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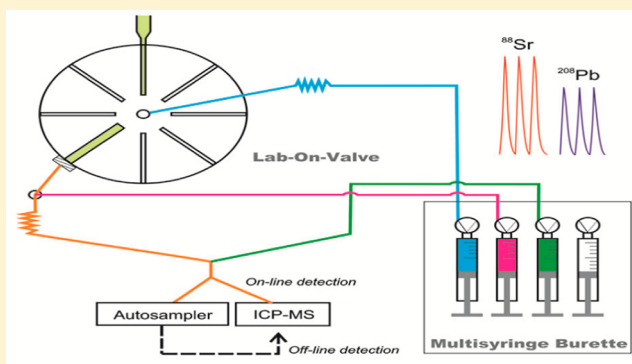
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ABSTRACT: A new automated, sensitive, and fast system for the simultaneous online isolation and preconcentration of lead and strontium by sorption on a microcolumn packed with Sr-resin using an inductively coupled plasma mass spectrometry (ICP-MS) detector was developed, hyphenating lab-on-valve (LOV) and multisyringe flow injection analysis (MSFIA). Pb and Sr are directly retained on the sorbent column and eluted with a solution of 0.05 mol L⁻¹ ammonium oxalate. The detection limits achieved were 0.04 ng for lead and 0.03 ng for strontium. Mass calibration curves were used since the proposed system allows the use of different sample volumes for preconcentration. Mass linear working ranges were between 0.13 and 50 ng and 0.1 and 50 ng for lead and strontium, respectively. The repeatability of the method, expressed as RSD, was 2.1% and 2.7% for Pb and Sr, respectively. Environmental samples such as rainwater and airborne particulate (PM₁₀) filters as well as a certified reference material SLRS-4 (river water) were satisfactorily analyzed obtaining recoveries between 90 and 110% for both elements. The main features of the LOV-MSFIA-ICP-MS system proposed are the capability to renew solid phase extraction at will in a fully automated way, the remarkable stability of the column which can be reused up to 160 times, and the potential to perform isotopic analysis.



1. INTRODUCTION

Naturally occurring isotopic ratios of some elements, such as strontium and lead, are very useful for characterizing different sources and to provide background information to different application fields,¹ for instance, geochronological and archeological studies,² also in food samples³ and in environmental studies.⁴ There are a variety of techniques and methods with different schemes of separation to quantify Pb and Sr, most of them include many steps, and these analytes are determined in different fractions which imply more reagents and time-consuming operations. Lead is one of the most studied contaminants among heavy metals, due to its presence in the environment and to its adverse effects on health which include neurological damage and suppression of hemoglobin biosynthesis.^{5,6} Lead isotope ratios are important for different application fields, especially for the investigation of lead isotope variation for environmental monitoring.⁷ Strontium has very seldom been used for environmental studies probably because in comparison to Pb it is not so toxic.⁸ However, its determination has shown to be useful since Sr isotope ratios

allow the traceability of base cations in rainwater.⁹ Besides, in combination with Pb, isotopic analysis allows the discovery of the provenance of atmospheric heavy metals collected directly on filters.¹⁰ Therefore, lead and strontium isotopic systems can be used as environmental tracers to identify pollution sources, representing a powerful information tool in environmental studies.

The capabilities of inductively coupled plasma mass spectrometry (ICP-MS) for performing precise isotope ratio measurements are nowadays well-known. Instrumental progress in this field has permitted to obtain highly reliable isotope ratio data, very useful for many environmental applications.¹¹ There are a variety of methods for Pb and Sr quantification by ICP-MS.^{12–15} ICP-MS analysis requires a high degree of purification, low level blanks, and high yields, an isolation

Received: January 8, 2013

Revised: July 1, 2013

Accepted: July 24, 2013

Published: July 24, 2013

procedure being necessary, i.e., a sample cleanup prior to isotopic ratio measurement. Solid phase extraction (SPE) is based on the use of ion-exchange resins, chelating resins, and hydrophobic materials, for the enrichment of analytes and the removal of interfering substances and matrix.¹⁶ Sr-resin is a chromatographic extraction resin which has proved to be an excellent sorbent for the separation and preconcentration of lead and strontium.^{17,18}

Hyphenation of SPE with flow analysis techniques makes possible the total or partial automation of many conventional analytical methods. On the one hand, lab-on-valve (LOV) facilitates integration of various analytical units in the valve and provides great potential for miniaturization of the entire instrumentation.¹⁹ In addition, the LOV unit allows a flexible fluid manipulation, what leads to its more attractive feature which is the possibility of implementing bead injection (BI), that is to say the automatic renewal at will of the column.²⁰ On the other hand, the multisyringe flow injection analysis (MSFIA) system consists of the use of parallel moving syringes as liquid drivers; moreover, it overcomes the shortcomings of peristaltic pumping of pulsation, required recalibration of flow rates, and limitations regarding applicable reagents.²¹

Then, the main aim of this work was the development of a simple and selective method for the simultaneous isolation, preconcentration, and isotopic analysis of lead and strontium. Therefore LOV and MSFIA techniques were combined with SPE via Sr-resin and ICP-MS: using ammonium oxalate as a unique eluent. Two different operational modes are proposed: the off-line and online modes. A fully automated LOV-MSFIA system coupled to ICP-MS is achieved with online detection decreasing the risk of analyte losses and contamination of the samples. However, the off-line detection mode was also used to increase the analysis frequency. The potential of the proposed system as a tool for the isotopic analysis of lead and strontium in environmental samples was studied.

2. EXPERIMENTAL SECTION

2.1. Reagents and Standard Solutions. As blanks are a critical concern for Pb and Sr measurements by ICP-MS, all chemicals used were of analytical reagent grade. Millipore quality water was used throughout this work. Nitric acid (65% w/w) was obtained from Scharlau (Barcelona, Spain) as well as standard solutions of Pb, Sr, Ag, and Bi (1000 mg L⁻¹ in 2% HNO₃) for ICP, which were utilized to prepare diluted solutions for quantitative analyses. ¹⁰⁹Ag and ²⁰⁹Bi were added as internal standards for Pb and Sr, respectively, to correct possible instrument drifts.

The LOV-microcolumn was packed with Sr-resin (50–100 μm) from Triskem Industries (France) and glass fiber prefilters from Millipore (Madrid, Spain) were used to retain the beads within the column. A solution of 2 mol L⁻¹ HNO₃ was used as column conditioner.

A 0.05 mol L⁻¹ solution of ammonium oxalate monohydrated (Scharlau) was employed as the eluent reagent and was prepared dissolving 3.55 g of ammonium oxalate in 500 mL of water.

All glassware were carefully cleaned, soaked in 10% (v/v) HNO₃ during 24 h before being rinsed with Millipore water and ready to be used.

2.2. Samples. Samples of rainwater and particulate airborne were analyzed using the proposed method. Rain water samples were filtered through 0.45 μm filters. Particulate airborne filters were digested using a closed-vessel microwave digestion device

(MLS-47100 StartD). An 8 mL portion of HNO₃ and 2 mL of H₂O₂ were added to the particulate airborne filters for their digestion. A certified reference material of river water SLRS-4 (Institute for National Measurement Standards, Canada) was also analyzed.

To ensure retention of lead and strontium on the column packed with Sr-resin, all samples were prepared in a 2 mol L⁻¹ HNO₃ concentration.

2.3. Manifold and Software. A schematic depiction of the proposed MSFIA-LOV system is shown in Figure 1. The LOV

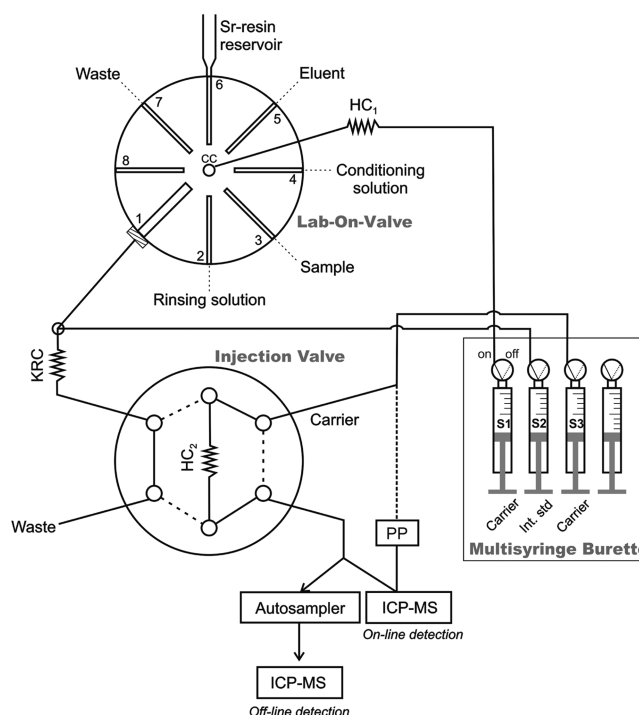


Figure 1. MSFIA-LOV-ICP-MS system scheme for lead and strontium isotopic analysis: (C) column; (CC) central conduit; (HC) holding coil; (KRC) knotted reaction coil; (PP) peristaltic pump; (S) syringe.

microconduit (Sciware Systems, Palma de Mallorca, Spain), fabricated from methylmethacrylate encompassing eight integrated microchannels (1.5 mm i.d./16 mm length, excepting the bead column channel whose dimensions were 2.8 mm i.d. and 16 mm length) was mounted atop of an eight-port multiposition selection valve (SV; Crison Instruments, Barcelona, Spain).

The central port of the valve in the LOV system is made to address the peripheral ports (1–8) of the unit and was connected to a 10 mL glass syringe (S1) (Hamilton, Switzerland) via a holding coil (HC₁), whose function is the sequential aspiration of the various constituents for the bead injection (BI) process, through the central communication channel (CC) of the selection valve.

Channel 1 of the LOV unit serves as column and was automatically packed with an appropriate amount of Sr-resin (0.035 g) in order to avoid compaction and overpressures in the system. To contain the sorbent within the cavity of the LOV module and prevent it from escaping, the outlet of the column was furnished with a glass fiber prefilter (Millipore) retaining the beads while allowing the solution to flow freely. A 5 mL plastic syringe was mounted vertically on port 6 of the integrated microsystem and was utilized as a reservoir of the

resin. The peripheral port configuration was as follows: port 2 (rinsing solution, 0.05 mol L⁻¹ ammonium oxalate), port 3 (sample in 2 mol L⁻¹ HNO₃), port 4 (conditioning solution, 2 mol L⁻¹ HNO₃), port 5 (eluent solution, 0.05 mol L⁻¹ ammonium oxalate), and port 7 (waste).

MSFIA comprises basically a multisyringe buret (BU 4S; Crison Instruments, Spain) with programmable flow rates equipped with three glass syringes of 10 (S1), 1 (S2), and 10 mL (S3) (Hamilton, Switzerland). S1 contained distilled water and was connected to the central port of LOV, S2 contained the internal standard solution of Ag and Bi, and S3 also contained distilled water; this syringe was only employed in the on line approach and was connected to a peripheral port of the injection valve. Each syringe has a three way solenoid valve (N-Research, USA) at the head, which facilitates the application of multicommutation schemes (on, inline flow; off, to reservoirs). In addition, an injection valve (InjV) (Crison Instruments, Spain) integrated in the same selection valve module was used to drive the flow in the desired way, i.e. "load position" allows the sample loading into the holding coil (HC₂) and "inject position" allows the sample dispensing to the autosampler (off-line detection) or to the ICP-MS (online detection).

The flow network was constructed with 0.8 mm i.d. PTFE tubing including a 6 m holding coil (HC₂), corresponding to a volume of 3 mL and a knotted reaction coil (KRC) of 0.062 m, i.e. 0.030 mL of volume. KRCs enhance the mixing due to the major contribution of secondary toroidal flows. The holding coil (HC₁) connected to the LOV was constructed with 1.5 mm i.d. and 6.25 m length PTFE tubing with a volume capacity of 11 mL. All connections were made by means of PVDF connectors, except cross-junction, which were made of methacrylate.

The operation control of instrumentation was carried out using the software package AutoAnalysis 5.0 (Sciware Systems).

2.4. ICP-MS Instrument. Quantitative analyses were carried out using an Elan DCR-e (Perkin-Elmer). The sample introduction system consisted of a multichannel peristaltic pump, a cross-flow nebulizer (Perkin-Elmer), and a Scott spray chamber. Instrument settings are shown in Table 1. Signals of ⁸⁸Sr and ²⁰⁸Pb were used to optimize the proposed methodology, since these isotopes have the most relative abundance in nature, 82.58% for ⁸⁸Sr and 52.4% for ²⁰⁸Pb. In order to correct instrumental drift, ¹⁰⁹Ag and ²⁰⁹Bi were used as internal standards. Thus, the rates between counts of ⁸⁸Sr/¹⁰⁹Ag and ²⁰⁸Pb/²⁰⁹Bi were used as signal. The proposed methodology was tested in offline and online modes. The ICP-MS method utilized for the quantification and isotopic analysis of Pb and Sr was set in steady state signal mode for the off-line detection approach and in transient signal mode for the online detection. When the system was coupled to the ICP-MS, this instrument was controlled as a peripheral device of the LOV-MSFIA system using the software package AutoAnalysis. The synchronism of ICP-MS with the LOV-MSFIA system was performed through the digital output of the multisyringe buret. A relay interface (Sciware Systems) was used to trigger the events input of the ICP-MS.

2.5. Analytical Procedure. The hyphenation of LOV and MSFIA allowed the simultaneous isolation and preconcentration of Pb and Sr, followed by ICP-MS detection in off-line and online approaches. The analytical procedure of the proposed LOV-MSFIA-ICP-MS system is summarized in Table 2 and briefly described below.

Table 1. Instrumental Settings for the ICP-MS

		offline detection	online detection
radio frequency power gas flow	forward	1100 W	1100 W
	plasma	15 L min ⁻¹	15 L min ⁻¹
	auxiliary	1.2 L min ⁻¹	1.2 L min ⁻¹
	nebulizer	0.95 L min ⁻¹	0.95 L min ⁻¹
acquisition parameters (all analysis)	dwelt time	0.05 s	0.05 s
	scan mode	peak-hop transient	peak-hop transient
	sweeps per reading	20	15
	MCA channels per spectral-peak	1	1
	resolution/amu 10% peak maximum	0.7	0.7
	signal processing	steady state signal processing: average	transient signal processing: average
	reading per replicate	1	1
	replicates	3	4
	baseline readings	0	5
	isotopes measured	⁸⁸ Sr, ⁸⁷ Sr, ⁸⁶ Sr ²⁰⁸ Pb, ²⁰⁷ Pb, ²⁰⁶ Pb, ²⁰⁴ Pb	⁸⁸ Sr, ⁸⁷ Sr, ⁸⁶ Sr ²⁰⁸ Pb, ²⁰⁷ Pb, ²⁰⁶ Pb, ²⁰⁴ Pb
	internal standards	¹⁰⁹ Ag, ²⁰⁹ Bi	¹⁰⁹ Ag, ²⁰⁹ Bi

First, the column is automatically loaded with Sr-resin, and then, it is conditioned with 1 mL of 2 mol L⁻¹ HNO₃. The InjV is stated in load position directing the reagents to the waste. Once the column is ready, *x* mL of standard or sample are dispensed toward the column. Afterward, Pb and Sr retained on the column are simultaneously eluted with 2.6 mL of 0.05 mol L⁻¹ ammonium oxalate. Then, 0.26 mL of Ag and Bi solution is mixed with the eluent in the KRC. Up to this point, the InjV is in load position to ensure that the eluate and internal standard solution are loaded into the HC₂. Then, the InjV is activated (injection mode) and the mixture of eluate and internal standards is addressed to the autosampler (off-line mode) or directly into the ICP-MS (online mode), through S3 in off-line mode or the peristaltic pump of the ICP-MS in online mode. Finally, a single cleanup stage is carried out to avoid contamination of the column and to enlarge its lifetime. In order to change the sample and to avoid memory effects, 1 mL of the new sample (port 3) is aspirated into HC₁, and 2 mL are discarded toward waste (port 7). When the change of the resin is required, the column is regenerated by replacing the beads automatically. The used resin is loaded into the HC₁ and sent to waste, then new resin is loaded into the HC₁ from the resin reservoir (port 6) and dispensed at port 1 with InjV in load position (to waste) for filling the column.

2.6. Optimization of Experimental Conditions. In order to optimize the operational conditions of the proposed LOV-MSFIA-ICP-MS system, a series of experiments were conducted using multivariate optimization technique. The acidic medium of the sample was established at 2 mol L⁻¹ nitric acid, as in previous works.^{17,22} The same concentration was also utilized for column conditioning.

First, a screening of the independent variables and their possible interactions was carried out by a two level full factorial design (2^k),^{23,24} entailing 19 experiments. The range for each factor was chosen according to previous experiments results. Thus, the potentially critical variables for Pb and Sr extraction and preconcentration that were taken into consideration were the following: the eluent concentration (studied range: 0.005–

Table 2. Automated Procedure for Simultaneous Isolation and/or Preconcentration of Pb and Sr

step	LOV position	MSFIA			flow rate (mL min ⁻¹)	InjV position
		S1	S2	S3		
offline detection (steady signal mode)						
1. Resin loading						
(a) Loading beads into HC ₁	6	on	off	off	1.5	load
(b) Filling the column	1	on	off	off	2	load
2. Conditioning of Sr-resin						
(a) Loading 1 mL of 2 mol L ⁻¹ HNO ₃ into HC ₁	4	on	off	off	10	load
(b) Dispensing 1.3 mL of conditioner into the column	1	on	off	off	2	load
3. Sample loading						
(a) Loading <i>x</i> mL sample into HC ₁	3	on	off	off	10	load
(b) Dispensing <i>x</i> mL of sample through the column	1	on	off	off	2	load
4. Elution of Pb and Sr						
(a) Loading 2.6 mL of 0.05 mol L ⁻¹ ammonium oxalate into HC ₁	5	on	off	off	10	load
(b) Dispense 2.6 mL of eluent through the column and simultaneous addition of internal standard (0.26 mL of Ag and Bi solution)	1	on	on	off	1.3	load
5. Loading into the holding coil (HC ₂)	1	on	on	off	1.3	load
6. Injection to the autosampler	1	off	off	on	1.3	inject
7. Rinsing the column						
(a) Loading 1.5 mL of rinsing solution	2	on	off	off	10	load
(b) Dispense through the column 1.7 mL	1	on	off	off	2	load
8. Change of sample						
(a) Loading 0.5 mL of new sample into HC ₁	3	on	off	off	10	load
(b) Discarding 1 mL to waste	7	on	off	off	10	load
9. Beads replacing						
(a) Loading old beads into HC ₁	1	on	off	off	2	load
(b) Discarding old beads	7	on	off	off	10	load
(c) Loading new beads into HC ₁	6	on	off	off	1.5	load
(d) Filling the column	1	on	off	off	2	load
online detection (transient signal mode)						
Steps 1–5 are the same						
6. Injection to ICP-MS ^b						
(a) Wait 300 s	1	off	off	off	1.3	inject ^c
(b) Isotopes lecture	1	off	off	off	1.3	inject ^c

^aMSFIA: S1, distilled water; S2, Ag and Bi standard; S3, distilled water. ^bICP-MS activation through the events input. ^cThe flow is driven by the ICP-MS peristaltic pump.

0.07 mol L⁻¹), eluent volume (studied range: 1–3 mL), sample loading flow rate (studied range: 0.6–2 mL min⁻¹), and elution flow rate (studied range: 0.6–2 mL min⁻¹). The evaluation of the screening results (ANOVA table, *p* value, Pareto chart, etc.), allowed the identification of the variables which had a significant influence in the determination of Pb and Sr (analytical response) and to discard those with negligible effects.²⁵ Then, a face centered central composite design (CCD) was performed in order to find the critical values of the significant variables. Three center points were included to identify any irregularities, such as the loss of linearity in the center of the interval in both studies. The Statistica 6.0 software was employed for the entire multivariate analysis. All optimization experiments were carried out in the off-line detection mode.

3. RESULTS AND DISCUSSION

3.1. Optimal Working Conditions. Results of the screening experiments (ANOVA table, *p* value, and Pareto chart) showed that the sample loading flow rate did not have a significant influence upon the analytical signal of Pb and Sr within the experimental domain. However, a small increase in

the analytical signals was observed at 1.3 mL min⁻¹, so this value was set for further experiments. The other three variables (eluent concentration, eluent volume, and elution flow rate) and the curvature were significant. Nonetheless, opposite trends and a higher influence upon Pb signal were observed. So, these three variables were optimized by a CCD, keeping the experimental domain as wide as possible.

The range of elution flow rate in the CCD was established taking into account that minimum value is the lowest flow rate allowed by this MSFIA system, while the maximum value is that not causing overpressure on the column. The ranges of eluent volume and eluent concentration were similar to those of screening, because these were the widest ranges possible for the used detector. A total of 17 experiments were carried out, including 3 central points. The ANOVA table of the CCD showed that these variables were not significant for strontium in the studied experimental domain, whereas the three variables tested were significant for lead determination in the same experimental domain. Considering these results and that both analytes are isolated and eluted simultaneously in the proposed method, the critical values obtained for lead in the CCD were taken as critical values in order to obtain the optimal conditions

for both elements. Data were adjusted to a linear-quadratic model with interactions of second order with $r^2 = 0.9595$ for lead. Moreover the residuals histogram and the fit between observed vs predicted values showed satisfactory results. The critical values are summarized as follows: ammonium oxalate concentration of 0.05 mol L^{-1} , 2.6 mL of eluent volume, and a stripping flow rate of 1.3 mL min^{-1} . They were used as optimized conditions in all experiments throughout this work.

3.2. Figures of Merit. Analytical parameters were established under reached optimal experimental conditions and are summarized in Table 3. Mass calibration curves were

Table 3. Analytical Parameters of the Optimized Method for the Simultaneous Determination of Sr and Pb by the MSFIA-LOV-ICP-MS System (Offline Detection Mode)

analytical parameters	lead	strontium
detection limit (ng)	0.04	0.03
detection limit (ng L^{-1})	4	12
quantification limit (ng)	0.13	0.10
regression coefficient (r^2)	0.9998	0.9998
repeatability (%) ($n = 10$)	2.2	2.7
reproducibility (%) ($n = 5$)	4	2.3
resin durability (injections)	160	160
preconcentration volume	Up to 10 mL	Up to 2.5 mL
linear working range (ng)	$0.13\text{--}50$	$0.1\text{--}50$
injection throughput (h^{-1}) ^a	$5\text{--}9$	$5\text{--}9$

^aDepending on the sample volume to preconcentrate.

used since with the proposed system it is possible to preconcentrate different sample volumes. Mass calibration curves (counts of analyte/counts of internal standard ratio vs mass in nanograms of Pb and Sr) with statically satisfactory results were obtained as $y = 0.22x + 0.05$ ($r^2 = 0.9998$, $n = 10$) for $^{208}\text{Pb}/^{209}\text{Bi}$ and $y = 0.51x + 0.15$ ($r^2 = 0.9998$, $n = 11$) for $^{88}\text{Sr}/^{109}\text{Ag}$. Linear working ranges were $0.13\text{--}50 \text{ ng}$ and $0.1\text{--}50 \text{ ng}$ for Pb and Sr, respectively. The proposed method provides high versatility allowing the loading of variable sample volumes, $1\text{--}10 \text{ mL}$ for Pb and $0.5\text{--}2.5 \text{ mL}$ for Sr. This allows the analysis of environmental samples in a wide concentration range of $0.013\text{--}50$ and $0.04\text{--}100 \mu\text{g L}^{-1}$ for Pb and Sr, respectively. Comparing with previous developed methodologies, our working ranges are significantly wider.^{26,27}

Limits of detection (LOD) achieved were 0.04 and 0.03 ng for Pb and Sr, respectively. Both values were calculated from three times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve. Moreover, considering the maximum preconcentrable sample volume (10 and 2.5 mL , for Pb and Sr, respectively), these can be expressed in concentration units as 4 ng L^{-1} for lead and 12 ng L^{-1} for strontium (see Table 3). As can be seen in Table 4, these LODs are lower than those reported by previous methods which also utilized preconcentration. Besides, with the proposed method, lead and strontium can be simultaneously determined. Regarding strontium, the LOD achieved is up to 3 or 5 orders of magnitude lower than those reported in previous methods; moreover, these previous methods do not allow strontium isotopic analysis.^{26,28} When comparing methods for lead determination, our LOD is better than the ones obtained in previous works.^{7,27,29}

Moreover, the proposed LOV-MSFIA system is able to renew the column at will in a fully automated way without requiring the analyst intervention, what results in high

Table 4. Comparison of LODs with Previous Works Based on Preconcentration Procedures Using Different Detectors

detection system	LODs (ng L^{-1})		ref
	Pb	Sr	
LOV-MSFIA-ICP-MS	4	12	present work
FI-ICP-TOFMS	6		7
ICP-OES ^a	1.53×10^4		29
ICP-MS ^a	30		27
UV-vis ^a		2.5×10^4	26
LOV-MSFIA-ICP-OES		1.8×10^3	30
HPCIC-UV-vis ^a		3.25×10^6	28

^aManual method.

reproducibility. In fact, the reproducibility of the method was determined for results obtained in different working days, changing the packing of the resin column and utilizing a solution of 15 ng of total Pb and Sr. Thus, in the case of Pb, the reproducibility was 4%, expressed as RSD; whereas it was 2.3% for strontium, which is quite similar (2.6%) to the one attained by a LOV-ICP-OES system for strontium determination.³⁰

The repeatability of the proposed methodology can be related to the lifetime of the column and was obtained without changing the column packing and making consecutive injections of a solution that contained 15 ng of both analytes. Thus, it was estimated that the lifetime of the column is 160 injections for the simultaneous determination of Pb and Sr, with recoveries above 95%. The repeatability of the proposed method was 2.2% and 2.7% ($n = 10$) for lead and strontium, respectively, expressed as RSD. The frequency of extraction was of 9 injections h^{-1} when 1 mL of sample was loaded onto the column and 5 injections h^{-1} when preconcentrated 10 mL of sample was used. These values only represent the sample pretreatment time, since the ICP-MS has an injection throughput of 50 injections h^{-1} .

It should be noticed that the frequency obtained in the proposed method was improved in comparison with batch procedures, e.g. only lead preconcentration in a batch method can require 50 min ³¹ as well as a higher amount of resin (0.4 g) per sample and higher volumes of reagents ($10\text{--}25 \text{ mL HNO}_3$, 2 mol L^{-1}). The proposed LOV-MSFIA system on the contrary reduces the reagent consumption (1 mL HNO_3 , 2 mol L^{-1}) including the amount of resin (0.035 g) and its reuse up to 160 times.

3.3. Validation. A certified reference river water material SLRS-4 (Institute for National Measurement Standards) was analyzed to validate the present automated system. The certified values for lead and strontium were 0.086 ± 0.007 and $26.3 \pm 3.2 \mu\text{g L}^{-1}$, respectively. Portions of 10 and 1 mL of sample were injected for Pb and Sr, respectively. The results for three replicates ($n = 3$) were 0.086 ± 0.018 and $26.12 \pm 0.03 \mu\text{g L}^{-1}$ for Pb and Sr, respectively. These values are expressed as mean value $\pm 2 \text{ SD}$ (standard deviation). The *t*-test for comparison of means revealed that there were no significant differences at the 95% confidence level between the values obtained with the proposed methodology and the certificated values.

3.4. Application to Environmental Samples. In order to demonstrate the applicability and reliability of the proposed method, two rain waters and three particulate airborne samples were analyzed. Each sample was analyzed directly and with two levels of spike (0.2 and $5 \mu\text{g L}^{-1}$ of Pb and Sr). In all cases, recoveries of lead and strontium were in the range of 90–110%

Table 5. Analysis of Rain Water and Particulate Airborne (PM₁₀) Samples

sample ^a	sample ID	added ($\mu\text{g L}^{-1}$)		found ($\mu\text{g L}^{-1}$)		recovery (%)	
		Pb	Sr	Pb	Sr	Pb	Sr
rain water	Manacor			<LOD	8.46 \pm 0.18		
		0.2	0.2	0.249 \pm 0.011	8.67 \pm 0.19	108	105
		5	5	4.74 \pm 0.15	12.97 \pm 0.10	94	90
	Inca			<LOD	11.85 \pm 0.05		
		0.2	0.2	0.25 \pm 0.04	12.04 \pm 0.06	110	95
		5	5	5.06 \pm 0.18	16.13 \pm 0.18	101	90
particulate airborne	Palmanyola 1			5.5 \pm 0.2	4.69 \pm 0.02		
		0.2	0.2	5.67 \pm 0.06	4.89 \pm 0.12	101	100
		5	5	10.39 \pm 0.06	9.1 \pm 0.2	101	91
	Palmanyola 2			4.47 \pm 0.02	3.39 \pm 0.06		
		0.2	0.2	4.65 \pm 0.04	3.470 \pm 0.010	90	102
		5	5	9.4 \pm 0.2	8.52 \pm 0.19	99	105
	Palmanyola 3			2.73 \pm 0.04	4.54 \pm 0.09		
		0.2	0.2	2.81 \pm 0.11	4.5 \pm 0.2	106	102
		5	5	7.69 \pm 0.10	8.95 \pm 0.03	101	92

^aResults are expressed as the mean value \pm standard deviation ($n = 3$).

Table 6. Pb and Sr Isotopes Ratios in Rain Water and Particulate Airborne Filters (PM₁₀) Samples Analyzed by the Proposed Method

sample	sample ID	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	⁸⁷ Sr/ ⁸⁶ Sr
rain water	Manacor	<LOD	<LOD	<LOD	<LOD	0.7122
	Inca	<LOD	<LOD	<LOD	<LOD	0.7133
particulate airborne	Palmanyola1	17.1707	15.6952	35.8215	2.0862	0.7164
	Palmanyola 2	17.0453	15.3059	36.0006	2.1121	0.7068
	Palmanyola 3	16.7796	14.6667	33.9542	2.0235	0.7190

(Table 5). These satisfactory recoveries are mainly due to the high selectivity of the Sr-resin and to the absence of interfering elements in the analyzed sample types, e.g. not high calcium contents. Although other authors have reported calcium interferences, thanks to the use of 2 mol L⁻¹ nitric acid as sample medium, calcium is weakly retained in the Sr-resin, and its retention is 3 orders of magnitude lower than Sr and Pb.³² Therefore, no additional step was necessary to remove interferences, and considering previous works^{30,33} and the good results obtained, we did not carry out a study of interferences.

Results proved that this MSFIA-LOV-ICP-MS method can be used to determine concentrations of lead and strontium in a wide concentration range including trace levels with a high and remarkable reproducibility, together with low consumption of Sr-resin, long lifetime of the column, and good recoveries. In addition, different stages of elution were avoided and the cleanup of the sample was carried out in a single step in comparison with previously developed methods in which Sr-resin was also exploited for the isolation of lead and strontium.^{17,34–36} Ammonium oxalate had been previously reported in bibliography for lead elution³⁷ and experimentally, we found that both Sr and Pb can be simultaneously eluted avoiding separation steps when exploiting a selective detector, such as ICP-MS.

3.5. Pb and Sr Isotope Ratios. As mentioned before, the stable isotopes ratios of Sr and Pb, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁶Pb, and ⁸⁷Sr/⁸⁶Sr are becoming a widely used tool in different areas related to environmental studies, since these make possible the identification of the sources of atmospheric resuspended soil particles.^{4,10,38} Thus, in order to demonstrate the applicability of the proposed MSFIA-LOV-ICP-MS methodology, several rain and airborne samples were

analyzed (Table 6). The precision of isotope ratio measurements is improved with the use of mass discrimination correction in the ICP-MS. The ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁶Pb ratios of the present study (mean values between 14.6667 and 15.6952 and between 2.0235 and 2.1121, respectively) and ⁸⁷Sr/⁸⁶Sr ratios (mean values between 0.7164 and 0.7190) were obtained. Other authors found values for ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁶Pb ratios of 15.608⁸ and 2.1132,³⁹ respectively; whereas for ⁸⁷Sr/⁸⁶Sr they found a value around of 0.7132. Rain water samples were analyzed, but we could not establish the isotopic ratios of lead due to the concentrations of lead in these samples were below the LOD. However, ⁸⁷Sr/⁸⁶Sr ratios were obtained (0.7122 and 0.7133). These values exhibit a small variation in comparison with measurements of samples obtained of precipitations collected for two stations in eastern Canada¹⁰ (⁸⁷Sr/⁸⁶Sr: 0.707–0.710).

3.6. Online Detection Method. An important advantage of the use of flow analysis systems is the versatility provided. This feature allows the use of an assembly (sample pretreatment system) offline or online connected to the detection system.

A fully automated system LOV-MSFIA coupled to ICP-MS is achieved with online detection, decreasing the risk of analyte losses and contamination of the samples. The online coupling of the LOV-MSFIA system with the ICP-MS was performed through the digital output of the multisyringe buret and a relay interface with the ICP-MS.

A mass calibration curve was constructed (counts of analyte/counts of internal standard ratio vs mass in nanograms of Pb and Sr) with statically satisfactory results as $y = 0.27x + 0.11$ ($r^2 = 0.9998$, $n = 10$) for ²⁰⁸Pb/²⁰⁹Bi and $y = 0.6x + 0.2$ ($r^2 = 0.9998$, $n = 10$) for ⁸⁸Sr/¹⁰⁹Ag. Linear ranges of the curves were

0.3–60 ng and 0.1–60 ng for Pb and Sr, respectively. The limit of detection was 0.08 and 0.03 ng for Pb and Sr, respectively (calculated from $3\sigma_b/\text{slope}$).

The injection frequency (including the sample treatment and the online detection) was between 5 and 3 injections h^{-1} varying the sample volume from 1 to 10 mL. The ICP-MS method utilized for the quantification of Pb and Sr was set in *transient signal* mode, requiring more time (300 s) for the reading of all the isotopes. This explains the decrease of the injection frequency, and also, it can result in an inconvenience due to argon gas consumption, which is a critical concern when using ICP-MS. By contrast, with offline detection, the ICP-MS works in *steady signal* mode, requiring less time of reading. In consequence, the consumption of argon gas decreases at the same time that analysis frequency increases.

Thus, considering the similar LODs obtained by the offline and the online approaches and establishing a compromise between the sampling frequency and argon gas consumption, offline mode was selected as the best option.

Thereby, the hyphenation of flow-based techniques, selective extraction resin, and ICP-MS detection allowed the simultaneous isotopic analysis of Sr and Pb. In addition, automation of the whole procedure, e.g. the loading, cleaning, and refill of the column, provided a high reproducibility to the system. Two operational modes were tested, i.e. online and offline detection. Furthermore, the method offers excellent analytical performance ensuring good accuracy. Therefore the proposed method is presented as a potential tool for Pb and Sr isotopic analysis in environmental samples.

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Notes

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ACKNOWLEDGMENTS

This work was funded by the Spanish Ministry of Science and Innovation (CTQ2010-15541 project) and by the Balearic Government (43/2011 cofinanced by FEDER funds). B.B. acknowledges the National Council of Science and Technology in México (CONACYT) for the allowance of a grant.

REFERENCES

- (1) Åberg, G.; Fosse, G.; Stray, H. Man, nutrition and mobility: A comparison of teeth and bone from the Medieval era and the present from Pb and Sr isotopes. *Sci. Total Environ.* **1998**, *224*, 109–119.
- (2) Elburg, M. Sources and processes in arc magmatism: the crucial role of water. *Geol. Belg.* **2010**, *13*, 119–134.
- (3) García-Ruiz, S.; Moldovan, M.; Fortunato, G.; Wunderli, S.; García-Alonso, I. Evaluation of strontium isotope abundance ratios in combination with multi-elemental analysis as a possible tool to study the geographical origin of ciders. *Anal. Chim. Acta* **2007**, *590*, 55–66.
- (4) Ruiz, J.; Leal, I.; García, I.; Sanz-Medel, A. Isotope ratio measurements using gas chromatography inductively coupled plasma mass spectrometry for the assessment of organolead sources. *J. Anal. At. Spectrom.* **2001**, *16*, 475–480.
- (5) Elçi, L.; Arslan, Z.; Tyson, J. Determination of lead in wine and rum samples by flow injection-hydride generation-atomic absorption spectrometry. *J. Hazard. Mater.* **2009**, *162*, 880–885.
- (6) Karadjova, I.; Lampugnani, L.; D'ulivo, A.; Onor, M.; Tsalev, D. Determination of lead in wine by hydride generation atomic fluorescence spectrometry in the presence of hexacyanoferrate(III). *Anal. Bioanal. Chem.* **2007**, *388*, 801–807.
- (7) Benkhedda, K.; Goenaga, H.; Adams, F. C. Determination of total lead and lead isotope ratios in natural waters by inductively coupled plasma time-of-flight mass spectrometry after flow injection on-line preconcentration. *Anal. Chim. Acta* **2004**, *506*, 137–144.
- (8) Lahd, M.; Stille, P.; Millet, M.; Perrone, T. REE characteristics and Pb, Sr and Nd isotopic compositions of steel plant emissions. *Sci. Total Environ.* **2007**, *373*, 404–419.
- (9) Schmitt, A. D.; Stille, P. The source of calcium in wet anthropogenic deposit: Ca-Sr isotope evidence. *Geochim. Cosmochim. Acta* **2005**, *69*, 3463–3468.
- (10) Simonetti, A.; Gariépy, C. Isotopic evidence of trace metal sources and transport in easter Canada as recorded from wet deposition. *J. Geophys. Res.* **2000**, *105*, 12,263–12,278.
- (11) Krupp, E. M.; Pécheyran, C.; Pinaly, H.; Motelica-Heino, M.; Koller, D.; Young, S. M. M.; Brenner, O. F. X. Isotopic precision for a lead species (PbEt₄) using capillary gas chromatography coupled inductively coupled plasma-multicollector mass spectrometry. *Spectrochim. Acta, Part B* **2001**, *56*, 1233–1240.
- (12) Dehelean, A.; Voica, C. Determination of lead and strontium isotopes ratios in wines by inductively coupled plasma mass spectrometry. *Rom. J. Phys.* **2011**, *57*, 1194–1203.
- (13) Miyazaki, T.; Vaglarov, B. S.; Takei, M.; Suzuki, M.; Suzuki, H.; Ohsawa, K.; Chang, Q.; Takahashi, T.; Hirahara, Y.; Hanyu, T.; Kimura, J.-I.; Tatsumi, Y. Development of a fully automated open-column chemical-separation system—Columnspider—and its application to Sr-Nd-Pb isotope analyses of igneous rock samples. *J. Miner. Petr. Sci.* **2012**, *107*, 74–86.
- (14) Monna, F.; Loizeau, J. L.; Thomas, B. A.; Guéguen, C.; Favarger, P. Y. Pb and Sr isotope measurement by inductively coupled plasma-mass spectrometer: efficient time management for precision improvement. *Spectrochim. Acta, Part B* **1998**, *53*, 317–1333.
- (15) Widory, D.; Liu, X.; Dong, S. Isotopes as tracers of sources of lead and strontium in aerosols (TSP & PM 2.5) in Beijing. *Atmos. Environ.* **2010**, *44*, 3679–3687.
- (16) Mohammadhosseini, M.; Saber Tehrani, M. Solid Phase Extraction and Determination of Trace Amounts of Lead(II) using Octadecyl Membrane Disks Modified by a New Schiff's Base and Flame Atomic Absorption Spectrometry. *J. Chin. Chem. Soc.-Taipei* **2006**, *53*, 1119–1128.
- (17) Deniel, C.; Pin, C. Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements. *Anal. Chim. Acta* **2001**, *426*, 95–103.
- (18) Smet, I.; Muynck, D.; Vanhaecke, F.; Elburg, M. A. From volcanic rock powder to Sr and Pb isotope ratios: a fit-for-purpose procedure for multi-collector ICP-MASS spectrometric analysis. *J. Anal. At. Spectrom.* **2010**, *25*, 1025–1032.
- (19) Luque De Castro, M. D.; Ruiz-Jiménez, J.; Pérez-Serradilla, J. A. Lab-on-valve: a useful tool in biochemical analysis. *TrAC, Trends Anal. Chem.* **2008**, *27*, 118–126.
- (20) Avivar, J.; Ferrer, L.; Casas, M.; Cerdà, V. Fully automated lab-on-valve-multisyringe flow injection analysis-ICP-MS system: an effective tool for fast, sensitive and selective determination of thorium and uranium at environmental levels exploiting solid phase extraction. *J. Anal. At. Spectrom.* **2012**, *27*, 327–334.
- (21) Horstkotte, B.; Elsholz, O.; Cerdà, V. Review on Automation using Multisyringe Flow Injection Analysis. *J. Flow Injec. Anal.* **2005**, *22*, 99–109.
- (22) Varga, Z.; Wallenius, M.; Klaus, M.; Keegan, E.; Millet, S. Application of Lead and Strontium Isotope Ratio Measurements for the Origin Assessment of Uranium Ore Concentrates. *Anal. Chem.* **2009**, *81*, 8327–8334.
- (23) Araujo, P.; Brereton, R. Experimental design I. Screening. *TrAC, Trends Anal. Chem.* **1996**, *15*, 26–31.
- (24) Escudero, L.; Cerutti, S.; Olsina, R.; Salonia, J.; Gasquez, J. Factorial design optimization of experimental variables in the on-line separation/preconcentration of copper in water samples using solid

phase extraction and ICP-OES determination. *J. Hazard. Mater.* **2010**, 1–3, 218–223.

(25) Lundstedt, T.; Seifert, E.; Abramo, L.; Thelin, B.; Nyström, A.; Pettersen, J.; Bermang, R. Experimental design and optimization. *Chemom. Intell. Lab. Syst.* **1998**, 42, 3–40.

(26) Idriss, K. A.; Sedaira, H.; Ahmed, S. S. Determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content of Portland cement by derivative ratio spectrophotometry. *Talanta* **2009**, 78, 7.

(27) Sabarudin, A.; Lenghor, N.; Liping, Y.; Furusho, Y.; Motomizu, S. Automated Online Preconcentration System for the Determination of Trace Amounts of Lead Using Pb-Selective Resin and Inductively Coupled Plasma–Atomic Emission Spectrometry. *Spectrosc. Lett.* **2006**, 39, 669–682.

(28) Nesterenko, E. P.; Nesterenko, P. N.; Paull, B.; Meléndez, M.; Corredor, J. E. Fast direct determination of strontium in seawater using high-performance chelation ion chromatography. *Microchem. J.* **2013**, 111, 8–15.

(29) Zougagh, M.; García De Torres, A.; Vereda Alonso, E.; Cano Pavón, J. M. Automatic on line preconcentration and determination of lead in water by ICP-AES using TS-microcolumn. *Talanta* **2004**, 62, 503–510.

(30) Rodríguez, M.; Avivar, J.; Ferrer, L.; Leal, L.; Cerdà, V. Automated total and radioactive strontium separation and preconcentration in samples of environmental interest exploiting a lab-on-valve system. *Talanta* **2012**, 96, 96–101.

(31) Tewari, P. K.; Singh, A. K. Preconcentration of lead with Amberlite XAD-2 and Amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry. *Talanta* **2002**, 56, 735–744.

(32) Horwitz, E.; Chiarizia, R.; Dietz, M. A novel strontium-selective extraction chromatographic resin. *Solvent Extr. Ion Exc.* **1992**, 10, 313–336.

(33) Jakmunee, J.; Sooksamiti, P.; Geckies, H.; Grudpan, K. Flow injection sample pretreatment for determination of lead by flame atomic absorption spectrophotometry. *Anal. Sci.* **2001**, 17, 1415–1420.

(34) Grahek, Z.; Rosmaric, M. M. Determination of radioactive strontium in seawater. *Anal. Chim. Acta* **2006**, 534, 271–279.

(35) Landstetter, C.; Sinojmeri, M.; Katzlberger, C.; Achatz, A. Determination of Sr-90 and Pb-210 in freshwater fish in Austria; Austrian Agency for Health and Food Safety: Vienna, **2011**; www.ages.at.

(36) Makishima, A.; Nath, B. N.; Nakamura, E. New sequential separation procedure for Sr, and Pb isotope ratio measurement in geological material using MC-ICP-MS and TIMS. *Geochem. J.* **2008**, 42, 237–246.

(37) Sooksamiti, P.; Geckeis, H.; Grudpan, K. Determination of lead in soil samples by in-valve solid-phase extraction-flow injection flame atomic absorption spectrometry. *Analyst* **1996**, 121, 1413–1417.

(38) Herut, B.; Srinsky, A.; Katz, A. Strontium in Rain Water from Israel: sources, isotopes and chemistry. *Earth Planet. Sci. Lett.* **1993**, 120, 77–84.

(39) Lee, H. C.; Kim, M. K.; Jo, W. K. Pb isotopic ratios in airborne PM10 of an iron/metal industrial complex area and nearby residential areas: Implications for ambient sources of Pb pollution. *Atmos. Res.* **2011**, 99, 462–470.