Determination of Lead in Frying Oils by Direct Current Plasma Atomic Emission Spectrometry

Hosny Ibrahim
Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

Two methods for determination of lead in frying oils by direct current plasma-atomic emission spectrometry were investigated. The first method is based on the formation of an oil-water emulsion followed by aspiration of the sample directly into the plasma. The second method involves extraction of lead from oil into an aqueous ethylene diamine tetraacetic acid phase before measurement. The methods were applied to the determination of lead in used frying oil samples collected from different parts of Cairo, Egypt.

KEY WORDS: Atomic absorption spectrometry, direct current plasma-atomic emission spectrometry, emulsion, frying oils, solvent extraction.

The standard procedure for determining lead in oils requires ashing of the sample to obtain an aqueous solution, followed by the analysis of the metal by spectrophotometry, atomic absorption spectrometry or other suitable technique. With vegetable oils, the common ashing techniques are time-consuming and may lead to serious errors due to losses from spattering, foaming and volatilization (1). Dry ashing technique was used by Ybanez (2) for determination of Pb, Cd, Cu and Zn in animal fats by atomic absorption spectrometry. Dijkstra (3) determined trace elements, including lead in oils dissolved in kerosine by direct current plasma emission spectrometry. However, appreciable instability of the instrument was observed and regular measurements were required to detect drift in the output signal. Moffett (4) studied the parameters and conditions required for the determination of lead and other trace metals in palm oil by furnace atomic absorption spectrometry.

The main objective of this study was to develop simple methods for determination of lead in vegetable oils and to assess the degree and extent of lead contamination in used frying oils (cottonseed oil) under circumstances in which lead compounds from automobile exhaust constitute a major source of lead pollution. The study reports the optimum experimental conditions for the use of direct current plasma-atomic emission spectrometry (DCP-AES) in the determination of lead in oils.

EXPERIMENTAL PROCEDURES

Instrumentation. A Spectraspan V Emission Spectrometer (Beckman Instruments, Inc., Fullerton, CA) was used with the standard cross-flow and Echelle grating monochromator. Instrumentation specification and typical operating conditions were followed as cited in the Beckman Handbook (5). The plasma and grating positions were adjusted to maximize the lead emission signal for the 368.4 nm line while aspirating a 10 μg/mL solution of lead into the plasma.

Chemicals and reagents. All reagents were of AnalaR grade and all aqueous solutions were prepared with distilled deionized water. Standard solutions were freshly prepared as required from a stock solution containing 100 μg/mL lead. Working standards of 0.1 and 5 μg/mL of lead as lower and upper standards were prepared by appropriate dilution with 1% v/v nitric acid.

Oil samples containing known amounts of lead were prepared by adding aliquots of a standard lead solution (in xylene) to lead-free vegetable oil. Lead-free oil purchased was the purest grade available and the absence of lead was confirmed by a recommended method (2). Standard lead solution in xylene (100 μg/mL) was prepared by dissolving 0.1830 g of AnalaR lead acetate in 10 mL anhydrous acetic acid and diluting with xylene to one liter.

Emulsogen MS-12 lipophilic surfactant (Hoechst, Frankfurt, Germany) was used as a 10% benzene solution and the 23 lauryl ether (Brij 35) hydrophilic surfactant (Aldrich Chemical Co., Milwaukee, WI) was prepared as a 4% aqueous solution.

Analytical procedures: Emulsion method. In this method the analyte addition technique must be used to increase the analyte content in the emulsion to be in the linear response range of emission signal.

In a 50-mL volumetric flask, about 0.1 g of oil is accurately weighed, followed by the addition of Emulsogen MS-12 solution (2 mL), lauryl ether solution (5 mL) and distilled water (25 mL). After shaking vigorously for 5 min, 1 mL of aqueous standard lead solution (50 ppm) is added along with 1 mL ethanol (to prevent foaming) and made to volume with distilled water. The mixture is shaken again for 2 min and aspirated directly into the plasma.

Emulsions containing known amounts of lead were used for calibration of the instrument.

Extraction method. In a 150-mL separatory funnel, 25 g of oil is accurately weighed, followed by 50 g of aqueous 10^{-3} M ethylene diamine tetraacetic acid (EDTA) solution adjusted to pH 2 with 0.1% v/ nitric acid. The solutions were shaken and equilibrated for 2 hr. After settling, aliquots from the aqueous layer were taken for measurements by DCP. Aqueous standard lead solutions were used for instrument calibration.

Dry ashing method with atomic absorption spectrometry (2). Lead in oil was recovered by dry ashing the sample, dissolving the ash in 4% nitric acid, and determining lead in the solution with a Perkin-Elmer atomic absorption spectrometer (Model 2380, Perkin-Elmer, Norwalk, CT) in an air-acetylene flame at 271.0 nm.

RESULTS AND DISCUSSION

Stability and composition of the emulsion. In the present investigation attempts were made to obtain the optimum hydrophilic-lipophilic balance (hlb) by mixing the Emulsogen MS-12 lipophilic surfactant and the hydrophilic lauryl ether, as described by Hernandez-Mendez (6). Balanced emulsions stable for at least 5 hr are obtained when they contain 0.4% of each lipophilic and hydrophilic surfactant. The optimum oil-water ratio is conditioned by the sensitivity of DCP measurements and the stability of the

TABLE 1

Recovery of Lead from Oil by Direct Current Plasma and Atomic Absorption Spectrometry

Lead content (μg/g)	Lead found by analysis					
	μg/g[a]	Recovery(%)[a]	μg/g[b]	Recovery(%)[b]	μg/g[c]	Recovery(%)[c]
0.200	0.211	105.5	0.186	93.3	0.182	91.0
0.250	0.262	104.8	0.238	95.2	0.240	96.0
0.500	0.520	104.0	0.472	94.4	0.460	92.0
1.000	1.032	103.2	0.965	96.5	0.955	95.5
1.500	1.550	103.3	1.469	97.9	1.430	95.3
2.500	2.530	101.2	2.400	96.0	2.410	96.4
5.000	5.152	103.0	4.880	97.6	4.700	94.0
7.500	7.517	100.1	7.350	98.0	7.312	97.0
10.000	10.109	101.0	9.737	97.4	9.540	95.4

[a]Emulsion formation method with DCP-AES.

[b]Solvent extraction method with DCP-AES.

[c]Dry ashing technique with atomic absorption spectrometry (2).

emulsions (6). About 0.1 g of oil in a total volume of 50 mL is suitable.

Extraction pH. The pH of the aqueous layer was found to affect the sensitivity and the extent of lead extraction and was found to be optimum at pH 2 with 93–98% extraction efficiency.

Evaluation of the methods. The concentrations of lead in oil samples were determined by both of the above-mentioned procedures. A side-by-side comparison of the results and precision of these methods was made with the standard dry ashing method (2). The results of these analyses are shown in Table 1. Relatively higher standard deviation values were obtained from the emulsion method. This may be attributed to the low stability of the plasma in organic matrices because organic vapors tend to cool the plasma, which results in analyte signal depression (7). However, the results are still in good agreement with those obtained by other methods. The detection limits, calculated from three times the standard deviation from blanks, are 0.12 μg/g and 0.08 μg/g for emulsion and extraction methods, respectively.

Application of the methods. Samples of used frying oils (cottonseed oil) were obtained from restaurants at 14 separate locations in Cairo. The lead concentration in each sample was determined by both of the cited methods, and the average concentrations are shown in Table 2. The results show that the samples collected from heavy traffic sites contain higher concentrations of lead than those collected from quiet areas. The World Health Organization (WHO) recommends a maximum of 0.05 μg lead per 1 g of food or drinking water (8). Generally, the lead content in all samples exceeds these limits.

Results show that the concentration of lead in oil samples cooled after use in open air for several hours are much higher than those obtained from oil pans during frying (Table 2). All oil samples were obtained from oils used for nearly the same interval of time. The lower lead content of hot samples is attributed to the volatilization of the lead compounds during frying. Recontamination of oil with lead from the dust-fall takes place on cooling in open air. Studies on air pollution in Cairo have shown that the lead content ranges from 0.3 to 1.0 μg/g in the dust-fall over the districts of the city (9). Thus it is advisable to cover the frying-pans after use to protect the oil from polluted dust-fall.

TABLE 2

Lead Content of Used Frying Oils

Samples from heavy traffic areas (Lead content, μg/g)		Samples from quiet areas (Lead content, μg/g)	
Open air[a]	Frying[b]	Open air	Frying
1.18	0.46	0.79	0.51
2.11	0.31	0.51	0.44
1.45	0.55	0.91	0.47
1.11	0.47	0.64	0.32
1.16	0.42	0.56	0.33
2.02	0.31	0.73	0.52
1.93	0.30	0.83	0.44

[a]Samples obtained from oil pans cooled in open air for several hours.

[b]Samples obtained from oil pans during frying.

REFERENCES

1. Labuza, T.P., and M. Karel, *J. Food Sci. 32*:572 (1967).
2. Ybanez, N., M.L. Cervera, R. Montoro and R. Catala, *Rev. Agroguim. Tecnol. Aliment 27*:590 (1987).
3. Dijkstra, A.J., and D. Meert, *J. Am. Oil Chem. Soc. 59*:199 (1982).
4. Moffett, J.H., and K.G. Brodie, *Int. Lab. 16*:48 (1986).
5. *Handbook of Spectral Lines Characteristics for the DC Plasma/Echelle Systems, Vol. 1*, Beckman Instruments, Inc., Fullerton.
6. Hernandez-Mendez, J., L. Polo-Diez and A. Bernal-Melchor, *Anal. Chim. Acta 108*:39 (1979).
7. Montaser, A., and D.W. Golightly, in *Analytical Atomic Spectrometry*, VCH Publishers, Inc., New York, 1987, p. 182.
8. *Guidelines For Drinking Water Quality, Vol. 1, Recommendations*, World Health Organization, Geneva, 1984, p. 53.
9. Hindy, K.T., and S.A. Farag, *Environ. Pollut., Ser. B 5*:247 (1983).

[Received January 23, 1991; accepted June 13, 1991]