



# Towards broadening thermospray flame furnace atomic absorption spectrometry: Influence of organic solvents on the analytical signal of magnesium



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## ABSTRACT

This study demonstrates the influence of the solvent when thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is employed for the determination of elements of low volatility, taking magnesium (Mg) as leading case. Several organic solvents/water solutions of different characteristics (density, surface tension, viscosity, etc.) and proportions were employed for the TS-FF-AAS analytical determination. To this end, solutions containing methanol, ethanol and isopropanol in water were assayed. Measurements were performed at different acetylene/air ratios of the combustion flame and then, the corresponding response surfaces were obtained. Methanol/water 75% v/v as carrier and a fuel rich flame were found as the most sensitive alternative.

In the light of these findings and in order to explain the changes on the analytical signal, the influence of the solvent characteristics, the sample droplet size and the redox environment was studied. An estimation of the temperature of different zones of the heated flame furnace based on a modified signal ratio pyrometry method was analyzed for comparative purposes. A full discussion is provided throughout the paper.

Once obtained the best conditions for analysis, Mg was determined in samples of effervescent vitamin tablets comparing two different solvents. The tablets were dissolved in methanol/water 75% v/v and ethanol/water 75% v/v and then, directly introduced in the TS device. The methanol/water 75% v/v dissolution yielded a slightly higher sensitivity when compared to ethanol/water and thus, the latter was selected due to its lower toxicity. The obtained figures of merit are: LOD ( $3\sigma_b$ ):  $0.021 \text{ mg L}^{-1}$ ; LOQ ( $10\sigma_b$ ):  $0.068 \text{ mg L}^{-1}$ , sensitivity:  $0.086 \text{ L mg}^{-1}$ ; RSD%: 3.55, dynamic linear range  $0.068\text{--}5 \text{ mg L}^{-1}$ . Comparison of the results was performed by flame atomic absorption spectrometry (FAAS), showing a good agreement (95% confidence level,  $n = 5$ ). Whilst the FAAS approach needed sample mineralization as no complete solubility was attained with both alcohol/water solvents, TS allowed direct introduction of the sample with an excellent recovery of the analyte after spiking. The whole TS procedure was more economic (lower amount of reagents and wastings, lower time of operation) and faster ( $60 \text{ h}^{-1}$  sampling throughput) than FAAS.

Nonetheless, the main objective of this work is to show that an analytical signal different from zero can be obtained for Mg via TS by simply choosing the adequate operational variables that allow an optimization of the mass transfer of the analyte into the atomizer and a favorable dynamics of desolvation/atomization.

This approach could broad TS analytical capabilities to other elements of lower volatility as it is shown here for the case of Mg.

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## 1. Introduction

Thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is a method of analysis proposed by Gaspar and Berndt [1] where a liquid sample is transported through a ceramic

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capillary towards a perforated metallic tube (mostly nickel) located over a combustion flame in the optical path of an atomic absorption spectrometer. This arrangement allows the complete sample introduction and an increased residence time of the analyte in the furnace, improving sensitivities for the volatile elements (Cd, Zn and Pb) [2–10]. Nonetheless, a drawback of this technique is that a fraction of the flame energy is wasted on solvent vaporization producing a cooler environment in the atomization cell. This is why most of the literature in thermospray (TS) reports the analytical determination of elements of low atomization temperatures or derivatization strategies for the less volatile ones [11–16].

Since the early works of Berndt et al. up to date, no Mg determination by TS-FF-AAS was reported due to the lack of sensitivity [13,15]. This is probably because the environment inside the perforated atomization cell and its lower temperature –when compared to the premixed air/acetylene flame–, produce a decrease in the atomic population.

This work seeks for the first time alternatives to control the cooling of the atomization cell, providing at the same time a suitable redox environment able to minimize the amount of oxygen and thus, the amount of oxygenated compounds that magnesium is prone to produce. In this way, the addition of organic compounds seemed to be capable of consuming oxygen by combustion. At the same time, the reduction of the droplet size should enable a more favorable desolvation/atomization dynamics.

Even though this is not the first time that organic compounds are employed as carriers in TS, the literature [16–18], mostly refer to applications of sample introduction into mass spectrometers where the reduction of the droplet size becomes an important advantage. Few approaches for elemental determination were reported up to date [19].

In this work, several mixtures of the solvents methanol, ethanol and isopropanol in water at different air/acetylene ratios were assayed. Their combined effect on Mg signal was evaluated by obtaining the surface responses. Calculations of the droplet sizes of the solvents mixtures and temperature estimations of the different zones of the perforated flame furnace were also performed as tools to explain their joint effect on the desolvation/atomization dynamics. Estimations of temperature were based on the two color thermometry method [20–23] which was modified by the authors for this particular purpose. The findings were employed to hypothesize about the sample behavior inside the furnace as it is explained throughout the manuscript.

Once obtained the operational variables giving the best performance, Mg was determined in Berocca<sup>®</sup> effervescent vitamin tablets. The samples were simply dissolved in either ethanol/water or methanol/water mixtures and then, directly introduced into the TS device. Validation was performed via FAAS after microwave digestion since it was not possible to prevent the nebulizer clogging by direct dissolution in alcohol/water. Results were in good agreement. Costs and economy of the analytical determination reveal that TS could be an excellent alternative not only for Mg but to other elements of lower volatility.

## 2. Experimental

### 2.1. Reagents and materials

All solutions were prepared with analytical grade chemical reagents and double deionised water (DIW) obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). All glassware was washed with EXTRAN (Merck, Darmstadt Germany) 1% v/v and kept in 10% (v/v) HCl (Merck) with further cleaning with DIW.

Mg standard solutions were prepared daily by appropriate dilutions of 1000 mg L<sup>-1</sup> stock standard solution (Merck).

Organic solvents methanol, ethanol and isopropanol were Merck p.a.

Concentrated nitric acid was Merck p.a.

### 2.2. Instrumental

A flame atomic absorption spectrometer Shimadzu AAS 6800 (Kyoto, Japan) equipped with a hollow cathode lamp of Mg as radiation source and a deuterium lamp for background correction was used. Instrumental conditions were those provided by the manufacturer. An air/acetylene flame was used under different oxidant/fuel ratios: acetylene was varied between 1 and 3.5 L min<sup>-1</sup> whilst air flow rate was kept constant at 24 L min<sup>-1</sup> since no changes in air flow rate are allowed by the Shimadzu spectrometer. The optimal values of acetylene flow rate were 2.5 L min<sup>-1</sup> and 3.0 L min<sup>-1</sup> for ethanol and methanol, respectively. These values were employed throughout the experiments.

Transient signals were recorded in the peak height mode. Sharpness and tallness of the obtained signals made unnecessary the use of peak area mode.

A closed-vessel microwave oven (MDS-2000, CEM Corporation, USA), equipped with temperature and pressure probes, was used in the samples digestion procedure. The mineralization program was that provided by the manufacturer.

The TS-FF-AAS system was assembled with a peristaltic pump of eight channels and six rollers (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), a six-ports rotatory valve VICI (Valco Instruments, Houston, TX, USA), 0.5 mm i.d. PTFE<sup>®</sup> tubings, a ceramic capillary (0.5 mm i.d., 6 cm length) and a perforated (six holes) nickel flame furnace atomizer placed on an air/acetylene flame with the assistance of a homemade steel holder (see Fig. 1).

The nickel tube (Inconel 600<sup>®</sup> alloy, Camacam, São Paulo, Brazil) composition was >72% (m/m) Ni, 14–17% (m/m) Cr and 6–10% Fe as major constituents. The dimensions were 9.7 mm i.d. and 100 mm length.

Temperature estimations were carried out with a Nikon D3100 digital camera. Digital photographs of the heated tube were obtained between 600 and 1000 °C at intervals of 50 °C. A muffle (Heraeus) was employed for changing the temperature of the tube for calibration purposes. “Color” measurements were performed at fixed sensitivity and exposure values, Shutter speed of 1/10 s and an aperture of 6.3 were considered optimal for the temperature range employed for calibration.

Image processing was performed with MATLAB 8.0

### 2.3. Procedure

#### 2.3.1. Analytical methodology

Whole tablets of Berocca<sup>®</sup> (about 5 g weight) were microwave digested in nitric acid following the program provided by the

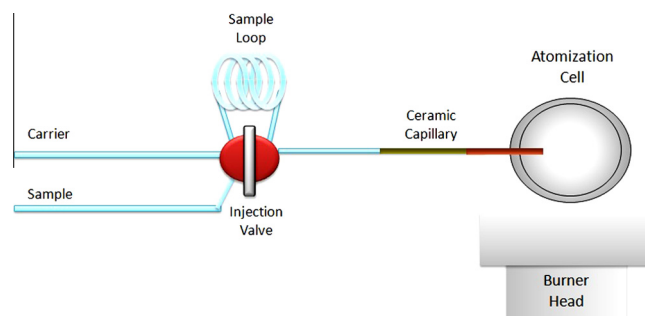


Fig. 1. TS-FFAAS experimental setup. Different proportions solvent/water were employed as carriers at a constant flow rate of 0.9 mL min<sup>-1</sup>.

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