APPLICATION NOTE

Atomic Absorption

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Toxic Trace Metals in Edible Oils by Graphite Furnace Atomic Absorption Spectrophotometry

Introduction

Graphite furnace atomic absorption spectrophotometry (GFAAS) has been widely applied to the determination of trace elements in food due to its selectivity, simplicity, high sensitivity, and its capability for accurate determinations in a wide variety of matrices. Edible oils are generally low in trace element concentrations, however, metals such as arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), and selenium (Se) can be found and are known for their toxicities which affect the health of consumers. The determination of toxic elements from naturally occurring or production-contamination sources in oils can be determined by using GFAAS or inductively coupled plasma mass spectrometry (ICP-MS). When only a few elements are being analyzed, GFAAS is the preferred choice. It is easy to learn, faster in setting up, and simpler to use than ICP-MS. GFAAS is also lower in initial capital investment and has a lower operating and maintenance cost. Sample pretreatment procedures for edible oils are normally required prior to instrumental analysis in order to eliminate the organic matrix. Wet, dry or microwave digestion, dilution with organic solvent, and extraction methods can be time consuming and require more operator training than a direct analysis method.

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This method reports the development of a direct analysis method for edible oil samples using GFAAS without digestion. The advantages of using this method include small sample volume, direct introduction of samples, high sensitivity, and rapid analysis times. The application of GFAAS to arsenic, lead and cadmium analysis in edible oils was performed. The optimal pyrolysis and atomization temperatures, limit of detection, quality control (QC) checks and recoveries were studied in order to develop a rapid and accurate method.

Experimental Conditions

Instrumentation

The measurements were performed using the PerkinElmer PinAAcle™ 900T atomic absorption spectrophotometer (PerkinElmer, Inc., Shelton, CT, USA) (Figure 1) equipped with an AS 900 graphite furnace autosampler and WinLab32™ for AA software running under Microsoft® Windows™ 7 operating system.

Figure 1. PerkinElmer PinAAcle 900T atomic absorption spectrophotometer equipped with AS 900 graphite furnace autosampler.

The PerkinElmer PinAAcle 900T has a high-efficiency, true double-beam optical system and solid-state detector which provide outstanding signal-to-noise ratios. The system features longitudinal Zeeman-effect background correction for the graphite furnace, doubling the amount of light throughput by eliminating the need for a polarizer in the optical system. The use of standard transversely heated graphite atomizer (THGA) tubes provides uniform temperature distribution across the entire length of the graphite tube. By employing the latest analytical concepts of the Stabilized Temperature Platform Furnace™ (STPF) technique and the instrumental advances of THGA tubes, chemical interferences are overcome allowing for faster, simpler direct calibration.

The analytical conditions (Table 1) and the graphite furnace temperature programs (Table 2) are given below. A heated injection at 90 ˚C was used for all three elements. Standard (non-endcapped) pyrolytically coated THGA tubes (Part No. B3000641) were used for all analyses. The autosampler cups were soaked in 20% nitric acid overnight to minimize sample contamination, and were thoroughly rinsed with deionized water before use. Prior to unknown sample analysis, a five-point calibration curve (four standards and one blank) using isopropyl alcohol (IPA) was constructed for each analyte. By employing the latest analytical concepts of the Stabilized Temperature Platform Furnace (STPF) technique and the instrumental advances of THGA tubes, chemical interferences are overcome allowing for faster, simpler direct calibration.

Table 1. **Analytical conditions for analyzing several toxic metals in edible oils on the PinAAcle 900T.**

Analyte	As	Pb	Cd
Wavelength (nm)	193.70	283.31	228.80
Slit Width (nm)	0.7	0.7	0.7
Lamp Type	EDL	EDL	HCL
Signal Processing	Peak Area	Peak Area	Peak Area
Read Time (sec)	3	3	2
Standard/Sample Volume (µL)	20	20	20
Diluent Volume (µL)	4	4	5
Matrix Modifier	5 µg Pd + 0.5 µg Mg	5 µg Pd + 0.5 µg Mg	5 µg Pd + 0.5 µg Mg
Matrix Modifier Volume (µL)	5	5	5
Injection Temp (˚C)	90	90	90
Pipet Speed (%)	40	40	40
Calibration Equation	Linear Through Zero	Linear Through Zero	Linear Through Zero
Standard Concentration (µg/L)	0, 20, 30, 40, 50	0, 20, 30, 40, 50	0, 0.5, 1.0, 1.5, 2.0
QC Concentration (µg/L)	10	10	0.4
Automatic Spike Conc. (µg/L)	10	10	0.5

Table 2. **Temperature programs for analyzing several toxic metals in edible oils on the PinAAcle 900T.**

Analyte	As			Pb			Cd		
Furnace Program	**Temp (˚C)**	**Ramp (s)**	**Hold (s)**	**Temp (˚C)**	**Ramp (s)**	**Hold (s)**	**Temp (˚C)**	**Ramp (s)**	**Hold (s)**
Drying 1	110	1	20	110	1	20	110	1	20
Drying 2	150	10	10	150	10	10	150	10	10
Drying 3	450	10	20	450	10	20	450	10	20
Pyrolysis	1100	10	20	900	10	20	550	10	20
Atomization	2300	0	3	1900	0	3	1800	0	2
Clean Out	2500	1	5	2500	1	5	2500	1	5

BOC = 2 s for all samples

Standards and Sample Preparation

Single-element PerkinElmer Pure Calibration Standards (Part Nos. As: N9300180; Pb: N9300175; Cd: N9300176) were used as the stock standards for preparing working standards and quality control check standards. All standards were prepared with IPA (VWR, Normapur Reagent grade) by volume/volume (v/v) dilution.

A mixture of 1000 mg/L Pd and 100 mg/L Mg was used as the chemical modifier for all elements. The chemical modifier was prepared by weighing 0.1430 g of Pd(II) acetylacetonate (Aldrich, 99%, MW=304.62) and pipetting 1 mL of Mg oil standard (Conostan, 5000 µg/mL) and dissolving with 50 mL of xylene (Panreac, reagent grade).

Five edible oils (palm, sesame, sunflower, soybean and rice bran) were purchased from a local supermarket and were used without any pre-treatment. All oil samples were carefully diluted 20 times (v/v) with isopropyl alcohol in polypropylene vials (Part No. B0193234).

Results and Discussion

The calibration curves for all elements returned an r^2 value ≥ 0.997 (Figure 2). Direct calibration for the analysis of oil samples has several advantages over the method of standard additions. Direct calibration results in less operator error, lower cost, and shorter analysis times than with standard additions or matrix matched standards.

An overlay of the peak plots for the standards (red), QC checks (green), and oil samples (various colors) taken on the PinAAcle 900T spectrometer are shown in Figure 3 (Page 4). Although there is a difference in appearance times for some elements, when using the conditions listed above and calculating for peak area, the results are accurate and precise.

The results for the direct analysis of edible oils using GFAAS to detect toxic metals are shown in Table 3 (Page 4). All oils showed concentrations less than the detection limit for lead and cadmium. The soybean oil showed a concentration of 4.28 µg/L arsenic. All others showed concentrations less than the detection limit.

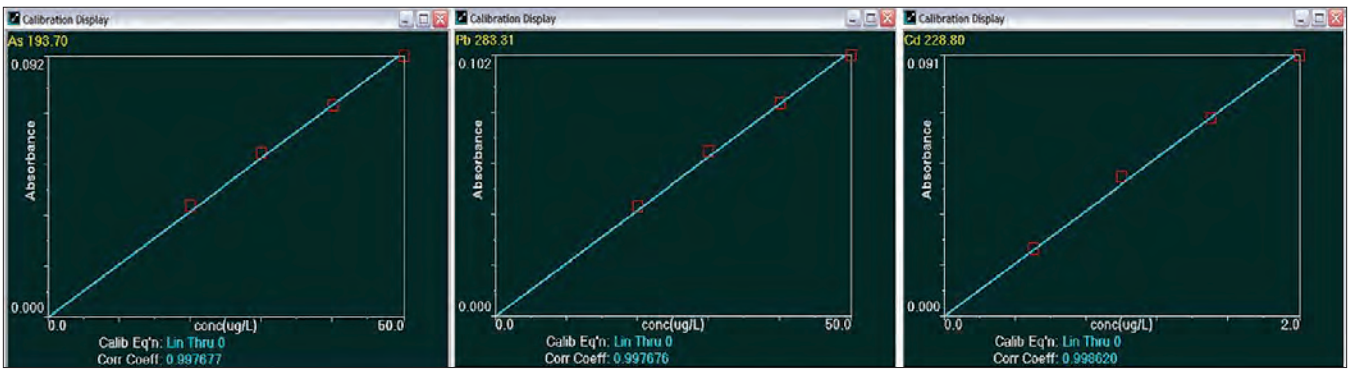

Figure 2. Direct calibration curves for the determination of As, Pb, and Cd in edible oils.

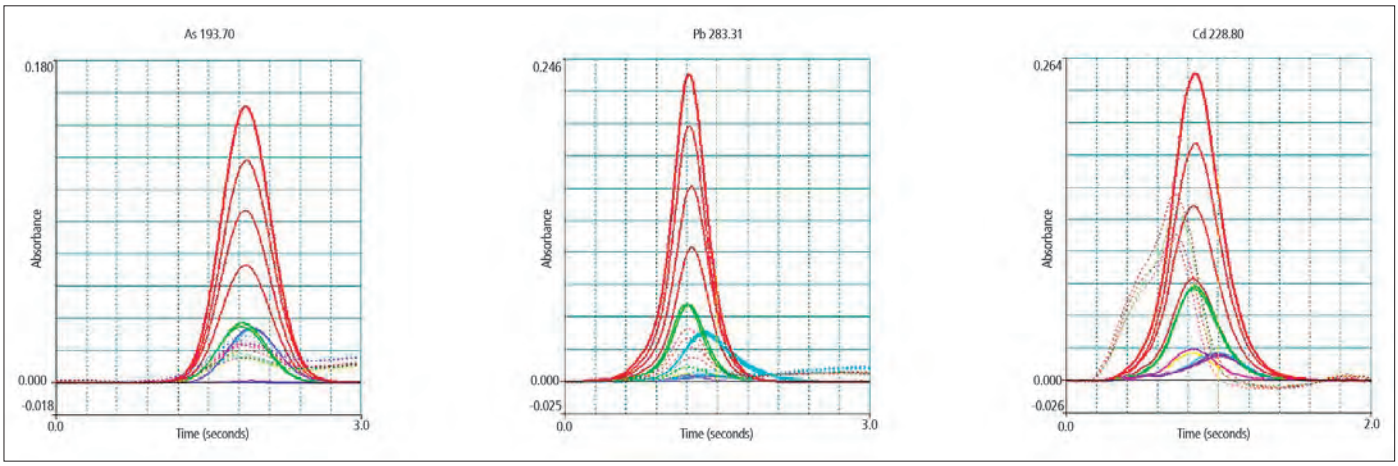

Figure 3. Peak overlays for standards (red), QC checks (green), and samples (various colors) run on the PinAAcle 900T for the analysis of As, Pb, and Cd in edible oils by direct calibration. Solid lines are the analytical signal after background correction (AA-BG); dotted lines are the background signal (BG).

***Table 3.* Result for direct edible oils metals analysis using GFAAS.**

Analyte	As	Pb	Cd
Palm Oil (µg/L)	< MDL	< MDL	< MDL
Sesame Oil (µg/L)	< MDL	< MDL	< MDL
Sunflower Oil (µg/L)	< MDL	< MDL	< MDL
Soybean Oil (µg/L)	4.28	< MDL	< MDL
Rice Bran Oil (µg/L)	< MDL	< MDL	< MDL

Method detection limits (MDLs) were calculated based on 3 times the standard deviation of seven (for Cd and As) or five (for Pb) replicates of the IPA blank. The result was then multiplied by 20, in regards to the 20x sample dilution, to estimate the MDL in standard/sample units. Table 4 shows the resulting MDLs of the PinAAcle 900T spectrometer in analyzing difficult oil matrices at lower concentrations.

***Table 4.* Method detection limits (MDLs) for the analysis of edible oils using the PinAAcle 900T.**

Analyte	As	Pb	Cd
MDL (µg/L)	3.4	3.0	0.42

The goal of this method was to develop a simple and direct method for the quantitative analysis of various toxic metals in edible oils using GFAAS without any sample pretreatment. The validity of the developed method has been verified by incorporating various QC checks and spike recovery checks throughout the analysis. As shown in Table 5, the QC samples showed good recoveries between 98-110%, well within acceptable limits. In addition, individual samples of oil were spiked for either As, Pb, or Cd in concentrations of 10 µg/L, 10 µg/L and 0.5 µg/L respectively. The recoveries for the individual spiked oils were between 93-112% (Table 5) meeting the guidelines of ±15%.

***Table 5.* Recoveries of QC checks and spiked samples for the direct analysis of edible oils using GFAAS.**

	% Recovery		
Analyte	As	Pb	Cd
QC1	104	110	107
QC2	98.4	110	109
QC3	104	109	109
Spike Recovery – Palm Oil	93.9	106	109
Spike Recovery – Sesame Oil	94.8	93.2	112
Spike Recovery – Sunflower Oil	98.8	93.5	108

Conclusions

A direct injection method for the quantitative analysis of toxic elements in edible oil samples was developed. With the THGA tube design, accuracy and sample throughput are improved by reducing the need of time-consuming sample pretreatment. The unique optical system, solid-state detector (which is highly efficient at low wavelengths), THGA, STPF technique, and longitudinal Zeeman background correction, all contribute to the ability of the PinAAcle 900T spectrometer to provide highly accurate, fast and reproducible results with difficult matrices such as edible oils. The PinAAcle 900Z (Longitudinal Zeeman Furnace only) spectrometer can also be used for this application.

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