

A New Technique for the Direct Analysis of Combustible Solids by Flame Atomic Absorption Spectrometry

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Uma nova técnica é sugerida para a análise de sólidos por Espectrometria de Absorção Atômica (EAA) em chama. Uma alíquota da amostra, de 0,1 a 10,0 mg colocada sobre uma plataforma de grafite, é situada sob o foco de três lâmpadas infravermelhas. A combustão da amostra é iniciada por um flash das lâmpadas e a fumaça contendo os elementos mais voláteis é transportada para a chama por uma corrente de ar. Foram estudadas as condições variáveis, como o fluxo de ar, a estequiometria da chama, a altura de observação na chama e os efeitos de matriz para a determinação de chumbo, cádmio, zinco e cobre. Foi obtida boa concordância entre os valores de concentrações encontrados e os recomendados para diferentes materiais biológicos de referência. As sensibilidades, em área de pico, foram cerca de uma ordem de grandeza melhores do que as obtidas pela técnica da chama convencional. O dispositivo proposto é facilmente adaptável a qualquer espectrômetro de absorção atômica.

A new technique for the direct analysis of solids by Flame-AAS is described. The sample, 0.1 to 10.0 mg on a graphite platform, is placed under the focus of three infrared lamps. The combustion of the sample is started by a flash of the lamps and the smoke containing the more volatile elements is transported to the flame by an air stream. Variables conditions, like the air flow, the flame stoichiometry and observation height and the matrix effect for the determination of lead, cadmium, zinc and copper were studied. Very good agreement of the found concentrations with the recommended ones for different biological reference materials was obtained. The sensitivities, in peak area, were about one order of magnitude better than those of the conventional flame technique. The proposed device is easily adaptable to any flame atomic absorption spectrometer.

Key words: *flame atomic absorption spectrometry, combustible solids, direct analysis, biological materials.*

Introduction

The flame-AAS was originally proposed as a technique for the analysis of liquids samples. For solid samples, the dissolution procedure may cause contamination or loss of the analyte and is time consuming. Besides, when the analyte concentration is low, it may require high purity reagents, clean rooms and a skilfull and experienced analyst. The direct analysis of solids diminishes the contamination and loss risks and allows a less tedious analysis. Also, as the dilution associated to the sample dissolution is avoided, less amount of sample is needed.

Most of the publications on the direct analysis of solids by AAS uses electrothermal atomization in the graphite furnace¹. The sample may be introduced in the furnace using special tools or as suspension, when the use of an autosampler is convenient. The calibration with aqueous analytical solutions frequently is not possible, even using the Stabilized Temperature Platform Furnace (STPF) concept, due to interference problems. In most cases, solid samples

of similar composition need to be used for the calibration.

Some suggestions for the direct analysis of solids by flame-AAS are reported in the literature. The solid sample may be either directly introduced in the flame^{2,3} or as fine suspension through the nebulizer system⁴⁻⁶. In this case, the main problems are the blockage of the nebulizer and the incomplete volatilization of the particles in the flame. L'vov⁷ has shown that, to obtain a detection limit of about 10⁻⁶%, the sample should be introduced at a rate of 1gs⁻¹, what is not feasible. In spite of not having a large utilization, the direct analysis of solids by flame AAS was used for a number of applications⁸⁻¹⁶.

Another possibility is to vaporize the sample externally and introduce the vaporized sample into the flame through the nebulizer. The vaporization may be accomplished by electrical arc, spark or electrothermally. These techniques were reviewed by Kantor¹⁷. Also laser radiation was used for the vaporization¹⁸. By separating the vaporization and atomization processes, these techniques have less background at-

tenuation. Another way to combine the electrothermal vaporization with the flame-AAS is to use a graphite boat containing the solid sample, which is electrothermally heated inside the flame, just below the optical path. This possibility was recently reviewed by Stupor¹⁹.

A general problem with the direct analysis of solids is the heterogeneity of the sample, since only small amount of it is weighted. Usually the sample must be finely divided to ensure good homogeneity and, for a better precision, a larger number of replicates is needed.

In spite of the problems with the homogeneity of the sample and with the calibration of the method, the direct analysis of solids by AAS is receiving increasing interest from the analyst, as can be seen by the increasing number of publications each year.

This work is a contribution to the direct analysis of combustible solids, where the vaporization of the sample is achieved by infrared lamps in a sample device and the atomization is effected in a flame.

Experimental

The device for the introduction of solids in the flame used in this work is shown in Figure 1 and is a modification of that described by Berndt²⁰. The graphite platform having on his top a previously weighted amount of the sample, 0.1 to 10.0 mg, is manually placed inside of a quartz tube, under the focus of three infrared lamps (in series, 15V, 150W each), circularly distributed around the quartz tube. A previously chosen air stream flows through, the tube. The lamps (OSRAN, Hallogen Bellaphot), with a focal length of 3 cm, are connected to a power supply with several outlets. A teflon tap placed at the end of the quartz tube avoids the flow of the gases from the mixture chamber of the burner to the quartz tube. The tap is open as soon as the air stream is connected to the system, after placing the platform inside the tube. A flash of the lamps initiates the burning of the sample inside the tube. The air flow provides oxygen for the combustion and also transports the smoke resulting from the burning of the sample to the mixture chamber and from there to the flame, where the elements present in the smoke are atomized. The described system will be referred as the "combustion technique".

The system is easily adaptable to any atomic absorption spectrometer with a premix burner. Most of our results were obtained using a Varian Techtron AA6 Atomic Absorption Spectrometer. Also a non-commercial spectrometer with a McPherson 2051 monocromator and a personal Commodore 8096 computer was used. Only air-acetylene flame was used in this work and background correction was not needed.

For comparison, the non-certified materials used as sample were also analysed by GFAAS after dissolution. The sample solution were measured using either a Perkin-Elmer 4000 Atomic Absorption equipped with a Perkin-Elmer Graphite Furnace HGA 500 or a Perkin-Elmer Atomic Absorption Spectrometer AA 1100 equipped with a Perkin-Elmer Graphite Furnace HGA 300 and a Perkin-Elmer Autosampler AS-40. The STPF conditions and temperature programs recommended by the manufacture were used.

The following certified reference materials were used: Orchard Leaves (NBS No. 1571), Pine Needles (NBS No. 1575), Tomato Leaves (NBS No. 1573), Spinach (NBS No. 1570), Fish Meal²¹, Oyster Tissue (NBS No. 1566). Non-certified samples were also used. Also synthetic samples from Cellulose Hyphan were prepared²².

When necessary, the samples were further pulverized and homogenized using a ball mill. All concentration values shown in this work are based on the dry weight, which was determined by independent measurements. The water content was in the range 3 to 6%.

For the GFAAS measurements, the samples were dissolved mostly by a method proposed by Sperling²³ using, about 5 mg of sample and a sulfonitric solution (1:3) at 60 °C during 12h in closed 1.5 ml Eppendorf vessels, or by acid digestion in Perkin-Elmer Autoclave-3, using the condition recommended by the manufacturers.

The water was de-ionized and the acids were of high purity (Ultrex from Baker) or reagent grade acids purified by subdistillation.

All glassware was washed with water, then submitted to nitric vapors for several hours acid and finally washed three times with de-ionized water.

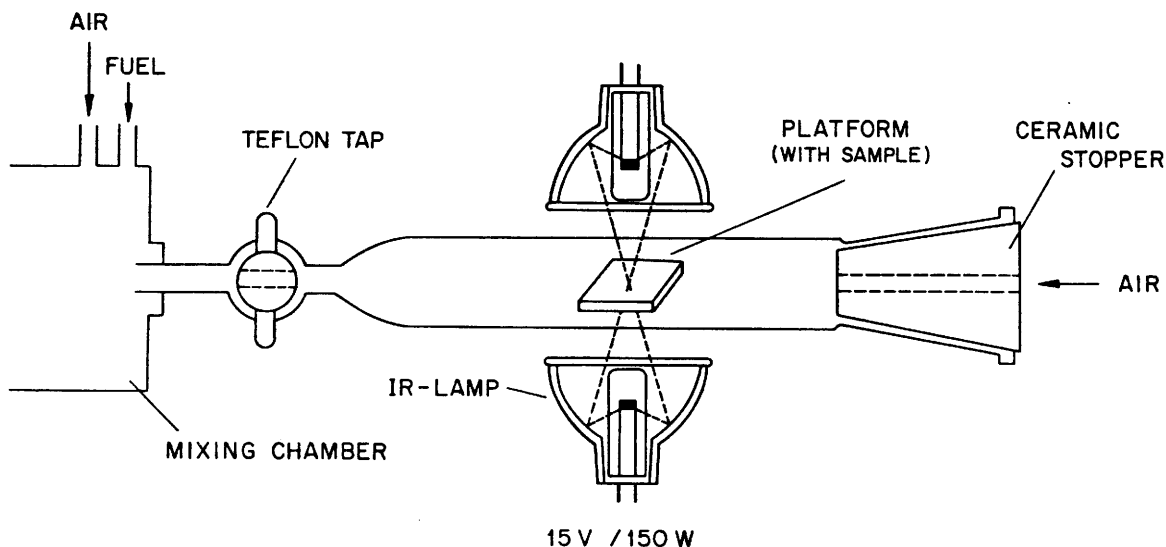


Figure 1. The burning system of the combustion technique.

Results and Discussion

The effect of different air flows in the integrated absorbance is shown in Figure 2. As expected, for very low flows the signals are lower due to an incomplete burning of the sample, since there is not enough oxygen available. Also for air flows higher than 6 l min^{-1} , there is a decrease in the signal, not shown in Figure 2, due to a lower residence time of the aerosol in the flame. The optimum air flow range depends not only on the element, Figure 2 (a), but also on the matrix, Figure 2(b).

For the elements and matrices studied, in relation to a reducing flame, an oxidizing flame gives the same or higher

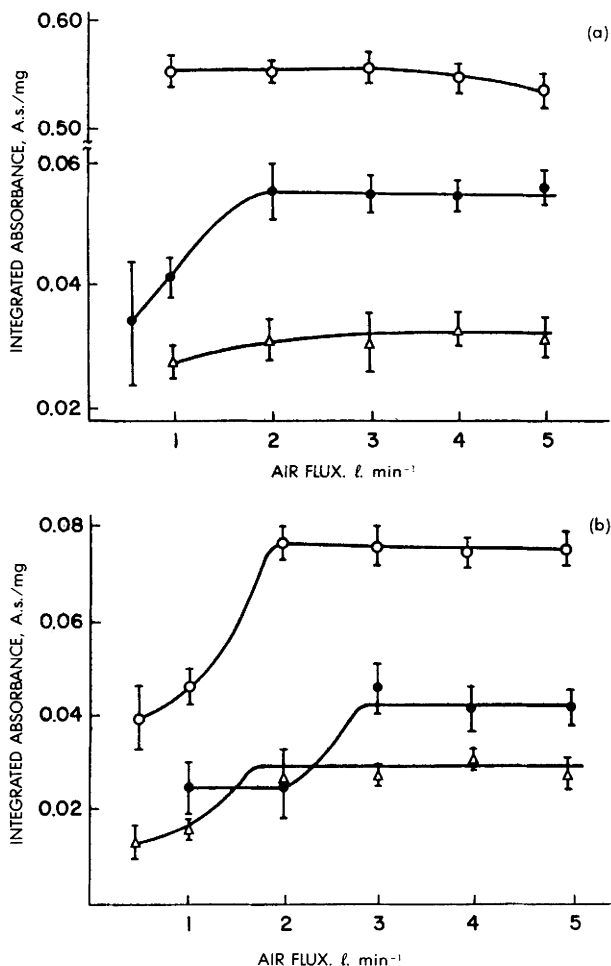


Figure 2. Variation of the integrated absorbance with air flux: (a), different elements, (○) Zn, (●) Pb and (Δ) Cu NBS Orchard Leaves; and (b), cadmium in (○) NBS Tomato Leaves, (●) NBS Spinach Leaves and (Δ) grass.

results as shown in Figure 3. Also the oxidizing flame leads to a larger linear range of the analytical curves.

The division line of the primary zone with the secondary zone was taken as observation height zero. The effect of the observation height on the sensitivity, for some elements in some matrices are shown in Figure 4. For most cases, higher integrated absorbances were obtained at height zero what could imply that good consumption of the aerosol was achieved. This was also suggested by the fact that virtually no background attenuation could be measured. Figure 4(b), show that the effect depends on the matrix, even for similar matrices.

Table 1 shows the characteristic masses (ng/0.0044 A.s) for different elements in different matrices. The values were

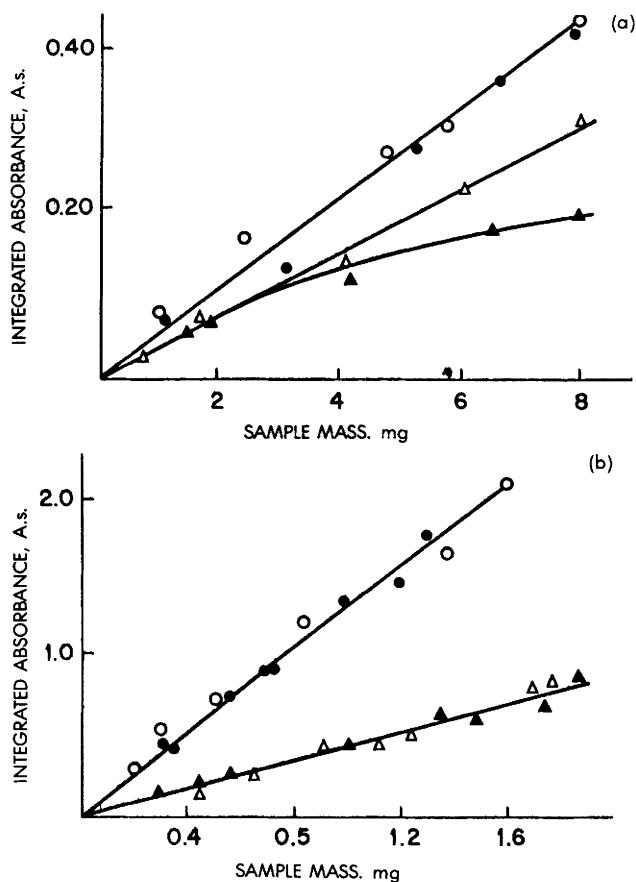


Figure 3. Influence of the flame stoichiometry: (a), Cd in NBS Tomato Leaves, (○) oxidizing flame, (●) reducing flame, and Cd in NBS Spinach Leaves, (Δ) oxidizing flame, (▲) reducing flame; (b), Zn in NBS Orchard Leaves, (○) oxidizing flame, (●) reducing flame and Zn in Tomato Leaves, (Δ) oxidizing flame, (▲) reducing flame.

Table 1. Characteristic Mass, ng/0.0044 A.s, obtained for Pb, Cd, Zn, and Cu in different matrices using the combustion technique.

Matrix	ELEMENTS			
	Pb	Cd	Zn	Cu
Orchard Leaves	4.6 ± 0.3	nd	0.25 ± 0.01	1.4 ± 0.1
Tomato Leaves	4.3 ± 0.9	0.20 ± 0.01	0.20 ± 0.01	1.3 ± 0.1
Spinach Leaves	4.5 ± 0.9	0.21 ± 0.02	nd	1.2 ± 0.1
Oyster Tissue	nd	0.21 ± 0.02	nd	0.9 ± 0.1

nd = not determined

obtained from the analytical curves, integrated absorbance versus sample mass, using at least eight different masses for each curve. For the same element, the differences are small, allowing the conclusion that no matrix effect occurred.

Since no matrix effect was detected, the calibration can be performed using any one of the materials listed in Table 1 as a calibration sample for the others. Table 2 shows, as an example, the concentrations of lead in different reference materials, taking the Orchard Leaves as the calibration sample and using the best observation height and air flow and an oxidizing flame. Very good agreement in relation to the certified values were obtained. Also non-certified grass sample were analysed. In this case, grass samples analysed by GFAAS after dissolution were used as the calibration standards. Figure 5 shows the analytical curves for zinc and cad-

mium in grass samples. Very good agreement was obtained using the combustion technique in comparison to the results obtained by GFAAS, as shown in Table 3.

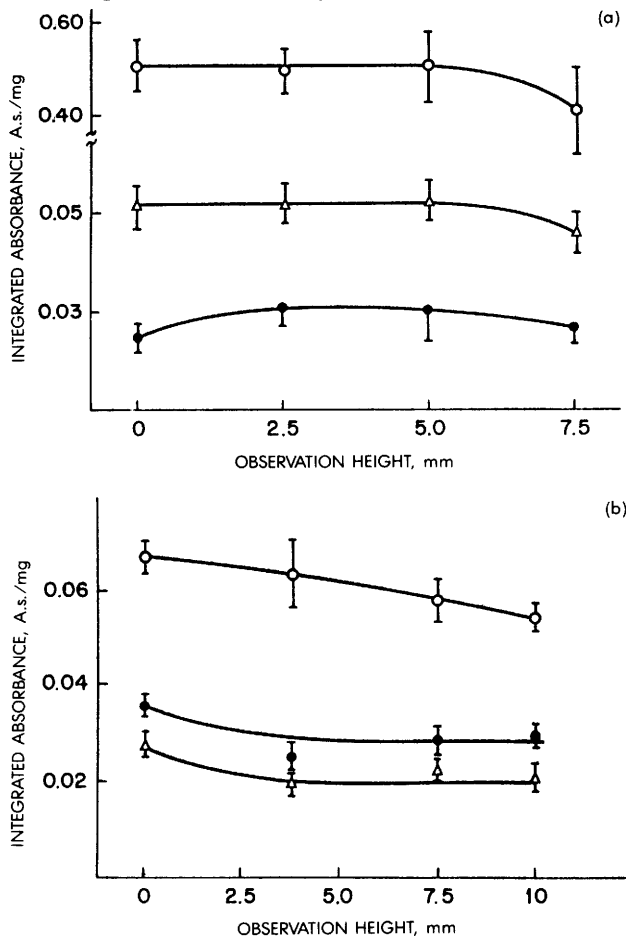


Figure 4. Variation of the integrated absorbance with the observation height: (a) different elements, (○) Zn, (Δ) Pb and (●) Cu, in NBS Orchard Leaves; and (b), Cd in (○) NBS Tomato Leaves, (●) NBS Spinach Leaves and (Δ) grass.

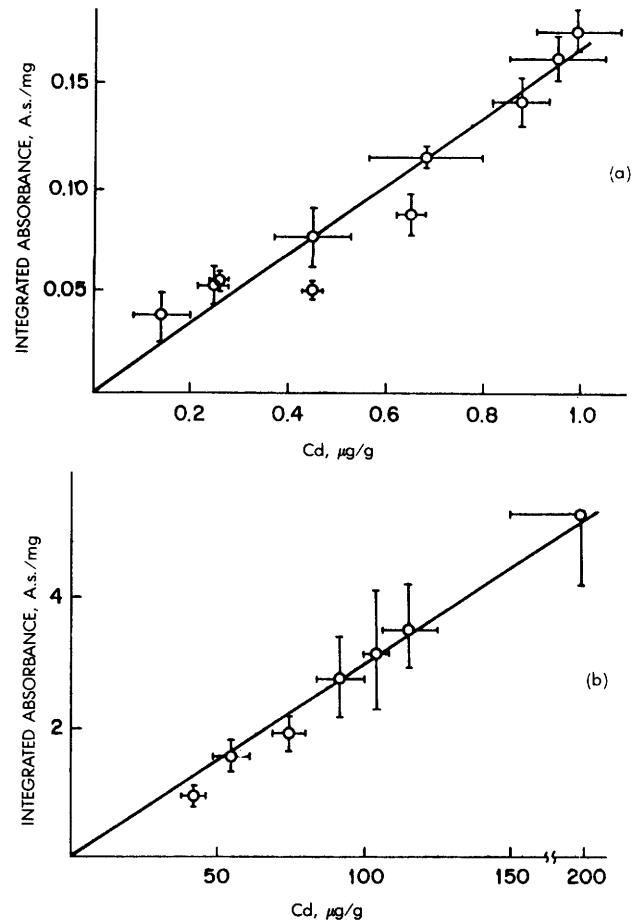


Figure 5. Analytical curve for the determination of Zn in grass samples. Each point is the mean of 5 measurements. Standard deviations are shown.

Figure 6 shows the peak shapes for mercury, cadmium, copper and lead in different materials. A double peak was obtained for cadmium and lead, but not for mercury and copper. The combustion process is sufficient to transfer all mercury to the smoke but it is not for cadmium and lead, which are further released by the heating of the platform, after the combustion, producing a second peak. For copper, probably because the platform does not reach a temperature high enough to vaporize the copper oxide, after the combustion, only a peak was observed. This also explains the small improvement in the sensitivity for this elements in comparison to that of the flame-AAS (Table 4). As long as integrated absorbances are used, the double peak does not disturb the analytical results.

Table 2. Concentration of Pb in different materials, taking NBS Orchard Leaves as standard.

Sample	Found μg/g	Certified μg/g
Pine Needles	9.9±0.2	10.8±0.5
Tomato Leaves	5.9±1.3	6.3±0.3
Spinach Leaves	1.2±0.2	1.2±0.2
Fish Meat	2.7±0.5	2.6±0.3

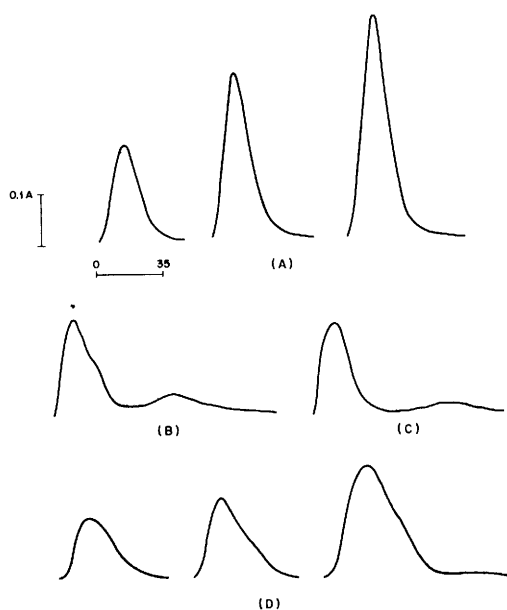
Table 3. Grass Analysis: concentrations, in $\mu\text{g/g}$, obtained by the combustion technique and by GFAAS.

Grass Sample	Combustion Technique			GFAAS		
	Cd	Pb	Cu	Cd	Pb	Cu
1 A	0.76±0.1	25±4	nd	0.85±0.06	26±3	nd
2 A	0.76±0.1	17±2	9.6±0.2	0.75±0.14	18±2	12±3
3 A	0.50±0.05	31±5	13.3±1.2	0.46±0.04	28±1	15.5±0.6
4 A	0.23±0.02	nd	8.6±1.2	0.24±0.06	nd	2.0±0.1
5 A	0.03±0.02	8±1	7.5±0.8	0.03±0.03	8±1	7.8±1.5
24	1.69±0.02	20±1	nd	1.53±0.07	22±1	nd
25	0.36±0.06	4±1	7.2±0.4	0.29±0.01	3.0±0.2	7.1±2.4
36	1.04±0.02	16±1	6.8±1.0	0.97±0.01	15±2	7.9±2.5
42	nd	11±2	3.2±0.5	nd	8.0±0.2	3.9±1.0

nd = not determined.

Table 4. Characteristic mass (ng/0.0044 A.s) and detection limit for the combustion technique (mean value) and for the conventional flame AAS.

Element	Comb. Tec. (a)	Characteristic Mass		Factor (b/a)	Detection Limit	
		Flame AAS (b)			Comb. Tec. (ng)	Flame AAS ($\mu\text{g/ml}$)
Bi	5.6	5.0	9	4.1	0.06	
Cd	0.2	2.5	12	0.30	0.0006	
Cu	1.4	9.0	6.4	12.5	0.003	
Hg	54	750	14	—	0.2	
Pb	4.4	50	11	16.2	0.02	
Tl	5.0	50	10	12	0.02	
Zn	0.2	1.8	9.0	9.8	0.002	

**Figure 6.** Peak profiles, absorbance vs. time: (A) Hg in Cellulose Hyphan, increasing masses; (B) Pb in NBS Orchard Leaves; (C) Cd in NBS Tomato Leaves; and (D) Cu in coffee powder, increasing masses. Chart record speed: 50 cm/min.

The proposed technique can be applied only to the more volatile elements. Besides cadmium, copper, zinc and lead, also mercury, bismuth and thallium, for example, can be detected, but since their concentrations in the available samples were below the detection limit, their determinations were not studied.

These elements include some of the most important ones concerning environmental and toxicological problems. The technique is applicable to combustible solid samples covering frequently analysed samples, such as plants, food, biological tissues, etc.

The characteristic masses and detection limits of volatile elements, using the combustion technique and the conventional flame-AAS are shown in Table 4. For mercury, bismuth and thallium, synthetic samples using Cellulose Hyphan were analysed. As can be seen, the sensitivity using the proposed technique is about one order of magnitude better than those of the conventional flame-AAS. It is important to remember that the detection limits of the combustion technique are related to the sample mass (no dilution) while those reported for the conventional flame technique are obtained from aqueous standards, and so applicable only to the final form of a solid sample, that is, after dissolution. The characteristic masses and detection limits given in Table 4 do not consider the dilution necessary for the dissolution, which is required for the flame technique but not for the proposed technique.

The combustion technique proposed in this work offers advantage concerning costs and simplicity of the pre-vaporization device, in relation to others, which also use the separation of the vaporization and atomization processes¹⁹. The device can be easily built in the laboratory and utilizes commercially available lamps.

In this technique a mixture of the sample with a combustible material as previously suggested by Venghiattis²⁴, is not required, since the sample is combustible itself. In this way, contamination problems can be easily avoided. Since an air-acetylene flame is used as the atomizer, also alignment and flame stability and shape are not changed in relation to the conventional flame-AAS. Besides, in our technique, only a small aliquot of the sample is used and, after the combustion, the smoke is transported to the nebulizer by an air stream and is further diluted in the flame, resulting in insignificant background attenuation. Thus, a background correction is not necessary. Since, only small matrix effects were detected, calibration does not require the same matrix of the sample, which is another advantage of our proposed technique.

Conclusions

A simple device is proposed for the direct determination of volatile elements in combustible solid samples. The device is easily adaptable to any atomic absorption spectrometer with a premix burner and could also be coupled to ICP emission atomic spectrometers. In comparison to the conventional flame-AAS, the dissolution of the sample is not required, avoiding contamination problems and loss risks, and the sensitivity is about one order of magnitude better. Since matrix effect were not observed similar matrix can be used as a calibration standard. Also background correction is not necessary allowing the use of a simpler instrumentation.

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