cooled for 20 min at +4 ◦C in refrigerator. Then it was centrifuged for 20 min at 2500 rpm. Surfactant-rich and aqua phases were separated by simple decantation. Surfactant-rich phase was diluted with 1.0 mL 1.0 mol L^{-1} HNO_3 in methanol to decrease the viscosity. At the end, the final volume reached 5 mL by adding 1.0 mol L^{-1} HNO_3 solution. Metal concentration of final solution was determined by flame atomic absorption spectrometer in acetylene/air flame. The calibration curves were developed under the optimum conditions of the cloud point extraction procedure.

1.6. Analysis of real samples

50 mL water was placed into a centrifugation tube. 1 mL of 4.0 % isopropyl xanthate solution was added to each sample in order to form an isopropyl xanthate precipitate and co-precipitation. pH of this solution was adjusted to 9 by adding NH_4Cl. The tube was kept for 20 min. The precipitate was centrifuged at 2500 rpm for 20 min and the supernatant was discarded. A small precipitate adhered to the bottom of the tube. Then, 1mL of 1 mol L^{-1} HNO_3 was added to dissolve the precipitate. At the end, an amount of 5.0 or 10.0 mL solution was obtained by adding 1 mol L^{-1} HNO_3. The analyte ions in this solution were determined by flame atomic absorption spectrometer.

2. Results and discussion

To determine the optimal condition for maximum extraction efficiencies of analytes, some analytical parameters including pH, surfactant concentrations, incubation temperature, sample volume, and interfering ions were examined.

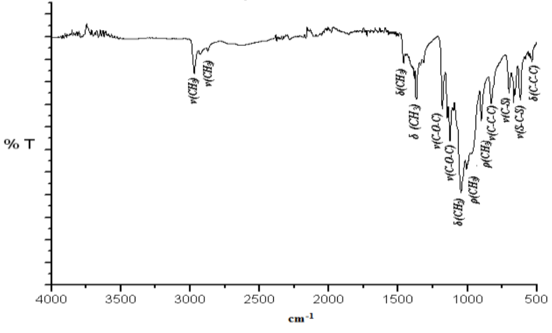

Fig. 1. FTIR spectrum of xanthate

The metal complex of the xanthate is given by in figure 2 and also FTIR spectrum is given by figure 1. The C-S vibrations are observed at 669-617 cm^{-1}, the C-O-C vibration is observed at 460 cm^{-1}, the C-C-O vibrations are seen at 394-363 cm^{-1}, and also the characteristic vibration of the O-C-S is observed at 280 cm$^{-1.}$

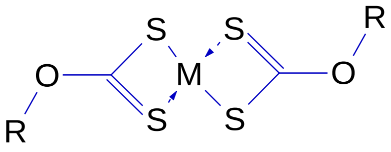

Fig. 2. Metal-xanthate complex

1.1. *Effect of pH*

The effect of pH on the extraction systems was investigated for the range of 2–10. The micelles phase has not occurred between pH 2 and 6. The results are illustrated in Fig. 3. Optimum pH for proposed extraction system was obtained to be 9.

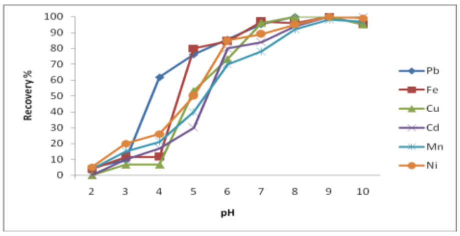

Fig. 3. Effects of pH on the recoveries of analyte (*N*= 3)

1.2. *Effect of isopropyl xanthate*

The concentration of surfactant that is used in the CPE is a critical factor. Thus, the amount of isopropyl xanthate was investigated for the range of 2-7 mL (4%, v/v) for extraction performance. The results are illustrated in Fig. 4. At zero point isopropyl xanthate concentration, absorbance of metals was also zero. Absorbance values of analyte metal ions were approximately the same between 3 and 6 mL of surfactant (5.0 mL of 4% (v/v) isopropyl xanthate was used).

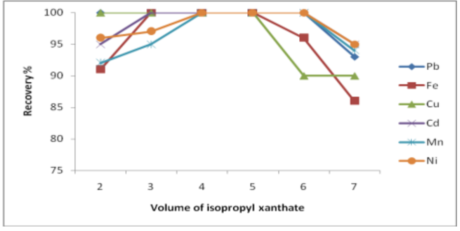

Fig. 4. Volume of isopropyl xanthate on the recoveries (*N*= 3).

1.3. *Effect of temperature*

In cloud point extraction system, extraction temperature is a crucial parameter for micelleus formation. The effect of equilibration temperature was investigated from 30˚C to 50 ˚C. It has been observed that the separation of the two phases was not complete at temperatures lower than 40 ˚C. Over 40 ˚C, the recoveries had approximately the same value (Fig. 5). The incubation time was kept at 20 minutes, which is sufficient for the completion of the physicochemical processes. Thus incubation temperature was determined to be 40 ˚C.

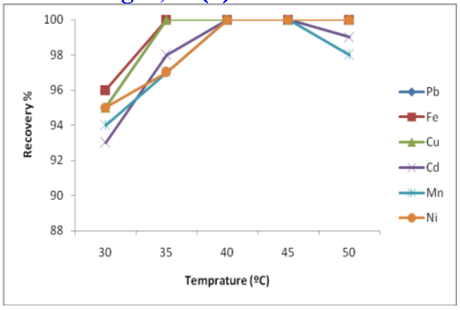

Fig. 5. Effect of temperature (N=3).

2.1. *Effect of standing time in refrigerator*

The effects of standing time in refrigerator for cloud point extraction on the recoveries of analytes were also examined. The results are given in Fig. 6. Analyte ions were quantitatively recovered between 15 and 25 min of standing times. After 10 mL, the recovery values were not quantified. For further studies, standing time for cloud point extraction was selected as 20 min.

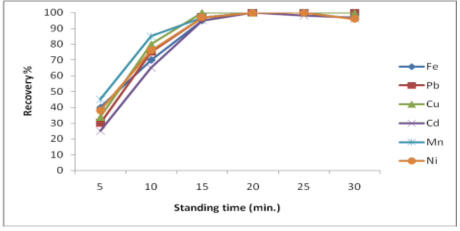

Fig. 6. Effect of standing time in refrigerator (N=3).

2.2. *Centrifuge time*

The effects of centrifuge time on the recoveries of the analyte ions were examined for the range of 5–30 min at 2500 rpm. The results are illustrated in Fig. 7. Quantitative recoveries were obtained for all analytes in the range of 15–30 min. Subsequent works were performed using 20 min as centrifuge time.

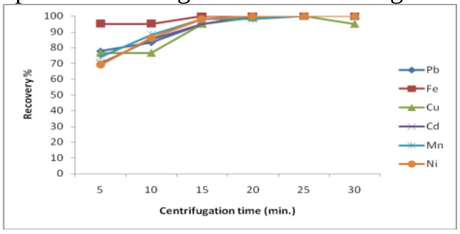

Fig. 7. Centrifuge time (N=3).

2.3. *Centrifuge velocity*

The effects of centrifuge velocity on the recoveries of the analyte ions were examined for the range of 1000-3000 rpm. The results are illustrated in Fig. 8. Quantitative recoveries were obtained for all analytes in the range of 1500–3000 rpm. All subsequent works were performed at 2500 rpm as centrifugation velocity.

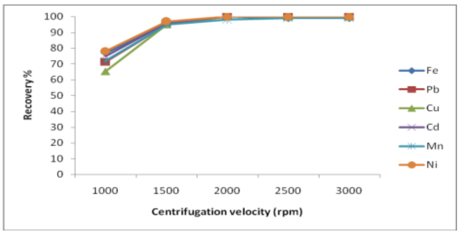

Fig 8. Centrifuge velocity (N=3).

2.4. *Effect of sample volume*

Sample volume might be one of the important analytical factors to obtain high pre-concentration. The effect of sample volume was examined for sample volume range of 5-10–400 mL (Fig. 9). Investigated trace metal ions were recovered quantitatively in all ranges (5–400 mL).

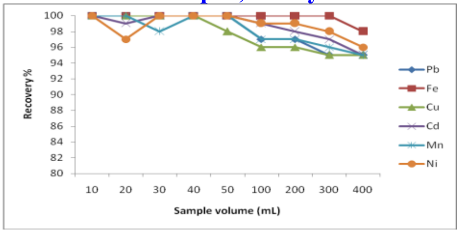

Fig. 9. Effects of volume on the recoveries (N=3).

1.4. *Interferences*

The interferic effects of cation and anion were examined under optimized conditions. The results showed that metal recoveries were almost quantitative in the presence of examined matrix ions (Table 2). The quantitative recovery was between 95-105%.

Table 2 Tolerance levels of the matrix ions (*N*=3).

Matrix Ion	Element Pb	Fe	Cu	Cd	Mn	Ni
NO_3^{2-}	2000	2000	2000	1500	1000	1500
Na^+	10000	10000	15000	15000	10000	10000
Al^{3+}	75	75	100	50	50	50
Cl^-	8000	10000	10000	8000	6000	8000
$SO4^{2-}$	1000	1000	1000	1000	1000	1000
Mg^{2+}	800	1000	1000	1000	800	1000
Ni^{2+}	20	30	30	30	20	-
K^+	2000	3000	3000	3000	2000	3000
PO_4^{2-}	800	800	1000	800	800	800
Fe^{2+}	15	-	25	15	15	15
Cr^{3+}	20	30	30	10	10	20
Zn+	20	20	20	20	20	20
Ca^{2+}	2000	2000	3000	2000	2000	2000
Cu^{2+}	20	30	-	20	20	20
Pb^{2+}	-	20		20	20	20

1.5. *Detection limits*

In model solutions, standard deviations of atomic absorption spectrometric measurements for analyte ions were between 0.3 and 1.7 %. The detection limits, which were set as three times the standard deviation (n = 10) of the blank sample are displayed at Table 3. The detection limits (3σ) of Pb(II), Fe(III), Cu(II), Cd(II), Mn(II) and Ni(II) were 0.5, 0.3, 0.7, 1.5, 0.8 and 1.7 μgL^{-1}, respectively.

Table 3 Limit of detection values for the analytes (N= 10).

Analytes	Limit of dedection (mgL^{-1})
Pb	0.5
Fe	0.3
Cu	0.7
Cd	1.5
Mn	0.8
Ni	1.7

1.6. *Analysis of standard reference materials*

The cloud point extraction procedure, presented in this study, was applied to Bovine Liver 1577-b of Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) and Ni(II) ions. The results are given in Table 4. Most of the results are in line with the certificated values except cadmium, nickel and lead. The relative standard deviations of Fe(III), Cu(II), and Mn(II) are lower than 10.0.

Table 4 Application of the method to the standard reference materials (*N*=3).

Element	Bovine Liver 1577-b Certified value (μg/g)	Observed value (μg/g)
Pb	0.129 ± 0.004	BDL
Fe	184 ± 15	187 ± 10
Cu	160 ± 8	157 ± 7
Cd	0.500 ± 0.030	BDL
Mn	10.5 ± 1.7	10.2 ± 2.5
Ni	-	-

BDL, below the detection limit.

$^* x \pm t.s./\sqrt{5}, p = 0.95$.

1.1. *Analysis of real samples*

The cloud point extraction procedure was applied to the separation and determination of Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) and Ni(II) in different water samples. The results are given in Table 5. In order to show the validity of the methodology, trace elements such as Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) and Ni(II) were also tested with real water samples. The results are tabulated in Table 5.

Table 5 Levels of analyte ions in various samples after application of precipitation Procedure (*N*=5).

Table 5 Levels of analyte ions in various samples after application of coprecipitation procedure (N=5).

Sample	Concentration (mg/L) Fe	Pb	Cu	Cd	Mn	Ni
Gölcük(Creater lake)	0.30(±0.1)[a]	0.73(±0.2)	0.75(±0.2)	BDL	0.82(±0.2)	BDL
Beypınarı(Spring water)	0.20(±0.1)	0.81(±0.4)	BDL	BDL	BDL	BDL
Arpaözü(Spring water)	0.20(±0.1)	BDL	BDL	BDL	BDL	BDL
Kuşkayası(Spring water)	0.20(±0.1)	BDL	BDL	BDL	BDL	BDL
Çayıralan(Spring water)	0.22(±0.1)	0.73 (±0.3)	BDL	BDL	BDL	BDL
İncesu(Barrage)	BDL	0.53(±0.1)	BDL	BDL	0.84(±0.3)	BDL

BDL: below the detection limit.

[a] Mean ± S.D.

2. Conclusion

The proposed cloud point extraction method, which is using isopropyl xanthate as surfactant, is proven to be an efficient, simple and rapid separation and pre-concentration method that can be used for Pb(II), Fe(III), Cd(II), Mn(II), Cu(II) and Ni(II) in several matrices and water samples. Effects of the extraction procedure were investigated for analytical parameters such as pH, surfactant concentration and incubation temperature and matrix ions. The accuracy of the method was assessed through recovery experiments and reference materials. Pre-concentration factor (80) of the developed method is better than other methods. The detection limits of the method are comparable with the literature, such as cloud point extraction, solid-phase extraction and co-precipitation [28–30]. Simultaneous separation and pre-concentration of all six elements is one of the most important advantages of the proposed method, which has been applied on different matrices.

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