Original Research Article

Direct atomic absorption spectrometry determination of arsenic, cadmium, copper, manganese, lead and zinc in vegetable oil and fat samples with graphite filter furnace atomizer

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ABSTRACT

The article presents the results of optimization of operation parameters, investigation of analytical characteristics and the abilities of a graphite filter-furnace (FF) atomizer for the direct electrothermal atomic absorption spectroscopy (ET AAS) determination of trace amounts of Mn, As, Pb, Cu, Cd and Zn in some vegetable oils and fats. The effect of pyrolysis and atomization temperatures of the graphite FF atomizer on atomic absorbance values of the listed elements at their evaporation from some organic solutions in the presence of a Pd-Mg chemical modifier (CM) was investigated. For the ET AAS determination of As, Pb, Cd and Zn with Pd-Mg CM, the temperature of the graphite FF atomizer for the pyrolysis step can be raised by 250–350 °C. This mode allows to eliminate the background absorption, to increase the sensitivity of the elements to be analyzed and to enhance the total content of vegetable oils or fats in organic solutions up to 0.5 g mL^{-1}. The obtained limits of quantification for Mn, As, Pb, Cu, Cd and Zn were 0.002, 0.004, 0.004, 0.002, 0.0008, 0.0004 mg kg^{-1}, respectively. The relative standard deviation (RSD) varied between ~3 and 8% and the time of one element determination did not exceed ~3–5 min. The reliability of the proposed method was checked using the reference method. A paired Student's t-test showed no significant difference between the results obtained by both methods on a 95% confidence level.

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1. Introduction

The content of metals in vegetable oils and fats is an important criterion of their quality. Mn, As, Pb, Cu, Cd and Zn are the most often determined elements in vegetable oils and fats and their maximum allowable concentrations referring to human health are well documented (Codex, 1995). Atomic absorption spectrometry (AAS) is one of the most effective official techniques for food analysis that was outlined in many standards in order to control health assessment in food trading (EN 14084, 2003; EN 14546, 2005; EN ISO 6869, 2000; EN ISO 8294, 1999; EN ISO 12193, 2004; EN ISO 15774, 2001). Oils and fats are specific analytic samples that consist of nearly totally organic substances. This fact may cause spectral interferences, which leads to time-consuming sample mineralization procedures for accuracy improvements (Betz et al.,

1980; Gücer and Massmann, 1983). To eliminate or reduce these interferences, various means and techniques are being offered: the separation of the elements to be determined from interfering components (Anwar et al., 2004; Khan et al., 2007; Price et al., 1970), chemical modifiers (CM) (Bozhanov and Karadjova, 2008; Karadjova et al., 1998, 2005; Karadjova and Venelinov, 2002), L'vov platform (Karadjova et al., 1998, 2005; Karadjova and Venelinov, 2002; Lacoste et al., 1999), addition of oxygen to the protective gas (Nash et al., 1983), Zeeman-effect background correction (Karadjova et al., 1998; Nash et al., 1983; Chen et al., 2003), and the Stabilized Temperature Platform Furnace (STPF) concept (Slavin et al., 1981).

According to EN ISO 8294 (1999), EN ISO 12193 (2004), and EN ISO 15774 (2001), such volatile elements as Pb and Cd, must be determined with the presence of chemical modifiers (lecithin – 2% (m/v) for Pb, and PdCl$_2$ – 0.1% (m/v) for Cd), while for Cu a chemical modifier is not needed in case of the analysis of vegetable oils and fats.

A different approach for the electrothermal atomic absorption spectroscopy (ET AAS) determination of some elements in complex
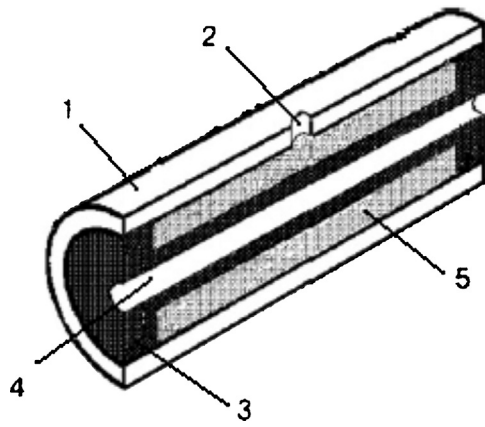
Fig. 1. Filter-furnace atomizer: (1) Pyrolytically coated graphite furnace (length-28 mm; diameter-6 mm); (2) dosing hole (diameter-1 mm); (3) graphite filter (the length and external diameter of the central part – 20 and 4 mm, respectively); (4) internal hole – analytical zone (diameter-2.5 mm) and (5) ring cavity.

Table 1
Operation parameters of FF atomizer heating for ET AAS determination of Mn, Cu and Cd As, Pb, Zn with Pd-Mg CM in vegetable fats and oils.

Step	Temperature (°C)	Ramp (°C s⁻¹)	Hold (s)	Ar flow rate (mL min⁻¹)
Drying	110	15	15	250
Pyrolysis	Mn (1000) As (1050)[a] Pb (1000)[a] Cu (1000) Cd (750)[a] Zn (1050)[a]	100	45	250
Pyrolysis[b]	Mn (1000) As (1050) Pb (1000) Cu (1000) Cd (750) Zn (1050)	0	3	0
Atomization	Mn (2500) As (2300) Pb (2100) Cu (2300) Cd (1700) Zn (1800)	FP[c]	7 7 5 9 5 5	0
Cleaning	2600	1000	3	400

[a] With addition of Pd-Mg CM.
[b] The argon flow is interrupted in this stage to prevent loss of the element at atomization step.
[c] FP – full power.

matrices was proposed by D. Katskov and his co-workers (Becker et al., 2011; Damin et al., 2009; Katskov et al., 1996) using a graphite filter-furnace (FF) atomizer. This device has several advantages for the analysis of organic-matrix solutions, which are summarized in a review (Katskov, 2007), including Pb and Cd determination in edible oils with the transverse heated filter atomizer (THFA) (Canário and Katskov, 2005). First of all, the graphite FF atomizer provides ∼2–2.5-fold increase in sensitivity in comparison with a platform. The main reason for a higher sensitivity of the graphite FF atomizer is the smaller volume of the filter tube in which absorption takes place, and hence the higher atom cloud density. In addition, the porous graphite filter tube greatly restricts the entrance of molecules into the absorption volume, which significantly reduces background absorption,

whereas atoms can pass separately. A wider range of sample volumes that can be introduced into the graphite FF atomizer provides additional advantages of this atomizer compared with the platform.

Up until now, except for the study by Canário and Katskov (2005), the direct ET AAS determination of Mn, As, Pb, Cu, Cd and Zn
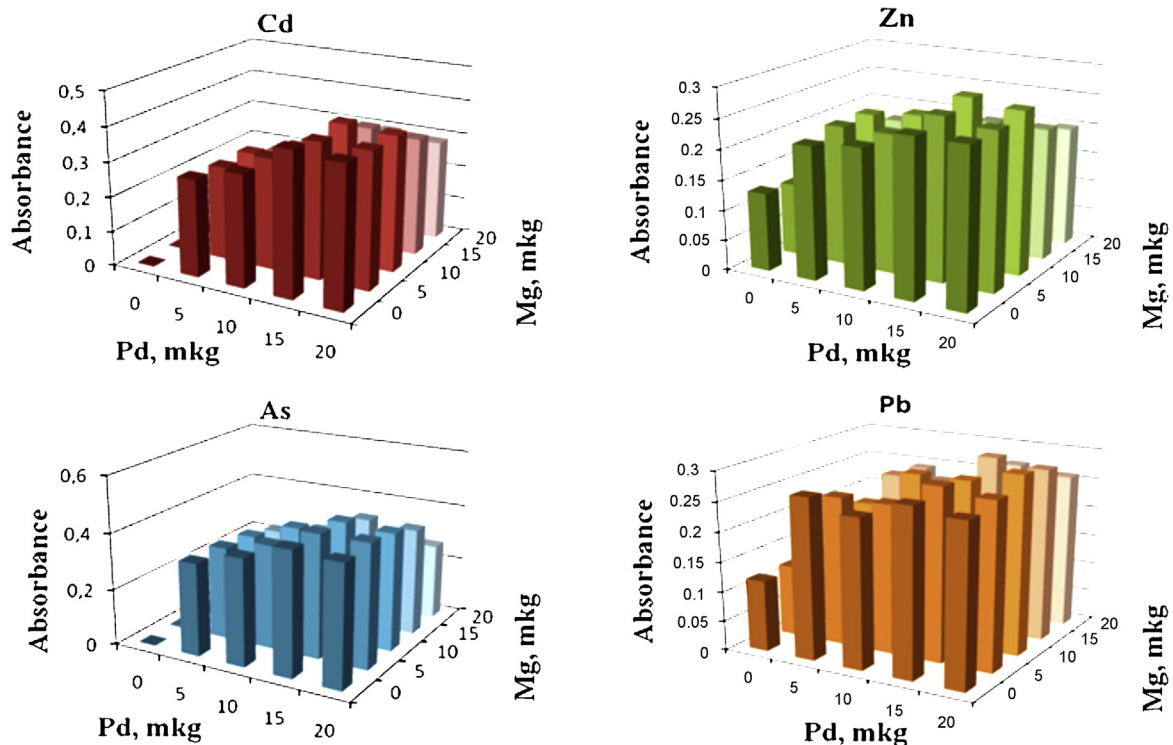

Fig. 2. Dependence of the Pb, As, Zn and Cd absorbance signals on the combined effects of various amounts of Mg and Pd added to an aqueous standard solutions of 0.3, 0.5, 0.03, 0.12 ng listed elements respectively.