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

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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 μg 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

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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.

2.6. Calibration strategy

The analysis of spirit samples was performed using ethanol matched standards and internal standardization. Sc was selected as internal standard since it is not usually present in spirits and it has shown a good behavior in wine analysis [12].

3. Results and discussion

3.1. MWTN preconcentration-nebulization process

Fig. 1 shows the system pressure and signal profiles obtained for several analytes in a given matrix when operating with the MWTN under different P_{MW}. In this experiment, P_{MW} was increased from P_{MW1} to P_{MW2} for a given period of time (preconcentration time) and then switched back to the initial P_{MW} conditions. From Fig. 1, three different signal regions can be distinguished. First, at P_{MW1} (Fig. 1a), MWTN operates as a conventional thermal nebulizer thus affording a continuous emission signal. Next, when P_{MW} is increased from P_{MW1} to P_{MW2} (Fig. 1b), analyte signal completely disappears and the system pressure gradually rises up. In these conditions, the microwave energy per solvent mass liquid unit (EMR) is high enough to completely evaporate the sample solvent inside the capillary thus precipitating the non-volatile analytes on the capillary walls. Finally (Fig. 1.c), when switching back to P_{MW1}, EMR is again reduced. Therefore, the liquid fraction evaporated inside the capillary is reduced and the remaining liquid fraction re-dissolves the analyte deposited. As a result, an analyte-enriched aerosol is generated and transported to the atomization cell thus affording a sudden transient signal increase before reaching the initial stationary signal and pressure values.

The above discussed results point out the capability of the MWTN to work in two different operation modes just by a judicious selection of the experimental conditions: (i) as a conventional microwave-based thermal nebulizer [13–15]; and, (ii) as analyte preconcentration and nebulization device. To characterize the behavior of the MWTN as preconcentration-nebulization device in ICP-AES, a systematic study of the variables controlling the full process (i.e., solvent composition and nature, P_{MW}, preconcentration time, Q_l and nozzle diameter) on the integrated Mn emission signal was studied.

3.2. Characterization of the MWTN in ICP-AES

3.2.1. Influence of the solvent composition and microwave power

Fig. 2 shows the influence of the ethanol concentration on the Mn net emission signal (257.610 nm) afforded by the MWTN when operating at different P_{MW}. As shown in this figure, signal behavior strongly depends on both the solvent composition and the P_{MW} used. Thus, when operating at 100 W, Mn emission signal continuously increased with ethanol concentration. At 290 W the opposite behavior is observed and no signal was obtained for pure ethanol solution. An intermediate situation is observed when operating at 180 W since analyte signal peaked for the ethanol 80% w w^{-1} solution. Similar results were observed when operating with methanol and *i*-propanol solutions, irrespective of the analyte considered (Co, Ca, Pb, Cd, etc.).

Results shown in Fig. 2 are inconsistent with the previous findings obtained when running the MWTN with inorganic acid solutions for which signal always increased when increasing P_{MW} values and acid concentration [13–15]. To explain these behaviors, the influence of both P_{MW} and alcohol concentration on the MWTN aerosol generation process must be considered. Thus, the higher the P_{MW} and the alcohol concentration, the higher the heating efficiency (i.e. EMR) and then, the amount of solvent evaporated inside the system [15]. As a consequence, finer aerosols are generated (see Table 2) and higher amount of analyte

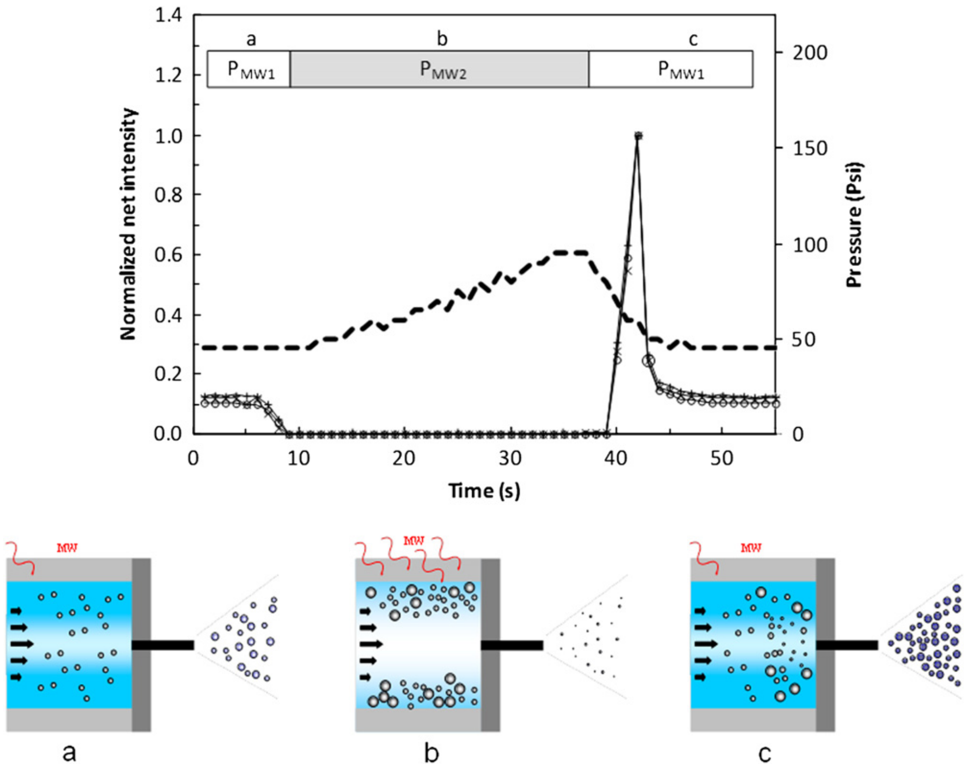

Fig. 1. Influence of MW power on the analyte signal profile (continuous line) and HPLC pump pressure read-out (dotted line) obtained with the MWTN when modifying the microwave power applied. Analytes: (+) Mn, (○) Co and (x) Ca. P_{MW1}: 100 W; P_{MW2}: 180 W; solvent: Pure ethanol; Q_l: 1.4 mL min^{-1}; nozzle diameter: 300 µm. ICP-AES view mode: radial.

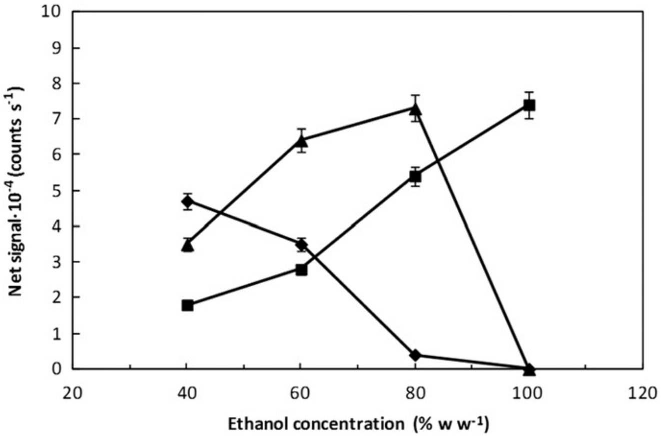

Fig. 2. Influence of ethanol concentration on the Mn emission intensity obtained with the MWTN operating at different microwave power values: (■) 100 W; (▲) 180 W; (◆) 290 W; Q_l: 1.4 mL min^{-1}; nozzle diameter: 200 μm. ICP-AES view mode: radial.

Table 2
Influence of the alcohol nature and concentration on the median of the volume drop size distribution (D_{50}) of the aerosols generated by the MWTN at different microwave powers. Q_l: 1.1 mL min^{-1}; nozzle diameter: 200 μm.

Solvent concentration (w w^{-1})	D_{50} (μm)		
	100 W	180 W	290 W
Ethanol 40%	73.90	48.20	26.43
Ethanol 60%	46.89	22.29	20.30
Ethanol 80%	27.67	15.40	12.94
Ethanol 100%	25.71	14.68	12.52
Methanol 100%	21.84	11.94	9.17
i-propanol 100%	34.65	19.76	15.59

can be transported to the plasma. Therefore, an increase in the analytical signal is expected. Nonetheless, when the solvent fraction evaporated is high enough, analyte retention within the capillary is also favoured thus reducing the amount of analyte reaching the plasma (and then, the signal). Operating with the MWTN at 100 W, stable Mn emission signals were registered for periods longer than 1 h, irrespective of the ethanol solution tested. This result points out that preconcentration is negligible at these conditions and the MWTN behaves exclusively as a nebulizer. However, when using P_{MW} above 100 W, emission signal progressively decreased with time. This observation suggests that a fraction of the analyte introduced in the system is being retained within the MWTN capillary (preconcentration). Signal loss rate increases when increasing P_{MW} and alcohol concentration. In fact, Mn signal instantaneously disappeared at 290 W and ethanol concentrations above 80% w w^{-1}, thus indicating a complete analyte preconcentration within the MWTN capillary.

Results shown in Fig. 2 point out that MWTN is not able to preconcentrate the analyte contained in diluted alcohol solutions. Similarly, no preconcentration was observed operating with diluted nitric and hydrochloric acid solutions at different P_{MW} values. These behaviors can be explained taking into account that water, due to its higher boiling point, requires a higher EMR values than alcohols to completely vaporize the solvent. As a consequence, analyte cannot be efficiently retained on the capillary walls using the current MWTN design.

Taking into account the results above discussed, the next experiments were performed with pure alcohol solutions. First, the microwave-based device was operated at 100 W MW power (P_{MW1}) to ensure an adequate sample nebulization avoiding analyte preconcentration. Next, the applied MW power was increased up to 290 W (P_{MW2}) to rapid enhance the EMR and promote the analyte preconcentration inside the PTFE capillary. After a given time (preconcentration time) operating at these conditions, P_{MW} was fixed again at 100 W. Emission signals were measured during the whole process and the area of the peak obtained was manually integrated.

3.2.2. *Preconcentration time*

Fig. 3 shows the influence of preconcentration time on the Mn emission signal obtained for the MWTN running with different alcohol solutions. From these data it can be derived that signal increases when increasing the preconcentration time, irrespective of the alcohol solution tested. These results are the expected taking into account that when higher the preconcentration time, higher the amount of analyte retained within the system. In general terms, analyte signal was almost proportional to preconcentration time. Thus, when preconcentration time was increased from 30 to 90 s (i.e. 3 times), emission signal improved on average 2.7 times for all the alcohol solution tested. Small differences between preconcentration time increment and signal improvement can be attributed to analyte losses during the aerosol transport to the atomization cell [20] rather than to changes in the preconcentration process.

Preconcentration factor was estimated using the ratio between the sensitivities obtained with the MWTN in preconcentration-nebulization mode and those operating the MWTN exclusively as a nebulizer (Table 3) [12]. Thus, considering a preconcentration time of 90 s and Q_l of 1.4 mL min^{-1}, a preconcentration factor of 13, on average, is afforded for the different elements tested. This preconcentration factor was similar to those previously reported for the TN in FAAS [12], electrochemical deposition [21,22] and liquid solid-phase extraction in ICP-AES [23,24]. To improve the preconcentration factor, preconcentration times longer than 90 s can be used. It must be taking into account that the maximum preconcentration time achievable will be determined by the capillary endurance, which finally depends on the sample composition (when higher the analyte and matrix concentration, the lower the preconcentration time required to break the capillary) and experimental variables used. Thus, it was observed that capillary used to go off when operating at system pressures above 350 psi. With the appropriate selection of the experimental conditions, capillary life-time was always higher than 2 months.

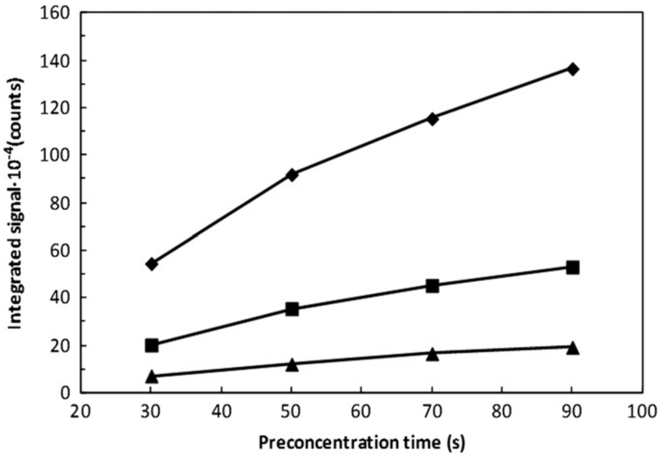

Fig. 3. Influence of the preconcentration time on the Mn integrated signal obtained with the MWTN for different pure alcohol solutions: (◆) methanol; (■) ethanol; (▲) *i*-propanol. P_{MW1}: 100 W; P_{MW2}: 290 W; Q_l: 1.4 mL min^{-1}; nozzle diameter: 200 μm. ICP-AES view mode: radial.

Table 3
Limits of detection and precision values obtained with the MWTN and PN. Ethanol; Q_l: 1.4 mL min^{-1}. MWTN (nebulization mode): P_{MW}: 100 W; nozzle diameter: 150 μm. MWTN (preconcentration-nebulization mode): P_{MW1}: 100 W; P_{MW2}: 290 W; nozzle diameter: 150 μm; preconcentration time: 90 s. ICP-AES viewing mode: axial view.

Element	Wavelenght (nm)	PN			MWTN					
					Nebulization mode			Preconcentration-nebulization mode		
		Sensitivity (counts L mg^{-1})	LOD (μg L^{-1})	RSD (%)	Sensitivity (counts L mg^{-1})	LOD (μg L^{-1})	RSD (%)	Sensitivity (counts L mg^{-1})	LOD (μg L^{-1})	RSD (%)
Al	396.153	14000	2	2	13000	3	3	150000	0.5	10
Ca	317.933	10000	4	1	12000	2	1	210000	0.3	5
Cd	228.802	7500	12	3	8000	10	3	90000	0.7	10
Cr	267.716	3500	50	2	3500	50	2	80000	2	6
Cu	327.393	18000	60	1	17000	70	2	200000	4	7
Fe	238.204	3800	120	2	4000	100	2	45000	8	6
K	766.490	40000	20	1	45000	20	1	475000	3	5
Mg	280.271	100000	0.4	1	100000	0.2	1	1100000	0.05	5
Mn	257.610	80000	0.4	1	75000	0.6	1	950000	0.06	5
Na	589.592	90000	0.8	1	95000	0.9	1	850000	0.1	5
Pb	220.353	1500	100	3	1500	100	2	30000	4	10
Zn	206.200	11000	8	2	10000	10	3	125000	0.2	8

Finally, from Fig. 3 it is also observed that, among the different alcohols tested, methanol provided the highest signals followed by ethanol and *i*-propanol. To explain these results, it must be considered that the signal afforded by the MWTN depends on the amount of analyte retained inside the capillary but also, once re-dissolved, on the characteristics of the aerosols containing it. In thermal nebulization the main solution property affecting the characteristics of the aerosols generated is the so-called expansion factor, i.e., the volume of gas produced by the evaporation of a unit of liquid solvent volume at its boiling point [25,26]. Thus, the higher the expansion factor, the higher the amount of energy available for aerosol generation. As a consequence, finer aerosols are generated and higher signals are expected. Among the different alcohols tested, methanol shows the highest expansion factor value (693) followed by ethanol (502) and *i*-propanol (382) [25] which agrees with the median of the aerosol volume distribution (D_{50}) and the signal trend shown in Table 2 and Fig. 3, respectively.

3.2.3. Influence of the sample uptake rate

Fig. 4 shows the influence of Q_l on the Mn emission signal obtained with the MWTN operating in preconcentration-nebulization mode. As shown in this figure, an increase in Q_l gives rise to higher signal values for all the solutions tested. These results are the expected taking into account that when Q_l is increased also increases: (i) the amount of analyte introduced (and then retained) in the capillary; and, (ii) the volume of the solution evaporated (as demonstrated by the higher pressure registered inside the capillary), thus giving rise to an increase in the energy available for aerosol generation. As a consequence, finer aerosols are generated and higher signals are obtained [13–15]. Finally, as expected from previous considerations (Section 3.2.2), Fig. 4 also reveals that the highest signals were obtained for methanol followed by ethanol and *i*-propanol.

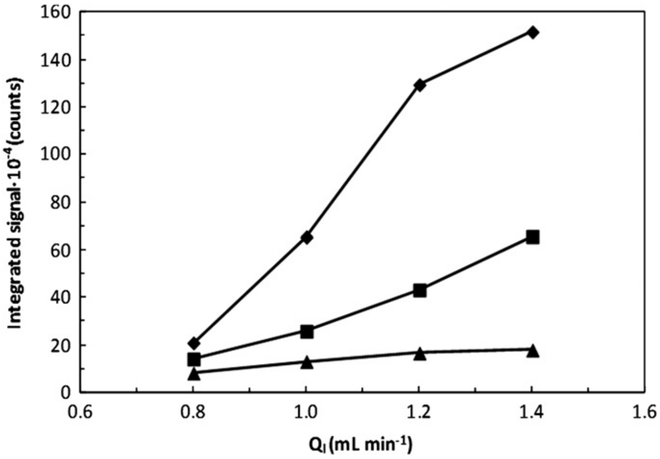

Fig. 4. Influence of Q_l on the Mn integrated signal obtained with the MWTN operating with different pure alcohol solutions: (◆) methanol; (■) ethanol; and, (▲) *i*-propanol. P_{MW1}: 100 W; P_{MW2}: 290 W; nozzle diameter: 200 μm; preconcentration time: 90 s; ICP-AES view mode: radial.

3.2.4. Influence of the nozzle inner diameter

Among the different variables controlling MWTN behavior, nozzle inner diameter has a great influence. For a given experimental conditions, the reduction of the nozzle or PTFE capillary diameter increases the system pressure. This fact leads to a higher gas and liquid streams velocity and thus, to a higher amount of energy available for aerosol generation. As a consequence, finer and more easily transported aerosols are generated, then resulting in higher signals [13,15]. As expected, when running the MWTN in preconcentration-nebulization mode with ethanol solutions, emission signal improved 4.3 and 12.6-fold when switching from a nozzle inner diameter of 300 μm to 200 μm and to 150 μm, respectively. Similar behavior was observed for methanol and *i*-propanol solutions.

3.3. Analytical figures of merit

3.3.1. Limits of detection

Table 3 shows limits of detection (LOD) obtained for pure ethanol solutions when operating the MWTN in both nebulization and preconcentration-nebulization modes. LOD obtained using a pneumatic nebulizer (PN) are also included for comparison. As it is shown in Table 3, MWTN preconcentration-nebulization mode provides LOD about 10 times (on average) lower than those afforded by the device operating in nebulization mode or the PN. According to Boumans, [27,28] LOD depends on blank relative standard deviation and signal background ratio (SBR) values. The former parameter was similar for both MWTN working modes. However, differences in the SBR values between both systems were noticeable. Thus, MWTN preconcentration-nebulization mode always shows higher SBR values (9 times on average) than

MWTN nebulization mode. These results are in agreement with the observed improvement in LOD.

It is interesting to note that when operating with pure alcohol solutions, LOD obtained with the MWTN operating in nebulization mode were of the same order of magnitude than those with the PN. These results can be explained taking into account that the use of organic solutions [15]: (1) improve the pneumatic aerosol generation process due to its low surface tension; and, (2) negatively affects the thermal nebulization since its low expansion factor compared to water (i.e., 1700) leads to a reduction in the amount of energy available for aerosol generation [25]. As a consequence, no significant differences on sensitivity and SBR were observed between both systems (Table 3).

3.3.2. Precision

Table 3 also shows relative standard deviation values (RSD) of the emission intensity obtained with the MWTN in preconcentration-nebulization mode. As it is shown in this table, RSD values were always between 5% and 10%. These values are higher than those obtained using MWTN nebulization mode and PN (i.e., 1–2%) and it can be attributed to the irreproducibility of the analyte preconcentration process within the capillary as well as the impossibility to monitor transient signals with the spectrometer employed [29]. Experiments performed introducing the sample discontinuously by means of an injection valve, indicate that signal RSD increases from 1 to 2% up to 4%. Therefore, it seems to be clear that current precision shown by the MWTN in preconcentration-nebulization mode is expected to be improved when using the appropriate software design.

3.3.3. Sample throughput

MWTN preconcentration-nebulization mode is able to analyze up to 20 samples per hour. Sample throughput for the MWTN is similar to that shown by other reported on-line preconcentration devices [30,31].

3.4. MWTN versus thermospray

From the above discussed results and those previously reported by Choi et al., [12] it seems to be clear the capability of thermal based nebulizers to operate as on-line preconcentration devices in atomic spectrometry techniques. Nevertheless, several differences between the MWTN and the TN can be highlighted: (1) MWTN offers a superior solvent vaporization control (i.e., preconcentration process) than TN. As a result, significantly better precisions are afforded by the MWTN; (2) TN requires the use of an injection valve to avoid stainless steel capillary degradation. Thus, the amount of analyte retained within the capillary (and hence, the enrichment factor) is limited by the loop sample volume. However, MWTN is able to introduce the sample continuously and, as a consequence, higher enrichment factors can be obtained; and, (3) MWTN sample throughput is not limited by blockage problems and a no wash-out step is required to prevent capillary obstruction unlike TN. From the above made considerations, it is clear that the MWTN is superior to the TN for on-line preconcentration purposes in atomic spectrometry techniques.

3.5. Elemental analysis of spirit samples

To validate the use of MWTN as on-line preconcentration-nebulization device, the multi-element analysis of different commercial spirit samples in ICP-AES has been performed. The control of elemental composition of alcoholic beverages is of great economical significance to ensure product quality and prevent toxicological issues [32]. ICP-AES has been widely employed in this field but limits of detection are sometimes not low enough to quantify some elements of interest present at ultra-trace levels.

Spirit samples use to present a wide range of ethanol concentrations. As it has been pointed out previously, to ensure a rapid and efficient preconcentration procedure using the MWTN, ethanol solutions with concentrations above 80% w w^{-1} are recommended. To obtain the appropriate ethanol concentration content, the spirit samples analyzed in this work were diluted 4 times with pure ethanol. MWTN experimental conditions were selected as a compromise between the analytical figures or merit and capillary durability. Thus, experimental conditions chosen with MWTN were those affording minimum LODs (i.e., 1.4 mL min^{-1} Q_l and 150 μm nozzle diameter). Preconcentration time was increased up to 120 s to partially offset sample dilution and improve LODs. Longer preconcentration times were not considered to avoid capillary damage.

First of all, a recovery test was performed to evaluate analysis accuracy since no spirit certified material is available in the market. Recovery values for all the elements studied ranged from 93 ± 3 to 107 ± 5%. Calibration graph showed a good linearity up to 1000 μg L^{-1}. However, preconcentration reproducibility for standards below 1 μg L^{-1} was poor (i.e., about 20%).

Table 4 shows the results for the elemental analysis of different spirit samples obtained with the MWTN operating with and without analyte preconcentration. As shown in this table, both operation modes provided similar results. Among the different elements studied in the present work, only Na, K, Ca, Mg, Fe and Cu were quantified in the spirit samples. Al, Cd, Cr, Mn, Pb and Zn concentration levels were below LODs (Table 3), regardless MWTN mode employed. Despite dilution required, MWTN in preconcentration-nebulization mode allowed to quantify a higher number of elements than the MWTN nebulization mode due to its lower LODs. In fact, the high signals obtained for Na, K and Ca

Table 4
Analyte concentration values obtained in different spirit samples operating the MWTN in nebulization and in preconcentration-nebulization modes. Solvent: pure ethanol; Q_l: 1.4 mL min^{-1}; nozzle diameter: 150 μm. MWTN (nebulization mode): P_{MW}: 100 W. MWTN (preconcentration-nebulization mode): P_{MW1}: 100 W; P_{MW2}: 290 W; preconcentration time: 120 s. ICP-AES viewing mode: axial (unless otherwise stated).

Beverage	Measurement mode	Analyte concentration (mg L^{-1})					
		Na	K	Ca	Mg	Fe	Cu
Gin(G1)	Nebulization	2.47 ± 0.04	< LOD	0.62 ± 0.02	0.041 ± 0.002	< LOD	< LOD
	Preconcentration-nebulization	2.6 ± 0.3*	0.094 ± 0.008	0.61 ± 0.02	0.050 ± 0.009	0.15 ± 0.04	0.092 ± 0.008
Gin (G2)	Nebulization	64.6 ± 1.2	0.39 ± 0.03	0.050 ± 0.002	0.44 ± 0.03	< LOD	< LOD
	Preconcentration-nebulization	63 ± 4*	0.38 ± 0.07	0.055 ± 0.008	0.49 ± 0.07	0.24 ± 0.05	0.075 ± 0.007
Anisete	Nebulization	36.9 ± 1.6	< LOD	7.7 ± 0.4	2.7 ± 0.2	1.85 ± 0.14	< LOD
	Preconcentration-nebulization	34 ± 4*	0.25 ± 0.04	8.3 ± 0.7*	2.7 ± 0.4	2.1 ± 0.3	0.12 ± 0.02
Liquor	Nebulization	23.4 ± 0.9	33.5 ± 1.4	1.49 ± 0.04	0.50 ± 0.02	< LOD	< LOD
	Preconcentration-nebulization	26 ± 3*	40 ± 4*	1.31 ± 0.08*	0.63 ± 0.08	0.18 ± 0.04	0.110 ± 0.010

* ICP-AES radial viewing mode.

with MWTN in preconcentration mode makes necessary to use radial rather than axial view mode to avoid detector saturation. In general, the concentration of trace elements in the spirits samples analyzed was similar to those previously reported [33–35] and below the maximum values established and Spanish [36] authorities.

4. Conclusions

Results shown in the present work demonstrate the high versatility of the MWTN as sample introduction device in ICP-AES. MWTN can be running in two different modes just by the appropriate selection of the experimental conditions: either as a thermal nebulizer or as on-line preconcentration-nebulization device. Operating mode selection will depend on the LOD required to perform a given analysis.

The analytical behavior of the MWTN strongly depends on the solvent nature and composition, MW power, preconcentration time, sample uptake rate and inner nozzle diameter. Operating at its optimum conditions, MWTN preconcentration-nebulization device provide LODs up to one order of magnitude lower than those obtained running with the nebulization mode. The device was successfully applied to the multi-element analysis of spirits samples in ICP-AES.

When compared with other preconcentration procedures described in the literature, MWTN arrangement is simpler and greener, since analyte preconcentration is efficiently performed without the use of additional reagents and complex treatments. The main drawback is related with the difficulty of the device to operate with diluted alcohol and inorganic acid solutions. This inconvenient could be solved by an appropriate re-design of the MWTN. We are currently working on this topic in our laboratory.

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