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# Determination of lead and cadmium in water samples by cloud point extraction prior to flame atomic absorption spectrometry determination

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## Abstract

Pb and Cd in water samples were determined by cloud point extraction (CPE) with sodium diethyldithiocarbamate (DDTC) as the chelating agent and octylphenoxypolyethanl (Triton X-114) as the surfactant prior to flame atomic absorption spectrometry (FAAS) determination. The main factors of affecting the extraction and detection processes were optimized. The preconcentration of 10 mL of standard solutions gave enhancement factors of 35 and 75 and the detection limits of 9.41 and 0.40 ng mL$^{-1}$ for Pb and Cd, respectively. The proposed method was applied satisfactorily to the determination of Pb and Cd in seawater and lake water. Good agreement was obtained between the added and measured analyte amounts through the recovery of experiments.

***Keywords:*** Cloud point extraction; Flame atomic absorption spectrometry; Lead; Cadmium; Diethyldithiocarbamate

## 1. Introduction

Pb and Cd are at the top of the most toxic elements in environment. The excessively intake of Pb and Cd, even in low levels, can lead to serious problems and hazardous risks for humans, plants and animals. Pb and Cd elements in water are mainly from the waste water produced by metallic mine, smelt factories, battery factories and other chemical plants which pollute the water resources seriously. Hence, the determinations of trace Pb and Cd in water samples is increasing importance in order to monitor the quality of water resources and decrease the harm to humans, plants and animals.

As to the determination of metal elements, although flame atomic absorption spectrometric (FAAS) method is a powerful analytical tool for determining trace metal elements, the direct determination of trace Pb and Cd in water samples is difficult due to various factors, particularly low concentration and matrix effects. Therefore, in order to achieve accurate, reliable, and sensitive results, a preconcentration step is essential prior to analysis. The widely used techniques for preconcentration of Pb and Cd include: coprecipitation [1, 2], solid-phase extraction [3], solvent extraction [4], ion-exchange [5], membrane filtration [6], cloud point extraction [7, 8] and so on. Among these methods, cloud point extraction (CPE) has become a widely researched method for the preconcentration of trace metal elements because it is a safe, simple, rapid and inexpensive method compared with other common preconcentration methods.

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In recent years, CPE has been used for the extraction and preconcentration of many common metal ions: Cu, Hg, Co, Ni, Pb, Fe [9-14] and even rare metal ions: Dy, La, Eu, Lu, U, Th, Zr, Hf [14-16]. Meanwhile, CPE is also used for the treatment of contaminated environmental compartments, particularly water samples and soils.

In CPE for metal preconcentration studies, the surfactant and the chelating agent chosen are critical in attaining highest extraction percentages. As to various surfactants, octylphenoxypolyethanl (Triton X-114) is a more popularly used surfactant because of its low cloud point, high viscosity, low toxicity and cost. Diethyldithiocarbamate (DDTC) used in this work as the chelating agent can complex with some metal irons fast, such as Mn, Zn, Fe, Co, Ni, Cu, Cd, Pb and Hg [17]. It also has ever been used in CPE to complex with Cd, Cu and Ni [18, 19]. Making a comprehensive view of the forgoing statement, we made an extended and further study to determine the levels of Pb and Cd in environmental water samples.

In this paper, Pb and Cd were determined by CPE with DDTC as the chelating agent and Triton X-114 as the surfactant prior to FAAS determination. The main factors affecting the cloud point extraction were investigated in detail. Phase separation can be achieved at relatively low temperature without using electrolytes and the extraction efficiencies are high resulting in low detection limits and high enrichment factors. The accuracy is assessed by means of recovery experiments. The developed method was applied to the determination of Pb and Cd in seawater and lake water with satisfactory results.

## 2. Experimental

### *2.1. Materials*

The nonionic surfactant octylphenoxypolyethanl (Triton X-114) was obtained from sigma and was used without further purification. 5% (w/v) Triton X-114 solution was made that 5.0 g of Triton X-114 was dissolved in a 100-mL volumetric flask with doubly distilled water filled to the mark. Stock standard solutions of 1000 mg $L^{-1}$ metal ions of Pb and Cd were prepared by dissolving appropriate amounts of nitrate salts in 1.0% nitric acid. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Mg, Na Ca, K, Al, Fe, Co, Ni, Cu, Zn and Mn, which were used in interference HPO study, were made with respective stock standard solutions prepared with their metal nitrate salts or chloride salts through appropriate dilution. A solution of $1.0\times10^{-3}$ mol $L^{-1}$ of sodium diethyldithiocarbamate (DDTC) (analytical reagent grade, Guangzhou Chemical Reagent Factory) was prepared by dissolving of appropriate amounts of this reagent in ethanol. A stock buffer solution was prepared by dissolving appropriate amounts of $K_{24}$ and $KH_2PO_4$ (analytical reagent grade, Sinopharm Chemical Reagent Com. Ltd) in doubly distilled water. All the other reagents were of analytical reagent grade. Water was doubly distilled.

### *2.2. Apparatus*

A 3200 flame atomic absorption spectrometer (Analysis Instrument Factory of Shanghai, Shanghai, China) and cadmium and lead hollow-cathode lamps (KY-1, Electric and Optic Apparatus Com. Ltd., Shanghai, China) as radiation sources, was used to measure absorbances of all analytes. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The air and the acetylene flow rates, the burner height and the lamp current were adjusted in order to obtain the maximum absorbance signal. A centrifuge (Model 0406-1, Shanghai Surgical Instruments Factory, Shanghai, China) was used to accelerate the phase separation. A PHS-3C digital pH meter with a combined glass and calomel electrode was used to adjust the pHs of all sample solutions and to make buffer solutions. A galvanothermy thermostatic bather was used to control the desired temperature so as to achieve the phase separation. A KQ218 ultrasonic cleaning (Kunshan Ultrasonic Instruments Com. Ltd, Jiangsu, China) was used to complete dissolution of the final extract into the dilution solution. Vessels used for trace analysis were soaked in 10% nitric acid for at least 24 h and washed.

### 2.3. Recommended procedure

For cloud point extraction, aliquots of 10 mL of the standard or sample solution containing the analyte, DDTC and Triton X-114 buffered at a suitable PH were left to stand in a thermostated bath for suitable temperature and time. Separation of the two phases was accomplished by centrifuging at 3500 rpm for 10 min. On cooling in an ice-bath, the surfactant-rich phases became viscous and were retained at the bottom of the tubes. The aqueous phases can be easily discarded by inverting the tubers. In order to decrease the viscosity of the surfactant-rich phases and facilitate the aspiration prior to the FAAS determination, 0.05 mL of an acidified methanol solution of containing 0.10 mol $L^{-1}$ $HNO_3$ was added to the surfactant-rich phase and then put the obtained solutions into an ultrasonic cleaning bath for 1.0 min to ensure the complete dissolution of the final extracts. The samples were introduced into flame by conventional aspiration.

## 3. Results and discussion

### 3.1. Effect of pH on CPE

Because the pH plays an important role in metal complex formation and subsequent extraction, pH of the analyte solution is a critical factor and should be optimized. The effect of pH upon the complexes formation was studied using sodium acetate solution by addition of NaOH (0.2 mol $L^{-1}$) or HCl (0.5 mol $L^{-1}$) solution to adjust pHs. Fig. 1 shows the effect of pH on the analytical signals of the cloud extraction of Cd and Pb complexes. It can be seen that the extraction was almost quantitative in the range of pH 8.9-10 for Pb and pH 8.0-9.4 for Cd. Hence, the value of pH 9.0 was chosen for both of the analytes.

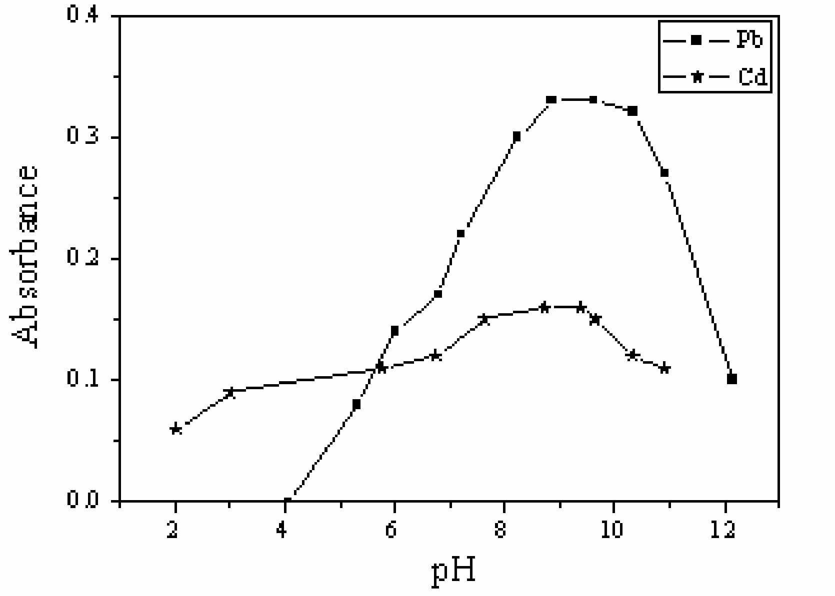

**Fig. 1.** Effect of pH on CPE, conditions: 300 ng $mL^{-1}$ Pb, 5 ng $mL^{-1}$ Cd; $1.0\times10^{-7}$ mol $L^{-1}$ DDTC; 0.07% (w/v) Triton X-114; equilibrium temperature 45 °C; equilibrium time 15 min.

### 3.2. Effect of amount of DDTC

The concentration of the chelating agent has to compensate sufficiently for any consumption of the reagent by metals. The effect of the amount of DDTC on the analytical signal was examined and the results are shown in Fig. 2, which shows the variation of absorbances of the analytes as a function of DDTC concentration from $1.0\times10^{-10}$ to $5.0\times10^{-7}$ mol $L^{-1}$. The absorbance reaches near quantitative extraction efficiency following the increase of DDTC concentration up to a $5.0\times10^{-8}$ mol $L^{-1}$ for both Pb and Cd. Hence a DDTC concentration of $1.0\times10^{-7}$ mol $L^{-1}$ was chosen for subsequent experiments.

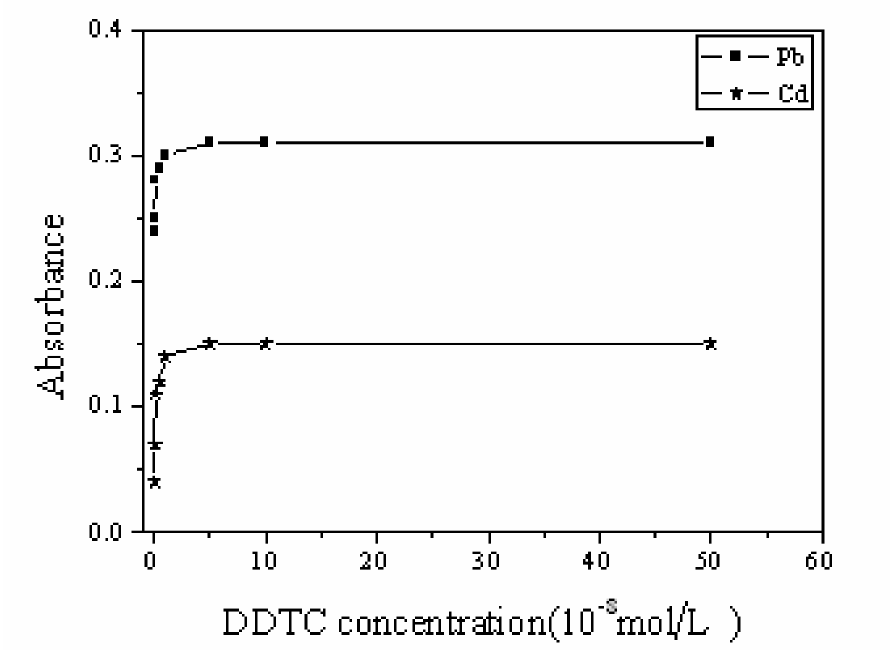

**Fig. 2.** Effect of amount of DDTC on CPE, conditions: 300 ng $mL^{-1}$ Pb, 5 ng $mL^{-1}$ Cd; pH=9.0; 0.07% (w/v) Triton X-114; equilibrium temperature 45 °C; equilibrium time 15 min.

### *3.3. Effect of Triton X-114 concentration*

A successful cloud point extraction procedure should maximize the extraction efficiency by minimizing the phase volume ratio, which improves its concentrating ability [20]. The effect of Triton X-114 concentration was investigated between 0.04 and 0.4% (w/v) and the results was shown in Fig. 3. Quantitative extraction was observed when the Trion X-114 concentration reached 0.05% for Cd and Pb. With the increase of Trion X-114 concentration, the signals became to decrease, which can be explained that an increase in surfactant amount also increases the volume of the micellar phase that makes the concentration of the analyte in the enrichment phase decrease and the viscosity of the surfactant phase increase. Hence larger amount of the surfactant made the absorbance decrease. The concentration of 0.07% (w/v) was chosen for subsequent experiments.

### *3.4. Effect of the equilibration temperature and time*

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. Temperature seems to play an additional role in enhancing preconcentration efficiency, as it is reported that applying elevated temperatures leads to dehydration of the micelle, increasing the phase–volume ratio and thus the signal enhancement [21]. On the other hand, it appears that the phase volume ratio of non-ionic surfactants decrease as the equilibration temperature increase just as Safavi et al. reported [22]. Fig. 4 shows the effect of equilibration temperature on CPE. The cloud point temperature appeared at 25 °C, without adding electrolyte. The equilibration temperature of 45 °C is chosen for both analytes.

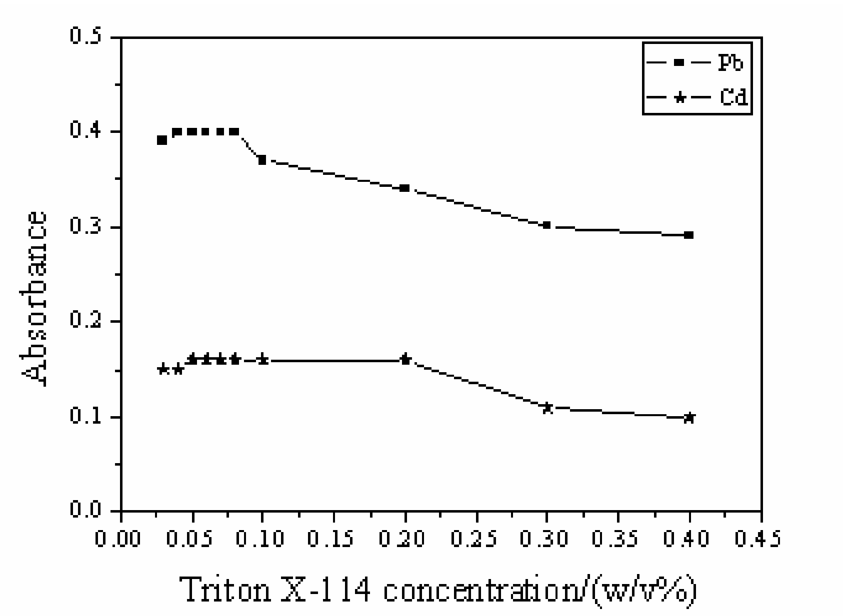

**Fig. 3.** Effect of Triton X-114 concentration on CPE, conditions: 300 ng mL$^{-1}$ Pb, 5 ng mL$^{-1}$ Cd; 1.0×10$^{-7}$ mol L$^{-1}$ DDTC; pH=9.0; equilibrium temperature 45 °C, equilibrium time 15 min.

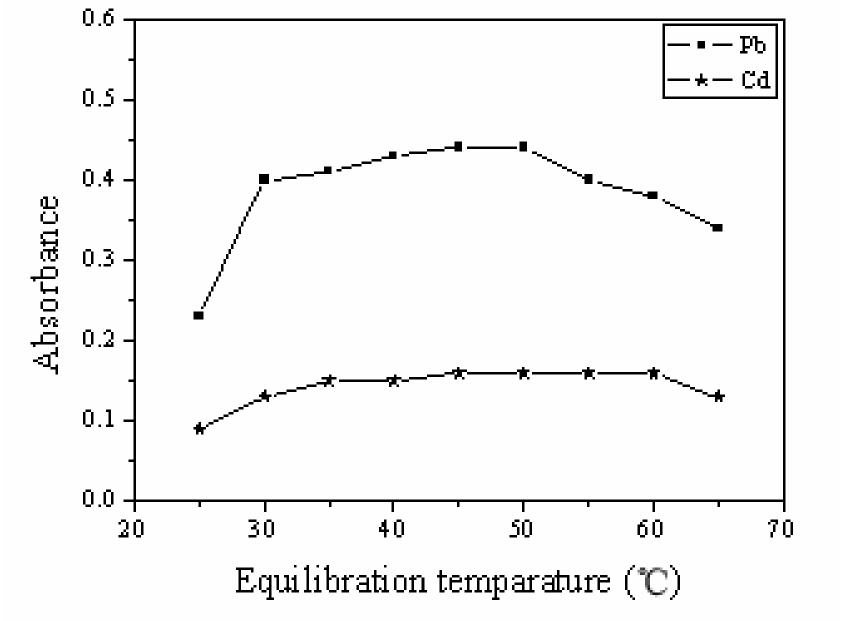

**Fig. 4.** Effect of equilibration temparature on CPE, conditions: 300 ng mL$^{-1}$ Pb, 5 ng mL$^{-1}$ Cd; 1.0×10$^{-7}$ mol L$^{-1}$ DDTC; 0.07% (w/v) Trion X-114; pH=9.0; equilibrium time 15 min.

### *3.5. Effect of the equilibration temperature and time*

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. Temperature seems to play an additional role in enhancing preconcentration efficiency, as it is reported that applying elevated temperatures leads to dehydration of the micelle, increasing the phase–volume ratio and thus the signal enhancement [21]. On the other hand, it appears that the phase volume ratio of non-ionic surfactants decrease as the equilibration temperature increase just as Safavi et al. reported [22].

Fig. 4 shows the effect of equilibration temperature on CPE. The cloud point temperature appeared at 25 °C, without adding electrolyte. The equilibration temperature of 45 °C is chosen for both analytes. The equilibration and centrifugation times were studied within the range of 5-25 min. Times of 15 and 10 min were chosen as optimal times for equilibration and centrifugation, respectively.

### *3.6. Effect of viscosity on the analytical signals*

Since the surfactant-rich phase obtained after CPE is very viscous owing to the high concentration of Trion X-114, methanol solution containing 0.10 mol $L^{-1}$ nitric acid was used to dissolve the surfactant rich phase in this work. The obtained solutions were then put into an ultrasonic cleaning bath for 1.0 min to complete absolutely dissolution of the final extracts. There is an optimum volume for added methanol solution with respect to the analytical signals. If added volumes of methanol solution are not enough, the signals are lower owing to the greater viscosity, however for larger added volumes, the surfactant rich phases were excessively diluted resulting that the absorbances decreased. The volume of 0.05 mL was chosen as the optimum volume for both of the two analytes through comparing the analytical signals obtained by adding different volumes of acidified methanol solution.

### *3.7. Characteristics of the method*

Analytical characteristics of the proposed CPE-FAAS for Cd and Pb were summarized in Table 1. The calibration curves were obtained by preconcentrating 10 mL of standard solutions under the optimum experimental conditions. Table 1 shows the parameters of calibration graphs, the detection limits calculated as three times the standard deviation (3σ) of the blank signal and the enhancement factor defined as the concentration ratio of analyte in the final diluted surfactant rich phase extracted ready for FAAS determination and in the initial solution. Further improvement in enhancement factor is also feasible, either by increasing the amount of the sample solution or/and by suitably decreasing the amount of the diluting agent.

**Table 1**
Analytical characteristics of the method.

| | Pb | Cd |
|---|---|---|
| Linear range (ng $mL^{-1}$) | 0-300 | 0.5-35 |
| r | 0.995 | 0.996 |
| R.S.D. (%) (n=5) | 3.16 (90) [a] | 7.58(2.5) |
| LOD [b](ng $mL^{-1}$) | 9.41 | 0.40 |
| Enhancement factor [c] | 35 | 75 |

[a] Values in parentheses are the $Pb^{2+}$ and $Cd^{2+}$ concentrations (ng $mL^{-1}$) for which the R.S.D. was contained.

[b] L.O.D.: calculated as the ratio of three times the standard deviation (3σ) of the blank signals with the slope (S) of the linear equation, which can be showed as the expressions of 3σ/S.

[c] Enhancement factor: the absorbance ratio of analyte in the final diluted surfactant-rich extract for FAAS determination and in the initial solution.

### *3.8. Interferences*

The effect of foreign ions on the determination of Pb and Cd by the proposed method was investigated. An ion was considered as an interferent when it caused a variation in the absorbance of the sample greater than ± 5%. To perform this study, 10 mL of solution containing Pb (300 ng $mL^{-1}$) or Cd (5 ng $mL^{-1}$) and interferent ions in different interferent-to-analyte ratios were tested under the optimum conditions. The effect of foreign ions was shown in Table 2. As the results show large excess amounts of common cations and anions do not interfere on the determination of trace quantities of Cd and Pb by considering the concentration range of elements in water samples.

**Table 2**
Effects of foreign metal ions on the preconcentration and determination of Pb (300 ng mL$^{-1}$) and Cd (5 ng mL$^{-1}$) promising the recovery of 95-105%.

| Ions | Ion/Pb ratio (w/w) | Ion/Cd ratio (w/w) |
|---|---|---|
| $Cl^-$ | 10000 | 10000 |
| $SO_4^{2-}$ | 800 | 1000 |
| $PO_4^{3-}$ | 1000 | 1000 |
| $CO_3^{2-}$ | 1000 | 800 |
| $K^+$ | 4000 | 1000 |
| $Na^+$ | 4000 | 1000 |
| $Ca^{2+}$ | 2000 | 1000 |
| $Mg^{2+}$ | 2000 | 100 |
| $Al^{3+}$ | 2000 | 100 |
| $Mn^{2+}$ | 100 | 100 |
| $Fe^{3+}$ | 100 | 100 |
| $Co^{2+}$ | 80 | 50 |
| $Ni^{2+}$ | 80 | 50 |
| $Cu^{2+}$ | 80 | 50 |
| $Zn^{2+}$ | 80 | 50 |
| $Cd^{2+}$ | 80 | - |
| $Pb^{2+}$ | - | 50 |

### *3.9. Determination of Pb and Cd in water samples*

The proposed method was applied to assess the contents of Pb and Cd in seawater and river water. Water samples were filtered to remove suspended particulate matter and then 10 mL of each of the samples were preconcentrated under the optimum conditions. In addition, to estimate the accuracy of the method, different certain amount of the analytes were added to 10 mL samples and the resulting solutions were submitted to the preconcentration procedure. The results are given in Table 3. Good agreement was obtained between the added and measured analyte amounts. It can be seen that recoveries in the range of 93.9-104.0% were obtained. So the accuracy of the proposed method was confirmed.

**Table 3**
Analytical results for Pb and Cd in water samples.

| Cations | Samples | Added (ng mL$^{-1}$) | Found (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| Pb | Sea water | 0 | 3.98 ± 0.00 | - |
| | | 144 | 148 ± 3.85 | 98.4 |
| | | 287 | 281 ± 7.70 | 96.6 |
| | Lake water | 0 | 8.26 ± 3.11 | - |
| | | 144 | 143 ± 6.67 | 93.9 |
| | | 287 | 288 ± 3.85 | 97.4 |
| Cd | Sea water | 0 | 0.58 ± 0.14 | - |
| | | 2.39 | 2.97 ± 0.19 | 99.8 |
| | | 4.76 | 5.40 ± 0.00 | 101 |
| | Lake water | 0 | 1.25 ± 0.00 | - |
| | | 2.39 | 3.63 ± 0.51 | 99.7 |
| | | 4.76 | 6.18 ± 0.38 | 103 |

## 4. Conclusion

A new method for determination of Pb and Cd in water samples is proposed by CPE with DDTC as the chelating agent and Triton X-114 as the surfactant prior to FAAS determination. Phase separation can be achieved at relatively low temperature without using electrolytes and the extraction efficiencies are high resulting in low detection limits and high enrichment factors. The accuracy is assessed by means of recovery experiments. The results show the utility and validity of the proposed method for the analysis of environmental water samples. This procedure may well be extended to other metal elements in water samples that can form complexes with DDTC.

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