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Journal Name

ARTICLE

Determination of Cadmium in commercial tobacco by EMFAAS.

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In this work we present the use of EMFAAS (Electrothermal Metallic Furnace Atomic Absorption Spectroscopy) for the determination of Cd in tobacco cigarettes of five commercial brands. Optimization of the experimental conditions was done by controlling the sample flow rate and the temperature of both, the injection capillar and the atomization cell. The determination was made in the whole cigarette and in filters and ashes of the cigarettes once consumed, cases in which the Cd concentration is much lower and its quantification more difficult. For the validation of the results, the ICP-OES technique was used, obtaining a good agreement within the experimental error. The results show that EMFAAS is a promissory tool for the determination of volatile analytes.

Introduction

Atomic Absorption Spectrometry (AAS) with different atomic vapour sources has proved to be a promissory tool for elemental determination at trace levels. Flame Atomic Absorption Spectrometry (FAAS) is a well established technique and one of the most employed in routine analysis¹. Nonetheless, when compared to other techniques for elements,² it cannot compete in terms of analytical performance, mainly sensitivity and limit of detection. Since the amount of sample that reaches the atomizer in FAAS is a serious constraint to improve sensitivity, Berndt et al³ developed TS-FF-AAS (Thermospray Flame Furnace Atomic Absorption Spectrometry) using a Ni tube heated by a combustion flame as atomization cell and a peristaltic pump to carry the liquid sample through a ceramic capillary towards the tube.

With the aim to avoid the use of combustion gases (air, acetylene), an electric method that takes advantage of Joule effect for heating the metallic tube was proposed in 2017.⁴ This method (EMFAAS for electrothermal metallic furnace atomic absorption spectroscopy) allows to control the temperature of the furnace by means of changing the voltage supplied to the metallic tube. This method not only makes operation more safety and economic, but also decreases significantly LODs (limit of detection) of volatile elements, making it a promissory tool for trace element determination.

EMFAAS also presents several advantages when compared to ETAAS (electrothermal atomic absorption spectrometry) either with tungsten coil or GFAAS (graphite furnace atomic absorption spectrometry). The most popular GFAAS shows a

better analytical performance but it requires high purity argon for proper operation and, in most cases, matrix modifiers (usually palladium nitrate) to prevent analyte co-volatilization with the sample matrix during pyrolysis. It is also known that the sample throughput with GFAAS (or tungsten coil) is extremely low (about ten samples per hour) whilst with EMFAAS we have attained 50 samples h⁻¹. Moreover, the employ of graphite furnaces working at high temperatures with samples in nitric acid (as in our case, see below) is much more expensive than the methodological alternative presented here. In the case of tungsten coil, the low temperatures attainable should be added to the inconveniences above.

The study of cadmium in different matrices becomes of relevance due its toxicity even at trace levels. Cd shows different routes of entry into the human body being the respiratory tract the most important.⁵ It induces damages in different organs⁶ and it is also one of the most potent carcinogen metals.⁷ Since cigarette smoking is one of the most common ways of Cd accumulation in the human body,⁸ cadmium determination in *Nicotiana tabacum* becomes of great concern at the moment of studying exposure to this contaminant. The leaves of this plant also contains other metals such as Mn, Zn (also analysed in this work).

Consequently, there are a good number of citations in the literature devoted to the determination of low levels of cadmium by means of atomic absorption spectrometry, usually coupled to different pre-concentration systems.⁹

In this work we present the employ of EMFAAS to determine Cd in commercial tobacco in five brands of commercial cigarettes. Samples of tobacco, filters and ashes of smoked cigarettes -where the amount of Cd is appreciably lower- were analyzed proving that EMFAAS is a promissory method for trace element determination in different kind of samples. Optimization of the different experimental conditions and the main figures of merit are showed. Comparison of the analytical results by ICP-AES is also provided.

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ARTICLE

Journal Name

Experimental

All solutions were prepared with analytical grade chemical reagents and double deionized water (DDW) obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). All glassware was washed with EXTRAN (Merck) 1% v/v and kept in 10% (v/v) HCl with further cleaning with DDW. Standard solutions of Cd were prepared by appropriate dilution of 1000 g L⁻¹ stock solutions (Merck Darmstadt, Germany). For digestion of the samples HNO₃ 65% (Merck) and H₂O₂ 8% v/v (Merck) were used.

Instrument

An atomic absorption spectrometer Shimadzu AA6800 (Shimadzu, Kyoto, Japan), hollow cathode lamps (Hamamatsu, Japan) and a deuterium lamp for background correction were employed throughout the measurements. Other instrumental conditions were those provided by the manufacturer. The EMFAAS system was assembled with a peristaltic pump with eight channels and six rollers (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), a six-port rotatory valve VICI (Valco Instruments, Houston, TX, USA), 0.5 mm i.d. polytetrafluoroethylene tubing, a ceramic capillary (0.5 mm i.d., 6 cm length) and the metallic flame furnace atomizers placed in the optical path of the spectrometer with the assistance of a homemade holder. An scheme of the instrument is shown in ESI.

500 µL of the sample solution were introduced into a carrier stream (DIW) and injected into the atomization cell at a flow rate of 1.8 mL min⁻¹. The solution was heated, above the vaporization temperature prior to entering the cell, by electric current on a nichrome wire coiled around the ceramic injection capillary. The heating was controlled by changing the applied voltage to the coil between 10 and 24 V to ensure full vaporization of the sample at different flow rates.

Sample Preparation.

Five cigarettes brands manufactured by different companies bought at a local store of Buenos Aires province, Argentina, were analyzed. The tobacco contained in 10 cigarettes (of each brand) was digested in a solution prepared with 20 mL of HNO₃ 65% and 10 ml H₂O₂ 8% v/v for 4hs at boiling point. The solution obtained after digestion was filtered and made up to 25 ml with DDW. The same procedure was done for 10 filters, 10 post-consumed filters and ashes obtained from 10 smoked cigarettes.

Samples for determination of Mn and Zn were prepared as Cd samples using the tobacco contained only in 1 cigarette and made up to 50 ml instead of 25 ml.

Results and discussion

Furnace temperature:

Analyte's signal depends on the temperature of the furnace where the atomization takes place. The electric current

flowing through the tube was varied by a current controller to increase the furnace temperature (heated by Joule effect). Figure 1 shows the influence of the temperature of the furnace on the analytical signal of Cd. As expected, the response increases with the furnace temperature due to a more efficient atomization of the analyte. Under the operative conditions, the heating system allows 1000 °C as maximum temperature.

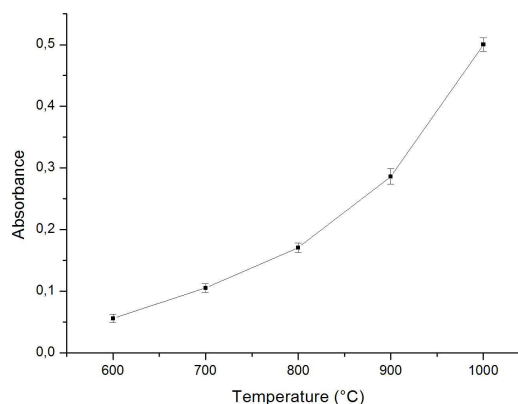


Figure 1. Effect of furnace temperature on analytical signal of Cd . (Cd concentration = 500 µg.L⁻¹; sample flow rate = 0.8 ml min⁻¹)

Effect of sample injection flow rate and temperature of the injection capillary:

Figure 2 shows the response surface for Cd obtained by modifying the experimental conditions of sample flow rate and temperature of the ceramic capillary, for a sample containing 500 µg.L⁻¹, keeping the furnace at the maximum temperature achievable.

While increasing the sample flow rate, keeping capillary temperature constant, the amount of analyte inside the furnace increases and the analytical signal reaches a maximum (See Figure 2). From this value onwards, even though a higher amount of sample reaches the furnace, the temperature inside the furnace decreases together with Cd response.

In order to improve the analytical signal by avoiding the cooling promoted by the sample injection at higher flow rates, the temperature of the injector capillary was modified by changing the voltage applied to a resistor which is coiled around the capillary.

A higher temperature of the injector not only diminishes the cooling of the furnace around the entrance of the liquid sample (which is observed as a considerable increment of the signal), but it also improves the sample vaporization efficiency and allows an efficient nebulization at higher sample flow rates.

This optimization of vaporization shifts the maximum sample flow rate to higher values at the time that increases the analytical response.

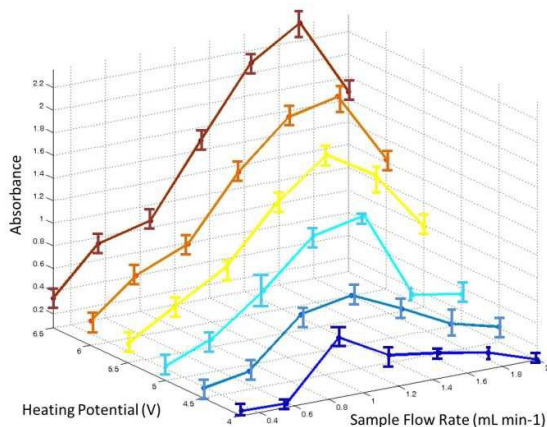


Figure 2. Analyte response at different sampling flow rates and ceramic capillary temperatures (Cd concentration = $500 \mu\text{g}\cdot\text{L}^{-1}$, furnace temperature: 1000°C).

Figures of merit:

For comparison purposes, the main figures of merit were calculated, and are shown in Table 1. A calibration curve was constructed under the optimum experimental conditions, showing a linear response ranging between 7 to $750 \mu\text{g}\cdot\text{L}^{-1}$. Analytical sensitivity ($0.010 \pm 0.003 \text{ L}\cdot\mu\text{g}^{-1}$) was also dramatically improved when compared to FAAS and it is close to that obtained with ICP-AES. EMFAAS presents the advantage of lower costs since it has no need of high purity argon in order to keep the plasma torch on during several hours.

An enhanced limit of detection (LOD) ($n=10$, $3s$) of 8.2 ng per gram of tobacco was attained in comparison to FAAS (140 ng/g).⁴ The calculated limit of quantification (LOQ) was $27 \mu\text{g/g}$ of sample. (5s).

A relative standard deviation (RSD %) of 4.5% was obtained for $n = 5$ at the $500 \mu\text{g}\cdot\text{L}^{-1}$ level.

Table 1. Figures of merit for Cd determined by EMFAAS.

LR (Lineal range, $\mu\text{g}\cdot\text{L}^{-1}$)	7-750
Sb (blank standard deviation)	0.0071
Sensitivity ($\text{L}\cdot\mu\text{g}^{-1}$)	0.010 ± 0.003
R^2	0.9914
LOD (ng/g sample)	8.2
LOQ (ng/g sample)	27
LOQ (ng Cd per cigarette)	17.6
%RSD	4.5

Sample analysis:

Figure 3 shows the results obtained for the determination of Cd contained in tobacco, post-consumed filter and ashes, and the calculated value of Cd contained in smoke, for five brands of commercial tobacco cigarettes. The new EMFAAS method was employed in all cases. Results are expressed as μg Cd per cigarette. Determination of Mn and Zn was also done for two brands of cigarettes (ESI).

For tobacco samples all brands presented similar amounts of Cd (250 ng / cigarette approximate), except for brand B (about 300 ng / cigarette). The analysis of post-consumed filters revealed that only a percentage of Cd close to 10% is retained by the filter. This behavior was observed in all the brands tested. Ashes produced after smoking were also analyzed, showing that almost 50 ng of Cd per cigarette remain in the ashes. This results shown that near 80% of Cd contained in tobacco remains in smoke.

The proposed method for Cd determination applied to the quantification of trace amounts of Cd in tobacco cigarettes was compared with ICP-OES. Results obtained are reported in Table 2).

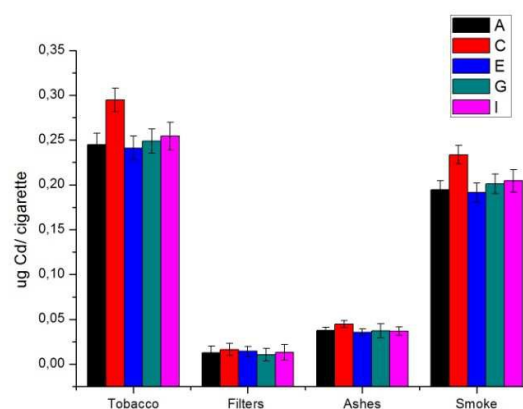


Figure 3. Amount of Cd / cigarette determined by EMFAAS in samples of tobacco, filters and ashes (post-consumption) and smoke (calculated by difference) in 5 brands of cigarettes.

Table 3 shows the percentage of recovery calculated for all the analyzed samples. As it is shown, the recoveries ranged between 96.01% - 105.09% for tobacco, 93.71% - 103.96% for ashes, and 94.40% - 108.28% for post-consumed filters. As expected, standard deviations (SD, $n = 5$) in samples containing lower amounts of the analyte was higher than in those containing higher (8.08% for post-consumed filters, $10 \mu\text{g}$ / cigarette approximate versus 3.40% for tobacco, $250 \mu\text{g}$ / cigarette approximate).

This results confirm that EMFAAS is a promissory tool for determination of trace of volatile elements in different kind of samples. Moreover, it is important to highlight that EMFAAS is a compact, inexpensive and safe alternative (keeps away pressurized gases) for volatile elements that can be applied successfully to different kind of real samples.

ARTICLE

Journal Name

Table 2 EMFAAS Cd determination in tobacco, filters and ashes (post-consumption) of tobacco cigarettes of five brands.

	Brand	µg of Cd / cigarette				Smoke*
		Tobacco	Filters	Post-Consumed Filters	Ashes	
EMFAAS	A	0.251	< LOQ	0.012	0.038	0.201
	B	0.295	< LOQ	0.016	0.042	0.234
	C	0.241	< LOQ	0.014	0.034	0.193
	D	0.239	< LOQ	0.012	0.037	0.190
	E	0.267	< LOQ	0.014	0.038	0.215
ICP-OES	µg of Cd / cigarette					
	Brand	Tobacco	Filters	Post-Consumed Filters	Ashes	Smoke*
	A	0.245	< LOQ	0.013	0.038	0.195
	B	0.295	< LOQ	0.016	0.045	0.234
	C	0.241	< LOQ	0.014	0.035	0.191
	D	0.249	< LOQ	0.010	0.037	0.201
E	0.254	< LOQ	0.013	0.037	0.205	

*(calculated by difference). ICP-OES results are presented for comparison purposes.

Table 3. Percentage of recovery (%rec) of Cd: EMFAAS vs ICP-OES determination (n = 5)

Brand	%rec (tobacco)	%rec (filters)	%rec (ashes)
A	102.60	98.53	101.54
B	99.90	95.76	93.71
C	99.83	94.40	95.67
D	96.01	112.63	99.12
E	105.09	108.28	103.96
Mean	100.69	101.92	98.80
SD	3.40	8.08	4.18
Temp	0.45	0.53	0.64

Conclusions

The findings show that EMFAAS is a promissory alternative for the determination of cadmium in tobacco. The possibility of reaching temperatures close to 1000°C allows obtaining a high sensitivity and low LOD, for volatile analytes in different types of samples. Heating of the injection capillary has allowed to increase the sample flow rate in order to obtain an optimized sensitivity derived not only from a lower cooling of the furnace but from a more efficient vaporization process of the sample before entering into the furnace. It is important to note that the use of a commercial equipment as an optical base for EMFAAS simplifies the setup and the analysis of the comparative data with FAAS. However, its use is not mandatory and an ideal EMFAAS equipment could use a very

compact optics, allowing to a simple relocation and portability of the entire system, given that no gases are needed to operate the equipment. In conclusion, we have demonstrated that EMFAAS is a good option for the measurement of volatile elements. EMFAAS can offer simplicity of use, a potential portability and a minimal preparation of the lab in order to operate in safe conditions.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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