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Electrothermal Metallic Furnace Atomic Absorption Spectrometry.

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We present an atomization system for atomic absorption spectrometry comprised by a stainless steel furnace heated by Joule effect by means of its intrinsic resistance. This new kind of furnace does not require any gases during operation. The sample is introduced with an independently controlled thermospray injector. The device outperforms conventional FAAS (Flame Atomic Absorption Spectrometry) for many analytes, giving a very safe, compact and inexpensive alternative for many analytical determinations. Full characterization of the system is presented, and theoretical simulations are contrasted with experimental data.

Introduction

Atomic Absorption Spectrometry (AAS) is one of the most widespread techniques for determination of trace elements since Alan Walsh introduced Flame Atomic Absorption Spectrometry (FAAS) in 1955.[1]

Since then, many changes of the original idea have been investigated and several new versions of AAS have been proposed with diverse success.[2,3]

The use of a flame in FAAS implies the acceptation of two drawbacks: a complex gas management system able to ensure a safe operation under every condition, and a short residence time of the sample into the optical path[4], given the fact that the flame is an open environment.

Electrothermal atomizers[5-8], mainly graphite furnaces[9,12], or tungsten coils[13-16] in a lower extent, became an excellent alternative to overcome the problems depicted above. Nonetheless, for these alternatives and regardless the employment of standardized temperature platform furnaces, transverse heating or matrix modification[17,18], high purity argon gas flow for protection of the heated cell is mandatory.

Another strategy to confine the sample into the optical path was proposed recently by Berndt[19] and refined by several groups.[20-25] This arrangement, known as *thermospray flame furnace atomic absorption spectrometry* (TS-FFAAS), allows the introduction of the totality of a liquid sample into a tube (or furnace) mounted over a combustion flame in the optical path of an atomic absorption spectrometer. The sample is injected *via* a peristaltic pump and transported to the flame furnace (FF) through a ceramic capillary directly heated by the flame, producing the so called *"thermospray"* (TS). The combination of the whole sample introduction and the confinement of the atomized sample has proven to optimize sensitivity for volatile elements when compared to FAAS with no need of major changes in the basic instrument

Inspired in FFAAS and ETAAS, we present the Electrothermal Metal Furnace Atomic Absorption (EMFAAS) approach that takes advantages of both techniques. EMFAAS employs a stainless steel alloy tube as furnace. This tube of relatively high electric resistivity is very well suited to be heated by conducting a high current through its body.

Thus, the high temperature of the furnace is attained with no need of burning or protecting gases. The total liquid sample introduction is performed with the assistance of a peristaltic pump and a ceramic thermospray injector which is heated electrically and independent from the furnace heating.

In this way, EMFAAS combines electrical heating of both the FF and the TS injector, keeping away from pressurized gases either for combustion, protection or typical pneumatic nebulisation of liquid samples.

Additionally, EMFAAS offers the simplicity and robustness of FAAS together with increased sensitivity for volatile elements as it will be shown here as proof of principle

Experimental

Materials and methods

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 all the analytes were prepared by proper dilution of 1,000 g L-1 stock solutions (Merck Darmstadt, Germany). A digital camera Samsung NX 1100 was used to take all the

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temperature images. The heating of the cell was performed by means of a commercial 700 W microwave oven transformer, in which the original secondary wiring was replaced by a two-turns coil of 7 mm diameter copper multifiber cable (automotive, for batteries).

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 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® 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.

In a typical experimental procedure, 500 μL of standard solution was introduced in a carrier stream (DIW) and injected into the atomization cell at a flow rate of 1.1mL min^{-1}. A Nichrome coil wounded around the ceramic injection capillary was used to heat the solution above the vaporization temperature prior to entering the cell. 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.

Temperature Measurements

A commercial digital camera was used to obtain the images of the cell during atomization heating. To overcome the intrinsic non linearity of the pixel values in images compressed to JPG with respect to the light intensity and to temperature, a two-step calibration process was followed. Image analysis was done using public access *ImageJ* software.[26]

Firstly, images of the heated cell were taken at constant diaphragm (f/8) and ISO 100 settings, varying the exposure time from 1 to 1/250 seconds. As the photon flux is linearly dependent with the exposure time, a calibration of pixel value vs. red or green intensity can be easily obtained. A polynomic expression is useful to perform this calibration. The results are given as supporting information.

As a second step, a relationship between light intensity of a given colour and the temperature must be found. Although in principle it is possible to use the theoretical dependence for a black body emission, better results can be obtained through empirical calibration of either red or green intensity vs. emission, or ratiometrically from the relationship between red/green values. In brief, the logarithm of emission intensity is rather linear with the temperature. The details are given as supporting information. Both, red or green can be used to obtain temperatures within 5% uncertainty. Ratiometric measurements yield similar results, but implies the use of perfectly steady images because the amount of red and green emission are strongly dependent on the temperature and thus several different exposures must be done for a given situation.

For the images presented in this work the green channel measurement was preferred.

Results and discussion

Figure 1 shows the general diagram of the Electrothermal Metal Furnace Atomic Absorption Spectrometer (EMFAAS) depicting their main building blocks. The heart of the system consists of a 10 mm inner diameter cylindrical tube (A) made of 304L Stainless Steel[27] alloy which is supported by two highly conductive copper pillars (B, C) connected to a controlled low voltage-high current source (D). A flow of water through a pair of holes in each pillar ensures that they remain at near-ambient temperature to prevent the heat for reaching the power supply cables (E). The pillars are separated using polycarbonate isolators from the aluminium base. At the front of the cylinder, a ceramic capillary (F) is introduced about 1-2 mm into the atomizer tube. This capillary is heated from the exterior by means of a Nichrome wire resistance coil (G) connected to a regulated voltage power supply (H). The sample (I) is fed into the capillary by means of a peristaltic pump (J).
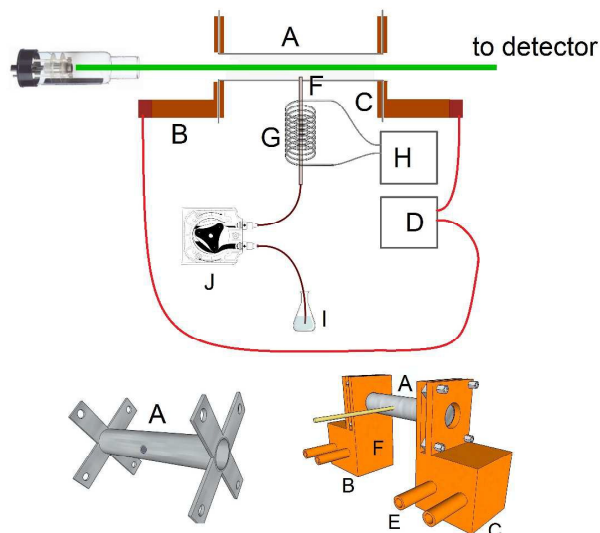

Figure 1. Scheme of the electrothermal atomization cell of EMFAAS. See text for details.

Stainless Steel (304L) presents a high electric resistivity, 0.72 x10^{-6} Ω.m at 20 ˚C and 1.16 x10^{-6} Ω.m at 660 ˚C around 60 times higher than that of copper. Together to its high mechanical, thermal and chemical resistance, this alloy constitutes a superb option for an electrothermal atomization cell. To achieve this goal, a 700 W AC transformer capable to generate around 1 Volt at several hundred Amperes was connected to the tube ends through the cooled copper pillars. The control of the overall power delivered to the cylindrical cell can be performed using a linear inductive autotransformer (variac) or changing the duty cycle of the primary coil of the

main transformer (220 VCA) using a phase controlled TRIAC (dimmer). The latter allows the possibility of temperature control using a calibrated K-type thermocouple and a thermostat for controlling the primary current. The thermal inertia of the heated cell guarantees that the 50 Hz cycle variation of the temperature at the cell walls is completely negligible. A similar phase controlled dimmer was used to control the injector heating.

For an 5 cm long furnace with both ends attached to refrigerated copper pillars through fins of about 2 cm long each, the total resistance was $R_L = 2.87$ mΩ. In a typical experiment a current i = 320 A circulates through the furnace, raising its central temperature to about 1000 ˚C. The voltage drop at the tube is V_L = 0.92 V. This low voltage implies that no hazard due to electric shocks is present in the equipment. At the involved high currents other voltage drops are important, such as the contact resistance between the pillars and the furnace (225 mV each contact) and on the cable itself (160 mV). Therefore, about 60% of the total power of 505 W is dissipated along the furnace, increasing its temperature. This figure could be easily enhanced by means of gold-plated contacts.

Figure 2 shows the cell geometry and its inset the obtained temperature profile as a false color picture registered with a digital RGB camera on the external wall of the atomization cell. The simulation performed with a finite differences algorithm (solved by a numerical procedure using *FlexPde 5.0* software, see Supporting Information) is shown with the same colour scale showing a good correspondence even for the simple model used.

injector due to vaporization heat of the sample. These temperature variations are responsible for changes of sensitivity at different injection flows. Figure 3 shows the signals obtained for several analytes at different injection flow rates. The response presents maxima around 1.1 mL min^{-1}, indicating that the cooling effect of the injection at higher flows can overcome the increment of the analyte
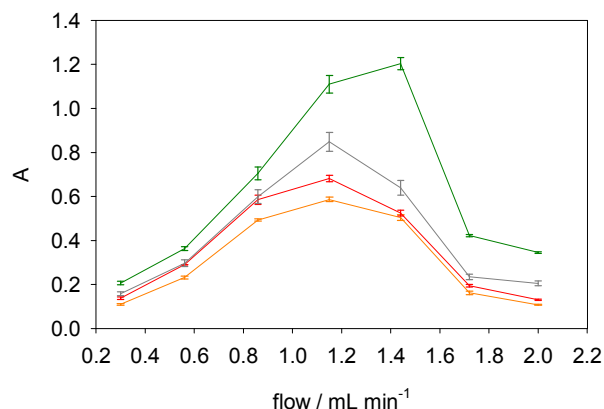
concentration in the atomization cell.

Figure 3. Signal change for several analytes in function of the injection flow rate. Green = Cd (100 µg L^{-1}). Grey = Zn (500 µg L^{-1}). Red = Cu (500 µg L^{-1}). Orange = Au (100 µg L^{-1}). T = 910 º.

In order to determine the magnitude of the cooling, temperature images were taken at different injection flows. Figure 4 shows the results. The top image corresponds to the Raw picture of the cell at maximum injection flow (1.2 mL min^{-1}). The false color pictures are the thermal images, from 0 (top) to 1.2 mL min^{-1} (bottom), showing that for this maximum flow corresponds a drop of about 90 ˚C at the coldest region.
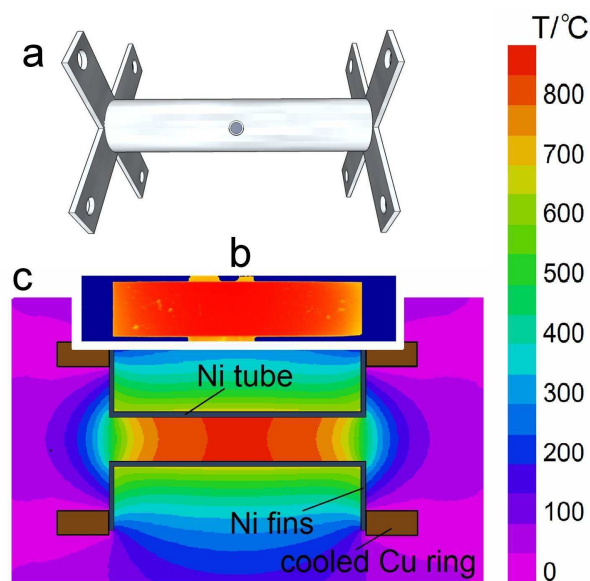

Figure 2: a) Furnace cell. b) False colour thermogram of the cell showing the temperature field. The temperature scale is depicted on the right. c) The colour-coded temperature field calculated with a finite differences software.

One of the typical characteristics of thermospray injection is the temperature drop that occurs at the position of the

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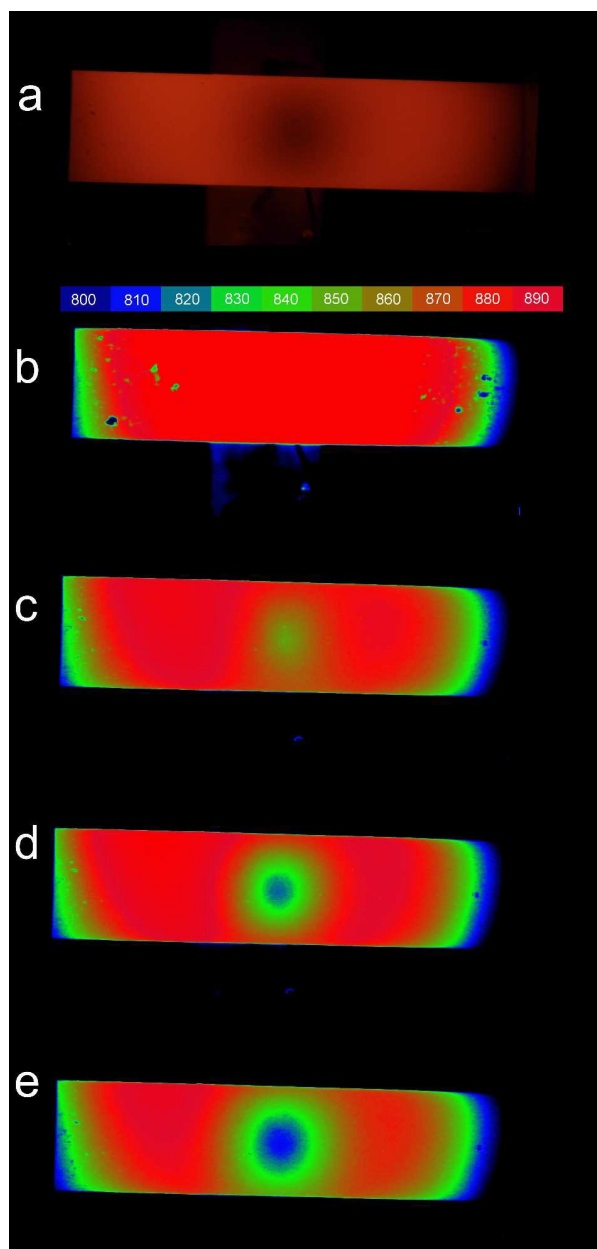

Figure 4: a) Raw RGB picture of the EMFAAS-cell at i = 320A during an injection flow of 1.2 mL min^{-1}. b-e) False color temperature fields of the EMFAAS-cell at 0, 0.6, 1.0 and 1.2 mL min^{-1} injection flows.

As shown in Tabla 1, the dynamic linear range is about two orders of concentration in most cases, and the repeatability expressed as RSD % is less than 5% (n=5). These figures of merit are comparable with those obtained by FAAS. Nevertheless, the LOD is up to 20 times lower than traditional FAAS for Cd. It is expected that even lower LODs can be obtained by raising the tube temperature, and/or extending the cell length. High temperature alloys like Kanthal® or metal-ceramic composites can help in increasing the maximum operation temperature.

Table 1: Figures of merit obtained by EMFAAS for several analytes in the conditions described in the text.   (For EMFAAS: injection volume = 500 mL, flow rate = 1.1 mL min^{-1}, T = 910 ˚C). Limits of detection are compared with those obtained by FAAS.

Element	LOD (μg L^{-1})		LR (μg L^{-1})		%RSD (n=5)
	FAAS	EMFAAS	EMFAAS		EMFAAS
Ag	30	15	50	1000	3.92
Au	40	29	96	1000	4.17
Cd	36	2	7	750	2.5
Cu	12	10	33	1000	3.43
K	26	24	79	2000	1.42
Pb	226	84	277	3000	2.58
Mn	90	87	287	3000	3.23
Zn	23	3	10	500	3.45

Conclusions

We have devised a new kind of electrothermal atomic absorption spectrometer which allows robust and sensitive measurements of several elements with improved figures of merit with respect to FAAS and a complete lack of any of the problems and nuisances due to the use of gases. The atomization is performed through a Joule effect self heating cell tube that can resist temperatures up to 1000 ˚C, enough to get good sensitivity for several analytes. The employment of cells of new metal-ceramic composite materials capable to work at 1600-1800 ˚C could broaden the analytical capabilities to a larger number of elements. The injection of samples through a heated capillary (thermospray injection) makes this approach fully compatible with flow systems. The independently electrically heated ceramic thermospray injector introduces a new variable to optimize the operation at different throughput rates. The compactness of EMFAAS, lacking any gas management which assures safe operative conditions, makes this kind of atomic spectrometry ideal for portable and in-field measurements. It is also as low cost bench for research, industry and education in AAS.
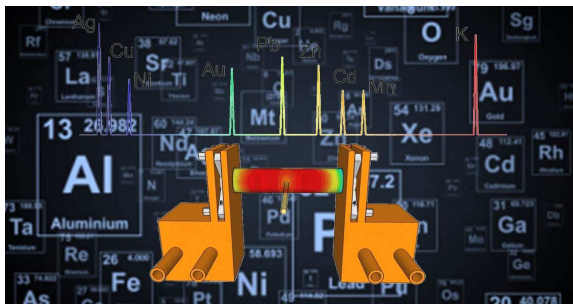
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