Turk J Chem
32 (2008) , 431 – 440.

Solid Phase Extraction of Cadmium in Edible Oils Using Zinc Piperazinedithiocarbamate and Its Determination by Flame Atomic Absorption Spectrometry

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Received 18.12.2007

A method was developed for preconcentration of cadmium with zinc-piperazinedithiocarbamate (ZnPDC) in edible oils and its determination by flame atomic absorption spectrometer (FAAS). The preconcentration method is based on the adsorption of the Cd(II) on to ZnPDC and the elution of them with mercury(II) nitrate. The accuracy of the method was tested with standard reference material (CONOSTAN S-21) and Cd added samples. Under optimum conditions, the recovery and the detection limit for cadmium were 99.67% (± 0.67) and 0.028 mg/L, respectively. The calibration curve was linear over the concentration range 0.1-3.0 mg/L ($r^2 = 0.9979$). The proposed method was applied to the oil standard and commercial edible oils.

Introduction

Many separation and preconcentration methods have been proposed for the determination of trace metals in various samples, including coprecipitation,[1,2] solvent extraction,[3,4] biosorption,[5,6] solid phase extraction,[7−13] electrochemical deposition,[14] and cloud point extraction.[15,16] Among the preconcentration methods, solid phase extraction (SPE) is one of the most effective multi-element preconcentration methods for trace metal analysis in edible oil, because of its simplicity, rapidity, and ability to attain a high enrichment factor. In addition, SPE methods remove the oil matrix that causes matrix smoke interference in atomic absorption spectrometry (AAS).

Edible fats and oils are frequently subjected to processing, including refining, bleaching, and deodorization, which inevitably makes the oils come into contact with metallic surface areas, often at high temperatures.[17]

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The content of metals and their chemical forms in edible oils depend on several factors. The metals might originate from the soil and fertilizers and be intimately incorporated in the oil.[18] Many reports have described the deleterious effects that trace metal contamination, particularly iron and copper, have on the flavor and oxidative stability of oil.[17,19,20]

Small amounts of metals in edible oils are well known to have serious deteriorative effects on the stability of these oils. The altered oil characteristics are expressed in changes in color, odor, and flavor. Copper and iron in particular greatly reduce the oxidative stability of oil. Therefore, accurate determination of trace metal contents is very important in evaluating deteriorating effects.[21]

Cadmium is a highly toxic element that accumulates in biologic systems and has a long half-life. Cadmium is not an essential element in plant nutrition; it is easily transferred from soil to plants, which are increasingly contaminated by cadmium from phosphate-based fertilizers.[22] Cadmium can also be present in edible oils and fats, as a result of contamination from the environment, the refining process, the storage tank, or the packing material (e.g., as a colorant or stabilizer in plastics).[23]

Fats and oils are particularly difficult to analyze for trace metals. Many of the usual methods of wet digestion are not recommended for use with high fat material because of associated safety hazards. The convenient direct method (solvent diluted oil samples are aspirated directly into an atomic absorption flame) is not sensitive below 0.3 ppm of each metal and is not suitable for solid fat or shortening samples. Determination of Cu in oil samples by direct aspiration with organic solvent using flameless atomization techniques gives lower detection limits than atomization with flame, which causes matrix smoke interference and metal volatilization. The char-ashing method is sensitive but inordinately time consuming.[24]

Several workers compared ashing, extraction, and solvent dilution and discussed the advantages and disadvantages of each procedure. Dry ashing is simple and direct, although several elements are partially lost during heating. Wet ashing causes no loss of inorganics but the risk of contamination and explosion (if perchloric acid is used) is higher. Various extraction methods, including acid extraction by hydrochloric acid or nitric acid and acid/EDTA extraction, have been used. Diluting the sample with methyl-isobutyl-ketone (MIBK) reduces the metal concentration, but it has some practical advantages: it is fast and simple, with little chance of contamination. Because of the very low metal contents, enrichment procedures using ashing or extraction methods may be more sensitive than diluting in addition to direct analysis.[21]

The dithiocarbamates, which are the half-amides of dithiocarbonic acid, were discovered as a class of chemical compounds early in the history of organo-sulfur chemistry. The N-substituted dithiocarbamates have found considerable use in analytical methods for heavy metals.[25] The dithiocarbamate extraction method has been one of the most widely used preconcentration techniques for trace metal analysis by AAS.[26−28]

This extraction method can be generally classified into 2 major categories: (I) Metal-dithiocarbamate complexes have been extracted into oxygenated organic solvents (e.g., MIBK) and the solvents have been analyzed directly. (II) Metal complexes extracted into oxygenated or chlorinated organic solvents (e.g., chloroform, MIBK) have been back-extracted by nitric acid, and the acid solution has been analyzed.

There are several drawbacks associated with the acid-back extraction of metal dithiocarbamates. The kinetics is generally slow and the efficiency of acid extraction is poor. Using a dilute mercury(II) solution instead of nitric acid overcomes the drawbacks mentioned above. This back-extraction method is based on the fact that the extraction constant of mercury(II) dithiocarbamate complexes is much greater than that of most of the common trace metals of environmental importance.[27]

Eckert,[29] in his discussion on the use of dithiocarbamates in heavy metal analysis, gives the order in which the complexes of metals with diethyldithiocarbamate increase in stability as follows: Mn, As(III), Zn, Sn(II), Fe(III), Cd, Pb, Bi, Co(II), Ni, Cu(II), Ag, and Hg(II). Thus, a metal-dithiocarbamate complex will be displaced by any other metal to the right of it in the series. The substitution of mercury(II) for other metals in the form of dithiocarbamate complex is extremely fast and the efficiency of recovery is nearly 100% for a number of metals. In addition, the back-extracted solution contains a low concentration of mercury(II) that is virtually interference free in AAS due to its high volatility.[27]

We report here an analytical method for the determination of Cd in edible oils that has been applied to the analysis of metallic contamination in several commercial edible oils. This method depends on using a solid (powder) zinc-piperazinedithiocarbamate (ZnPDC) for extraction and a mercury(II) nitrate solution for back-extraction to preconcentrate and separate cadmium from oil matrix components prior to the determination by flame atomic absorption spectroscopy (FAAS).

Experimental

Apparatus

An ATI UNICAM 929 flame atomic absorption spectrometer was used under the following conditions: a 10 cm l-slot burner, UNICAM cadmium hollow cathode lamps, an air-acetylene flame, a fuel gas flow of 1.50 L/min, a spectral bandwidth 0.5 nm, a burner height 7 mm, a lamp current of 7 mA, and a wavelength of 228.8 nm.

Reagent and solution

Zinc-piperazinedithiocarbamate (ZnPDC) was prepared according to a method given in the literature.[30] Piperazine (0.1 mol, 8.60 g; Merck, Schuchardt) was dissolved in diethyl ether (100.0 mL) and added to KOH (0.2 mol, 11.20 g; Merck) solution. Then 12.1 mL of carbon disulfide (0.2 mol; 99.5%, Merck) was added dropwise under stirring over 1 h in an ice bath. The mixture containing dipotassium piperazinedithiocarbamate (K_2PDC) was placed into a separatory funnel and the organic and aqueous phases were carefully separated. The aqueous phase containing K_2PDC was added slowly to $Zn(NO_3)_2$ solution (0.2 mol; Merck) at pH 5.0-5.5. The white precipitate ZnPDC was filtered off and washed with deionized water and dried at 60 °C. Then ZnPDC was washed with chloroform, carbon tetrachloride, acetone and n-hexane, in that order, and dried. A schematic diagram of the preparation of ZnPDC is given in Figure 1.

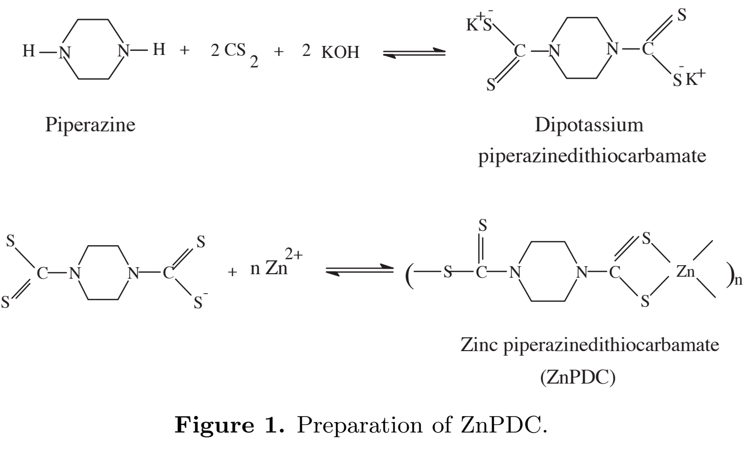

Figure 1. Preparation of ZnPDC.

A calibration graph was obtained by preconcentrating an appropriate amount of CONOSTAN Multi Element Oil Standard S-21 (containing 30 μg g^{-1} cadmium) under the experimental conditions.

Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. Oil samples were commercial purchases. All other reagents were of analytical reagent grade and they were used without further purification.

All glassware and centrifuge tubes were cleaned in concentrated nitric acid and carefully washed with deionized water.

General procedure

First, 20.00 g of edible oil was taken into a centrifuge tube and diluted up to 50 mL with n-hexane. After adding 0.10 g of ZnPDC to the mixture, it was stirred for 45 min. After centrifugation at 2800 rpm, the oil phase was removed with a pipette. The solid product containing the metal complex, which was collected at the bottom of the tube, was washed with n-hexane, acetone, and deionized water, consecutively. Then 2.0 mL of $Hg(NO_3)_2$ (0.3 mmol mL^{-1}; Aldrich, 98%) solution was added, followed by vigorous shaking by hand and then centrifugation. The aqueous phase was kept for FAAS measurements.

Results and Discussion

Although the adsorption mechanism of Cd on solid ZnPDC is not known, we estimate that it is similar to a metal-exchange reaction in the solid-phase extraction method (Figure 2).

$$M^{n+}_{(org)} + Zn(PDC)_{(s)} \rightleftharpoons M(PDC)_{(s)} + Zn^{2+}$$

$$M(PDC)_{(s)} + Hg^{2+}_{(aq)} \rightleftharpoons Hg(PDC)_{(s)} + M^{n+}_{(aq)}$$

Figure 2. Adsorption mechanism of Cd on solid ZnPDC.

Piperazinedithiocarbamate reagent is more suitable than other dithiocarbamates for the solid-phase extraction of metals in an organic matrix, because its chelate is polymeric, stable, and insoluble in water, and numerous organic solvents because of the 2-CS_2 groups.[25]

Convenient extraction and back-extraction parameters for separation and preconcentration of Cd in edible oils with ZnPDC solid-phase extraction were investigated. For the determination of the extraction parameters, oil standard was used.

Effect of amounts of ZnPDC

One gram of oil standard was put into a centrifuge tube and diluted with 3 mL of n-hexane. Increasing amounts of ZnPDC were added and the general procedure was applied. After back-extraction with 10 mL of Hg(II) (0.1 mmol mL^{-1}), the aqueous phase was kept for measurement by FAAS. The optimal amount of ZnPDC necessary for obtaining quantitative adsorption was found to be 0.05-0.10 g for cadmium (Figure 3).

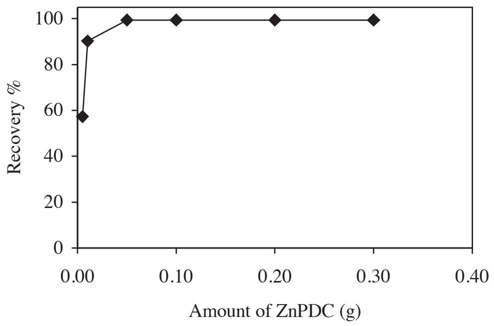

Figure 3. Effect of the amounts of ZnPDC on the recovery of cadmium. Oil standard: 1.00 g, n-hexane: 3 mL, back-extraction: 10 mL of 0.1 mmol mL^{-1} Hg(II). (N: 3).

Effect of organic solvent volume

Viscosity of edible oil is an important factor affecting the extraction efficiency since suspending of ZnPDC in oil causes bad stirring, centrifuging, and separation of the oily phase. For this reason, the viscosity of the oil must be low. For this purpose, 1.00 g of oil standard was diluted with n-hexane to different volumes and the developed method was applied. The ratio of oil to organic solvent should be 1:2 (Figure 4).

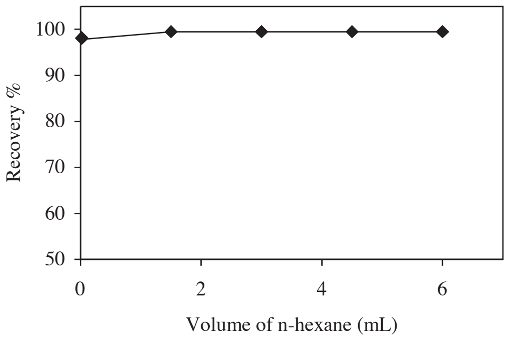

Figure 4. Effect of volume of n-hexane on the recovery of cadmium. Oil standard: 1.00 g, ZnPDC: 0.10 g. Back-extraction: 10 mL of 0.1 mmol mL^{-1} Hg(II). (N: 3).

Effect of extraction time and back-extraction time

For the practical use of the method developed in analysis, extraction time should not be too long. If extraction time is short, extraction yield is poor. Back-extraction time is another important factor for complete removal of trace metals on ZnPDC and for practical use of the method developed in analysis. Consequently, back-extraction time should not be long, but it should be long enough for exchanging of metals quantitatively. The effect of extraction and back-extraction time on the recovery of Cd was examined. The results are given in Figure 5 and 6. These results indicate that the quantitative extraction and back-extractions of Cd are completed in 40-45 min.

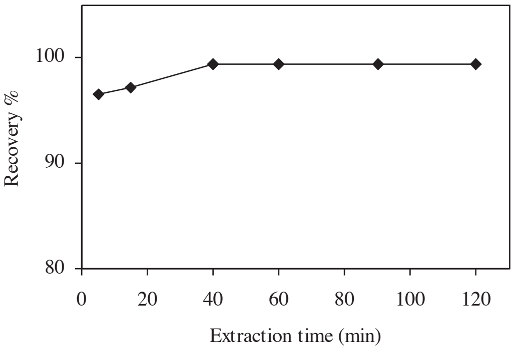

Figure 5. Effect of extraction time on the recovery of cadmium. Oil standard: 1.00 g, n-hexane: 3 mL, ZnPDC: 0.10 g. Back-extraction: 10 mL of 0.1 mmol mL^{-1} Hg(II). (N: 3).

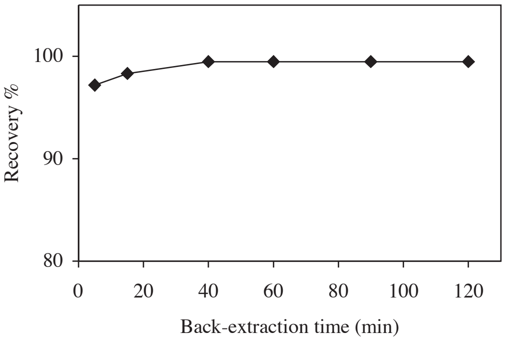

Figure 6. Effect of back-extraction time on the recovery of cadmium. Oil standard: 1.00 g, n-hexane: 3 mL, ZnPDC: 0.10 g. Extraction time: 45 min. Back-extraction: 10 mL of 0.1 mmol mL^{-1} Hg(II). (N: 3).

Effect of amount of Hg(II)

The amount of Hg(II) has a large effect on the recovery of Cd. To obtain quantitative recovery, the optimal amount of Hg(II) was more than 0.50 mmol (Figure 7)

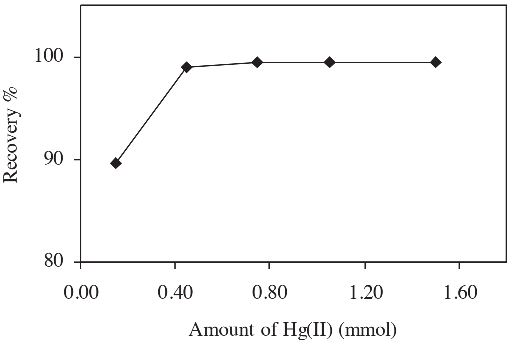

Figure 7. Effect of amount of Hg(II) on the recovery of cadmium. Oil standard: 1.00 g, n-hexane: 3 mL, ZnPDC: 0.10 g. Extraction time: 45 min. Back-extraction time: 45 min. Volume of Hg(II): 10 mL containing different amounts of Hg(II). (N: 3).

Method validation

In order to investigate the percentage recoveries of the proposed method, an appropriate amount of oil standard (1.00 g) was taken and diluted with n-hexane. The Cd content of solution was analyzed according to the procedure. In back-extraction 10 mL of $Hg(NO_3)_2$ (0.15 mmol mL^{-1}) solution was used. The results presented in Table 1 agree with the certified value.

Analytical performance

A calibration curve was constructed. For this purpose, the general procedure was applied to Conostan Multi Element Oil Standard and metal contents of back-extraction solutions were measured by FAAS at 228.8 nm. It was linear over the concentration range of 0.1-3 mg/L cadmium. The correlation coefficient obtained by the least squares method was 0.9979.

The detection limit was evaluated as the concentration corresponding to 3 times the standard deviation of the blank signal. The detection limit of Cd was estimated as 2.8 ng g^{-1}.

Analysis of the real samples

The procedure was applied to the determination of Cd(II) in different oil samples, including corn oil, olive oil, and sunflower oil, by spiking experiments. The results are given in Table 1.

Table 1. Determination of cadmium in spiked oil samples and multi-element oil standard (separation-preconcentration step: 20.00 g of oil, 30.0 mL of n-hexane, 0.10 g of ZnPDC, 2.0 mL, 0.3 mmol mL^{-1} of $Hg(NO_3)_2$).

Name of sample	Calculated cadmium in oil ($\mu g\ g^{-1}$)	Found* cadmium in oil ($\mu g\ g^{-1}$)	Recovery* %
Corn oil	-	7.77 ± 2.14	-
	0.50	0.58	100.0 ± 1.0
	1.00	1.05	97.2 ± 1.3
	1.50	1.55	98.1 ± 1.5
Olive oil	-	8.33 ± 1.65	-
	0.50	0.54	93.1 ± 2.2
	1.00	1.01	93.5 ± 1.2
	1.50	1.54	97.5 ± 1.5
Sunflower oil	-	8.20 ± 1.38	-
	0.50	0.55	94.8 ± 1.2
	1.00	1.01	93.5 ± 0.8
	1.50	1.53	96.8 ± 1.1
CONOSTAN multi-element oil standard (S-21)	30.0	29.9 ± 0.2	-

*Mean of 3 determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$)

In Table 2, the comparison of various methods for analysis of trace metals in different oil samples is given. The commonly used methods for the determination of metals in oil samples have some advantages and disadvantages. Direct aspiration is fast and there is little chance of positive contamination.[18] In addition, an oil-based metal standard must be prepared but it is difficult in routine analyses. On the other hand, AAS suffers from the presence of a complex organic matrix, which causes severe suppression of the analyte signal. Although char-ashing[31,32]gives accurate results for several metals, it is time consuming and recovery is poor. Compared with acid extraction or char-ashing in terms of recovery, extraction time, and efficiency, the proposed method is more advantageous. In this method, metals are both separated from the oil matrix and preconcentrated for determining by AAS. It has the advantage that ZnPDC is insoluble in water and organic solvents. No other adsorbent such as active carbon, naphthalene, or XAD-2 resin is necessary. It may also be used for the preconcentration of trace metals in other organic materials, beverages, or liquids.

Table 2. Comparison of various methods for analysis of trace metals in different oil samples.

Oil sample	Metal	Method	Tec.	DL	PF	Recovery %	Ref.
Olive oil	Al, Cd, Cr, Cu, Mn,Ni, Pb, Fe	Direct injection	ETAAS	10-100 ng g^{-1}	-	95-100	13
Sunflower oil	Cd	Direct aspiration	ETAAS	0.4 ng g^{-1}	-	101	18
Soybean, peanut oil	Cu, Zn	Acid-extraction	ETAAS	9-12 ng g^{-1}	2	81-95	19
Corn, soybean, sunflower oil	Cu	Solid-phase extraction	FAAS	0.24 pg g^{-1}	10	91-96	21
Soybean, glyceride oil	Cu, Fe	Char-ashing	ETAAS	$<$ 9 ng g^{-1}	6	87-98	27
Corn, olive, sunflower oil	Cd	Solid-phase extraction	FAAS	2.8 ng g^{-1}	10	93-100	Present work

HMDC-HMA: N,N-Hexamethylenedithiocarbamic acid-hexamethyleneammonium, PF: Preconcentration factor, ETAAS: Electrothermal atomic absorption spectrometry, EDTA: Ethylenediaminetetraacetic acid, DL: Detection limit

Conclusions

Direct analysis of trace metals in fats and oils by FAAS is difficult due to low concentrations of analytes and effects of the complex organic matrix, which causes suppression of the analyte signal.[33] Therefore, separation-preconcentration procedures may be used for eliminating matrix effects and improving the detection limit. Compared with the acid extraction and direct injection techniques in terms of matrix matching, recovery, and efficiency, the solid-phase extraction procedure with ZnPDC is very simple, rapid, precise, accurate, and reliable for the preconcentration of Cd from edible oils. The method was successfully applied to FAAS determination of Cd in various oil samples. This method also may be used for the determination of cadmium in different organic matrixes, such as engine oil and organic solvents.

Acknowledgment

The authors are grateful for the financial support from the Unit of the Scientific Research Projects of Ondokuz Mayıs University.

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