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A COMPARISON OF ETV AND LA FOR THE DETERMINATION OF TRACE ELEMENTS IN SOLID SAMPLES BY MIP OES

PORÓWNANIE METOD ETV I LA OZNACZANIA PIERWIASTKÓW ŚLADOWYCH W PRÓBKACH STAŁYCH Z ZASTOSOWANIEM MIP OES

Abstract: The performance of electrothermal vaporization (ETV) and laser ablation (LA) of dry aerosols as sample introduction systems for microwave induced plasma optical emission spectrometry (MIP OES) are compared and evaluated in terms of detection limits, precision and accuracy for the determination of trace elements (Ca, Cd, Cu, Fe, Mg, Mn, Sr, Zn) in the same solid micro samples. In MIP OES both radiation sources can be independently adjusted to optimize the sampling process and then its subsequent excitation. A univariate approach and simplex optimization procedure were used to obtain the best signal/noise (S/N) ratio and derive analytical figures of merit. A comparison using a Student's *t*-test between the results obtained by both ETV/LA-MIP OES methods for trace elements, and concentrations in standard reference material (SRM) and certified reference materials (CRMs) showed that there was no significant differences on a 95 % confidence level. The detection limits of the tested elements in solid samples by ETV/LA-MIP OES were in the range of 0.1 to 11 $\mu\text{g g}^{-1}$ for all elements determined, while the corresponding absolute values in the range of ng. The precision of the results for ETV-MIP OES and LA-MIP OES varied between 2 and 4 % and 3 and 7 %, respectively. The linear dynamic ranges in the ETV/LA-MIP OES are extend over three decades of concentration. The methods were validated by the analysis of NIST SRM 2711 Montana Soil, NRCC CRM PACS-2 Marine Sediment and NRCC CRM TORT-2 Lobster Hepatopancreas of different matrix composition and by the standard addition technique.

Keywords: microwave induced plasma optical emission spectrometry, electrothermal vaporization, laser ablation, simultaneous determination, trace elements

Introduction

Microwave induced plasmas (MIPs) have been used as atomization and ionization sources in optical emission spectrometry (OES) since the 1950's due to their versatility to operate with different gases or mixtures of them, operational simplicity and low gas consumption and is well established method for the analysis of a wide variety of liquid samples. The MIP OES offers some attractive characteristics, such as its unique features of high excitation efficiency for metal and non-metal elements, capability of working with various gases (Ar, He, N₂, air), capabilities for simultaneous determination of elements, low cost for instrumentation and maintenance, and convenience of operation [1]. This technique

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usually require a sample preparation step in order to promote the dissolution/decomposition of the solid material prior to element determination. However, when this method is applied to the analysis of solid or powder samples in their conventional form, decomposition of the sample material is necessary. Particularly for refractory, inorganic materials the decomposition is often difficult and sometimes even impossible. In general, this time consuming procedure represents a considerable limitation to the limits of detection (LOD) leading to deteriorated limits of quantification (LOQ) and a source of systematic errors, both caused mainly by contamination and/or analyte loss (blanks) [2]. From this point of view, direct solid sample analysis is an attractive approach, improving sample throughput and mitigating the risks of analyte loss and contamination. For these reasons, methods for the direct analysis of solids/powders/slurries are of great interest. One of the approaches found effective is thermal vaporization (TV). This technique presents the potential for elemental mapping, micro homogeneity studies, and may be a solution for challenging applications, as in some cases the sample preparation step or amount of sample is a limiting factor. It is for this reason that electrothermal vaporization (ETV) and laser ablation (LA) techniques have been developed for sample introduction into the MIP, which were used for the direct determination of impurities in solids/powders/slurries at the trace or ultratrace level [3-5].

ETV sample introduction requires the generation of dry sample aerosol, transport of the aerosol and introduction into the plasma for the direct analysis of solid materials. The system used for the production of such aerosol is simple and efficient, introducing reproducible amounts of analyte into the plasma and producing no memory effects. In addition, ETV has the ability to use thermal programming, allowing selective removal of sample matrix constituents, thereby eliminating or reducing spectroscopic interferences that would otherwise arise from the matrix. A variety of systems were built and used in the last three decades. In most of the designs, the sample aerosol is transported through about 30-60 cm of plastic tubing to the base of the injector tube of the MIP torch. ETV sample introduction devices used for MIP OES have been discussed in detail by Matusiewicz [4]. Most vaporization cells were based on atomizers already available at that time for graphite furnace atomic absorption spectrometry (GF AAS), including graphite rods, cups, tubes and platforms. In practice, the transformation of a graphite furnace originally designed for AAS monitoring for its subsequent use as an ETV unit is relatively straightforward. Since the early work of Matusiewicz and Koprás [6], a variety of commercially available graphite furnaces have been modified for combination with MIP OES instruments and numerous applications have been reported. Concerning commercially available ETV units, the device manufactured by Perkin-Elmer (HGA 600 MS) was the most frequently used for many years, but its production has been discontinued. Nowadays, only the device manufactured by Spectral Systems (ETV 4000) is currently available [7]. This manufacturer offers the possibility of coupling these ETV devices for solid sampling with inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP MS) instruments. However, there is no results report based on the use of this unit with MIP OES.

LA has been investigated for MIP sample introduction with some success. Leis and Laqua published two papers on the excitation of a laser-produced plume in an MIP and determination of some elements in metal samples [8, 9]. LA-MIP OES, although known for a couple of years, is not an established method such as the commercially available LA-ICP OES [10]. The advantage of this technique is that, as with ETV, a two-step process is used.

The laser is used to volatilize and atomize the sample before it is introduced into the plasma for excitation, thus overcoming any problems with low thermal temperatures in the MIP. The sample is transferred from the laser ablation cell to the plasma via a carrier gas that is usually the support gas. In the past, some features of LA-MIP OES, e.g., detection limits of metals, element correlations from shot-to-shot and the possibility of internal standardization in metals and glass samples, have been described [3]; minimal loss of sample occurs during the vaporization stage. The main problem with laser ablation is lack of precision due to the shot-to-shot variation in laser power and its nonlinear effect on the ablation process. To overcome this several different normalization techniques have been investigated. A major advantage of this technique is that it can be used for solid or powder samples, which is important, for example, in the analysis of materials where complete sample destruction is a disadvantage.

Comparing results given by two analytical methods is a common task in analytical sciences. However, a more precise comparison of the analytical properties described in the literature is hardly possible because each sample introduction system is used in combination with its own spectral apparatus and detector, resulting in differences in the analytical figures of merit which are not necessarily due to the atomization/excitation sources themselves.

In order to have similar conditions for the measurement of detection limits and matrix effects we used the same solid (powder) samples, the same spectral apparatus and the same detector for both sample introduction systems. The conditions were different with respect to the dry aerosol production (ETV) and to the size of the observation zones (LA).

The aim of this study was to evaluate and compare, under optimized conditions, the analytical performance of ETV and LA of dried aerosols as complimentary analyte introduction techniques for the determination of trace elements (Ca, Cd, Cu, Fe, Mg, Mn, Sr, Zn) in solid micro samples of various composition. An objective evaluation of both vaporization/ablation units is obtained as the same signal recording equipment is used. A performance study of the elaborated ETV/LA-MIP OES systems were carried out in order to validate and characterized the both methods in terms of detection limits, precision and accuracy by analyzing different reference materials (NIST 2711, NRCC PACS-2, NRCC TORT-2).

Materials and methods

Instrumentation

A Carl Zeiss Echelle spectrometer (Model PLASMAQUANT 100) using fiber-optical light-guides and photomultiplier tubes (PMT) and the TE₁₀₁ microwave plasma resonant cavity assembly, as an excitation source, was used.

The plasma is viewed axially with the axis of the plasma perpendicular to the plane of the entrance slit. The microwave generator is connected by means of a flexible cable to the rectangular resonant cavity of the TE₁₀₁ design. The torch is a quartz tube made of Suprasil (Heraeus, Hanau, Germany). Instrument settings and operational parameters used for the experimental MIP OES system are summarized in Table 1. A schematic diagram of the entire experimental setup is shown in Figure 1.

The samples for analysis were weighed using an M2P microanalytical balance (Sartorius, Göttingen, Germany) with a resolution of 1 µg (electronic weighing range up to 2 g).

Homogenization was performed using a centrifugal ball mill (Testchem-S, Pszów, Poland).

A laboratory hydraulic press with 13 mm diameter press molds (Testchem, Pszów, Poland) was used for the preparation of sample pellets.

Table 1

Equipment and operating conditions

Parameter	Value/setting
<i>Microwave plasma spectrometer</i>	
Mounting	Czerny-Turner in tetrahedral set-up
Focal length [mm]	500
Spectral range [nm]	193-852
Order lines	28th-123rd
<i>MIP OES parameters</i>	
Microwave frequency [MHz]	2450
Microwave power [W]	100-220, variable
Microwave cavity	TE ₁₀₁ rectangular, water cooled
Microwave generator	700 W, MPC-01 (Plazmatronika Ltd., Wrocław, Poland)
Plasma viewing mode	Axial
Plasma torch, axial position	Quartz tube, 3.0 mm i.d., air cooled
<i>OES data acquisition</i>	
Argon plasma gas flow rate [cm ³ min ⁻¹]	100-500, variable
Read	On-peak
Integration time [s]	0.1
Background correction	Fixed point
Determination	Simultaneous
Number of replicates	3
Wavelength [nm] (line type)	Ca 393.366 (II), Cd 226.502 (II), Cu 324.754 (I), Fe 238.204 (II), Mg 285.213 (I), Mn 257.611 (II), Sr 407.771 (II), Zn 213.857 (I)

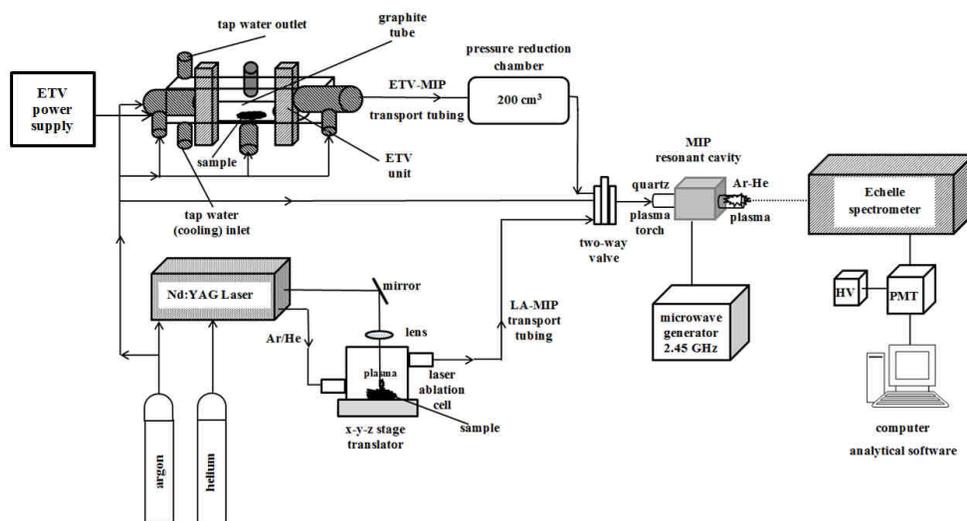


Fig. 1. Component diagram of the elaborated ETV/LA-MIP OES systems

ETV sample introduction system

For ETV sample introduction, a Spectral system 4000 ETV electrothermal vaporizer (Spectral systems, Fürstentfeldbruck, Germany) was used. The ETV 4000 unit consists of a commercially available graphite tube furnace, power supply, gas supply and water cooler. The resistively heated graphite furnace is placed between two water-cooled brass components. Graphite furnace is placed inside the transparent glass casing inside which carrier argon gas flows. Argon was also supplied into the furnace through the graphite furnace closure element, it is used to transfer the sample in the gas phase to plasma source. The power supply delivers currents up to 400 A and enables to achieve temperatures of the graphite tube in the interval between 50 and 3000 °C. Temperature programming of the graphite furnace is carried out by the built-in microcomputer of the equipment by specifying the duration time of the heating steps and the value of the electric current passing through the furnace. The flows for inner (carrier) gas and bypass gas are mass-flow controlled. During the heating cycle, argon gas flow removes all vapors in the graphite tube. The ETV unit was interfaced to the MIP via a two-way Teflon valve switching gas flows. The valve was used in order to avoid extinguishing the plasma during sample introduction. The transfer line between the ETV and the valve was an 50 cm long, 3 mm id Teflon lined Tygon tube (Cole-Parmer Instruments Co., USA). In addition, it was considered important to connect the pressure-reducing chamber of 200 cm³ capacity with ETV apparatus to minimize the impact of the volatile products of electrothermal vaporization on the plasma stability. The experimental parameters are shown in Table 2.

Table 2

Operating experimental conditions for the electrothermal vaporization and laser ablation devices

Parameter	Value/setting
<i>Operating conditions of the electrothermal vaporization device</i>	
Instrument	ETV 4000
Carrier argon flow rate [dm ³ min ⁻¹]	0.2
Secondary gas flow rate [dm ³ min ⁻¹]	0.5
Drying temperature [°C]	90, ramp 5 s, hold 30 s
Drying temperature [°C]	120, ramp 5 s, hold 15 s
Pyrolysis temperature [°C]	350, hold 15 s
Vaporization temperature [°C]	2700, hold 8 s
Cleaning temperature [°C]	3000, hold 5 s
Amount of sample [mg]	3-6
<i>Operating conditions of the laser ablation system</i>	
Instrument	LA J 200
Wavelength [nm]	266
Maximum laser output energy [mJ]	25
Repetition rate [Hz]	10
Scanning speed [mm s ⁻¹]	10
Spot size [μm]	75
Carrier gas flow (He) [dm ³ min ⁻¹]	0.5
Make-up gas flow (Ar) [dm ³ min ⁻¹]	0.5

LA sample introduction system

Experiments were performed using a femtosecond laser ablation instrument (LA J200, Applied Spectra Inc., Fremont, CA) equipped with a 266 nm frequency quadrupled Nd:YAG laser. The laser ablation system LA J 200 comprises a neodymium laser

(Nd:YAG UV 266 nm) with a maximum output energy of 25 mJ and a repetition rate of 1 to 20 Hz, the single volume chamber-type allowing the use of plug-in modules of different shapes in order to adapt the chamber to the optimal mixing vaporized particles and timing of its flushing and two cameras (macro camera - preview the entire sample in the chamber, and a micro camera for observation of details enabling the enlarged image). The flow of the carrier gas and the additional (argon and helium) was carried out by means of a double gas mass flow controller.

The output of the laser ablation system was connected to a microwave induced plasma excitation source via a two-way switching valve made of Teflon. Therefore a standard set of spray chamber including a nebulizer was removed and replaced with an adaptive tip made of PTFE, which allowed the insertion of the Teflon tubing connecting LA unit with the two-way switching valve, while the quartz plasma torch was directly connected to the opposite outlet of switching valve. The connection of a LA apparatus with excitation source was achieved by using of a 100 cm Teflon lined Tygon tubing (6 mm od, 3 mm id) to limit the adsorption of the sample constituents on the inner parts. The main task of the two-way valve was to ensure the plasma stability and to prevent destruction of quartz plasma torch during samples introduction caused by the air aspiration into the system. Setting the two-way valve in the auxiliary gas flow position allowed to maintain stable operation of the MIP plasma. Ablation of the sample material was performed under a constant helium gas flow, which was subsequently mixed with argon as make-up gas using a glass T-piece in close proximity of the ablation chamber outlet. Helium gas flow was optimized in preliminary experiments to obtain the shortest possible washout times. For measurement, each sample was placed along the axis of symmetry one centimeter from the cell outlet. The experimental parameters are shown in Table 2. The laser operating conditions were optimized in terms of both sensitivity and absence of segregation effects for the evaluated samples (Table 3).

Table 3
Optimum operating conditions for ETV/LA-MIP OES measurement^a of trace elements in solid materials obtained by simplex and univariate methods

Parameter (variable)	Boundary limits of parameters, range	Univariate method	Simplex method	Chosen values
<i>Optimum operating conditions for ETV-MIP OES</i>				
Forward power [W]	100-220	200	195	200
Carrier argon flow rate (ETV) [cm ³ min ⁻¹]	100-1200	800	810	800
Secondary gas flow rate (ETV) [cm ³ min ⁻¹]	100-600	500	500	500
Argon plasma gas flow rate [cm ³ min ⁻¹]	100-300	250	250	250
<i>Optimum operating conditions for LA-MIP OES</i>				
Forward power [W]	100-220	180	175	180
Argon gas flow rate (LA) [cm ³ min ⁻¹]	200-1200	500	495	500
Helium gas flow rate (LA) [cm ³ min ⁻¹]	200-1200	500	500	500
Argon plasma gas flow rate [cm ³ min ⁻¹]	100-500	300	310	300
Laser output energy [mJ]	10-25	20	21	20
Spot size [μm]	50-175	75	75	75

^a Response, peak height of the element emission intensity

Reagents, chemicals and gases

Compressed, pure argon and helium gases (N-50 purity, 99.999 %) obtained from BOC GAZY (Poznan, Poland) were used without further purification, following the reduction of pressure to about 300 kPa (3 bar).

Microcrystalline cellulose was purchased at highest purity grade from Sigma-Aldrich (Steinheim, Germany). ICP Multi-element Standard Solution IV (CertiPURs, Merck, Darmstadt, Germany) was used for analysis using standard addition technique. Water was initially deionized (DEMIWA 5 ROSA, Watek, Czech Republic) and then doubly distilled in a quartz apparatus (Heraeus Bi18, Hanau, Germany).

Quality control

Applicability of the method described and the methods accuracy in this work was evaluated by the analysis of three reference materials (RMs), which were chosen to represent solid sample matrices: PACS-2 (Marine Sediment) and TORT-2 (Lobster Hepatopancreas) supplied by the National Research Council of Canada (NRCC, Ottawa, Canada), and NIST 2710 (Montana Soil) supplied by NIST (Gaithersburg, MD, USA). The certified reference values are available for the chosen elements for assessment of the quality assurance and method validation. All solid reference materials were used as bottled, without further grinding and sieving.

Sample preparation

Reference materials for ETV-MIP OES analysis were placed in the graphite cup and weighed using an analytical microbalance (masses not exceeding 10 mg). Samples were introduced manually to the ETV furnace using pliers. For calibration, standard addition technique was used.

Pellets for LA-MIP OES analysis were all prepared following the same procedure: 200 mg of the sample was mixed with 200 mg of binder; homogenization of the mixture was achieved by centrifugal ball mill. Microcrystalline cellulose with particles of 20 μm diameter was purchased at highest purity grade. The microcrystalline cellulose was chosen as a binder because is easy to handle and free of trace elements; homogenization time was 2 minutes. Homogenized mixture was then pressed into 13 mm diameter pellets by applying a force of 30 MPa for 30 s with resulting thickness of about 2 mm.

ETV/LA-MIP OES analysis

The plasma was ignited by momentarily inserting an isolated high purity tantalum wire into the discharge tube and was allowed to warm up for a period of about 15 min prior to analysis. A microwave power of 200 and 180 W for ETV-MIP OES and LA-MIP OES, respectively, were selected and the reflected power was tuned to minimum.

With the aid of the two-way valve in the MIP "plasma bypass" position, it was possible to load samples into the ETV furnace without disturbing the plasma. Sample masses of 2 to 5 mg were weighed into the sample graphite boats. After loading the sample, the 2-way valve placed in the "aerosol transport" position allows transfer of analytes to the plasma. Subsequently, the analytes were vaporized by heating the furnace up to 2700 °C, and the released vapors were finally transported into the MIP for excitation by the Ar carrier gas. The emission intensity peaks were recorded at the appropriate lines. During the ashing and cleaning step, the 2-way valve was positioned in a way that directed the stream of gases

from the ETV system to the waste, thus avoiding the deposition of carbonaceous materials on the interface of the MIP OES instrument. Simultaneous background measurements for each element were applied (which is required for the standard addition technique). Finally, the graphite furnace was cleaned by heating at 3000 °C. The furnace was maintained at room temperature during the loading of samples. Instrumental settings and operational parameters with the use of the experimental ETV-MIP OES system is shown in Tables 1-3. Analytical blanks were also carried through the entire procedure outlined above, to correct for possible contaminants in the reagents and graphite boats. Quantification of elements was made from the method of standard additions. All detection limits were calculated for raw, in smoothed data based on a 3σ criterion of the blank counts.

Laser ablation of the sample material was performed under a constant helium/argon gases flow. Coupling of spectrometer was established using a 1.0 m-long Teflon tubing with an inner diameter of 3.0 mm *via* two-way valve into which supporting argon gas line was connected. The auxiliary gas flow allowed to maintain stable operation of the MIP plasma during samples replacement in the ablation chamber. Laser ablation parameters were optimized in preliminary experiments to ablate the complete sample material in one run of analysis while maintaining the integrity of the sample material surrounding the area of the incident laser beam. A laser spot size of 75 μm and laser energy of 20 mJ were selected to be appropriate for the performed investigations; this value provided a good trade-off between time-efficient measurement and emission signals intensities. While all instrumental settings for the LA device were kept constant throughout all measurements, the MIP OES had to be tuned on a daily basis to obtain best sensitivity for the measurements. Typical measurement parameters are summarized in Tables 1-3.

Signal processing

As with the manufacturer's software package the evaluation of transient signals was not possible. Twelve selected analogous outputs of the amplifiers connected to the photomultiplier of the polychromator and additionally the analogs output of the monochromator by the ETV/LA data station. A separate program multichannel MIP OES transient signal detection software developed in our laboratory was employed. This makes the PLASMAQUANT 100 suitable for a method combining MIP OES with ETV and LA devices. This software can handle transient signals (allow us to follow the profile of the transient emission signals that result from ETV/LA sample introduction) from all the 12 channels of PLASMAQUANT 100 simultaneously and had real time graphic observation function. Integration time of each data point could be varied from 0.1 to 2.5 s and the maximum number of points could go up to 10^6 . It should be noted that the ETV 4000 graphite furnace and J200 LA system are controlled by the separate computers, and no triggering between their introduction systems and the PLASMAQUANT 100 spectrometer is available. Therefore, data acquisition on the spectrometer was manually triggered prior to vaporization or ablation of the samples. Since similar results were obtained with either peak height or peak area, analytes were quantified only by peak heights, besides the subtraction of background signals, reported hereafter, as recorded on a Comma Separated Values (CSV) file.

Results and discussion

General remarks

In this study, two spectrochemical methods aiming at the determination of trace elements in international reference materials were compared. The results of the ETV-MIP OES - LA-MIP OES comparison show that in terms of analytical figures of merit; ETV-MIP OES is comparable to LA-MIP OES and thereby in principle a viable alternative for bulk analysis of solid samples. In view of the overall reliability of the reference standards, their use as a measure of the accuracy of the methods described is practicable. Consequently, the use of such materials during routine analysis constitutes a rigorous check of the accuracy and precision and may indicate the presence or absence of gross systematic errors.

The variance of the data of this investigation can be attributed to the described instrumental procedures. We realize that is not fully justified since the procedures described herein include several pre-instrumental preparatory steps which may introduce errors: sample heterogeneity, sample mixing and graphite furnace packing in the ETV-MIP OES analysis or pellet homogeneity in LA-MIP OES analysis. Nevertheless, the data suggest that such errors are minimal. Consequently, these comparisons might be considered as an assessment of the described instrumental analytical methods. However, the possibility that at least some of the erratic variations may be due to the above mentioned limitations cannot be eliminated.

Simplex optimization of operational variables

In view of the simultaneous multi-element capability of ETV/LA-MIP OES, optimum parameters for single determination of all analytes were compared and, in effect, compromise conditions were selected for a simultaneous determination, provided that the selected value was not totally unsuitable for a particular element. Optimization of all operating conditions simultaneously by simplex procedures was undertaken in these initial investigations. Preliminary experiments were conducted with ETV/LA-MIP OES of aqueous multi-element standard solution containing Ca, Cd, Cu, Fe, Mg, Mn, Sr and Zn introduced to the graphite boats (ETV) or mixed with cellulose for pellets preparation (LA).

Two different types of experimental variables affect the methods. These are as follows: first, variables controlling the emission response in the ETV/LA-MIP OES, i.e., the microwave forward power of the microwave generator and secondly, the argon/helium carrier flows, that regulate transport. Followed by univariate searches for the optimum values of applied power and carrier gas flow rates, a multivariate simplex optimization was used to establish the optimum experimental parameters for low detection limits of selected elements. Simplex optimization is a quick and efficient method of optimizing various interrelated variables of the same sample, hence this optimization strategy was used, taking into account the fact that many experimental parameters are interrelated and cannot be optimized in a single stage to achieve the maximum overall S/B ratio intensity for a simultaneous optimization of the four for ETV and six for LA parameters. The optimization was complete in 24 steps, which took approximately 2 h. Table 3 lists the optimum values that the simplex and univariate experiments indicated for each of the ten factors studied. In addition, the maximum and minimum levels of the variables to be investigated are also shown in Table 3. Table 3 list the optimum values that the simplex and univariate experiments indicated for each of the ten factors studied. In addition, the

maximum and minimum levels of the variables to be investigated are shown in Table 3. The effectiveness of the simplex procedure was confirmed with univariate searches, which assisted in the verification showing that the optimum lay near the simplex value. Table 3 lists the optimum values that the experiments indicated for each of the ten factors studied.

Analytical figures of merit

The optimization of wavelength was not carried out because the wavelengths used for the determination were pre-selected by the producer of the polychromator.

With the use of established experimental parameters as shown in Table 3, the analytical performance of the both methods were evaluated. The conventional definition of limit of detection (LODs) is inappropriate in solid sampling, since no realistic blank (for both ETV and LA) can be measured. On the other hand an empty boat, in terms of ETV, and cellulose pellet, in terms of LA, can be used as "zero-mass" signal to calculate the limits of detection. The zero-mass signal was measured 10 times and averaged. The final limits of detection (3σ) are based on the raw, unsmoothed data reported in Table 4. Emission signals were evaluated by measuring the peak height. The detection limits of the tested elements in solid samples by ETV/LA-MIP OES were in the range of 0.1 to 11 $\mu\text{g g}^{-1}$ for all elements determined, while the corresponding absolute values in the range of ng. Therefore, is no major change in DL's and other analytical figures of merit. Detection limits obtained by an identical or similar technique for all elements are not available.

Table 4
Analytical figures of merit

Parameter	Ca	Cd	Cu	Fe	Mg	Mn	Sr	Zn
Analysis wavelength [nm]	393.366	226.502	324.754	238.204	285.213	257.611	407.771	213.857
Detection limit (3σ) of ETV-MIP OES system [$\mu\text{g g}^{-1}$]	0.5	1.3	1.0	1.2	0.8	0.5	0.1	1.4
Absolute detection limit ^a (3σ) of ETV-MIP OES system [ng]	2.5	6.5	5.0	6.0	4.0	2.5	0.5	7.0
Precision ^b /% RSD	3	3	2	3	2	3	3	4
Detection limit (3σ) of LA-MIP OES system [$\mu\text{g g}^{-1}$]	1.5	2.9	2.1	11	1.1	1.6	1.7	5
Precision ^b /% RSD	4	6	5	7	3	4	3	6

^a For sample weights of 5 mg, ^b Peak height, % relative standard deviation (RSD), $n = 3$

Precision and accuracy of the two methods were evaluated by analyzing the reference materials. Precision, expressed as a relative standard deviation (RSD) for five consecutive replicates at analyte concentrations approximately 50-fold higher than the procedural LOD, was evaluated for each introduction system. The good accuracy was attained with the ETV/LA-MIP OES systems by the standard addition technique. Precision is satisfactory for both procedures and the standard deviation is comparable to that of the reference materials; the precision of the results for ETV-MIP OES and LA-MIP OES varied between 2 and 4% and 3 and 7%, respectively. These values may be considered satisfactory, especially owing to the large number of parameters governing the performance of the coupled technique. In

other words, this reflects the cumulative imprecision of all of the sample solid handling, transfer of dry aerosols, excitation and detection steps.

In general, no statistical difference (*t*-test, 95% of confidence level) was observed between the results obtained by ETV-MIP OES and LA-MIP OES, showing that the proposed methods are suitable for the quantification of trace elements in solid samples.

As it is possible to observe in Table 4, the obtained LODs by ETV-MIP OES were in the same order of magnitude as those obtained for LA-MIP OES, except for Fe and Sr, which were about ten times lower than those obtained by LA-MIP OES, likely due to incomplete ablation.

As a rough estimation, three to four orders of magnitude can be assessed as linear working range for solid sampling ETV/LA-MIP OES methods.

Method validation

To evaluate the accuracy and precision of the sample introduction system tested on the determination of the elements in three reference materials (RMs) were selected because they were closest in nature to real environmental and biological samples. The results obtained for the analysis of RMs by ETV/LA-MIP OES method are summarized in Table 5 and 6 and are based on processing 3 replicate test samples. Certified values and relative error values are also given. Table 5 and 6 showed a good agreement between results of ETV-MIP OES and LA-MIP OES analysis of three reference materials. The results obtained by the standard addition technique agree with certified values for all the three reference materials, indicating that calibration against the standard addition technique produce accurate results. For most of the elements, a *t*-test (based on the 95 % confidence level) shows no statistically significant difference between mean and recommended values.

All experimental concentrations agreed fairly well with the certified interval element values. Although no interference study was undertaken, it is obvious that there are no systematic errors due to the presence of the matrices. The precision of the results for ETV-MIP OES and LA-MIP OES varied between 2 and 4 % and 3 and 7 %, respectively. Finally, the results obtained in the analysis via ETV/LA-MIP OES can be considered satisfactory.

Table 5
Analysis (concentrations in $\mu\text{g g}^{-1} \pm \text{SD}$ of three parallel determinations) of reference materials using ETV-MIP OES system

Element	Montana Soil NIST 2711		Marine Sediment PACS-2		Lobster Hepatopancreas TORT-2	
	Found value	Certified value	Found value	Certified value	Found value	Certified value
Ca	27600 \pm 2580	28800 \pm 800	17680 \pm 2420	19600 \pm 1800	- ^a	-
Cd	37.4 \pm 3.4	41.70 \pm 0.25	2.05 \pm 0.12	2.11 \pm 0.15	24.8 \pm 3.1	26.7 \pm 0.6
Cu	108 \pm 13	114 \pm 2	281 \pm 30	310 \pm 12	95 \pm 14	106 \pm 10
Fe	27500 \pm 3250	28900 \pm 600	38100 \pm 4900	40900 \pm 600	101 \pm 13	105 \pm 13
Mg	9800 \pm 1270	10500 \pm 300	13210 \pm 1450	14700 \pm 1300	-	-
Mn	605 \pm 66	638 \pm 28	409 \pm 44	440 \pm 19	12.7 \pm 1.9	13.6 \pm 1.2
Sr	221.5 \pm 26	245.3 \pm 0.7	242 \pm 32	276 \pm 30	42.5 \pm 4.9	45.2 \pm 1.9
Zn	319.1 \pm 38.0	350.4 \pm 4.8	321 \pm 39	364 \pm 23	169 \pm 22	180 \pm 6

^a Not certified

Table 6

Analysis (concentrations in $\mu\text{g g}^{-1}$ \pm SD of three parallel determinations) of reference materials using LA-MIP OES system

Element	Montana Soil NIST 2711		Marine Sediment PACS-2		Lobster Hepatopancreas TORT-2	
	Found value	Certified value	Found value	Certified value	Found value	Certified value
Ca	28850 \pm 1155	28800 \pm 800	18820 \pm 962	19600 \pm 1800	- ^a	-
Cd	39.85 \pm 2.4	41.70 \pm 0.25	2.08 \pm 0.11	2.11 \pm 0.15	25.5 \pm 1.5	26.7 \pm 0.6
Cu	111 \pm 7	114 \pm 2	298 \pm 15	310 \pm 12	102 \pm 6	106 \pm 10
Fe	28410 \pm 1983	28900 \pm 600	39600 \pm 1650	40900 \pm 600	103 \pm 7	105 \pm 13
Mg	10120 \pm 405	10500 \pm 300	14210 \pm 853	14700 \pm 1300	-	-
Mn	626 \pm 31	638 \pm 28	415 \pm 26	440 \pm 19	12.9 \pm 1.0	13.6 \pm 1.2
Sr	239.0 \pm 7.2	245.3 \pm 0.7	259 \pm 14	276 \pm 30	43.2 \pm 2.8	45.2 \pm 1.9
Zn	339.8 \pm 23.8	350.4 \pm 4.8	338 \pm 15	364 \pm 23	175 \pm 11	180 \pm 6

^a Not certified

Conclusions

The conditions used for the solid sampling methods ETV-MIP OES and LA-MIP OES were optimized for application to simultaneous multi-element determination of trace elements in reference material powders.

The two considered methods permitting the solid samples to be analyzed directly, have been characterized and proved to be effective for the determination of trace elements in solid samples; in fact both procedures allow to obtain accurate results for the analysis of a reference materials (PACS-2 (Marine Sediment), TORT-2 (Lobster Hepatopancreas), NIST 2710 (Montana Soil)). The proposed screening methods requires no extensive sample preparation, such as sample digestion, extraction and pre-concentration. The methods advantages are short analysis time, no use of solvents (no chemical waste, no potential health damage and can be considered as a green analytical techniques) and good limits of detection. Only one thermal pretreatment step is sufficient for the analytical samples.

Optical emission spectrometric measurements of the trace elements in different matrices, have shown that the coupling of a setup for electrothermal vaporization or/and laser ablation of solid samples in an atmospheric pressure argon/helium with an microwave induced plasma is a powerful technique for simultaneous multi-element analysis. Applicability of the developed procedure was demonstrated by the successful analysis of the trace elements Ca, Cd, Cu, Fe, Mg, Mn, Sr and Zn in three different RMs (NIST 2711, NRCC PACS-2, NRCC TORT-2). A relatively good agreement was found between the two methods and with the reference values. The only requirements are samples in solid or powdered forms and the existence of reference materials with suitable element contents. Results obtained by ETV-MIP OES were generally in agreement with those obtained by LA-MIP OES and the LODs for ETV-MIP OES (for 5 mg of sample) were lower or in the same order of magnitude as those obtained by LA-MIP OES.

The results show that ETV/LA-MIP OES methods has a great potential for the determination of trace elements of parts-per-million ($\mu\text{g g}^{-1}$) level in analytical powder samples with satisfactory analytical results.

Although ETV and LA sample introduction methods have similarities in several principal aspects, they are best suited to different types of sample forms. Therefore, it is not an unrealistic ambition to have both of these techniques in laboratories of wide analytical

scope. These two techniques can be good co-operators in addition to being strong competitors.

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