On-line microwave-based preconcentration device for inductively coupled plasma atomic emission spectrometry: Application to the elemental analysis of spirit samples

Guillermo Grindlay*, Luis Gras, Vicente Hernandis, Juan Mora

Department of Analytical Chemistry, Nutrition and Food Sciences, University of Alicante, P.O. Box 99, 03080 Alicante, Spain

ABSTRACT

A microwave-based thermal nebulizer (MWTN) has been employed for the first time as on-line preconcentration device in inductively coupled plasma atomic emission spectrometry (ICP-AES). By the appropriate selection of the experimental conditions, the MWTN could be either operated as a conventional thermal nebulizer or as on-line analyte preconcentration and nebulization device. Thus, when operating at microwave power values above 100 W and highly concentrated alcohol solutions, the amount of energy per solvent mass liquid unit (EMR) is high enough to completely evaporate the solvent inside the system and, as a consequence, the analyte is deposited (and then preconcentrated) on the inner walls of the MWTN capillary. When reducing the EMR to the appropriate value (e.g., by reducing the microwave power at a constant sample uptake rate) the retained analyte is swept along by the liquid-gas stream and an analyte-enriched aerosol is generated and next introduced into the plasma cell. Emission signals obtained with the MWTN operating in preconcentration-nebulization mode improved when increasing preconcentration time and sample uptake rate as well as when decreasing the nozzle inner diameter. When running with pure ethanol solution at its optimum experimental conditions, the MWTN in preconcentration-nebulization mode afforded limits of detection up to one order of magnitude lowers than those obtained operating the MWTN exclusively as a nebulizer.

To validate the method, the multi-element analysis (i.e. Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn) of different commercial spirit samples in ICP-AES has been performed. Analyte recoveries for all the elements studied ranged between 93% and 107% and the dynamic linear range covered up to 4 orders of magnitude (i.e. from 0.1 to 1000 $\mu g\,L^{-1}$). In these analysis, both MWTN operating modes afforded similar results. Nevertheless, the preconcentration-nebulization mode permits to determine a higher number of analytes due to its higher detection capabilities.

1. Introduction

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a widely employed technique for trace and ultra-trace analysis due to its high dynamic range, multi-element capabilities and low limits of detection. However, sample throughput is often limited by manual and labor-intensive sample preparation methodologies (digestion, extraction, etc.) [1]. Analysis automation and sample throughput can be easily improved by means of on-line methodologies [2–6]. Among them [7,8], column-based solid phase extraction is one of the most popular and efficient ones. By the appropriate selection of the sorbent material characteristics, selective and high analyte enrichment efficiency can be accomplished. Nonetheless, the analytical performance is usually limited in long term due to: (i) volume changes (i.e. swelling or shrinking) on the sorbent material; (ii) increase in the back pressure due to tighter packing of the column material; and (iii) deactivation of the surface and/or loss of functional groups [8]. In addition, the use of non-polar volatile solvents for analyte elution has negative effects on plasma characteristic [9]. A different alternative for analyte preconcentration is on-wall adsorption/retention of non-charged metal complexes by means of knotted reactors [10]. In these procedures, analyte retention within the capillary is achieved by merging of the sample solution with a complexing or precipitating reagent. Then, after a washing step, the complex/precipitate is released with the appropriate eluent (usually diluted nitric acid) and introduced into the plasma. In the late 80's, Robinson et al. [11,12], reported the use of a thermospray nebulizer (TN) as an on-line preconcentration device for samples with a low matrix content. TN was able to retain (i.e., preconcentrate) the analyte on the capillary walls when operating at strong vaporization

* Corresponding author. Tel.: +34 965903400x1242.
  E-mail address: guillermo.grindlay@ua.es (G. Grindlay).

conditions (i.e., high capillary temperatures and/or low sample uptake rates). Switching back to softer conditions allows analyte redisolution thus obtaining a transient signal. TN on-line preconcentration device provides sensitivities up to 50 times than those typically obtained in Flame Atomic Absorption Spectrometry, thus, making feasible the analysis of Cu at ultra-trace levels in river water samples [12]. Nonetheless, several non-overcoming drawbacks make difficult its use for routine analysis: (1) very poor signal precision; (2) prone to blockage; and, (3) high memory effects [12].

Microwave radiation (MW) has been successfully employed as an alternative energy source for thermal nebulizers [13–15]. MW offers some unique advantages when compared to conventional electric heating, mainly: (i) better and faster control of the operating conditions, mainly applied power; and (ii) minimization of the contamination risk and improved system life-time and reproducibility due to the use of a PTFE capillary instead of the stainless steel one. From the above mentioned characteristics, it seems possible to use a microwave-based thermal nebulizer (MWTN) as an on-line preconcentration device for ICP-based techniques. Up to now, MW has been widely employed to assist extraction-preconcentration methodologies [16–18] but no description of a fully microwave-based preconcentration-nebulization device is reported in the literature.

The purpose of the present work is to characterize the behavior of a MWTN as on-line preconcentration device in ICP-AES. To this end, the influence of the key experimental variables (i.e. MW power, solvent composition, sample uptake rate and nozzle diameter) on the ICP-AES analytical figures of merit has been evaluated. To validate the proposed method, the multi-element analysis (i.e. Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn) of different commercial spirit samples in ICP-AES has been performed. Results have been compared with those obtained using the MWTN operating in the conventional nebulization mode.

2. Experimental

2.1. Sample introduction systems

A complete description of the MWTN can be found elsewhere [15,19]. Sample was supplied to the system by means of an HPLC pump (Model 1500, Chrom Tech, Apple Valley, Minessota, USA). Microwave power (P_{MW}) (i.e. 100–290 W), sample uptake rate (Q_l) (i.e. 0.8, 1.0, 1.2 and 1.4 mL min^{-1}) and nebulizer nozzle inner diameter (i.e. 150, 200 and 300 μm) were the variables studied. PTFE capillary dimensions were kept constant (1 m PTFE capillary length with an inner diameter of 500 μm) [15].

In order to evaluate the results obtained with the MWTN, a pneumatic concentric nebulizer (PN) (Model TR-30-K2, Meinhard, Santa Ana, California, USA) was also employed. The sample was delivered to the PN by means of a peristaltic pump (Model Minipulse 3, Gilson, Villiers-Le-Bel, France) and organic resistant tubes (SC0323 (i.d. 038 mm), Ismatec SA., Labortechnik-Analytik, Glattbrugg, Switzerland).

All the nebulizer arrangements were coupled to a home-made thermostated cyclonic spray chamber (inner volume 33 cm^3) operated at −5 °C by means a thermostated bath (Haake F3-K, Haake Mess-Technik GmbH U Co, Karlsruhe, Germany). In addition, a Peltier condenser (30 cm length × 0.8 cm id) operating at −30 °C was attached to the spray chamber exit in order to avoid plasma extinction. A rotameter (Cole-Palmer Ins. Co., Chicago, Illinois, USA) was used in all cases to control the aerosol carrier/nebulizer gas flow. When operating with the MWTN, the aerosol carrier gas flow was introduced into the spray chamber by means of a T-joint placed at the nebulizer entrance.

Table 1
ICP-AES operating conditions.

Plasma forward power/ W	1450
Argon flow rate/ L min^{-1}:	
Plasma	15
Auxiliary	0.5
Nebulizer/Carrier	0.5
Sample uptake rate/mL min^{-1}	Variable
View mode	Axial/radial (15 mm)
Injector inner tube diameter/mm	0.8
Integration time/ms	20
Readings/replicates	10/3

2.2. ICP instrumentation

ICP-AES measurements were performed using a PerkinElmer Optima 4200 ICP-AES system (PerkinElmer, Shelton, CT, USA). Table 1 shows the operating conditions used. Transient signals afforded by the MWTN when operating as on-line preconcentration-nebulization device were manually integrated using Excel® software since the ICP-AES software used does not allow doing it automatically. For the remaining arrangements tested through this work, a continuous signal was registered by the spectrometer.

2.3. Aerosol drop size distributions measurements

Aerosols generated by the MWTN were characterized by means of a laser Fraunhofer diffraction system (Model 2600c, Malvern Instruments Ltd., Malvern, Worcestershire, UK). All measurements were made at 1 mm from the nebulizer tip. A lens with a focal length of 63 mm, which enables the system to measure droplets with diameters between 1.2 and 118 μm, was used. Calculations were performed by means of Malvern software version B.0D which transforms the energy distribution into aerosol drop size distribution using a model-independent algorithm that does not preclude any particular distribution function. A set of five replicates was performed in each case, being the precision of these measurements always lower than 4%.

2.4. Reagents

High purity water (i.e. with conductivity lower than 18 MΩ cm^{-1}) obtained from a Milli-Q water system (Millipore Inc., Paris, France), methanol, ethanol and i-propanol solutions (Merck, Darmstadt, Germany) were used throughout the work.

Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn mono-elemental solutions (Merck, Darmstadt, Germany) were employed to prepare test solutions and calibration standards as well as to spike the samples for recovery studies. In addition, Sc monoelemental solution (J.T. Baker, Deventer, Netherlands) was employed for internal standardization purposes.

All glassware and polypropylene flasks were soaked with nitric acid 10% w w^{-1} overnight and rinsed with deionized water prior to use. Test solutions and calibration standards were daily prepared.

2.5. Samples

A set of four different alcoholic beverages purchased in local markets were analyzed: two gins (G1: 32% w w^{-1} ethanol; G2: 30.4% w w^{-1} ethanol), one anisette (38.5% w w^{-1} ethanol) and one liquor (36% w w^{-1} ethanol). All the samples were diluted 1:4 prior to the analysis with pure ethanol.