Analytical Methods

PAPER

Aluminium as chemical modifier for the determination of lead in sugar cane spirits using electrothermal atomic absorption spectrometry

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Aluminium was used as a chemical modifier for the determination of lead in sugar cane spirit samples by electrothermal atomic absorption spectrometry (ET-AAS). Pyrolysis temperature, pyrolysis time and atomisation temperature were 800 °C, 20 s and 1800 °C, respectively. The aluminium mass was 3 μg. Lead was quantified with limits of detection and quantification of 0.14 and 0.47 μg L^{-1}, respectively, and a characteristic mass of 24 pg. Analyte addition experiments demonstrated that external calibration can be performed with aqueous standards. The precision, expressed as relative standard deviation (RSD%), was 3.11% for a sample with a lead concentration of 3.00 μg L^{-1}. There is currently no certified reference material for sugar cane spirits, so a standard reference material of orchard leaves was used to confirm accuracy. The proposed method was used to determine the lead content of five sugar cane spirit samples from Salvador City, Brazil. Their lead contents varied from 3.00 to 19.61 μg L^{-1}. The samples were also analysed by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion in a closed system. No statistical difference was observed between the results obtained by both methods.

1. Introduction

Several chemical modifiers have been proposed for the determination of lead by electrothermal atomic absorption spectrometry (ET-AAS), with palladium–magnesium yielding the best results. This modifier allows for a pyrolysis temperature of 1200 to 1400 °C, which enables separation of most concomitant elements.[1–5] Ammonium phosphate is another common modifier, but lower pyrolysis temperatures must be used.[1] Alternative chemical modifiers for lead determination include the platinum group metals (*i.e.*, palladium, platinum, iridium, ruthenium and rhodium) and carbide-forming elements (*i.e.*, zirconium, niobium, tantalum and tungsten), which are permanent modifiers.[6,7] Gomes and co-workers evaluated seven of these modifiers for the determination of lead in sugar cane spirits: Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$, Ir, Ru, W, Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$ + Ir, Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$ + Ru and Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$ + W. The Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$ + W and Pd(NO$_3$)$_2$/Mg(NO$_3$)$_2$ + Ir gave the best results, with characteristic masses of 28 and 29 pg.[8] Neto and co-workers proposed a method for the simultaneous determination of arsenic, lead and copper in sugar cane spirits by ET-AAS using a W-coated platform and Pd–Mg(NO3)$_2$ as a modifier.[9] Citric acid[10] and other organic acids have also been proposed as

chemical modifiers for lead, and 8-hydroxyquinoline-5-sulfonic acid was recently used as a chemical modifier for its determination in cereals.[11] Another method used tungstate as a permanent chemical modifier for the determination of lead and cadmium in water after preconcentration by liquid-phase microextraction.[12]

Cachaça is a Brazilian sugar cane spirit that is appreciated worldwide. Several papers have been published on quantifying organic and inorganic species in this beverage.[13,14] For example, Silva and co-workers determined antimony and chromium by ET-AAS using ruthenium as a permanent modifier,[15] and Pereira *et al.* determined copper by fast sequential flame atomic absorption spectrometry and internal standards.[16]

Several researchers have proposed using aluminium as a chemical modifier.[17–22] Docekalova *et al.* investigated the effect of various chemical modifiers, including aluminium nitrate, on the ET-AAS analytical signal during selenium determination.[17] Tsai *et al.* tested several chemical modifiers for copper[18] and cadmium[19] determination in nickel-based alloys by ET-AAS. Aluminium chloride was tested between the inorganic modifiers. Other authors have used aluminium and nickel as chemical modifiers to determine gallium in aluminium alloys and fresh water samples by ET-AAS. Sensitivity improved 2.3 times with aluminium as a modifier.[20] Carrion *et al.* evaluated the performance of aluminium as a matrix modifier for the determination of lead in aluminium-based alloys by ET-AAS. They observed that lead can be strongly retained by aluminium at low pyrolysis temperatures (700 °C), and the integrated absorbance signal was lower when aluminium was not present. Lead retention also

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increased with the amount of aluminium added.[21] Ince and Akman evaluated the effects of aluminium salts on the determination of manganese by ET-AAS. They concluded that aluminium salts form refractory compounds between aluminium and manganese (*e.g.*, spinel $MnAl_2O_4$) that shift the absorption signals of manganese to higher temperatures. If the pyrolysis temperature was below 800 °C, aluminium chloride altered the vaporisation mechanism of manganese.[22]

In the present paper, aluminium was used as a chemical modifier for the determination of lead in sugar cane spirits by ET-AAS. The parameters: modifier mass, pyrolysis temperature and atomisation temperature were optimised by univariate methodology. The procedure was then applied in the determination of lead in samples from Brazilian cities.

2. Experimental

2.1. ET-AAS instrumental parameters

Lead determination by ET-AAS was performed on a ZEEnit 600 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with a transverse-heated graphite tube atomiser and Zeeman-effect background correction. Transversely heated pyrolytic graphite coated tubes with PIN platforms were used for all analyses. A lead hollow cathode lamp (Varian, Mulgrave, VA, Australia) was used as the radiation source with a current of 3 mA, wavelength of 283.3 nm and spectral bandwidth of 1.2 nm. An MPE 60 furnace autosampler (Analytik Jena) was used for sample introduction. Argon with a purity of 99.997% (White Martins, Salvador, Brazil) was used as the purge gas with an internal flow rate of 2.0 L min^{-1} during all steps except atomisation, when internal flow was stopped. Analytical signals were measured as integrated absorbances, A_{int} (peak area). Table 1 shows the optimised graphite furnace temperature program.

2.2. ICP-MS instrumental parameters

ICP-MS analysis was performed on a quadrupole XSeries II inductively coupled plasma mass spectrometer (Thermo Scientific, Germany) fitted with a standard concentric nebuliser, a Peltier cooled spray chamber option and an Xs interface. The Xs+ mode was used for ion extraction, and the instrument was operated under standard conditions without use of the collision cell. Argon (99.997%, White Martins, Salvador, Brazil) was used as the carrier gas. Table 2 presents the ICP-MS operational conditions. The isotope monitored was 208.

Table 1 Temperature program used for lead content determinations; an internal gas flow rate of 2.0 L min^{-1} was used in all stages except during atomization, when the gas flow was turned off

Step	Temperature/°C	Ramp/°C s^{-1}	Hold time/s
Drying	110	15	10
Drying	120	10	15
Drying	140	5	10
Pyrolysis	800	50	20
Atomization	1800	FP[a]	4
Cleanout	2550	FP	5

[a] Full power.

2.3. Reagents and solutions

Deionised water obtained from a Milli-Q system (Millipore, Bedford, USA) with a specific resistivity of 18 MΩ cm was used to prepare all solutions and standards. All reagents were of analytical grade. Nitric acid solutions were prepared by appropriate dilution from concentrated nitric acid (Merck, Darmstadt, Germany). Working standards were prepared immediately before use by serial dilution from a 1000 mg L^{-1} lead stock solution (Merck) in 0.05% nitric acid. Three microlitres of a 1000 mg L^{-1} ICP-MS aluminium solution (Merck) were used as the modifier, which resulted in an aluminium mass of 3 μg.

Calibration solutions for quantification by ICP-MS were prepared from 0 to 25 μg L^{-1} for each analyte measured in 2% ultrapure nitric acid. Scandium-45, ^{72}Ge, ^{103}Rh and ^{205}Tl were used as internal standards at 50 μg L^{-1}.

2.4. Samples

Spirit samples were purchased at supermarkets in Salvador City, Brazil in October 2010. For ET-AAS analysis, sample solutions were prepared by diluting 4.95 mL of the original samples with 50 μL of 50% nitric acid solution (v/v).

For ICP-MS analysis, samples were heated to 70 °C to eliminate ethanol, diluted to 10 mL with ultrapure water and digested by 200 μL of concentrated nitric acid in a digester block with a reflux system (cold finger[23]).

3. Results and discussion

3.1. Optimisation of instrumental conditions for lead determination in sugar cane spirits with aluminium as a chemical modifier

Experimental conditions for drying time, drying temperature, gas flow and clean step were fixed at the recommendation of the instrument manufacturer and are shown in Table 1. First, the amount of aluminium as a chemical modifier was determined by testing 1.0, 2.0, 3.0, 4.0 and 5.0 μg. Experiments were performed at a pyrolysis temperature of 700 °C, pyrolysis time of 20 s and atomisation temperature of 1800 °C. The analytical signals were relatively constant while aluminium masses changed from 2.0 to 5.0 μg. Three micrograms were ultimately established as the modifier mass used in this method.

Table 2 Typical settings of the ICP-MS

Incident power 1300 W
Extraction −184 V
Plasma gas flow 13 L min^{-1}
Nebulizer flow 0.89 L min^{-1}
Dwell time 10 ms (peak jump)
Sweeps/reading 100
Measurements 3–30 scans
Conditions $^{140}Ce^{16}O^+/^{140}Ce^+$ <2% and $^{137}Ba^{2+}/^{137}Ba^+$ <3%
Differential aperture (DA) −40.8 V
Standard mode
Isotope ^{208}Pb
Hexapole bias −4.0 V
Pole bias −3.7 V
DA −40.8 V
Signal ^{115}In (1 mg L^{-1}) > 40 kcps

The effect of pyrolysis temperature on lead absorbance was investigated with 20.0 μL of a sugar cane spirit sample solution, an atomisation temperature of 1800 °C, a pyrolysis time of 20 s and a pyrolysis temperature ranging from 600 to 1100 °C. Fig. 1 shows that from 600 at 800 °C, the analytical signals were constant. Therefore, 800 °C was selected as the optimised pyrolysis temperature for the subsequent lead determinations.

During optimisation of the atomisation temperature, pyrolysis time and temperature were fixed at 20 s and 800 °C, respectively. The atomisation temperature was varied from 1100 to 2300 °C. Considering the results shown in Fig. 1, the analytical signals remained constant from 1400 to 1800 °C. An atomisation temperature of 1800 °C was selected for future experiments because it yielded a lead absorption signal with good shape and a low background absorbance.

3.2. Validation studies

Using the optimised experimental conditions, we could directly determine lead in sugar cane spirits with limits of detection ($3\delta/s$) and quantification ($10\delta/s$), of 0.14 and 0.47 μg L^{-1}, respectively. δ represents the standard deviation of the blank solution and s is the slope of analytical curve.[24] A mass of 24 pg was obtained for a sample volume of 20 μL. Method calibration was evaluated by comparing the slope of the curve obtained with aqueous standards to that of analyte addition to a sugar cane spirit sample. There was a similarity between the curves, with determination coefficients >0.99 (Table 3). Therefore, this method can quantify lead using external calibration external with aqueous standards. The precision (expressed as relative standard deviation) of ten repetitive determinations of a sugar cane spirit sample with a lead concentration of 3.00 μg L^{-1} was 3.11%. Since no certified reference materials exist for sugar cane spirits, the accuracy of the method was evaluated on SRM 1571 (orchard leaves) furnished by the National Institute of Standard and Technology (NIST). We obtained a lead concentration of 44.67 ± 1.16 μg g^{-1} ($n = 3$) with this method, which is not statistically different from the
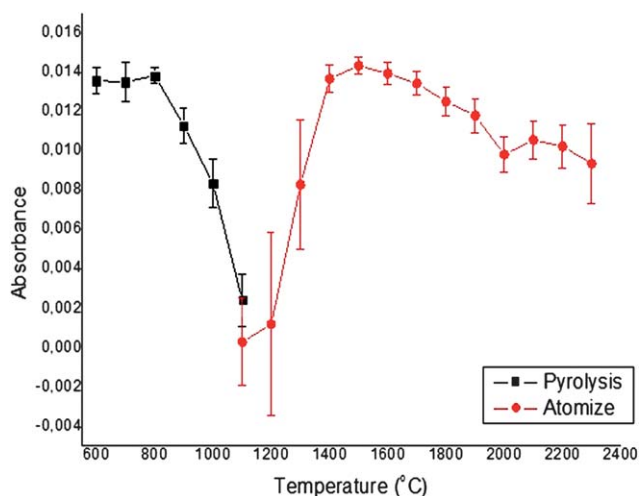
Table 3 Slopes of the analytical curves (L μg^{-1})

Analytical technique	Slopes
External calibration	0.004557 ± 0.000564
Analyte addition	0.004594 ± 0.000338

certified value of 45 ± 3 μg g^{-1} Pb based on a Student t-test at a confidence level of 95%.

Experiments employing ammonium phosphate as a chemical modifier were also performed with a pyrolysis temperature of 800 °C. Under these conditions, a characteristic mass of 22 pg was obtained, with limits of detection and quantification of 0.94 and 3.12 μg L^{-1}, respectively. Fig. 2A and B show the absorbance signals for lead and the background using 20 μL of a 25.0 μg L^{-1} lead solution. A and B represent 3 μg of aluminium and 5 μg of ammonium phosphate, respectively, as modifiers. In these figures, the background signal for aluminium was considerably lower than that of ammonium phosphate.

Preliminary studies evaluated the determination of lead by high-resolution continuum source graphite furnace atomic absorption spectrometry[25] (HR CS GFAAS) using aluminium as a chemical modifier and a pyrolysis temperature of 800 °C. The results were as follows: a characteristic mass of 15 pg, a limit of detection of 0.58 μg L^{-1} and a limit of quantification of 1.93 μg L^{-1}.
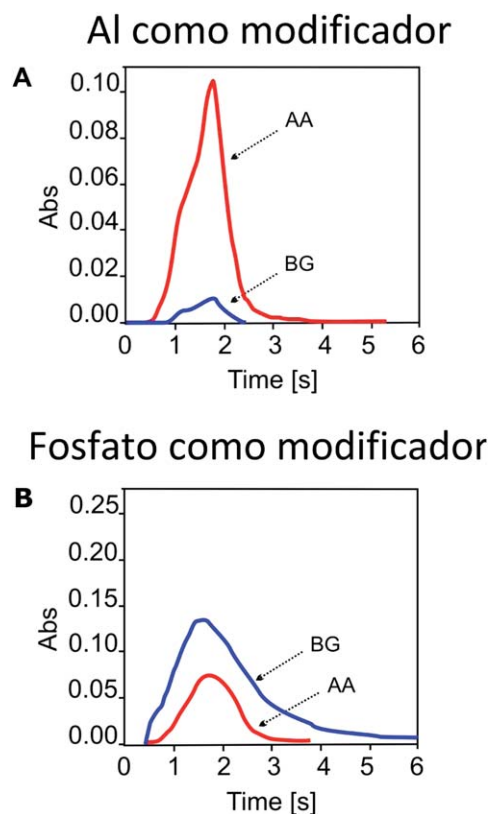

Al como modificador

Fosfato como modificador

Fig. 2 A – aluminium as chemical modifier; B – phosphate as chemical modifier.

Fig. 1 Pyrolysis and atomization curves for Pb using aluminium as chemical modifier.

Table 4 Determination of lead in sugar cane spirit samples ($n = 3$)

Sample	ET-AAS[a]/µg L^{-1}	ICP-MS[a]/µg L^{-1}
1	19.61 ± 0.16	19.82 ± 1.43
2	6.00 ± 0.47	6.21 ± 0.22
3	4.61 ± 0.79	4.72 ± 0.10
4	4.27 ± 0.68	4.15 ± 0.22
5	3.00 ± 0.38	2.79 ± 0.95

[a] Results expressed as interval confidence at 95% level.

3.3. Application

The ET-AAS method using aluminium as a chemical modifier was used to determine lead in five sugar cane spirit samples from several Brazilian cities. The results, expressed as 95% interval confidence levels, are shown in Table 4. The lead content in these samples varied from 3.00 to 19.61 µg L^{-1}, well below the maximum allowable level (Brazilian Ministry of Agriculture) of 200 µg L^{-1}.[26] These five samples were also analysed by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion in a reflux system (cold finger). Results (Table 4) from the two methods were compared by linear regression, and the confidence-interval equation is expressed as follows:

$$[\text{ICP-MS method}] = 1.02 \pm 0.04 \, [\text{ET-AAS method}] - 0.09 \pm 0.40$$

These results demonstrate that the calculated slope and intercept do not significantly differ from the "ideal" values of 1 and 0, respectively, and there is no evidence for a systematic difference between the two methods.

Using the optimised conditions, up to 500 firings were possible using the same tube without sensitivity losses. Preliminary studies also demonstrated that aluminium can be also used as a chemical modifier for the determination of cadmium.

4. Conclusions

An evaluation of the analytical parameters for the determination of lead in sugar cane spirits using an aluminium modifier demonstrates that this method is comparable to those using other recommended chemical modifiers. The proposed method displayed good precision, accuracy and sensitivity. In particular, the limits of detection and quantification and characteristic mass found in this work agree with those obtained during the determination of lead in antacids using phosphate as modifier.[27]

The concentrations of lead found in the samples analysed were below the maximum allowable limits set by the Brazilian Ministry of Agriculture. This work is timely, considering the high toxicity of lead and the high rate of consumption of this drink by Brazilians.

References

1 B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, 1999.
2 G. Chen and K. W. Jackson, *Spectrochim. Acta, Part B*, 1996, **51**, 1505.
3 B. Welz, G. Schlemmer and J. R. Mudakavi, *J. Anal. At. Spectrom.*, 1992, **7**, 1257.
4 M. S. S. Cerutti, L. D. Martinez, P. Smichowsk and R. A. Gil, *Talanta*, 2010, **82**, 523.
5 C. S. Nomura and P. V. Oliveira, *Anal. Methods*, 2010, **2**, 49.
6 J. B. B. da Silva, M. A. M. da Silva, A. J. Curtius and B. Welz, *J. Anal. At. Spectrom.*, 1999, **14**, 1737.
7 J. Yin, B. Hu, M. Bin, M. He, M. M. Zheng and Y. Q. Feng, *J. Anal. At. Spectrom.*, 2009, **24**, 76.
8 N. M. Caldas, J. L. RaposoJr, J. A. G. Neto and F. BarbosaJr, *Food Chem.*, 2009, **113**, 1266.
9 N. M. Caldas, S. R. Oliveira and J. A. G. Neto, *Anal. Chim. Acta*, 2009, **636**, 1.
10 J. C. P. de Mattos, A. M. Nunes, A. F. Martins, V. L. Dressler and E. M. de Moraes Flores, *Spectrochim. Acta, Part B*, 2005, **60**, 687.
11 S. Y. Huang and S. J. Jiang, *Anal. Methods*, 2010, **2**, 225.
12 R. E. Rivas, I. Lopez-Garcia and M. Hernandez-Cordobo, *Anal. Methods*, 2010, **2**, 1310.
13 M. S. F. Caruso and J. Alaburda, *J. Braz. Chem. Soc.*, 2009, **20**, 502.
14 I. Cesarino, G. Marino, J. D. Matos and E. T. G. Cavalheiro, *Talanta*, 2008, **75**, 15.
15 M. H. Canuto, H. G. L. Siebald, G. M. de Lima and J. B. B. Silva, *J. Anal. At. Spectrom.*, 2003, **18**, 1404.
16 K. Miranda, A. G. G. Dionisio and E. R. Pereira, *Microchem. J.*, 2010, **96**, 99.
17 H. Docekalova, B. Docekal, J. Komarek and I. Novotny, *J. Anal. At. Spectrom.*, 1991, **6**, 661.
18 S. J. J. Tsai, C. C. Shiue and S. I. Chang, *Spectrochim. Acta, Part B*, 1997, **52**, 1497.
19 S. J. J. Tsai, C. C. Shiue and S. I. Chang, *Spectrochim. Acta, Part B*, 1997, **52**, 55.
20 D. Ma, Y. Okamoto, T. Kumamaru and E. Iwamoto, *Anal. Chim. Acta*, 1999, **390**, 201.
21 N. Carrion, A. M. Itriago, M. A. Alvarez and E. Eljuri, *Talanta*, 2003, **61**, 621.
22 H. Ince and S. Akman, *Anal. Sci.*, 2004, **20**, 695.
23 S. L. C. Ferreira, R. M. de Jesus, G. D. Matos, J. B. de Andrade, R. E. Bruns, W. N. L. dos Santos, D. D. Cavalcante, M. G. R. Vale and M. B. Dessuy, *J. Braz. Chem. Soc.*, 2009, **20**, 788.
24 IUPAC Analytical Chemistry Division, *Spectrochim. Acta, Part B*, 1978, **33**, 242.
25 B. Welz, S. Morés, E. Carasek, M. G. R. Vale, M. Okruss and H. Becker-Ross, *Appl. Spectrosc. Rev.*, 2010, **45**, 327.
26 Ministry of Agriculture, Livestock and Supply, Instrução Normativa no. 13, in *DiárioOficial da União–Seção 1*, no. 124, Imprensa Nacional, Brasília, de 30 de Junho de 2005, pp. 3–4.
27 L. A. Portugal, G. D. Matos, D. C. Lima, G. B. Brito, A. P. Fernandes and S. L. C. Ferreira, *Microchem. J.*, 2011, **98**, 29.