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ScienceDirect

Food Chemistry 105 (2007) 236–241

Food Chemistry

www.elsevier.com/locate/foodchem

Tungsten permanent chemical modifier with co-injection of $Pd(NO_3)_2 + Mg(NO_3)_2$ for direct determination of Pb in vinegar by graphite furnace atomic absorption spectrometry

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Received 30 May 2006; received in revised form 19 October 2006; accepted 5 November 2006

Abstract

A tungsten carbide coating on the integrated platform of a transversely heated graphite atomizer (THGA®) used together with $Pd(NO_3)_2 + Mg(NO_3)_2$ as modifier is proposed for the direct determination of lead in vinegar by graphite furnace atomic absorption spectrometry. The optimized heating program (temperature, ramp time, hold time) of atomizer involved drying stage (110 °C, 5 s, 30 s; 130 °C, 5 s, 30 s), pyrolysis stage (1000 °C, 15 s, 30 s), atomization stage (1800 °C, 0 s, 5 s) and clean-out stage (2450 °C, 1 s, 3 s). For 10 µL of vinegar delivered into the atomizer and calibration using working standard solutions (2.5–20.0 µg L^{-1} Pb) in 0.2% (v/v) HNO_3, analytical curve with good linear correlation ($r = 0.9992$) was established. The characteristic mass was 40 pg Pb and the lifetime of the tube was around 730 firings. The limit of detection (LOD) was 0.4 µg L^{-1} and the relative standard deviations ($n = 12$) were typically <8% for a sample containing 25 µg L^{-1} Pb. Accuracy of the proposed method was checked after direct analysis of 23 vinegar samples. A paired *t*-test showed that results were in agreement at 95% confidence level with those obtained for acid-digested vinegar samples. The Pb levels varied from 2.8 to 32.4 µg L^{-1}. Accuracy was also checked by means of addition/recovery tests and recovered values varied from 90% to 110%. Additionally, two certified reference materials were analyzed and results were in agreement with certified values at a 95% confidence level.

Keywords: Lead; Vinegar; Graphite furnace atomic absorption spectrometry; Tungsten carbide coating

1. Introduction

Vinegar is a sour-tasting liquid made from the spontaneous acetous fermentation of wine, cider, beer, fruit juice, or nearly any other liquid containing alcohol (Prescott & Dunn, 1959). Consumers continue to daily use vinegars in a variety of ways, mainly as condiment to provide a special or unusual taste to foods. The physical and chemical properties of vinegars are essentially dependent from the geographical environment of production, which is affected either by natural or by human factors giving rise to a unique food product (Consonni & Gatti, 2004).

Vinegars may contain considerable levels of lead and this contamination is dependent on the raw materials or process by which vinegar is made (Acosta, Diaz, Hardisson, & Gonzales, 1993; Corradini, Marchesselli, Marchetti, Preti, & Biancardi, 1994; Ndung'u, Hibdon, & Flegal, 2004). Lead is one of the most studied metals and much information has been accumulated on human health problems caused by this toxic element. As foodstuffs may be considered an important intake source for Pb to humans, the accurate determination of this element in human feeding samples is important.

Graphite furnace atomic absorption spectrometry (GFAAS) is a suitable analytical technique for trace element determination due to its high selectivity and sensitivity, and capability for direct analysis with minimal sample

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0308-8146/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2006.11.003

preparation (Butcher & Sneddon, 1998; Jackson, 1999; Welz & Sperling, 1999).

Nevertheless, matrices of vinegar are rather complexes, typically containing organic compounds (e.g. carbohydrates, polyphenol, acetic acid, tartaric acid, citric acid, malic acid, ethanol, hydroxymethylfurfurale) and inorganic species (e.g. Na, K, Ca, sulfate, phosphate, etc.), which may cause errors in the analytical measurements for trace metal analysis (Welz & Sperling, 1999).

GFAAS was employed as a comparative technique for Pb determination by inductively coupled plasma mass spectroscopy (Ndung'u et al., 2004). Results of lead in digested and diluted vinegar did not agree, and poor precision was observed for diluted samples, that may be attributed to the inefficiency of the heating program of atomizer optimized using $NH_4H_2PO_4 + Mg(NO_3)_2$ as modifier for quantitative removal of matrix.

The modifiers $Pd(NO_3)_2$ and $NH_4H_2PO_4$ were evaluated for the determination of Pb in balsamic vinegar by GFAAS after dry and wet ashing, microwave digestion and simple dilution as sample treatments (Cochi et al., 2004). Chemometric approach suggested that better results were obtained for acid digests, particularly if closed-vessel microwave-assisted acid-digestion system is used.

Permanent chemical modifiers (Tsalev, Slaveykova, Lampugnani, D'Ulivo, & Georgieva, 2000) have been used as kind of a coating to graphite tube or platform surfaces in order to make simpler the analytical procedure and to avoid contamination introduced by the modifier (Bianchin et al., 2006; da Silva, da Silva, Curtius, & Welz, 1999). Among main benefits of permanent modifiers are shorter injection time, lower blanks, better limit of detection, increased lifetime of the graphite tube, and catalytic effects on matrix destruction, producing lower backgrounds (Acar, 2005; Barbosa, Lima, & Krug, 2000; Ortner et al., 2002; Volynsky, 1996). The modification of platform surface with stable carbide coatings (for example tungsten) may minimize the graphite deterioration. As a consequence, the use of tungsten as permanent modifier in GFAAS can increase the atomizers' lifetime. Additionally, the tungsten carbides may act as catalyst in the reduction of analyte oxides (Volynsky, 1996). Tungsten as a permanent chemical modifier has been evaluated to improve the analyte thermal stability and atomizer lifetime (Debenzo, Castro, Carrion, & Flores, 1986). There are several articles related to use of tungsten as modifier in different matrices, including waters (Freschi, Freschi, & Gomes Neto, 2006; Queiroz, Rocha, Knapp, & Krug, 2002), biological materials (Nomura, Silva, Nogueira, & Oliveira, 2005; Zanao, Barbosa, Souza, Krug, & Abdalla, 2002), environmental materials (Rosa et al., 2003; Vieira, Ribeiro, & Curtius, 2004), foodstuffs (Oliveira, Gomes Neto, Nóbrega, Correia, & Oliveira, 2005; Oliveira, Gomes Neto, Nóbrega, & Oliveira, 2005), fuels (Nakamoto, Ishimaru, Endo, & Matsusaki, 2004; Oliveira, de Moraes, Gomes Neto, & Lima, 2002).

Little attention has been given to the direct determination of lead in vinegar using *in situ* sample preparation. In this way, it is possible to have a direct reading of the metal concentration without any further manipulation of the sample. Likewise, procedures involving permanent chemical modifier for the determination of Pb in vinegar are not described in the literature.

This study reports a simple and fast method for the direct determination of Pb in vinegar using *in situ* sample decomposition using a graphite tube atomizer with W-coated platform. The performance of the proposed procedure was checked after analyzing different vinegar samples.

2. Materials and methods

2.1. Instrumentation

A Perkin–Elmer SIMAA® 6000 simultaneous multi-element atomic absorption spectrometer with longitudinal Zeeman-effect background correction, a THGA® atomizer and an AS-72 autosampler were used. Perkin–Elmer Lumina® hollow cathode lamp (HCL) was used for the determination of Pb at the analytical wavelength recommended by the manufacturer ($\lambda = 283.3$ nm) and lamp current of 10 mA. Argon (White Martins, Brazil) with 99.999% purity was used as purge gas throughout at a flow rate of 250 mL min^{-1}. It should be pointed out that the experiments were carried out using the STPF-concept (Slavin, Manning, & Carnrick, 1981) including Zeeman-effect background correction. The heating program of the THGA® atomizer used for the determination of Pb in vinegar is shown in Table 1. The heating program used to coat the platform with the W permanent modifier is described elsewhere (Freschi et al., 2006) that was adapted from the literature (Lima, Krug, & Jackson, 1998; Rademeyer et al., 1995). A volume of 50 μL of 1.00 g L^{-1} W stock solution was delivered onto the integrated platform and that heating program was run five times. All measurements were made with at least three replicates and are based on integrated absorbance.

Vinegar samples were digested by using a Perkin–Elmer-Anton Paar Multiwave® microwave oven (Graz, Austria) equipped with 50-mL quartz vessels.

2.2. Reagents, analytical solutions and samples

High purity de-ionized water obtained using a Millipore Rios 5®reverse osmosis and a Millipore Milli-Q Academic® deionizer system (resistivity 18.2 MΩ cm), and Suprapur® nitric acid (Merck, Darmstadt, Germany) were used throughout to prepare all solutions.

Permanent modifier solution (1.00 g L^{-1}) used to prepare the W-treated platform was obtained by dissolving 0.1794 g $Na_2WO_4 \cdot 2H_2O$ (Merck, Darmstadt, Germany) in 100 mL water.

Experiments involving thermal stabilization of Pb in presence of palladium nitrate and ammonium dihydrogenphosphate as conventional chemical modifiers were also carried out. Solutions containing 0.1% (m/v) Pd and 1%

Table 1
Optimized heating program for the direct determination of Pb in vinegar using W plus $Pd(NO_3)_2 + Mg(NO_3)_2$ as modifier

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow-rate (mL min^{-1})
1	110	5	30	250
2	130	5	30	250
3	1000	15	30	250
4	1800	0	5	0 (reading)
5	2450	1	3	250

Table 2
Optimized time-power program of the microwave oven for vinegar decomposition

Step	Initial power (W)	Final power (W)	Time (min)
1	100	600	5
2	600	600	5
3	1000	1000	10
4	0	0	15

(m/v) phosphate solutions were prepared by appropriate dilution of 10 g L^{-1} $Pd(NO_3)_2$ (Merck, Darmstadt, Germany) and 100 g L^{-1} $NH_4H_2PO_4$ (Merck, Darmstadt, Germany) stock solutions. Aliquots of 5 μL of Pd or phosphate and 3 μL of Mg were sampled and introduced onto the platform together with each aliquot (10 μL) of sample.

Lead working standard solutions in the 2.50–20.0 μg L^{-1} concentration range were prepared daily by appropriate dilution of the Normex® 1.00 g L^{-1} stock solutions (Carlo Erba, Milan, Italy).

All solutions and digested samples were stored in high-density polypropylene bottles (Nalgene®, Rochester, USA). Plastic bottles, autosampler cups, and glassware materials were cleaned by soaking in 10% (v/v) HNO_3 before use; all materials were rinsed abundantly in de-ionized water.

Vinegar samples were purchased at the local market in Araraquara, Brazil. All samples were analyzed without any previous treatment (direct analysis) and after microwave-assisted digestion. Two standard reference materials (1640 Trace Elements in Natural Water; 1643d Trace Elements in Water), from the National Institute of Standards and Technology (Gaithersburg, MD, USA) were also analyzed to furnish additional information to the method validation.

2.3. Procedure

For thermal behavior studies, an aliquot of 10 μL of sample was injected into the atomizer followed by 5 μL of 0.1% (m/v) Pd plus 3 μL of 0.1% (m/v) Mg chemical modifier solutions. For analysis, aliquots of 10 μL of working standard solutions and vinegar plus 5 μL of 0.1% (m/v) Pd plus 3 μL of 0.1% (m/v) Mg were directly delivered on the atomizer platform. All measurements of integrated absorbance were made at least in triplicates. The thermal stabilization studies of Pb during pyrolysis and atomization stages was investigated in vinegar containing 250 pg Pb using W-treated platform plus co-injection of $Pd(NO_3)_2 + Mg(NO_3)_2$. The proposed procedure was applied to lead determination in vinegar without treatment and after microwave-assisted digestion. For digestion, a volume of 5-mL of sample was transferred to quartz flasks followed by 2 mL of concentrated nitric acid + 1 mL of 30% (m/m) H_2O_2. Shown in Table 2 is the optimized time-power program of the microwave oven for vinegar decomposition. The digests were transferred to a 10-mL volumetric flask and the volume completed with de-ionized water.

In addition, recovery tests were also investigated by adding 20 μL of 1000 μg L^{-1} Pb in 10 mL samples in triplicate. Statistical tests used in the data processing (mean, standard deviations and precision) were done using the Microcal Origin® 7.0 program.

3. Results and discussion

Graphite furnace AAS with Zeeman-effect background corrector is an efficient technique to determine Pb at trace levels without sample preparation (Fernandes, Moraes, Gomes Neto, Nóbrega, & Oliveira, 2002; Freschi, Dakuzaku, Moraes, Nóbrega, & Gomes Neto, 2001). Lead and vinegar were selected after taking into consideration the importance of both in the analytical chemistry, food science and toxicology areas. The main characteristics considered for the evaluation and application of the proposed modifier were the pyrolysis and atomization temperatures, matrix effects, characteristic mass, repeatability, atomic signal profile, background level, and lifetime of graphite tube.

The electrothermal behavior of Pb in vinegar was evaluated by means of pyrolysis and atomization temperature curves using W-coated platform plus co-injection of $Pd(NO_3)_2 + Mg(NO_3)_2$. These curves, shown in Fig. 1,

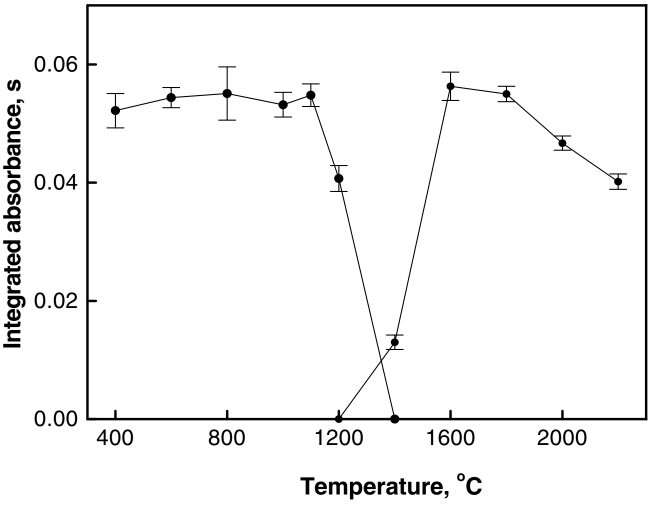

Fig. 1. Pyrolysis and atomization temperature curves for lead. Integrated absorbance refers to 25 μg L^{-1} Pb in vinegar sample.

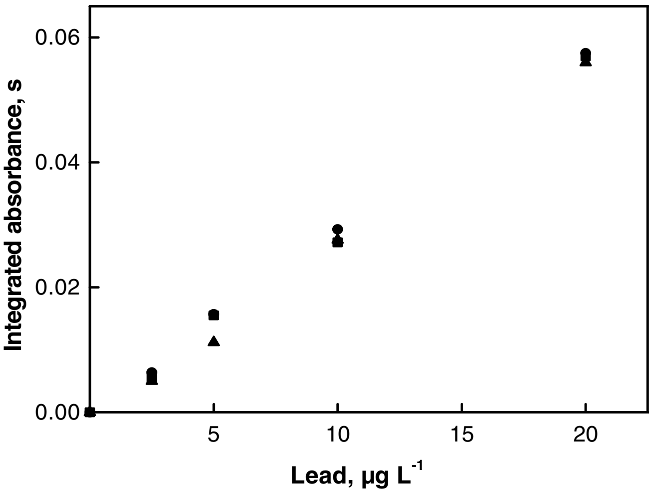

Fig. 2. Influence of the matrix on calibration for Pb. Curves correspond to analytical solutions prepared in 0.2% (v/v) HNO_3 (■), red wine vinegar (▲), and white wine vinegar (●).

were developed with the modifier by injecting 10 µL of vinegar containing 25 µg L^{-1} Pb plus 0.2% (v/v) HNO_3 solution. The maximum pyrolysis temperatures obtained in the presence of the $W + Pd(NO_3)_2 + Mg(NO_3)_2$ modifier was 1000 °C (Fig. 1). It should be pointed out that absorbance abruptly drops for temperatures greater than 1100 °C. For safer purposes, 1000 °C was adopted for further experiments. For comparison purposes, the influence of the conventional mixtures $Pd(NO_3)_2 + Mg(NO_3)_2$ and $NH_4H_2PO_4 + Mg(NO_3)_2$ were also evaluated and the optimum pyrolysis temperatures found were 1000 and 700 °C, respectively. The influence of variation of atomization temperature on absorbance was investigated in the 1200 – 2200 °C range after fixing the optimum pyrolysis temperature for the W-coated plus $Pd(NO_3)_2 + Mg(NO_3)_2$, and the mixtures $Pd(NO_3)_2 + Mg(NO_3)_2$ and $NH_4H_2PO_4 + Mg(NO_3)_2$. The atomization temperature was chosen after considering integrated absorbance value, peak profile, and repeatability. Therefore, the optimum atomization temperature was 1800 °C for W-coated plus $Pd(NO_3)_2 + Mg(NO_3)_2$, $Pd(NO_3)_2 + Mg(NO_3)_2$, and $NH_4H_2PO_4 + Mg(NO_3)_2$. The calculated characteristic mass values (m_0, in pg/0.0044A.s) for this sequence were 40, 46, and 74 pg Pb, respectively.

The absorbance-time profile for 250 pg Pb obtained in the presence of $W + Pd(NO_3)_2 + Mg(NO_3)_2$ modifier showed a narrow peak with rapid appearance time (0.5 s) and baseline restoration (2 s), revealing that the modifier provides one-step atomization. The background measured for $W + Pd(NO_3)_2 + Mg(NO_3)_2$, $Pd(NO_3)_2 + Mg(NO_3)_2$, and $NH_4H_2PO_4 + Mg(NO_3)_2$ were 0.0119, 0.0114, and 0.0080, respectively. Higher background was associated to the presence of Pd/Mg. but this was not a problem when a Zeeman-effect background corrector is used.

The matrix effects were evaluated by comparing the slopes between curves (Fig. 2) built up from aqueous (nitric acid) reference solutions $\{A^{Pb} = -0.0004 + 0.0029\ [Pb],\ r = 0.9996\}$, matrix-matched solutions with red wine vinegar $\{A^{Pb} = -0.0015 + 0.0029\ [Pb],\ r = 0.9995\}$, and matrix-matched solutions with white wine vinegar $\{A^{Pb} = -0.0002 + 0.0029\ [Pb],\ r = 0.9994\}$ in the 2.50–20.0 µg L^{-1} Pb range. No significant matrix effects were observed and errors associated to absorbance measurements by using calibration with aqueous reference solutions were usually lower than 3.8%, which is acceptable for trace and direct analysis of vinegar.

With 5 µg Pd + 3 µg Mg and 10 µL sample dispensed into the W-coated platform, pyrolysis temperature at 1000 °C and atomization temperature at 1800 °C, calibration curves in the 2.50–20.0 µg L^{-1} Pb ranges with good linearity were consistently obtained. The relative standard deviations ($n = 12$) were typically <8% for 25 µg L^{-1} Pb. The accuracy of the proposed method was checked after analysis of 23 commercial vinegar samples. A paired *t*-test showed that results were in agreement at 95% confidence level with those obtained for microwave-assisted digestion (Table 3). The levels of Pb varied from 2.8 to 32.4 µg L^{-1}. It is important to point out that these levels are close to those found (6.6–62 µg L^{-1}) in the literature for wine, garlic, apple and rice vinegars (Ndung'u et al., 2004). In addition, recoveries within 90% and 110% of spiked vinegars were found. Accuracy was also checked for Pb determination in standard reference materials from National Institute of Standards and Technology (1640 – trace elements in natural water; 1643d – trace elements in water). Results were in agreement at 95% confidence level with

Table 3
Results for lead ($n = 3$) in vinegar samples (mean ± SD) using the developed procedure without sample treatment and with the microwave-assisted acid-digestion procedure, and SRMs (mean ± SD) and recoveries (in %) for spiked vinegar samples

Simple	Certified values (µg L^{-1})	Pb found (µg L^{-1})		Recoveries (in %)
		Without treatment	Acid-digestion	
Vinegar 1		2.8 ± 0.3	3.0 ± 0.4	110
Vinegar 2		9.2 ± 0.7	8.1 ± 0.8	95
Vinegar 3		13.0 ± 1.0	12.8 ± 0.4	103
Vinegar 4		5.4 ± 0.4	4.8 ± 0.4	97
Vinegar 5		15.2 ± 1.2	14.3 ± 1.1	94
Vinegar 6		12.8 ± 1.0	13.0 ± 0.5	102
Vinegar 7		4.4 ± 0.4	5.0 ± 0.5	91
Vinegar 8		8.8 ± 0.9	9.4 ± 0.9	90
Vinegar 9		26.6 ± 1.9	24.2 ± 1.4	95
Vinegar 10		10.4 ± 0.8	11.7 ± 1.2	108
Vinegar 11		15.6 ± 1.2	13.6 ± 1.3	90
Vinegar 12		11.6 ± 0.9	10.5 ± 0.5	106
Vinegar 13		18.0 ± 1.5	20.2 ± 0.6	102
Vinegar 14		11.2 ± 0.9	10.2 ± 0.3	95
Vinegar 15		32.4 ± 2.6	30.3 ± 5.5	105
Vinegar 16		14.0 ± 1.1	11.9 ± 1.7	101
Vinegar 17		14.4 ± 1.2	16.2 ± 1.6	98
Vinegar 18		12.8 ± 1.0	12.8 ± 1.0	95
Vinegar 19		9.2 ± 0.7	9.9 ± 0.8	96
Vinegar 20		24.6 ± 2.0	22.5 ± 2.2	104
Vinegar 21		10.4 ± 0.8	10.8 ± 2.0	97
Vinegar 22		11.4 ± 0.9	10.7 ± 0.5	96
Vinegar 23		13.4 ± 1.1	13.2 ± 2.4	102
SRM1	18.15 ± 0.64	17.95 ± 0.28		
SRM2	27.89 ± 0.14	27.56 ± 0.34		

Numbers in parentheses represent % RSD.
SRM1: 1643d trace elements in water; SRM2: 1640 trace elements in natural water.

certified values of standard reference materials (Table 3). The limit of detection (LOD) and limit of quantification (LOQ) calculated for Pb are 0.4 and 1.4 μg L^{-1} Pb, respectively (Currie, 1999). In the particular case of Brazil, these limits are three and two orders of magnitude lower than that required by Health Department regulations (0.8 mg L^{-1} Pb).

The lifetime of W-coated platform was investigated by checking the repeatability of successive measurements of 25 μg L^{-1} Pb solution. The coating was stable up to around 250 firings for the first and second coating. A third re-coating allowed a further 230 firings. Hence, the graphite tube lifetime is around 730 firings.

4. Conclusion

This work presents an alternative method for direct determination of Pb in vinegar samples by graphite furnace atomic absorption spectrometry. The comparative results and recovery values of spiked samples indicated that no sample treatment was necessary to accurately determine lead in commercial vinegar samples. The limits of quantification obtained (1.4 μg L^{-1} Pb) exceeded the requirements of Brazilian Food Regulations (decree # 310-ANVS from Health Department), which establish the maximum permissible level for lead at 800 μg L^{-1} in vinegar, and with the proposed method up to around 18 measurements per hour can be done. It is important to point out that the atomizer lifetime was limited by the durability of the external wall of tube (the external wall usually deteriorates faster than the platform). For comparison purposes, the lifetime of graphite tube used in the direct determination of Pb in wine employing palladium plus magnesium as modifier was equivalent to 400 firings (Freschi et al., 2001).

Acknowledgements

The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Fundação para o Desenvolvimento da Unesp (FUNDUNESP) for financially supporting this work, and CNPq for fellowships to S.R.O and J.A.G.N.

References

Acar, O. (2005). Evaluation of V, Ir, Ru, V–Ir, V–Ru and W–V as permanent chemical modifiers for the determination of cadmium, lead, and zinc in botanic and biological slurries by electrothermal atomic absorption spectrometry. *Analytica Chimica Acta, 545*(2), 244–251.

Acosta, A., Diaz, C., Hardisson, A., & Gonzales, D. (1993). Levels of Cd, Pb, and Ni in different types of vinegars. *Bulletin of Environmental Contamination and Toxicology, 51*(6), 852–856.

Barbosa, F., Lima, E. C., & Krug, F. J. (2000). Determination of Arsenic in sediment and soil slurries by electrothermal atomic absorption spectrometry using W–Rh permanent modifier. *Analyst, 125*(11), 2079–2083.

Bianchin, L., Nadvorny, D., Silva, A. F., Vale, M. G. R., Silva, M. M., Santos, W. N. L., et al. (2006). Feasibility of employing permanent chemical modifiers for the determination of cadmium in coal using slurry sampling electrothermal atomic absorption spectrometry. *Microchemical Journal, 82*(2), 174–182.

Butcher, D. J., & Sneddon, J. (1998). Sample preparation: an introduction. In *A practical guide to graphite furnace atomic absorption spectrometry* (pp. 139–142). New York: John Wiley & Sons.

Cochi, M., Franchini, G., Manzini, D., Manfredini, M., Marchetti, A., & Ulrici, A. (2004). A Chemometric Approach to the Comparison of Different Sample Treatments for Metals Determination by Atomic Absorption Spectroscopy in Aceto Balsamico Tradizionale di Modena. *Journal Agricultural and Food Chemistry, 52*, 4047–4056.

Consonni, R., & Gatti, A. (2004). H NMR studies on Italian balsamic and traditional balsamic vinegars. *Journal of Agricultural and Food Chemistry, 52*, 3446–3450.

Corradini, F., Marchesselli, L., Marchetti, A., Preti, C., & Biancardi, C. (1994). Analysis of heavy metals in aceto balsamico tradizionale di modena by flame absorption spectroscopy. *Journal of AOAC International, 77*(3), 714–718.

Currie, L. A. (1999). Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC recommendations 1995). *Analytica Chimica Acta, 391*, 105–126.

da Silva, J. B. B., da Silva, M. A. M., Curtius, A. J., & Welz, B. (1999). Determination of Ag, Pb and Sn in aqua regia extracts from sediments by electrothermal atomic absorption spectrometry using Ru as a permanent modifier. *Journal of Analytical Atomic Spectrometry, 14*, 1737–1742.

Debenzo, Z. A., Castro, G., Carrion, N., & Flores, J. (1986). Preliminary-study on the recuperation of exhausted graphite tubes for the analysis of Cu and Cr by ET AAS. *Mikrochimica Acta, 1*(5–6), 311–324.

Fernandes, K. G., Moraes, M., Gomes Neto, J. A., Nóbrega, J. A., & Oliveira, P. V. (2002). Evaluation and application of bismuth as an internal standard for the determination of lead in wines by electrothermal atomic absorption spectrometry. *Analyst, 127*, 157–162.

Freschi, G. P. G., Dakuzaku, C. S., Moraes, M., Nóbrega, J. A., & Gomes Neto, J. A. (2001). Simultaneous determination of cadmium and lead in wine by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B, 56*, 1987–1993.

Freschi, G. P. G., Freschi, C. D., & Gomes Neto, J. A. (2006). Evaluation of Ir, Ru, and W as permanent modifiers for the simultaneous determination of As, Bi, Pb, Sb, and Se in natural water by electrothermal atomic absorption spectrometry. *Atomic Spectroscopy, 27*(1), 1–5.

Jackson, K. W. (1999). *Electrothermal atomization for analytical atomic spectrometry* (pp. 361–362). Weinheim: Wiley-VCH.

Lima, E. C., Krug, F. J., & Jackson, K. W. (1998). Evaluation of tungsten-rhodium coating on an integrated platform as a permanent chemical modifier for cadmium, lead, and selenium determination by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B, 53*(13), 1791–1804.

Nakamoto, Y., Ishimaru, T., Endo, N., & Matsusaki, K. (2004). Determination of vanadium in heavy oils by atomic absorption spectrometry using a graphite furnace coated with tungsten. *Analytical Sciences, 20*(4), 739–741.

Ndung'u, K., Hibdon, S., & Flegal, A. R. (2004). Determination of lead in vinegar by ICP-MS and GFAAS: evaluation of different sample preparation procedures. *Talanta, 64*, 258–263.

Nomura, C. S., Silva, C. S., Nogueira, A. R. A., & Oliveira, P. V. (2005). Bovine liver sample preparation and micro-homogeneity study for Cu and Zn determination by solid sampling electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B-Atomic Spectroscopy, 60*(5), 673–680.

Oliveira, A. P., de Moraes, M., Gomes Neto, J. A. G., & Lima, E. C. (2002). Direct determination of Al, As, Cu, Fe, Mn, and Ni in fuel ethanol by simultaneous GFAAS using integrated platforms pretreated with W–Rh permanent modifier together with Pd plus Mg modifier. *Atomic Spectroscopy, 23*(6), 190–195.

Oliveira, A. P., Gomes Neto, J. A. G., Nóbrega, J. A., Correia, P. R. M., & Oliveira, P. V. (2005). Determination of selenium in nutritionally relevant foods by graphite furnace atomic absorption spectrometry using arsenic as internal standard. *Food Chemistry, 93*(2), 355–360.

Oliveira, A. P., Gomes Neto, J. A., Nóbrega, J. A., & Oliveira, P. V. (2005). Internal standardization in graphite furnace atomic absorption spectrometry: Comparative use of As and Ge to minimize matrix effects on Se determination in milk. *Spectrochimica Acta Part B-Atomic Spectroscopy, 60*(5), 681–686.

Ortner, H. M., Bulska, E., Rohr, U., Schlemmer, G., Weinbruch, S., & Welz, B. (2002). Modifiers and coatings in graphite furnace atomic absorption spectrometry-mechanisms of action. *Spectrochimica Acta Part B, 57*, 1835–1853.

Prescott, S. C., & Dunn, C. G. (1959). *Industrial microbiology* (pp. 452–498) (3rd ed.). New York: McGraw-Hill.

Queiroz, Z. F., Rocha, F. R. P., Knapp, G., & Krug, F. J. (2002). Flow system with in-line separation/preconcentration coupled to graphite furnace atomic absorption spectrometry with W-Rh permanent modifier for copper determination in seawater. *Analytica Chimica Acta, 463*(2), 275–282.

Rademeyer, C. J., Radziuk, B., Romanova, N., Skaugset, N. P., Skogstad, A., & Thomassen, Y. (1995). Permanent iridium modifier for electrothermal atomic-absorption spectrometry. *Journal Analytical Atomic spectrometry, 10*(10), 739–745.

Rosa, C. R., Freschi, G. P. G., de Moraes, M., Gomes Neto, J. A. G., Nóbrega, J. A., Nogueira, A. R. A., et al. (2003). Tungsten permanent chemical modifier for fast estimation of Se contents in soil by graphite furnace atomic absorption spectrometry. *Journal of Agricultural and Food Chemistry, 51*(14), 3920–3923.

Slavin, W., Manning, D. C., & Carnrick, G. R. (1981). The stabilized temperature platform furnace. *Atomic Spectroscopy, 2/5*(1), 137–145.

Tsalev, D. L., Slaveykova, V. I., Lampugnani, L., D'Ulivo, A., & Georgieva, R. (2000). Permanent modification in electrothermal atomic absorption spectrometry – advances, anticipations and reality. *Spectrochimica Acta Part B, 55*, 473–490.

Vieira, M. A., Ribeiro, A. S., & Curtius, A. J. (2004). Slurry sampling of sediments and coals for the determination of Sn by HG-GF AAS with retention in the graphite tube treated with Th or W as permanent modifiers. *Analytical and Bioanalytical Chemistry, 380*(3), 570–577.

Volynsky, A. B. (1996). Catalytic processes in graphite furnaces for electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B, 51*, 1573–1589.

Welz, B., & Sperling, M. (1999). The techniques of atomic absorption spectrometry. In *Atomic absorption spectrometry* (third ed., pp. 15). Uberlinguer: Wiley-VCH, 362.

Zanao, R. A., Barbosa, F., Souza, S. S., Krug, F. J., & Abdalla, A. L. (2002). Direct determination of selenium in whole blood by electrothermal atomic absorption spectrometry using W-Rh-coated platform and co-injection of Rh as thermal stabilizer. *Spectrochimica Acta Part B-Atomic Spectroscopy, 57*(2), 291–301.