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 Spectrometry) for the determination of Cd in the 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 capillary and the atomization cell. The determination was made in the whole cigarettes, filters and ashes of the cigarettes once consumed, cases in which the Cd concentration is much lower and its quantification is more difficult. For the validation of the results, the ICP-OES technique was used, obtaining good agreement within the experimental error. The results show that EMFAAS is a promising tool for the determination of volatile analytes.

Introduction

Atomic Absorption Spectrometry (AAS) with different atomic vapour sources has been proved to be a promising 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 analysis.1 Nonetheless, when compared to other techniques for elemental determination,2 it cannot compete in terms of analytical performance, mainly sensitivity and the limit of detection. Since the amount of sample that reaches the atomizer in FAAS is a serious constraint to improving the sensitivity, Berndt et al.3 developed TS-FF-AAS (Thermospray Flame Furnace Atomic Absorption Spectrometry) using a Ni tube heated by a combustion flame as the atomization cell and a peristaltic pump to carry the liquid sample through a ceramic capillary towards the tube.

With the aim of avoiding the use of combustion gases (air and acetylene), an electrical method that takes advantage of the Joule effect for heating the metallic tube was proposed in 2017.4 This method (EMFAAS for electrothermal metallic furnace atomic absorption spectrometry) allows one 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 safe and economic, but also significantly decreases the LODs (limits of detection) of volatile elements, making it a promising tool for trace element determination.

EMFAAS also presents several advantages when compared to ETAAS (electrothermal atomic absorption spectrometry) either with a 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 a tungsten coil) is extremely low (about ten samples per hour) whilst with EMFAAS we have attained 50 samples h−1. Moreover, the use 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 the 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, the respiratory tract being the most important.5 It induces damage to different organs6 and it is also one of the most potent carcinogenic 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 when studying exposure to this contaminant. The leaves of this plant also contain other metals such as Mn and 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 use 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 promising method for trace element

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determination in different kinds of samples. Optimization of the different experimental conditions and the main figures of merit are shown. A comparison with the analytical results obtained by ICP-OES is also provided.

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 HNO\(_3\) (65%) (Merck) and H\(_2\)O\(_2\) (8% v/v) (Merck) were used.

Instruments

A Shimadzu AA6800 atomic absorption spectrometer (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 rotary 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 metallic flame furnace atomizers placed in the optical path of the spectrometer with the assistance of a homemade holder. A schematic diagram of the instrument is shown in the ESL.†

500 \(\mu\)L of the sample solution was 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 passing an electric current through a nichrome wire coiled around the ceramic injection capillary. The heating was controlled by changing the voltage applied to the coil between 10 and 24 V to ensure full vaporization of the sample at different flow rates.

Sample preparation

Five cigarette brands manufactured by different companies bought at a local store in 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 HNO\(_3\) (65%) and 10 mL of H\(_2\)O\(_2\) (8% v/v) for 4 h at the 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, and 10 post-consumption filters and ashes obtained from 10 smoked cigarettes.

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

Results and discussion

Furnace temperature

The analyte 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 the Joule effect). Fig. 1 shows the influence of the temperature of the furnace on the analyte signal of Cd. As expected, the response increases with the furnace temperature due to a more efficient atomization of the analyte. Under the operating conditions, the heating system allows 1000 °C as the maximum temperature.

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

Fig. 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 \(\mu\)g L\(^{-1}\), keeping the furnace at the maximum temperature achievable.

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

In order to improve the analyte signal by avoiding the cooling promoted by the sample injection at higher flow rates, the temperature of the injection capillary was modified by changing the voltage applied to the resistor which is cooled 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 analyte response.

![Fig. 1 Effect of furnace temperature on the analyte signal of Cd (Cd concentration = 500 \(\mu\)g L\(^{-1}\) and sample flow rate = 0.8 mL min\(^{-1}\)).](image-url)
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 and 750 μg L⁻¹.

The analytical sensitivity (0.010 ± 0.003 L μg⁻¹) was also dramatically improved when compared to FAAS and it is close to that obtained with ICP-OES. EMFAAS presents the advantage of lower costs since it has no need for high purity argon in order to keep the plasma torch on for several hours.

An enhanced limit of detection (LOD) (n = 10, 3 s) of 8.2 ng per gram of tobacco was achieved in comparison to FAAS (140 ng g⁻¹). The calculated limit of quantification (LOQ) was 27 μg g⁻¹ of sample (5 s).

A relative standard deviation (RSD%) of 4.5% was obtained for n = 5 at the 500 μg L⁻¹ level.

Sample analysis

Fig. 3 shows the results obtained for the determination of Cd contained in tobacco, post-consumption filters and ashes, and the calculated values of Cd contained in smoke for five brands of commercial tobacco cigarettes. The new EMFAAS method was employed in all the cases. The 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 per cigarette approximately), except for brand B (about 300 ng per cigarette). The analysis of post-consumption 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, and it was found that almost 50 ng of Cd per cigarette remains in the ashes. These results showed that nearly 80% of Cd contained in tobacco remains in the smoke.

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

Table 2 shows the percentage of recovery calculated for all the analyzed samples. As is shown, the recoveries ranged between 96.01% and 105.09% for tobacco, 93.71 and 103.96% for ashes, and 94.40 and 108.28% for post-consumption filters. As expected, standard deviations (SD, n = 5) in samples

<table>
<thead>
<tr>
<th>µg of Cd/cigarette</th>
<th>Brand</th>
<th>Tobacco</th>
<th>Filters</th>
<th>Post-consumption filters</th>
<th>Ashes</th>
<th>Smoke*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EMFAAS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A</td>
<td>0.251</td>
<td>&lt;LOQ</td>
<td>0.012</td>
<td>0.038</td>
<td>0.201</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.295</td>
<td>&lt;LOQ</td>
<td>0.016</td>
<td>0.042</td>
<td>0.234</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.241</td>
<td>&lt;LOQ</td>
<td>0.014</td>
<td>0.034</td>
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<td></td>
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<tr>
<td>D</td>
<td>0.239</td>
<td>&lt;LOQ</td>
<td>0.012</td>
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<tr>
<td>E</td>
<td>0.267</td>
<td>&lt;LOQ</td>
<td>0.014</td>
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<td><strong>ICP-OES</strong></td>
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<tr>
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<td>0.013</td>
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<tr>
<td>B</td>
<td>0.295</td>
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<td>0.016</td>
<td>0.045</td>
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<tr>
<td>C</td>
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<td>&lt;LOQ</td>
<td>0.014</td>
<td>0.033</td>
<td>0.191</td>
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<tr>
<td>D</td>
<td>0.249</td>
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<td>0.037</td>
<td>0.201</td>
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<tr>
<td>E</td>
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<td>&lt;LOQ</td>
<td>0.013</td>
<td>0.037</td>
<td>0.205</td>
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</table>

* (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)

<table>
<thead>
<tr>
<th>Brand</th>
<th>% rec (tobacco)</th>
<th>% rec (filters)</th>
<th>% rec (ashes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>102.60</td>
<td>98.53</td>
<td>101.54</td>
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<tr>
<td>B</td>
<td>99.90</td>
<td>95.76</td>
<td>93.71</td>
</tr>
<tr>
<td>C</td>
<td>99.83</td>
<td>94.40</td>
<td>95.67</td>
</tr>
<tr>
<td>D</td>
<td>96.01</td>
<td>112.63</td>
<td>99.12</td>
</tr>
<tr>
<td>E</td>
<td>105.09</td>
<td>108.28</td>
<td>103.96</td>
</tr>
<tr>
<td>Mean</td>
<td>100.69</td>
<td>101.92</td>
<td>98.80</td>
</tr>
<tr>
<td>SD</td>
<td>3.40</td>
<td>8.08</td>
<td>4.18</td>
</tr>
<tr>
<td>(T_{\text{exp}})</td>
<td>0.45</td>
<td>0.53</td>
<td>0.64</td>
</tr>
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</table>

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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Notes and references


Conclusions

The findings show that EMFAAS is a promising alternative for the determination of cadmium in tobacco. The possibility of reaching temperatures close to 1000 °C allows for obtaining a high sensitivity and low LOD for volatile analytes in different types of samples. Heating of the injection capillary has allowed the increase of the sample flow rate in order to obtain optimized sensitivity derived not only from a lowered cooling of the furnace but also from a more efficient vaporization process of the sample before entering the furnace. It is important to note that the use of 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 ideal EMFAAS equipment could use very compact optics, allowing 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, potential portability and minimal preparation of the laboratory in order to operate under safe conditions.

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