

Determination of Cd in Blood by Microwave-Induced Combustion Coupled to Flame Furnace Atomic Absorption Spectrometry

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Um sistema de combustão iniciada por microondas foi acoplado a um espectrômetro de absorção atômica com atomização em tubo metálico aquecido com chama (FF) do tipo ar-acetileno para a determinação de cádmio em sangue. Amostras de sangue liofilizado foram preparadas como comprimidos, posicionadas em um suporte de quartzo e introduzidas em uma câmara de vidro empregada para a etapa de combustão. A câmara foi acoplada ao tubo metálico usando tubos de politetrafluoroetileno e de quartzo. A ignição foi iniciada por irradiação microondas usando solução de nitrato de amônio adicionada em papel previamente descontaminado. Oxigênio foi usado na etapa de combustão e para o transporte dos produtos gerados até o tubo aquecido. Grafite em pó de alta pureza foi misturada com as amostras antes do preparo dos comprimidos. O volume da solução de NH_4NO_3 , a vazão de oxigênio, a estequiometria da chama, o tipo de suporte e a quantidade de massa de amostra foram avaliados. A calibração foi possível usando solução de referência adicionada a comprimidos de grafite de alta pureza, não sendo necessário o uso de material de referência certificado (CRM). Foi possível a combustão de até 56 mg de amostra, permitindo a obtenção de limite de quantificação de $0,018 \mu\text{g g}^{-1}$ e massa característica de 50 pg de Cd. Os valores dos brancos foram baixos (absorbância integrada menor que 0,01 s). Os resultados foram considerados satisfatórios com respeito à exatidão (concordância com valores de CRMs entre 95 e 99%) e à precisão (coeficiente de variação $< 12\%$). Até 15 determinações podem ser feitas por hora incluindo a etapa de pesagem.

Microwave-induced combustion system was coupled to a metallic flame furnace (FF) atomic absorption spectrometer and applied for cadmium determination in blood. Lyophilized blood samples were prepared as pellets, positioned on a quartz holder and introduced into a glass chamber used for the combustion step. The glass chamber was coupled to the metallic flame furnace by using polytetrafluoroethylene and quartz tubes. Ignition was performed by microwave radiation using ammonium nitrate solution added to a small piece of previously cleaned paper. Oxygen was used to assist the sample combustion and also to transport combustion products up to the FF heated by an air/acetylene flame. High purity graphite powder was mixed with samples before pellets preparation. The volume of NH_4NO_3 solution, oxygen flow-rate, flame stoichiometry, sample holder type and the sample mass range were evaluated. Calibration step was feasible using adsorbed reference solution in pelletized high purity graphite avoiding the use of certified reference material (CRM). Sample masses up to 56 mg could be used allowing quantification limit of $0.018 \mu\text{g g}^{-1}$ and characteristic mass of 50 pg Cd. Low values for blanks were obtained (integrated absorbance lower than 0.01 s) and results were considered satisfactory regarding to both accuracy (agreement with results using CRMs between 95 to 99%), and precision (relative standard deviation $< 12\%$). Up to 15 determinations can be performed *per* hour including the weighing step.

Keywords: flame furnace atomic absorption spectrometry, microwave induced combustion, cadmium determination, solid sampling, blood analysis

Introduction

Analysis of solid samples offers a number of important advantages partially by avoiding the dissolution step: the

risk of contamination as well as the risk of analyte loss is considerably reduced, the limit of detection (LOD) is improved as sample is not diluted and the use of corrosive or hazardous reagents is not required, resulting in both economic and environmental benefits.¹ Graphite furnace atomic absorption spectrometry (GF-AAS) has been currently used

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for solid sampling analysis²⁻⁴ allowing the achievement of low LODs for many analytes.^{5,6} In spite of better suitability of GF-AAS, flame atomic absorption spectrometry (FAAS) has been also used for solid sample introduction.⁷ In addition, the simplicity, availability in many laboratories and relative low cost can make FAAS an attractive technique for this purpose. However, this technique presents relatively low sensitivity and no commercial device suitable for solid sampling (SoS) analysis by FAAS is available up to now. Several approaches have been described to improve the sensitivity of conventional FAAS. Special systems have been used in order to increase the density of atoms in the optical path of the spectrometer as slotted-tube atom trap,⁸ high-temperature nebulization,⁹ beam injection flame furnace atomic absorption spectrometry,^{10,11} thermospray flame furnace atomic absorption spectrometry,¹²⁻¹⁵ and pneumatic nebulization flame furnace atomic absorption spectrometry.¹⁶ However, despite the good performance for liquids these procedures are not suitable for direct introduction of solid samples. In the case of solid introduction using FAAS another difficulty is related to the choice of a convenient analytical calibration procedure¹ and some problems have been reported if slurries are used for sample introduction using the pneumatic nebulizer.¹⁷ On the other hand, some works have demonstrated the feasibility of using solid sampling flame atomic absorption spectrometry (SoS-FAAS) for trace analysis.^{7,18-21} In these works, a conventional air/acetylene flame was used as atomizer and samples were weighed directly into a small polyethylene vial connected to a glass chamber. Air was used to transport ground samples as dry aerosol to a T-shaped quartz cell positioned above the burner in the optical path of spectrometer. In spite of good accuracy and relatively low LODs had been obtained with this system a limitation related to the small sample mass that could be introduced into the atomizer was reported.^{7,18-21} To overcome this problem, solid samples were introduced as pellets into a quartz cell for analysis by FAAS.²² With this system, samples up to 7 mg could be weighed into a small paper capsules and introduced into a quartz cell heated by an air/acetylene flame and LOD as low as 0.23 $\mu\text{g g}^{-1}$ was obtained for cadmium determination.

Some authors proposed to separate the sample vaporization step from atomization process. Infrared lamps were used to vaporize the analyte that was further transported to the flame or to a tube positioned above the burner of a conventional atomic absorption spectrometer. However, for the calibration step it was necessary the use of CRMs and the limitation of low masses still remained.^{23,24}

Recently, a novel system was proposed using microwave induced combustion (MIC) to the combustion of organic samples in closed quartz vessels pressurized with oxygen

with the ignition step being performed by microwave radiation. Samples were pressed as pellets and positioned on a small piece of low-ash filter paper that was previously placed on a quartz holder. About 50 μL of 6 mol L^{-1} ammonium nitrate solution is added as igniter, and the system is closed and pressurized with oxygen.^{25,26} The proposed mechanism is related to the heating of the NH_4NO_3 solution wetted-filter paper by microwave radiation. The fast heating allows the creation of a small flame that, in presence of a convenient oxygen-pressure, causes a complete combustion of sample. In this system, sample combustion is performed in less than one minute with minimum acid consumption.²⁷ Based in previous works,²⁵⁻²⁷ some authors proposed the combination of microwave induced combustion (MIC) system to a flame furnace (FF) for analysis of botanical samples by atomic absorption spectrometry (AAS).²⁸ For the combustion step, solid samples were introduced as pellets into a glass chamber using a quartz holder device. This chamber was coupled to a metallic FF by using polytetrafluoroethylene and quartz tubes. The glass chamber was positioned inside a microwave oven where the sample was combusted. Ignition was performed by microwave radiation using a small piece of paper wetted with few microliters of NH_4NO_3 solution. Oxygen was used to assist the combustion and also to transport the combustion products up to a heated FF positioned above an air/acetylene type burner and calibration was feasible by using reference solutions. Cadmium and Pb were determined in botanical samples as examples to demonstrate the potential of the proposed procedure for trace analysis. Moreover, with microwave-induced combustion flame furnace atomic absorption spectrometry (MIC-FF-AAS) system the LOD was improved by a factor of 50 and 12, respectively for Cd and Pb in relation to the conventional FAAS technique.

In the present work, MIC-FF-AAS was applied to Cd determination in blood samples in order to increase the analyte amount introduced into the atomizer in comparison with conventional flame-AAS atomizers. Accuracy was evaluated by using CRMs. Operational conditions were evaluated and results were compared to those using other devices proposed in the literature for SoS using flame heated systems.

Experimental

Instrumentation

Atomic absorption measurements for Cd determination were carried out using an atomic absorption spectrometer (Varian, Model SpectrAA 600, Mulgrave, Australia),

with deuterium lamp background correction system and a conventional burner (slit of 10 cm, air/acetylene flame). A cadmium hollow-cathode lamp was operated at 4 mA, wavelength was set at 228.8 nm and the spectral bandwidth was 0.5 nm. Integrated absorbance with an integration time of 30 s was used for signal evaluation.

A freeze dryer (Terroni Fauvel, Model LH 2000/3, São Carlos, Brazil) was used for blood lyophilization process. An ultra-micro balance (Sartorius, Model M2P, Goettingen, Germany) with a resolution of 1 µg and an electronic weighing range up to 2 g was used for sample weighing and a hydraulic press set at 1 ton (Specac, Model Hydraulic Press 15 ton, Orpington, England) was used to prepare the sample pellets.

For the combustion step, a microwave oven (Panasonic, Model NN-S52 B, Manaus, Brazil) with internal volume of 28 L and nominal maximum power of 900 W was used.

Closed polytetrafluoroethylene-perfluoroalkoxy (PTFE-PFA) vessels heated by microwave radiation (microwave oven Model ETHOS 1, Milestone, Sorisole, Italy) were used for conventional sample digestion. Cadmium determination was also performed by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, Model Sciex-Elan DRC II, Thornhill, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a quartz torch with a quartz injector tube (2 mm i.d.). Measurements were carried out according to the instructions of manufacturer.²⁹

Reagents and samples

All glass or quartz apparatus were soaked in 10% (v/v) HNO₃ solution for 24 h and washed with water before use. Water was distilled, deionized and purified using a Milli-Q system (Millipore Corp., Bedford, USA). Nitric acid (Merck, Darmstadt, Germany) was doubly distilled in a Model duoPUR 2.01E sub-boiling system (Milestone, Bergamo, Italy). Analytical grade hydrogen peroxide (30%, Merck, Darmstadt, Germany) was used as aid for samples digestion.

Calibration reference solutions for Cd were prepared immediately before use by dilution of a Titrisol® stock solution containing 1000 mg L⁻¹ in 2% (v/v) HNO₃ (Merck, Darmstadt, Germany). Ammonium nitrate solution (6 mol L⁻¹) was used as ignition aid.

High purity graphite powder (RWA, n° 431815/00, series X/62/403) was obtained from SGL Carbon (Bonn, Germany). Filter paper (2.2 cm², 25 mg) with low ash content (Black Ribbon Ashless, Schleicher & Schuell GmbH, Dassel, Germany) was used to aid the combustion process. The filter paper was cleaned with 10% (v/v) HNO₃

in an ultrasonic bath (Odontobrás, 100W, Model 1440D, Ribeirão Preto, Brazil) for 20 min and dried in an oven (Nova Ética, 820 W, Model 400/2ND 300, São Paulo, Brazil) by 2 h at 60 °C before use.

Human blood samples were obtained from a local hospital. Sodium citrate solution was added to the samples as anticoagulant. Samples were stored under freezing at -4 °C before use. For the initial development and optimization of the procedure, a spike correspondent to 0.19 µg mL⁻¹ Cd was performed to a sample of blood before lyophilization process.

Certified reference blood was not available and biological CRMs with different composition were used: dogfish muscle and liver DOLT-2 (NRCC, National Research Council Canada), non defatted lobster hepatopancreas LUTS-1 (NRCC), skim milk powder BCR-151 (IRMM, Institute for Reference Materials and Measurement), oyster tissue 1566a (NIST, National Institute of Standards & Technology) and oyster tissue 1566b (NIST).

Sample preparation

Human blood samples were defrost and lyophilized for 12 h, ground using an agate mortar and pressed (1 ton) to prepare pellets of 5 mm diameter. Pellets of lyophilized blood and pellets of lyophilized blood mixed with high purity graphite were also evaluated.

Sample digestion for ICP-MS

Cadmium determination was also performed by ICP-MS after sample digestion using closed vessels with microwave heating. About 80 mg of lyophilized human blood were digested in PTFE-PFA vessels, using 8 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide. After acid addition to samples the vessels were kept overnight. Then, vessels were closed and the decomposition was performed based on the manufacturer recommendation.³⁰ Digested samples were diluted with water to 25 mL in polypropylene vessels before analysis by ICP-MS.

Proposed MIC-FF-AAS procedure

A domestic microwave oven was modified in order to allow an oxygen flow entrance in the combustion chamber and to aid the transport of the combustion products up to the FF (Figure 1a). Microwave power that was effectively transferred to the oven cavity was determined according to a procedure previously described.³¹ For the combustion process, a borosilicate glass chamber (internal volume of 60 mL) and a quartz holder (2.5 cm length) were used. The glass chamber was connected by a PTFE glove

(3 mm i.d., 2 cm length) to a second glass chamber (expansion chamber). The expansion chamber was necessary to minimize eventual excessive pressure during the beginning of combustion. A PTFE tube (10 cm length, 3 mm i.d.) connected to a quartz tube (30 cm length and 3 mm i.d.) was used to the transport of combustion products inside the combustion chamber up to the FF. The end of this quartz tube was fitted to the FF (10 cm length, 11 mm o.d. and 9 mm i.d.), that was positioned 4 mm above the burner. The FF was home-made and it was produced from a metallic bar obtained from Camacam, Inconel 600, Brazil (72% Ni, 15% Cr, 8% Fe, 0.5% Cu and 0.3% Ti).

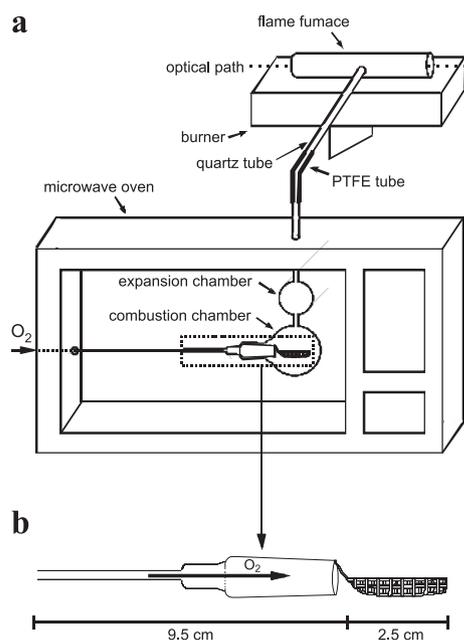


Figure 1. (a) MIC-FF-AAS device and (b) detail of quartz holder.

A pellet of lyophilized blood mixed with graphite was placed on a filter paper and it was wrapped with aid of polypropylene tweezers and positioned on the quartz holder. In order to have reproducible ignitions ammonium nitrate solution must be added to the extremity of filter paper close to the oxygen supply. After holder introduction into the combustion chamber oxygen was passed through the device (1 to 2.5 L min^{-1}) and microwave was irradiated using the maximum power. Combustion time was typically between 8 and 15 s. After ignition, the microwave radiation was stopped and atomic signals were recorded. Integrated absorbance (peak area) of 30 s was used throughout for the proposed MIC-FF-AAS procedure. After combustion has been finished the quartz holder was removed for a subsequent cycle of analysis. Calibration was evaluated by using reference solution added directly on the filter paper as described in previous work²⁸ or using reference solution added to high purity graphite powder pellets.

Results and Discussion

Optimization of operating conditions for MIC-FF-AAS

Initial experiments were performed by trying to introduce original blood samples (not lyophilized) directly into the metallic flame furnace. However, solid deposition in tube used for sample introduction was observed and results were not reproducible. On the other hand, preliminary tests using MIC-FF-AAS procedure for lyophilized samples were performed according to conditions described in previous work.²⁸ Pellets of lyophilized blood were wrapped with filter paper and placed on the sample holder. Ammonium nitrate solution (40 μL) was added to the paper and the sample holder was introduced into the glass chamber. Then, microwave irradiation was applied using the maximum power up to starting sample combustion (about 10 s). The maximum real power of microwave was 615 W and this condition was always used for the experiments by MIC-FF-AAS. Combustion products were transported to the FF and atomic signal was recorded. However, black particles remained after combustion inside the glass chamber and in the PTFE tube. It occurred due to sample falling through the holes in the basis of sample holder during the combustion. The quartz sample holder was changed with holes narrower than the previous type (Figure 1b). Using this holder the combustion process always occurred with complete combustion.

The influence of volume of 6 mol L^{-1} NH_4NO_3 solution was investigated from 10 to 50 μL . Volumes lower than 40 μL of ammonium nitrate solution were not sufficient to start the combustion process. With 40 or 50 μL of NH_4NO_3 solution the combustion process always occurred. This result was in agreement with results previously reported.²⁵ For further experiments, 40 μL of ammonium nitrate solution was selected.

Preliminary tests showed that characteristic mass of Cd was different for reference solution and solid sample. Addition of graphite has been proposed in direct solid sampling- graphite furnace atomic absorption spectrometry in order to allow sensitivities more close to those using reference solutions.³² In this work, tests were performed by mixing samples with 30 mg of high purity graphite powder and pressed as pellets. With this condition, results for characteristic mass were more similar between samples and reference solution added to graphite pellets used for calibration and graphite addition was used for further oxygen flow-rate, flame stoichiometry, calibration and sample mass evaluation.

The effect of oxygen flow-rate on characteristics mass of Cd was evaluated (Figure 2). For oxygen flow-rates

lower than 1.0 L min^{-1} (not shown in Figure 2) the ignition was not reproducible and the Cd signal was lower due to the incomplete burning of sample. For oxygen flow-rate higher than 2.0 L min^{-1} a decrease occurred in the analytical signal. This result was probably caused by dilution of analyte in gaseous phase. Better sensitivity and relative standard deviation (RSD) were obtained with O_2 flow-rate of 1 L min^{-1} and this condition was used for subsequent studies.

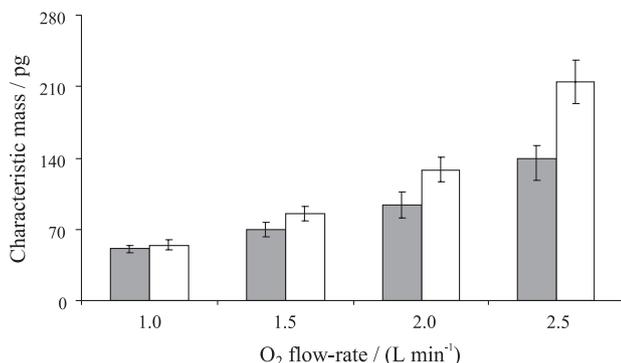


Figure 2. Characteristic masses obtained for (■) reference solution adsorbed in 30 mg of high purity graphite pellet and (□) pellets of 10 mg of solid sample mixed with 30 mg of high purity graphite for Cd with different oxygen flow-rate: air/acetylene, $16.0/2.0 \text{ L min}^{-1}$. Cd mass in reference solution added to graphite pellet was 5.0 ng and in solid sample was 6.2 ng ($n = 5$).

Flame stoichiometry

The influence of flame composition on Cd characteristic mass was investigated and results are shown in Figure 3. The following air/acetylene flow-rates were evaluated: $12.0/2.4$, $12.0/2.0$, $14.0/2.0$, $16.0/2.0$ and $18.0/2.0 \text{ L min}^{-1}$. Lower characteristic mass and standard deviation for Cd determination were obtained using air/acetylene flow-rates of $16.0/2.0 \text{ L min}^{-1}$. Background signals were always lower than 0.035 in peak height scale for all investigated flame composition. These results were similar to previous work using MIC-FF-AAS.²⁸ However, when compared with results of the present work, the small difference of chosen flame composition was probably due to the graphite presence in the pellet. Then, an air/acetylene flow-rate of $16.0/2.0 \text{ L min}^{-1}$ was applied for subsequent tests.

Calibration

Similar results for sensitivity were obtained if pellets for reference solutions and samples were prepared with 30 mg of graphite powder. With graphite addition good agreement between signals for reference solution and solid samples were obtained. The correlation coefficient for calibration curve up to 60 ng Cd was 0.9996 with the use of reference solution adsorbed in graphite pellets. Figure 4 shows the

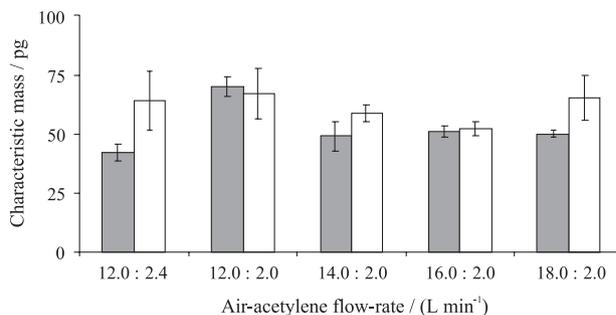


Figure 3. Characteristic masses obtained for (■) reference solution adsorbed in 30 mg of high purity graphite pellets and (□) pellets of 10 mg of solid sample mixed with 30 mg of high purity graphite for Cd with different flame stoichiometry. Oxygen flow-rate: 1 L min^{-1} . Cd mass in reference solution added to graphite pellet was 5.0 ng and in solid sample was 6.2 ng ($n = 5$).

typical signal using MIC-FF-AAS for Cd determination in lyophilized blood samples using graphite pellets. It can be observed that Cd signal was completely integrated in 15 s and background was relatively low (< 0.03 in peak height). The low background signal was compensated by the deuterium corrector and a more powerful corrector (e.g., based on Zeeman effect) was not necessary.

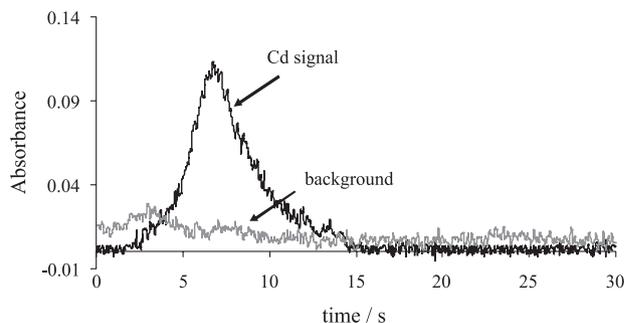


Figure 4. Analytical signal for Cd (6.2 ng) in lyophilized blood samples (10 mg) mixed with high purity graphite (30 mg). Flame stoichiometry: air/acetylene, $16.0/2.0 \text{ L min}^{-1}$. Oxygen flow-rate: 1 L min^{-1} .

Sample mass

In a similar way of a previous work,³³ a study was performed in order to evaluate the minimum and maximum limits feasible to apply the proposed procedure by MIC-FF-AAS (Figure 5). Pellets containing 2.7 to 90 mg of sample plus 30 mg of graphite were used and standard deviation was calculated using analysis of variance considering a confidence interval of 95% (Tukey-Kramer multiple comparisons test). Sample masses lower than 5 mg showed high dispersion of results probably due to heterogeneity of analyte in samples. With sample masses higher than 56 mg a black residue was observed in the glass chamber. This result was considered to be caused by incomplete sample combustion. In addition, memory effects were observed

using this condition and a cleaning step must be applied after each run. However, up to 10 runs using 56 mg of sample mass could be carried out without changes in analytical signal. Therefore, sample masses between 5 to 56 mg could be used in the present procedure.

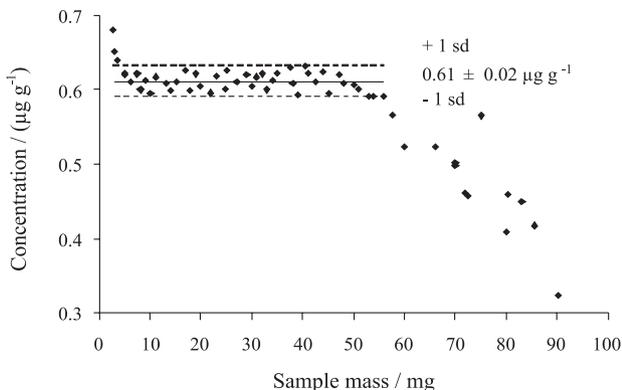


Figure 5. Influence of sample mass for Cd determination by MIC-FF-AAS, using pellets of different sample mass mixed with 30 mg of high purity graphite. Flame stoichiometry: air/acetylene, 16.0/2.0 L min⁻¹. Oxygen flow-rate: 1 L min⁻¹. Horizontal lines represent the mean and the standard deviation (sd) for the useful mass range.

Determination of Cd in human blood and in certified reference materials

Cadmium was determined in lyophilized human blood by MIC-FF-AAS and results were lower than 0.005 µg g⁻¹ (correspondent to < 1.6 µg L⁻¹ in blood samples). These results were confirmed by ICP-MS analysis with previous sample digestion. For lyophilized blood sample with Cd spike the results by MIC-FF-AAS and ICP-MS after digestion presented an agreement better than 95%. Cadmium was also determined in different biological CRMs (Table 1) and an agreement to the mean value of certified value between 95 to 99% was found for all certified reference samples (no statistical difference based on t-test, confidence level of 95%).

Comparison of MIC-FF-AAS procedure

Results using MIC-FF-AAS were compared with those from different procedures for biological sample analysis using FAAS^{22,24,28} and conventional graphite furnace atomic absorption spectrometry using diluted blood samples³⁴ (Table 2). The characteristic mass of Cd (0.05 ng) obtained with proposed procedure was the same or better than by a factor up to 50 in comparison with other works using FAAS systems.^{22,24,28} For MIC-FF-AAS the LOD (0.005 µg g⁻¹) was similar when using a similar procedure (0.003 µg g⁻¹)²⁸ but up to 40 times better than other procedures using FAAS systems.^{22,24} As expected, the LOD using GF-AAS³⁴ was

Table 1. Results for Cd determination using MIC-FF-AAS (results, in µg g⁻¹, represent the mean and respective standard deviation of results, n = 5)

CRM	Certified value	MIC-FF-AAS
IRMM BCR-151	0.101 ± 0.008	0.096 ± 0.010
NIST 1566a	4.15 ± 0.38	4.02 ± 0.32
NIST 1566b	2.48 ± 0.08	2.36 ± 0.22
NRCC DOLT-2	20.80 ± 0.50	20.64 ± 0.21
NRCC LUTS-1	14.2 ± 1.0	13.6 ± 1.6

Table 2. Characteristic mass, limit of detection and maximum sample mass used for different techniques for Cd determination

Technique	m ₀ / ng	LOD / (µg g ⁻¹)	Sample mass / mg	Reference
Conventional FAAS ^a	-	10 ^a	-	22
Conventional FAAS	2.5	-	-	24
SoS-FAAS	0.2	0.03	10	24
SoS-FAAS	0.34	0.23	7	22
GF-AAS ^b	-	0.00054 ^b	-	34
MIC-FF-AAS	0.05	0.003	60	28
MIC-FF-AAS	0.05	0.005	56	this work

^acalculated value considering the digestion of 100 mg of sample and dilution to 25 mL; ^bµg L⁻¹.

lower (0.00054 µg mL⁻¹). However, the obtained LOD using the proposed MIC-FF-AAS system was considered suitable for Cd determination in biological samples, as blood.

On the other hand, maximum sample masses were similar by using MIC-FF-AAS procedure²⁸ but higher than those reported in other works using FAAS.^{22,24} Relative standard deviation was lower than 12% and it was considered suitable for the proposed procedure.

In this work, the limit of quantification (10σ, n = 10) was 0.018 µg g⁻¹ and it was possible to perform up to 15 determinations in 1 h including the weighing step. Moreover, it was feasible the calibration using adsorbed reference solution in pelletized high purity graphite avoiding the use of solid CRMs.

Conclusions

Relatively low LOD and RSD were obtained using the proposed MIC-FF-AAS procedure for Cd determination in blood in view of the relatively high sample masses used (up to 56 mg). Calibration was carried out with reference solution added to graphite pellets which is an advantage in comparison with the use of CRMs for calibration. Moreover, the coupling of the MIC procedure to an inexpensive FF-AAS spectrometer makes this procedure

an alternative to more expensive techniques for direct solid sample analysis.

Acknowledgments

The authors thank to CAPES and CNPq for supporting this study.

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Received: March 17, 2009

Web Release Date: January 28, 2010