Determination of Copper in Edible Oils by Atomic Absorption Spectrometry after Lead Piperazinedithiocarbamate Solid-Phase Extraction and Potassium Cyanide Back-Extraction

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A trace level of copper is known to have an adverse effect on the stability of edible oils. The content of copper in edible oils depends on several factors. It might originate from the soil and fertilizers, or it might be incorporated during the production process. Also taking into account its metabolic role, the determination of copper in edible oils is very important. Oils are particularly difficult to analyze by AAS or other methods for trace metals because there are the same type difficulties in sample preparation. Three different techniques are used to analyze copper or other metals (such as Fe, Ni, Co, Zn) in oil. In the first, oil is decomposed by ashing¹ or charring, followed by high-temperature dry ashing.² The ash is then dissolved in a dilute acidic aqueous medium and the metals in the aqueous phase are measured by AAS. In the second method, oil diluted with MIBK,³⁻⁷ MIBK-nitric acid,⁸ tetrahydrofuran,⁹ 1,4-dioxane¹⁰ or BuNH₂-water-THF¹¹ is aspirated directly. In the third method, after the oil is extracted with nitric acid,^{12,13} nitric acid-EDTA^{14,15} or hydrochloric acid,¹⁶ the extracts are analyzed.

Several authors have discussed advantages and disadvantages of these techniques at length.^{15,17} In many cases, although the extraction method has the same advantages in the separation and preconcentration of metals in oil samples, the recoveries are poor for many metals. Moreover, the separation of phases is difficult, the enrichment factor is generally small, and the extraction time is long.

In this work, based on using a solid (powder) Pb-piperazinedithiocarbamate complex (PbPDC) for extraction and a potassium cyanide solution for back extraction, a new method is described for the preconcentration and separation of copper in edible oil samples prior to its determination by FAAS.

Experimental

Apparatus and reagents

An ATI UNICAM 929 flame atomic absorption spectrophotometer was used under the following conditions: A 10 cm 1-slot burner, a UNICAM copper hollow cathode lamp, a wavelength of 324.8 nm, an air-acetylene flame, a fuel gas flow of 1.2 l/min, a spectral bandwidth of 0.5 nm, a burner height of 7 mm, and a lamp current of 6 mA. PbPDC was prepared with potassium salt of piperazinedithiocarbamic acid (K₂PDC) and

Pb(NO₃)₂ according to a method given in the literature.¹⁸ A Cu(II) stock solution (1.000 mg ml⁻¹) in the aqueous phase was prepared by dissolving an appropriate amount of metallic copper (E. Merck, 99.5%) in concentrated nitric acid, evaporating to dryness and dissolving the residue in deionized water and completing up to 1000.0 ml with deionized water. Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. An organic copper stock solution (0.1 mg ml⁻¹) was prepared by dissolving an appropriate amount of copper(II) cyclohexanecarboxylate (Aldrich Chem. Co. 22818-4) in acetone. A dilute organic copper solution was prepared with the organic copper stock solution and acetone (0.01 mg ml⁻¹). Acetone (E. Merck, 99.9%) was purified by distillation. Oil samples were commercial purchases. All other reagents were of analytical reagent grade.

General procedure

First, 50.00 g of oil was taken into a beaker and diluted with 100.0 ml of acetone. After adding 0.50 g of PbPDC into the mixture, it was stirred at 30 min, and then filtered, washed with acetone and deionized water several times. A solid product containing the copper complex was taken into a syringe, and 5.00 ml of a potassium cyanide solution (0.1 mmol ml⁻¹) was added. After it was vigorously shaken by hand at 10 min, filtered by a syringe filter (Millipore SLMA-25 NB with pore-diameters of 0.45 µm), the aqueous phase was collected for a measurement by FAAS.

Results and Discussions

Solid-phase extraction

An appropriate amount of (150.0 ml) organic copper standard solution in acetone was taken, and its copper content was determined according to a general procedure.

The recovery results given in Table 1 show that PbPDC extracts the copper from the organic matrix effectively. Although the adsorption mechanism of copper on solid PbPDC is not known, we estimate that it is similar to a metal-exchange reaction in the solid-phase extraction method, which was applied in water samples.¹⁹

Piperazinedithiocarbamate reagent is more suitable than other

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Table 1 Determination of copper in an organic copper standard solution, spiked oil samples and multi element oil standard

Name of sample	Calculated copper in 5.00 ml final solution/ $\mu\text{g ml}^{-1}$	Found ^a in 5.00 ml final solution/ $\mu\text{g ml}^{-1}$	Recovery, %
Organic copper standard solution	0.50	0.48	96 $\pm$ 4
	1.00	0.97	97 $\pm$ 5
	1.50	1.44	96 $\pm$ 3
Soy bean oil	—	0.48 $\pm$ 0.06	—
	0.98	0.90	92 $\pm$ 7
	1.48	1.35	91 $\pm$ 2
	1.98	1.86	94 $\pm$ 3
Sunflower oil	—	0.57 $\pm$ 0.05	—
	1.07	0.97	91 $\pm$ 5
	1.57	1.46	93 $\pm$ 6
	2.07	1.95	94 $\pm$ 4
Corn oil	—	1.74 $\pm$ 0.08	—
	2.24	2.11	94 $\pm$ 2
	2.74	2.52	92 $\pm$ 5
	3.24	3.12	96 $\pm$ 5
CONOSTAN multi element oil standard (S-21)	3.00	2.97 $\pm$ 0.09	—

a. Mean of three determinations with 95% confidence level ($X \pm ts/\sqrt{N}$).

dithiocarbamates for the solid-phase extraction of copper in an organic matrix, because its chelates are polymeric, stable and insoluble in water, and numerous organic solvents by means of two-CS₂ groups.²⁰

Potassium cyanide is probably eluted by copper as a cyano copper(I) complex ([Cu(CN)₄]³⁻), and does not react with PbPDC.

Calibration curve, detection limit and determination limit

A standard Cu(II) solutions (0 – 10 $\mu\text{g ml}^{-1}$) were prepared with a Cu(II) stock solution and a potassium cyanide solution. The absorbance values of these solutions were measured by FAAS at 324.8 nm and a calibration graph was constructed. It was linear over the concentration range 0 – 6.0 $\mu\text{g ml}^{-1}$ of copper. The correlation coefficient (0.9987) was obtained by a least squares method.

The detection limit (2.4 ng ml⁻¹) and the determination limit (15.2 ng ml⁻¹) were evaluated as the concentration corresponding to three times and ten times the standard deviation of the blank signal, respectively. The blank solution was prepared with 150.0 ml acetone without copper according to the general procedure.

Determination of copper in spiked oil samples

Spiked oil samples were prepared by dissolving 50.00 g of oil in acetone and adding appropriate amounts of the organic copper standard solution (250, 500 and 750 μl) and completing up to 150.0 ml with acetone. The copper contents of these solutions were analyzed according to the procedure described above. The average recovery value in the oil samples with the additional copper content between 0.050 – 0.150 $\mu\text{g g}^{-1}$ was found to be around 93%.

Accuracy check with a standard material

An appropriate amount of (0.50 g) of CONOSTAN Multi Element Oil Standard S-21 (contain 30 ppm copper) was taken

and diluted with hexane. The copper content of the solution was analyzed according to procedure. It was shown that the results presented in Table 1 agreed with the certified value.

Determination of copper in real samples

The method was successfully applied to the determination of copper in some oil samples. Three different commercial oil samples were selected: soy bean oil, sunflower oil and corn oil. After 50.00 g of an oil sample was taken, it was diluted with acetone. The copper content of the solution was analyzed according to the general procedure. The results are given in Table 1.

To determine metals in oils by AAS, it is essential that a method be chosen in which a matched sample and a standard matrix can be prepared. The direct aspiration technique has the same advantages: rapidity and little chance of positive contamination, however, a standard in base oil of the known metal content must be prepared, which is difficult in routine analyses. On the other hand, experience has shown that AAS may be handicapped by the presence of a complex organic matrix, which causes severe suppression of the analyte signal.¹¹ Although the char-ashing technique gives accurate results for several metals, it is time consuming and the recovery is poor.²

Compared with the acid extraction techniques from the point of the recovery, extraction time and efficiency,^{12,15} the proposed method is more advantageous, and can be used for the determination of copper in oil samples by FAAS. It also may be used for the pre-concentration and determination of copper in other organic matrixes, such as organic solvents.

References

- W. G. Mertens, C. E. Swindells, and B. F. Teasdale, *J. Am. Oil Chem. Soc.*, **1971**, 48, 544.
- C. D. Evans, G. R. List, and L. T. Black, *J. Am. Oil Chem. Soc.*, **1971**, 48, 840.
- G. R. List, C. D. Evans, and W. F. Kwolek, *J. Am. Oil Chem. Soc.*, **1971**, 48, 438.
- P. Hocquellet, *At. Spectrosc.*, **1985**, 6(3), 69.
- H. J. Sun, *J. Am. Oil Chem. Soc.*, **1989**, 66, 540.
- M. M. Palvillo, T. Albi, and A. Guinda, *J. Am. Oil Chem. Soc.*, **1994**, 71, 347.
- G. Dalen, *J. Anal. At. Spectrom.*, **1996**, 11, 1087.
- J. T. Olejko, *J. Am. Oil Chem. Soc.*, **1975**, 33, 480.
- J. L. Fabec, *Anal. Chem.*, **1982**, 54, 2170.
- I. Karadjova, G. Zachariadis, G. Boskou, and J. Stratis, *J. Anal. At. Spectrom.*, **1998**, 13, 201.
- C. Lelievre, D. Hennequin, J. F. Lequerler, and D. Barillier, *At. Spectrosc.*, **2000**, 21(1), 23.
- R. A. Jacop and L. M. Klevay, *Anal. Chem.*, **1975**, 47, 741.
- C. M. Elson, E. M. Bem, and R. G. Ackman, *J. Am. Oil Chem. Soc.*, **1981**, 1024.
- H. Ibrahim, *J. Am. Oil Chem. Soc.*, **1991**, 68, 678.
- K. H. Wong, Y. S. Fung, and K. W. Fung, *Analyst*, **1980**, 105, 30.
- F. L. Coco, P. Monnotti, S. Rizzotti, and L. Ceccon, *Anal. Chim. Acta*, **1999**, 386, 41.
- L. T. Black, *J. Am. Oil Chem. Soc.*, **1975**, 52, 88.
- H. Cesur, T. K. Yazicilar, B. Bati, and V. T. Yilmaz, *Synth. React. Inorg. Met.-Org. Chem.*, **2001**, 31, 1271.
- H. Cesur and B. Bati, *Anal. Lett.*, **2000**, 33, 489.
- A. Hulanicki, *Talanta*, **1967**, 14, 1371.