Talanta 100 (2012) 21–26

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of lead in medicinal plants by high-resolution continuum source graphite furnace atomic absorption spectrometry using direct solid sampling

Jardes Figuerêdo Rêgo [a], Alex Virgilio [b], Joaquim A. Nóbrega [b], José A. Gomes Neto [a,*]

[a] São Paulo State University, Analytical Chemistry Department, P.O. Box 355, 14801-970 Araraquara, SP, Brazil
[b] Federal University of São Carlos, Department of Chemistry, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 4 July 2012
Received in revised form
24 August 2012
Accepted 27 August 2012
Available online 1 September 2012

Keywords:
Lead
Medicinal plant
Direct solid sampling
High-resolution continuum source graphite furnace atomic absorption spectrometry

ABSTRACT

A procedure is proposed for Pb determination in medicinal plants by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) using direct solid sampling. Among $Pd(NO_3)_2$, $Pd/Mg(NO_3)_2$, $NH_4H_2PO_4$ and the W-coated platform tested as chemical modifiers, $Pd(NO_3)_2$ presented the best performance. Calibration plots (10–1000 pg Pb) with regression coefficients better than 0.999 were typically obtained. Accuracy was checked for Pb determination in five plant certified reference materials. Results were in agreement with reference values at a 95% confidence level (paired *t*-test). Medicinal plant samples were analyzed by the proposed procedure and line-source GF AAS using slurry sampling as a comparative technique. The RSD was 10% ($n=3$) for a sample containing 0.88 μg g^{-1} Pb. The limit of quantification (dry mass) was 0.024 μg g^{-1}. The contents of Pb in medicinal plant samples varied in the 0.30–1.94 μg g^{-1} range.

1. Introduction

Quality control methods for medicinal plants are relevant since modern phytomedicine requires safety and efficacy of medicinal plant products for therapeutic use [1]. Besides active compounds, medicinal plant tissues may contain organic or inorganic hazardous compounds [2]. The determination of toxic metals such as lead in medicinal plants is relevant due to toxicity risks of this element and its compounds for human health [3]. Trace levels of lead usually found in plant materials require very sensitive and accurate analytical instruments.

Among atomic spectrometric techniques for trace analysis, graphite furnace atomic absorption spectrometry (GF AAS) is very attractive due to its capability for direct solid sampling (DSS) [4]. The main benefits of DSS are the minimum risk of contamination and analyte loss, high sensitivity, reduced overall time of analysis, consumption of non-hazardous reagents, and the least amount of waste [5].

The DSS has been used in GF AAS since the introduction of graphite atomizers [6]. However, most published papers related to DSS employed line-source graphite furnace spectrometers [7–9]. Moreover, some studies evaluating the use of chemical modifiers in the determination of Pb in different matrices as fuel ethanol [10], crude oil [11], ashes, coals, sediments, sludges, soils, and freshwaters [12] by using a transversely heated graphite atomizer (THGA) have been described.

The high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) enhanced and broadened the application of DSS due to its superior ability for background corrections based on the least-squares algorithm [7] and higher signal-to-noise ratios than those provided by line sources due to the high emission intensity of xenon short-arc lamps employed as the continuum radiation source [13]. Additionally, the availability of commercial instruments equipped with automatic solid sampler and integrated microbalance may eliminate errors caused by manual operations and reduce considerably the overall time of analysis.

DSS coupled to HR-CS GF AAS has been employed for elemental analyses of different matrices including crude oil [14], animal tissue [15–17], coal [18], grain [19], soil and sediment [20,21], geological [22], aquatic invertebrate [23], airborne particulate matter [24], polymer [25], activated carbon [26] and biological samples [27]. However, the determination of toxic trace metals in plant tissues is not described in literature.

This work reports a relatively simple, fast, and rugged procedure for Pb determination in medicinal plants by HR-CS GF AAS using DSS. Performance of the proposed procedure was checked after analyzing plant certified reference materials and a sort of medicinal plant. For comparison purposes, samples were also analyzed by line-source graphite furnace atomic absorption spectrometry using slurry sampling (SIS LS GF AAS).

* Corresponding author. Tel.: +55 16 33019611; fax: +55 16 33019692.
E-mail address: anchieta@iq.unesp.br (J.A. Gomes Neto).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.08.038

2. Materials and methods

2.1. Instrumentation

An Analytik Jena ContrAA 700 high-resolution atomic absorption spectrometer equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) as a continuum radiation source, a compact high-resolution double-Echelle grating monochromator with a spectral band width lower than 2 pm per pixel in the far ultraviolet range and a charge-coupled device (CCD) array detector were used throughout the work. The HR-CS GF AAS instrument is equipped with a transversely heated graphite furnace. Pyrolytic graphite-coated solid sampling tubes without a dosing hole were used. Samples were weighed directly onto the graphite platforms using a Sartorius WZ2PW micro-balance (Göttingen, Germany) with a precision of 0.001 mg. Sample-containing platforms were introduced into the atomization compartment by using a pair of tweezers from the Analytik Jena SSA 600 automated solid sampling accessory. White Martins high-purity (99.996%) argon (São Paulo, Brazil) was used as a purge and protective gas.

2.2. Reagents, analytical solutions and samples

High-purity water (resistivity 18.2 MΩ cm) obtained from a Millipore Rios 5^{TM} reverse osmosis and a Millipore Milli-Q Academic^{TM} system (Bedford, MA, USA) and Suprapur^{TM} nitric acid (Merck, Darmstadt, Germany) were used throughout to prepare solutions.

A 1.00 g L^{-1} W stock solution ($(NH_4)_2WO_4$, Merck) was used to coat the graphite platform. 10.0 g L^{-1} stock solutions of $Pd(NO_3)_2$, $Mg(NO_3)_2$ and $NH_4H_2PO_4$ (Merck) were employed as conventional modifier solutions. Solutions containing 0.1% (m/v) $Pd(NO_3)_2$, 0.1% (m/v) $Pd(NO_3)_2$+0.05% (m/v) $Mg(NO_3)_2$ and 1% (m/v) $NH_4H_2PO_4$ were prepared by appropriate dilution of stock solutions in 0.05% (m/v) Triton X-100 (Mallinckrodt Baker, Paris, KY, USA). Working standard solutions (10–1000 μg L^{-1}) were prepared in 0.1% (v/v) HNO_3 after appropriate dilution of the 1000 mg L^{-1} Pb stock solution (Merck).

For accuracy evaluation, the standard reference materials (SRM) 1515 Apple Leaves, 1570a Spinach Leaves, 3246 Ginkgo Biloba, 1547 Peach Leaves and 1575a Pine Needles from the National Institute of Standards and Technology (Gaithersburg, MD, USA) were analyzed.

The medicinal plants *Peumus boldus*, *Chamomilla recutita*, *Bacharis crispa*, *Equisetum ssp*, *Echinodorus grandiflorus*, *Melissa officinalis*, *Foeniculum vulgare*, *Panax ginseng*, *Annona muricata*, and *Mikania glomerata* were purchased at a local market in Araraquara city (SP, Brazil).

All samples were dried at 40 °C for 48 h in a forced air oven and ground in a cutting mill fitted with a 20-mesh screen at the bottom of the cutting chamber and thereafter powdered in a Spex 6750 cryogenic grinding mill (Metuchen, NJ, USA). A sample mass of 1.0 g was placed in a grinding vial (a polycarbonate cylinder supplied with two metallic end plugs), immersed in liquid nitrogen and ground by action of a magnetically driven stainless steel impactor. Samples were powdered by the impact of the magnetic bar oscillating in a magnetic field at 20 impacts per second. The grinding procedure was implemented with a first step of 2 min for sample freezing followed by two cycles with two stages of pulverization and cooling, in a total time of 4 min in order to obtain particles with average diameter below 50 μm.

2.3. Procedure

The thermochemical behavior of Pb was investigated in aqueous standard solution (470 pg Pb) and certified reference materials 1515 Apple Leaves and 1570a Spinach Leaves (ca. 0.5 mg) by means of pyrolysis and atomization temperature curves built up in absence and presence of the following modifiers: 5.0 μg $Pd(NO_3)_2$, 5.0 μg $Pd(NO_3)_2$+2.5 μg $Mg(NO_3)_2$, 50 μg $NH_4H_2PO_4$ and 200 μg W. Aliquots of 5.0 μL of conventional modifier samples and solutions were injected in sequence into the platform. The W-coated graphite platform was prepared according to a procedure described earlier [28], by injecting ten aliquots of 20 μL of a 1000 mg L^{-1} W standard solution onto the platform and submitting the graphite tube, after each injection, to the first four stages of the temperature program described in Table 1. After the last injection, when a total of 200 μg of W had been deposited, the entire program was run.

Analytical calibration curves in 10–1000 pg Pb intervals were built up using aqueous standard solutions. For the matrix effects evaluation, solid calibration experiments were done by using ca. 0.5 mg of 1515 Apple Leaves, 1570a Spinach Leaves, 3246 Ginkgo Biloba, 1547 Peach Leaves and 1575a Pine Needles which present different Pb contents.

Sample size and micro-homogeneity were investigated using ten mass intervals covering the mass range from 0.05 to 1.0 mg of 1575a Pine Needles and 3246 Ginkgo Biloba. Each mass interval represents the average weight of five sample masses. The homogeneity factor (H_e) was calculated according to literature [29]. Furthermore, the value of the minimum mass of sample to be analyzed was also determined.

For analysis by HR-CS GF AAS, sample masses (typically around 0.5 mg) were manually transferred to the solid sampling platforms, weighed and introduced into the atomization chamber automatically. The calibrations were performed employing the normal aqueous standard addition method. Aqueous standards and modifier solutions were injected manually onto the SS platform using micropipettes. The optimized heating program of the graphite tube is listed in Table 2. Although the most sensitive analytical line for Pb is at 217.001 nm, all atomic absorption measurements were carried out at 283.306 nm (less sensitive or secondary line). This line is preferred because it is less interfered by PO molecular structures. All measurements were based on the peak volume selected absorbance equivalent to three pixels and made in at least three replicates. Integrated absorbance values obtained with DSS were normalized for 1.0 mg of sample.

Table 1
Temperature program for the platform coating with W.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Ar flow rate (L min^{-1})
1	130	20	40	2.0
2	160	20	50	2.0
3	1000	100	25	2.0
4	1400	200	5	2.0
5	2000	1000	5	2.0

Table 2
Optimized heating program of atomizer for Pb determination in medicinal plants.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Gas flow rate (L min^{-1})
Drying 1	110	10	10	2.0 (Ar)
Drying 2	130	5	10	2.0 (Ar)
Ash	600	50	30	2.0 (air)
Cooling	100	no power	20	2.0 (Ar)
Pyrolysis	1300	100	10	2.0 (Ar)
Auto-zero	1300	0	5	0
Atomization	2200	3000	4	0
Cleaning	2500	500	5	2.0 (Ar)

SIS LS GF AAS was used as a comparative technique. Sample slurries containing a concentration of solids of 0.5% (m/v) were prepared in 0.2% (v/v) HNO_3+0.05% (v/v) Triton X-100. Immediately before sampling, the Ti ultrasound probe at 40% ultrasound amplitude was introduced into the auto-sampler cup containing slurries during 10 s to provide a uniform distribution of particles.

3. Results and discussion

3.1. Thermochemical behavior of lead using different chemical modifiers

The optimization of the pyrolysis and atomization temperatures is important in direct solid sampling mainly due to the influence of the matrix on the analyte signal. When aqueous calibration standards are involved, the heating program should be optimized to release the analyte from aqueous and solids similarly. Pyrolysis temperatures were varied in the 600–1600 °C range while the atomization temperature was fixed at 2000 °C. In absence of a modifier, Pb was stabilized up to 700 °C in aqueous and solid media. Despite the well-defined transient signals, the Pb absorbance reduced ca. 70% in the solid medium, revealing appreciable matrix effects. The presence of carbon residues inside the atomizer confirmed that the pyrolysis step would require improvements. In direct solid sampling, chemical modifiers can reduce matrix effects by (a) modifying the atomization mechanism of the analyte, often with increased thermal stability, and thus, higher pyrolysis temperatures can be established without significant analyte losses and (b) promoting the extraction of the analyte to the surface of the solid matrix, improving the conditions for atomic cloud generation. Therefore, the conventional chemical modifiers $Pd(NO_3)_2$, $Pd/Mg(NO_3)_2$, $NH_4H_2PO_4$, and the permanent modifier W (employed to coat the graphite platform) were evaluated to help the direct solid sampling and calibration with aqueous standards. The W-coated platform and $NH_4H_2PO_4$ allowed pyrolysis at temperatures of 900 °C and 1000 °C, respectively. In these conditions, the background was negligible, the peak profiles suggested single-stage atomization, but the sample residue still remained inside the atomizer. The use of $Pd(NO_3)_2$ or the mixture $Pd(NO_3)_2+Mg(NO_3)_2$ increased the pyrolysis temperature to 1300 °C but was ineffective in eliminating the sample matrix completely, even for a pyrolysis step as long as 50 s. After successive analytical cycles, the cumulative residue inside the atomizer impaired measurements due to light scattering. A soft brush could be used to remove the residue by manual handling. However, taking into consideration the facilities of the auto-sampler, a fully mechanized operation was preferred. An extra step comprising air-assisted pyrolysis at 600 °C during 30 s was added to improve matrix elimination [30]. This strategy was adequate to remove the matrix completely without analyte losses. In these conditions, no background was observed for W and $NH_4H_2PO_4$ modifiers. In the presence of $Pd(NO_3)_2$ or $Pd(NO_3)_2+Mg(NO_3)_2$, the low background absorption did not superpose the atomic absorption. This time-based spectra separation allowed analyte measurements without interference. The optimized pyrolysis and atomization temperatures for each modifier are presented in Table 3. Atomization temperatures were studied in the 1500–2500 °C range. The optimum atomization conditions were selected taking into account the atomic peak profile, repeatability, type and intensity of background, and sensitivity. The signal profile is an important feature: broad transient signals or the presence of double peaks may indicate difficulty in analyte vaporization/gas phase atomization.

Regarding atomization, the modifiers W or $NH_4H_2PO_4$ produced narrow transient peaks (typically 3 s from their appearance to baseline restoration) at 1700 and 1800 °C atomization temperatures, respectively. Shown in Fig. 1 are transient signals for Pb obtained in the presence of W (Fig. 1a) and $NH_4H_2PO_4$ (Fig. 1b). These signal profiles were similar to those obtained for Pd and Pd+Mg. Background was insignificantly low and the calculated repeatability (RSD) was 14% for W and 8.2% for $NH_4H_2PO_4$.

Transient signals for Pb in $Pd(NO_3)_2$ or $Pd/Mg(NO_3)_2$ were suitable only using atomization temperatures close to 2100 °C. It should be stressed that structured background appeared at atomization temperatures higher than 2400 °C, superposing atomic absorption signal. The RSDs of the determinations were 5.8% and 7.3% for $Pd(NO_3)_2$ and $Pd(NO_3)_2+Mg(NO_3)_2$, respectively.

Table 3
Pyrolysis (T_p) and atomization (T_a) temperatures, characteristic mass (m_o), and relative standard deviation (RSD) for Pb in aqueous and solid medium obtained with and without modifiers.

Modifier	T_p (°C)	T_a (°C)	m_o (pg)	RSD (%)	Structured background
None					
Aqueous	700	2000	16.2	5.8	No
1515 Apple Leaves	700	2000	19.3	15.5	Yes
1575a Spinach Leaves	700	2000	20.4	13.7	Yes
200 μg W					
Aqueous	1100	1700	13.4	3.9	No
1515 Apple Leaves	900	1700	15.3	14.4	No
1575a Spinach Leaves	900	1700	15.6	12.8	No
50 μg $NH_4H_2PO_4$					
Aqueous	1000	1800	8.9	3.3	No
1515 Apple Leaves	1000	1800	10.1	8.2	No
1575a Spinach Leaves	1000	1800	10.5	7.9	No
5 μg $Pd(NO_3)_2$					
Aqueous	1300	2200	12.7	2.1	No
1515 Apple Leaves	1300	2200	12.2	5.3	Yes
1575a Spinach Leaves	1300	2200	11.9	5.8	Yes
5 μg $Pd(NO_3)_2$/2.5 μg $Mg(NO_3)_2$					
Aqueous	1300	2200	14.8	3.6	No
1515 Apple Leaves	1300	2200	14.4	7.1	Yes
1575a Spinach Leaves	1300	2200	14.2	7.3	Yes

3.2. Matrix effects

The characteristic mass (m_o) is a useful parameter to check effectiveness of the heating program of the atomizer on minimization/elimination of matrix effects and was calculated as $0.0044m/A$, where m is the mass of analyte (pg) and A is the measured peak area. Analysis of Table 3 shows that the closest m_o values for aqueous and solid standards were obtained for $Pd(NO_3)_2$ and $Pd(NO_3)_2+Mg(NO_3)_2$. Thus, the optimized pyrolysis and atomization temperatures using those modifiers were efficient to circumvent matrix effects. Matrix effects were also evaluated by comparing slopes of calibration curves obtained from aqueous and solid standards in the presence of each modifier. The figures of merit of calibrations using aqueous and solid standards are depicted in Table 4. In spite of the fact that the lowest limit of detection was obtained with $NH_4H_2PO_4$ (4.2 pg), the slopes of curves corresponding to aqueous (4.88×10^{-4} s pg^{-1}) and solid (4.11×10^{-4} s pg^{-1}) calibrations were significantly different, showing that some matrix effects are still present. Thus, this modifier is not suitable to analyze solid samples using aqueous standards, otherwise errors close to 16% are found due to inadequate calibration. On the other hand, m_o values for Pb in both CRMs (10.1 and 10.5 pg) suggested some potential of $NH_4H_2PO_4$ for Pb determination using DSS and calibration with solid standards (Table 3). Similar slopes of calibration plots built up with solid and aqueous standards were obtained only for $Pd(NO_3)_2$ (3.50×10^{-4} s pg^{-1}—solid

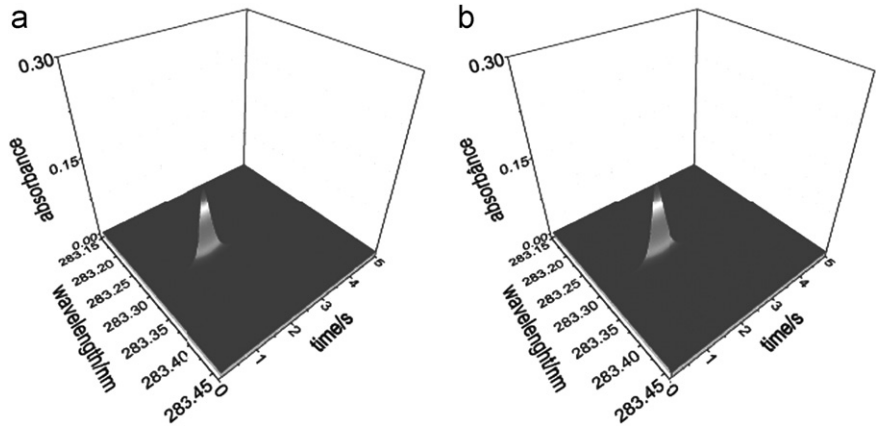

Fig. 1. Transient atomic absorption signals for Pb obtained in a W-coated platform (a) and $NH_4H_2PO_4$ (b).

Table 4
Figures of merit for calibration obtained with aqueous and solid standards using different modifiers.

Calibration	$Pd(NO_3)_2$	$Pd/Mg(NO_3)_2$	$NH_4H_2PO_4$	W-coated platform
Aqueous				
Slope (s pg^{-1})	3.47×10^{-4}	2.91×10^{-4}	4.88×10^{-4}	3.20×10^{-4}
R	0.9991	0.9968	0.9925	0.9974
LOD (pg)	7.3	11.7	4.2	8.5
RSD%	8.2	11	9.4	13
Solids				
Slope (s pg^{-1})	3.50×10^{-4}	2.86×10^{-4}	4.11×10^{-4}	2.79×10^{-4}
R	0.9989	0.9979	0.9772	0.9831
LOD (pg)	7.2	12.0	5.0	9.8
RSD%	12	14	18	15

and 3.47×10^{-4} s pg^{-1}—aqueous) and $Pd(NO_3)_2+Mg(NO_3)_2$ (2.86×10^{-4} s pg^{-1}—solid and 2.91×10^{-4} s pg^{-1}—aqueous). These findings strengthen potentialities of these modifiers to be employed for DSS combined with aqueous standard calibration. Limit of detection (LOD) was calculated using $3\sigma/S$, where σ is the standard deviation of ten successive measurements of the blank and S the slope of the calibration plot. Taking into consideration the lowest LOD and RSD acquired for $Pd(NO_3)_2$, this modifier was chosen for further studies.

3.3. Evaluation of minimum mass and homogeneity factor

DSS GF AAS is considered to be a microanalytical or ultra-microanalytical technique [31]. A large division of homogeneous materials may produce heterogeneous fractions, so the evaluation of the minimum sample size that statistically represents the entire sample is important [29]. The influence of sample size on accuracy and precision was studied by analyzing ($n=5$) different masses of 1575a Pine Needles (Fig. 2a) and 3246 Ginkgo Biloba (Fig. 2b) reference materials within the 0.05–1.0 mg range. For Pine Needles, more biased results were observed for sample masses lower than 0.2 mg. These may be explained by the low Pb contents for masses in the 0.05–0.2 mg range (8.4–33.4 pg), which are below or close to the limit of quantification (24.1 pg). Additionally, Fig. 3a reveals that masses of this CRM lower than 0.1 mg are inhomogeneous and should not be used. The best results were obtained for sample masses in the 0.2–0.8 mg interval (Fig. 2a). Sample masses higher than 0.8 mg inhibited the atomization of Pb and produced underestimated results. Sample amounts lower than 0.05 mg were not studied due to difficulties in handling very small amounts of samples manually. Sample masses greater than 1.0 mg may alter matrix decomposition and atomization kinetics of the analyte and

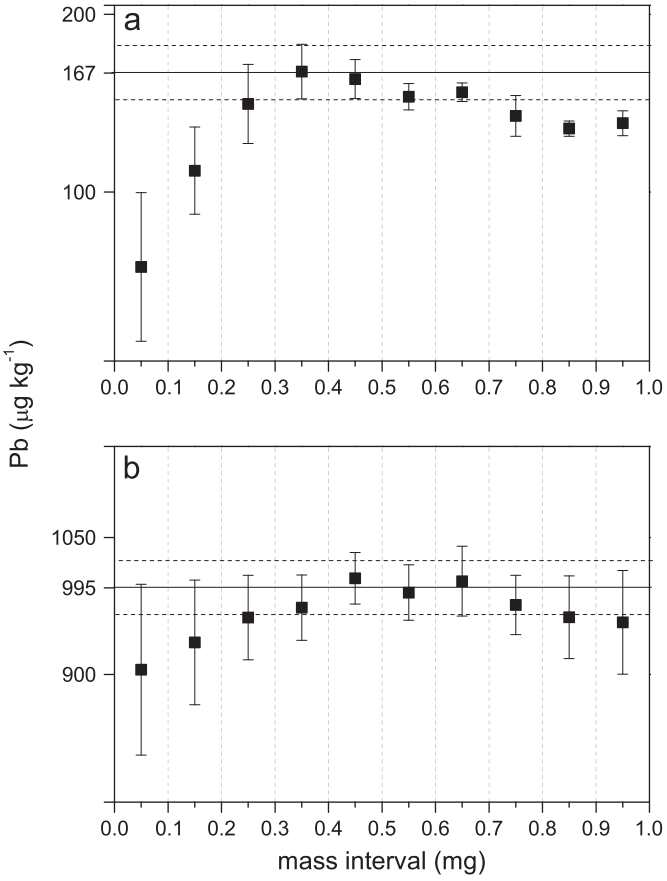

Fig. 2. Influence of sample mass on the precision and accuracy of Pb determination in 1575a Pine Needles (a) and 3246 Ginkgo Biloba (b).

were not tested. On the other hand, the high Pb content in Ginkgo Biloba (almost six times larger than that in Pine Needles) allowed the determination of Pb in the entire mass range (Fig. 2b). For masses of Ginkgo Biloba lower than 0.2 mg, the found Pb concentration (905 ± 94 ng g^{-1}) was in agreement with the reference value at 95% confidence level (t-test). It should be emphasized that the Ginkgo Biloba presented homogeneous for all mass intervals studied (Fig. 3b).

The homogeneity at micro scale may be evaluated by means of the homogeneity factor $H_e=S_H\times m^{1/2}$, in which S_H is the sampling uncertainty and m the sample mass [5]. Materials may be considered homogeneous when H_e is lower than 10. The 1575a

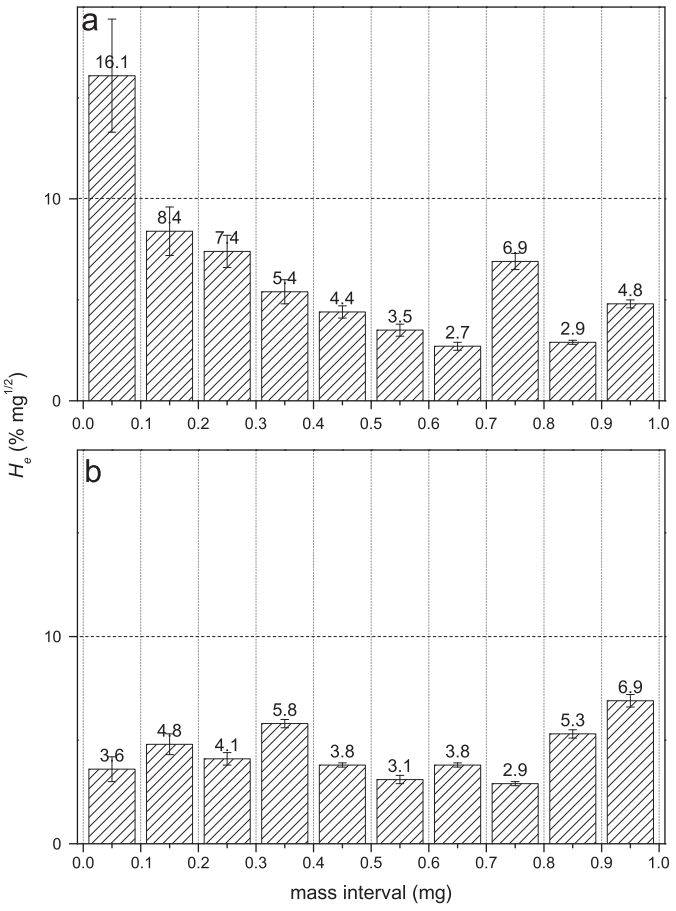

Fig. 3. Estimate of the homogeneity factor (H_e) for Pb in 1575a Pine Needles (a) and 3246 Ginkgo Biloba (b).

Pine Needles was considered to be homogeneous for sample masses higher than 0.1 mg since calculated H_e factors were below 10 (Fig. 3). Sample masses lower than 0.1 mg produced H_e=16.1 for the 1575a Pine Needles (Fig. 3a) and H_e=3.6 for 3246 Ginkgo Biloba (Fig. 3b). These findings may be explained by the different contents of Pb in CRMs. The higher the Pb content in the sample, the greater the probability of producing homogeneous distribution of analyte in the material, and the lower the RSD of measurements.

3.4. Analysis of medicinal plant samples

After optimization of the main parameters, the proposed procedure was applied to the direct determination of Pb in ten samples of medicinal plants. Determinations were carried out using the Pb line at 283.306 nm and peak volume selected absorbance of 3 pixels. Calibrations in the 10–1000 pg Pb mass range with regression coefficients better than 0.999 were typically obtained. Accuracy was checked for Pb determination in 1515 Apple Leaves, 1570a Spinach Leaves, 3246 Ginkgo Biloba, 1547 Peach Leaves and 1575a Pine Needles certified reference materials using calibration with aqueous and solid standards (Table 5). Results were in agreement at a 95% confidence level (paired *t*-test) with reference values. Indeed, ten medicinal plant samples were analyzed by the proposed procedure (Table 6). The concentration of Pb varied from 0.30–1.94 μg g^{-1}. These concentrations are comparable to those found in earlier works [32]. The RSD (n=3) was 10% for the sample *Echinodorus grandiflorus* containing 0.88 μg g^{-1} Pb. The limit of quantification (dry mass) was 0.024 μg g^{-1}. For comparison purposes, samples were also analyzed by SIS LS GF AAS. Results found for samples presenting a Pb concentration higher than 0.8 μg g^{-1} (limit of quantification) were in agreement with those obtained by DSS HR-CS GF AAS (Table 6).

Table 5
Results (ng g^{-1}) expressed as mean ± standard deviation for Pb in CRMs measured value (n=3) by DSS HR-CS GF AAS using aqueous (*A*) and solid (*S*) calibrations.

CRM	Certified value	Determined by	
		A	*S*
1515 Apple Leaves	470 ± 24	475 ± 22	482 ± 31
1570a Spinach Leaves	200[a]	204 ± 15	220 ± 29
3246 Ginkgo Biloba	995 ± 30	1004 ± 49	1139 ± 93
1547 Peach Leaves	870 ± 30	885 ± 41	861 ± 67
1575a Pine Needles	167 ± 15	166 ± 18	179 ± 20

[a] Non-certified (reference value).

Table 6
Results (μg g^{-1}) expressed as mean ± standard deviation for Pb in medicinal plant samples determined (n=3) by the proposed (DSS HR-CS GF AAS) and comparative (SIS LS GF AAS) methods.

Sample	DSS HR-CS GF AAS	SIS LS GF AAS
Peumus boldus	0.37 ± 0.04	< 0.8
Chamomilla recutita	0.30 ± 0.01	< 0.8
Bacharis crispa	0.94 ± 0.04	1.02 ± 0.18
Equisetum ssp	0.96 ± 0.02	1.06 ± 0.19
Echinodorus grandiflorus	0.88 ± 0.09	1.28 ± 0.07
Melissa officinalis	1.94 ± 0.06	1.91 ± 0.06
Foeniculum vulgare	0.76 ± 0.01	< 0.8
Panax ginseng	0.79 ± 0.04	< 0.8
Annona muricata	0.44 ± 0.01	< 0.8
Mikania glomerata	0.57 ± 0.01	< 0.8

4. Conclusions

The use of $Pd(NO_3)_2$ combined with air-assisted pyrolysis allowed calibration using aqueous standards in the direct analysis of plant materials for Pb determination by HR-CS GF AAS. The limit of quantification (dry mass) for Pb was 0.024 μg g^{-1}, almost 33-fold lower than the LOQ found by line-source GF AAS using slurry sampling. The proposed DSS-GF AAS for plant analysis is considered to be an environmentally friendly analytical procedure due to minimum waste generation and risk to analyst, short time (ca. 200 s) for one measurement, and hazardous reagents are not required.

Acknowledgments

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grant 09/52480-0) for financially supporting this work and Coordenação de Aperfeiçoamento Pessoal de Nível Superior (CAPES) for providing fellowships to J.F.R, and A.V. The authors are also grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for research-ships to J.A.G.N. and J.A.N.

References

[1] L.F. Verissimo, A.D. Bacchi, T. Zaminelli, G.H.O. Paula, E.G. Moreira, J. Braz., Pharmacogn. 21 (2011) 1163–1171.

[2] W.M. Bandaranayake, in: I. Ahmad, F. Aqil, M. Owais (Eds.), Modern Phytomedicine: Turning Medicinal Plants Into Drugs, John Wiley & Sons, Weinheim, 2007, pp. 25–57.
[3] M.M. Ozcan, A. Unver, T. Ucar, D. Arslan, Food Chem. 106 (2008) 1120–1127.
[4] M.A. Belarra, M. Resano, F. Vanhaecke, L. Moens, Trends Anal. Chem. 21 (2002) 828–839.
[5] U. Kurfürst, Solid Sample Analysis: Direct and Slurry Sampling Using GF-AAS and ETV-ICP, Springer, Berlin, 1998.
[6] L'vov B.V., Spectrochim. Acta Part B 17 (1961) 761–770.
[7] B. Welz, M.G.R. Vale, D.L.G. Borges, U. Heitmann, Anal. Bioanal. Chem. 389 (2007) 2085–2095.
[8] M.A. Belarra, I. Lavilla, J.M. Anzano, J.R. Castillo, J. Anal. At. Spectrom. 7 (1992) 1075–1078.
[9] C.S. Silva, C.S. Nomura, J.A. Nóbrega, P.V. Oliveira, Microchim. Acta 161 (2008) 109–114.
[10] D.R. Neves, S.R. Oliveira, J.F. Rêgo, D.L. Flumignan, J.E. Oliveira, J.A.Gomes Neto, At. Spectrosc. 31 (2010) 141–146.
[11] Z. Kowalewska, E. Bulska, A. Hulanicki, Spectrochim. Acta Part B 54 (1999) 835–843.
[12] E.C. Lima, J.L. Brasil, A.H.D.P. Santos, Anal. Chim. Acta 484 (2003) 233–242.
[13] B. Welz, D.L.G. Borges, F.G. Lepri, M.G.R. Vale, U. Heitmann, Spectrochim. Acta Part B 62 (2007) 873–883.
[14] I.M. Dittert, J.S.A. Silva, R.G.O. Araujo, A.J. Curtius, B. Welz, H. Becker-Ross, Spectrochim. Acta Part B 64 (2009) 537–543.
[15] D.L.G. Borges, A.F. Silva, B. Welz, A.J. Curtius, U. Heitmann, J. Anal. At. Spectrom. 21 (2006) 763–769.
[16] M. Resano, J. Briceno, M.A. Belarra, J. Anal. At. Spectrom. 24 (2009) 1343–1354.
[17] M. Resano, E. Mozas, C. Crespo, J. Briceno, J.D. Menoyo, M.A. Belarra, J. Anal. At. Spectrom. 25 (2010) 1864–1873.
[18] D.L.G. Borges, A.F. Silva, A.J. Curtius, B. Welz, U. Heitmann, Microchim. Acta 154 (2006) 101–107.
[19] L.M.G. Santos, R.G. Araujo, B. Welz, S.D. Jacob, M.G.R. Vale, H. Becker-Ross, Talanta 78 (2009) 577–583.
[20] L.M.G. Santos, B. Welz, R.G.O. Araujo, S.D. Jacob, M.G.R. Vale, A. Martens, I.B.G. Martens, H. Becker-Ross, J. Agric. Food Chem. 57 (2009) 10089–10094.
[21] J. Sardans, F. Montes, J. Penuelas, Soil Sediment Contam. 20 (2011) 447–491.
[22] I.M. Dittert, D.L.G. Borges, B. Welz, A.J. Curtius, H. Becker-Ross, Microchim. Acta 167 (2009) 21–26.
[23] J. Briceno, M.A. Belarra, K.A.C. De Schamphelaere, S. Vanblaere, C.R. Janssen, F. Vanhaecke, M. Resano, J. Anal. At. Spectrom 25 (2010) 503–510.
[24] R.G.O. Araujo, F. Vignola, I.N.B. Castilho, D.L.G. Borges, B. Welz, M.G.R. Vale, P. Smichowski, S.L.C. Ferreira, H. Becker-Ross, Spectrochim. Acta Part B 66 (2011) 378–382.
[25] M. Resano, J. Briceno, M.A. Belarra, Spectrochim. Acta Part B 64 (2009) 520–529.
[26] F.G. Lepri, D.L.G. Borges, R.G.O. Araujo, B. Welz, F. Wendler, M. Krieg, H. Becker-Ross, Talanta 81 (2010) 980–987.
[27] J. Sardans, F. Montes, J. Penuelas, Spectrochim. Acta Part B 65 (2010) 97–112.
[28] L. Bianchin, D. Nadvorny, A.F. Silva, M.G.R. Vale, M.M. Silva, W.N.L. Santos, S.L.C. Ferreira, B. Welz, U. Heitmann, Microchem. J. 82 (2006) 174–182.
[29] J. Pauwels, C. Hofmann, C. Vandecasteele, Fresenius' J. Anal. Chem. 348 (1994) 418–421.
[30] A.P. Oliveira, J.A. Gomes Neto, J.A. Nóbrega, P.V. Oliveira, Spectrochim. Acta Part B 60 (2005) 681–686.
[31] I.W.D. Hackh, R.L. Grant, C. Grant, Grant and Hackh's Chemical Dictionary, fifth ed., McGraw-Hill, Texas, 1987.
[32] E.D. Caldas, L.L. Machado, Food Chem. Toxicol. 42 (2004) 599–603.