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Automated total and radioactive strontium separation and preconcentration in samples of environmental interest exploiting a lab-on-valve system

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ABSTRACT

A novel lab-on-valve system has been developed for strontium determination in environmental samples. Miniaturized lab-on-valve system potentially offers facilities to allow any kind of chemical and physical processes, including fluidic and microcarrier bead control, homogenous reaction and liquid–solid interaction. A rapid, inexpensive and fully automated method for the separation and preconcentration of total and radioactive strontium, using a solid phase extraction material (Sr-Resin), has been developed. Total strontium concentrations are determined by ICP-OES and ^{90}Sr activities by a low background proportional counter. The method has been successfully applied to different water samples of environmental interest. The proposed system offers minimization of sample handling, drastic reduction of reagent volume, improvement of the reproducibility and sample throughput and attains a significant decrease of both time and cost per analysis. The LLD of the total Sr reached is 1.8 ng and the minimum detectable activity for ^{90}Sr is 0.008 Bq. The repeatability of the separation procedure is 1.2% ($n = 10$).

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1. Introduction

Strontium has four stable isotopes and several that are radioactive. The most significant strontium radioisotopes in the environment are ^{89}Sr and ^{90}Sr (beta emitters), because both are fission products with longer half-lives than the other radioisotopes. The main source of radiostrontium in the environment was atmospheric nuclear weapons testing. Strontium isotopes have biological significance because they are alkaline earth metals, and chemical analogs of calcium. Therefore, strontium can replace calcium in the biosphere and, through the food chain, reach humans, in whom it has a long residence time [1]. Thus, once strontium is assimilated, it is mainly accumulated in the bones. Stable and radioactive isotopes have been the subject of many investigations related to the treatment of bones [2], forensic science [3], archeology [4], the understanding of marine life [5] and cancer studies since radiostrontium damages the genetic material (DNA) [6], so its determination is of great interest not only in environmental samples but also in many other areas of knowledge.

In order to reduce the risk in the manipulation of radioisotopes in environmental samples, to improve the analysis time and to decrease the sample and reagent consumption, and so the radioactive waste generation, flow-analysis techniques have been widely and successfully applied to determine radioactive elements [7]. The combination of classical methods with modern instrumentation makes possible the total or partial automation of many conventional analytical methods in the radiochemical field, which, in practice, leads to simplicity, reliability and an improvement of the safety of the analyst. In particular, lab-on-valve (LOV) [8,9] brings to flow-based analysis the third generation, which significantly facilitates integration of various analytical units in the valve and provides great potential for miniaturization of the entire instrumentation. Moreover, its flexible fluid manipulation is suitable for delivering beads in flow-based manifolds (i.e. precise fluid manipulation by the LOV system and the channel configuration also make it a powerful platform for bead injection (BI)). In combination with the renewable surface concept, BI has been widely exploited for separation and preconcentration of analytes in the presence of complex matrix components [8]. Most importantly, the automated transport of solid materials in such a system allows their renewal at will and thus provides a high degree of repeatability.

The inductively coupled plasma optical emission spectrometry (ICP-OES) technique which offers fast multi-elemental analysis suffers from a poor sensitivity, because the concentration of some metals in environmental samples is below the detection limit of ICP-OES. To solve this problem, preconcentration separation procedures have been proposed [10]. ICP-OES is a detection technique that allows measuring total strontium (stable and radioactive) and possible interfering metals, being a useful screening tool.

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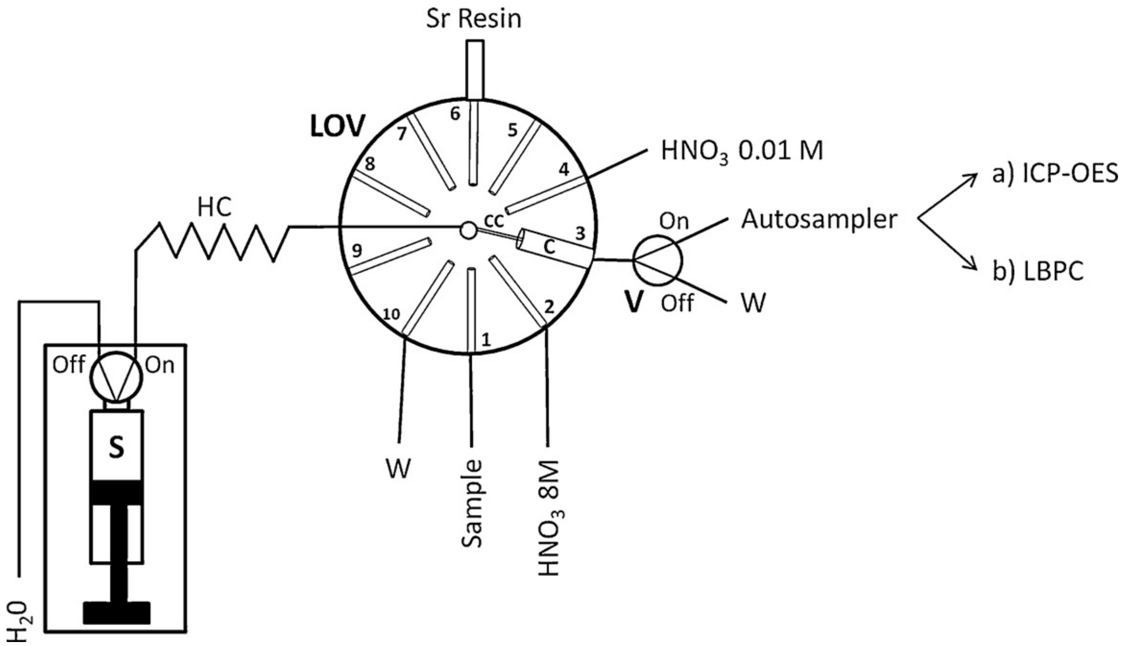

Fig. 1. Lab-on-valve system for strontium isolation and preconcentration: (a) ICP-OES total Sr determination and (b) low background proportional counter (LBPC) ^{90}Sr determination. S, syringe; LOV, lab-on-valve; HC, holding coil; V, solenoid valve; C, column; CC, central conduit; W, waste.

Low background proportional counters are an excellent detection technique for radioactive isotopes of strontium. However, this technique is rarely used for direct radiometric detection of beta emitters, because of its low capacity to discriminate between different beta particles. Since, beta particles from a single isotope are emitted with a range of energies, giving a spectrum that overlaps with those of other beta-emitting radioisotopes. So, beta emitters normally have to be previously isolated [7].

Solid phase extraction (SPE) is a widely used technique for the isolation and preconcentration of compounds or species from liquid samples, due to the short time required for extraction and the ease of handling [11]. Sr-Resin was selected as solid phase extraction material in the present work, since this resin is a high selective chromatographic material for Sr. Strontium extraction mechanism is based on nitrate complex formation.

Thus, the main aim of this work was the development of a rapid, selective, sensitive and automated method for the separation and preconcentration of total and radioactive strontium. Therefore, in this paper, a LOV system exploiting a solid phase extraction material (Sr-Resin) is presented.

2. Experimental

2.1. Reagents and standard solutions

All solutions were prepared from analytical grade reagents with Millipore quality water. Stock strontium standard solutions were prepared from $Sr(NO_3)_2$ 99%, Merck by appropriate dilution with 8 mol L^{-1} HNO_3.

Reagents and materials included HNO_3 65% Scharlau (Barcelona, Spain), 203.1 ± 0.3 Bq g^{-1} ^{90}Sr/^{90}Y in equilibrium secular, prepared in 1 mol L^{-1} HCl, certified by CIEMAT (Madrid, Spain, ref.1375/85298/99/MRI99N66). Sr-Resin 50–100 μm from Triskem Industries (France) and glass fiber prefilters from Millipore (Madrid, Spain).

All glassware were carefully cleaned, soaked in 10% (v/v) HNO_3 during 24 h and rinsed with Millipore water.

2.2. Samples

All water samples, mineral water, tap water, well water and seawater, were prepared in a final solution of 8 mol L^{-1} HNO_3. Groundwater and seawater were filtered through a membrane of 0.45 μm.

2.3. Manifold and software

The LOV system used is shown in Fig. 1. The LOV microconduit (Sciware, Palma de Mallorca, Spain), fabricated from methacrylate encompassing ten integrated microchannels (1.5 mm i.d./16.0 mm length, excepting the bead column channel made of 3.2 mm i.d.), was mounted atop of a ten-port multiposition selection valve (Crison Instruments, Barcelona, Spain).

The central port of the valve in the LOV system was connected to a 10 mL glass syringe (Hamilton, Switzerland) via a holding coil. The extraction system is a column located at the channel 3 of the LOV. The column is packed with 0.11 g of Sr-Resin (particle size 50–100 μm), achieving an adequate compaction grade to avoid 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. The suspension of extraction chromatographic resin was contained in a 5 mL plastic syringe, which was mounted vertically on port 6 of the integrated microsystem. Peripheral port configuration was: port 2 (8 mol L^{-1} HNO_3), port 4 (0.01 mol L^{-1} HNO_3), port 1 (sample) and port 10 (waste).

Port 3 is connected to a solenoid commutation valve V (MTV-3-N 1/4 UKG; Takasago, Japan) which helps drive the flow in the desired way (on: in line flow to sample collector; off: to waste).

The glass syringe is used as liquid driver and is mounted in a multisyringe burette (BU4S; Crison Instruments, Barcelona, Spain) with programmable flow rates. The syringe has a three-way solenoid valve (N-Research, Caldwell, NJ, USA) at the head, which facilitates the application of multicommutation schemes (on: in-line flow; off: to reservoir).

The flow network is constructed with 0.8 mm internal diameter PTFE tubing. The holding coil is constructed with 1.5 mm internal diameter PTFE tubing, corresponding to a volume of 8.5 mL. All connections are made by means of PVDF connectors.

The method and all instruments used to perform the extraction are automatically controlled by the software package AutoAnalysis 5.0 (Sciware, Palma de Mallorca, Spain)[1] [12]. The distinctive feature of this software based on dynamic link libraries (DLLs) at 32 bits is the possibility of using a single and versatile application without further modification for whatever instrumentation and detection system needed. It involves a basic protocol which allows the implementation of specific and individual DLLs, addressing the configuration of the assembled flow analyzer.

The detectors used in this work were an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 5300 DV, Perkin Elmer® Inc.) equipped with a Gem Tip Cross-flow pneumatic nebulizer (Waltham, MA, USA) and a low background proportional counter (Tennelec LB 4100) equipped with eight detectors, for total and radioactive strontium, respectively. Determination of total strontium was carried out by ICP-OES using next instrumental operating conditions: RF generator power 1300 W, frequency of RF generator 40 MHz, plasma argon flow 15 L min^{-1}, nebulizer argon flow 0.8 L min^{-1}, auxiliary argon flow 0.5 L min^{-1}, integration time 5 s and aspiration rate 1.5 mL min^{-1}. Wavelength (nm) for intensity measurements was 407.7 nm. All measurements were run in triplicate. While for the measurement of radioactive strontium a voltage of 1600 volt and a counting time of 1000 min were used.

2.4. Column conditioning

The extractant of the Sr-Resin is a crown-ether (4,4′(5′)-di-t-butylcyclohexano-18-crown-6) diluted in octanol [13,14]. It forms nitrate complexes with strontium. The formation of these complexes depends on the concentration of nitrate in the sample solution. The functionality of this resin has allowed its application to isolate and preconcentrate strontium in a variety of systems [15].

The resin needs to be conditioned with nitric acid of the same concentration as the sample medium. Optimal acid concentration for the retention of strontium is 8 mol L^{-1}, according to a previous work [16] and specifications of the manufacturer [15]. Thus, the resin is left at the syringe mounted as a bead reservoir in port 6 of the LOV with 8 mol L^{-1} HNO_3 solution. Once the resin is ready, on-column extraction and isolation of strontium are carried out automatically, ensuring high repeatability between replicates.

2.5. Analytical procedure

The complete operational sequence for strontium isolation and preconcentration is listed in Table 1, and summarized as follows:

Table 1
Automated procedure for strontium separation and preconcentration.

Step	Flow rate (mL min^{-1})	LOV position	V
Resin loading			
(a) Loading beads into HC	5	6	Off
(b) Filling the column	2	3	Off
Conditioning of Sr-Resin			
(a) Loading 2 mL of 8 mol L^{-1} HNO_3 into HC	5	2	Off
(b) Rinsing 2 mL on the column	2	3	Off
Sample loading			
(a) Loading *X* mL sample into HC	5	1	Off
(b) Rinsing *X* mL on the column	0.6	3	Off
Elimination of interferences			
(a) Loading 0.5 mL of 8 mol L^{-1} HNO_3 into HC	5	2	Off
(b) Rinsing 0.5 mL on the column	2	3	Off
Elution of strontium			
(a) Loading 5.125 mL of 0.01 mol L^{-1} into HC	5	4	Off
(b) Rinsing on the column	2	3	On
Change of sample			
(a) Loading 1 mL of new sample into HC	5	1	Off
(b) Discarding 2 mL to the waste	5	10	Off
Beads replacing			
(a) Loading old beads into HC	5	3	Off
(b) Discarding old beads	5	10	Off
(c) Loading new beads into HC	5	6	Off
(d) Filling the column	2	3	Off

1. Load of resin: the column is automatically loaded with resin. First, resin is loaded into the HC from the resin reservoir (port 6) which contains a saturated solution of the resin and dispensed at port 3 with V-off (to waste) to fill the column.
2. Conditioning of Sr-Resin: the CC is connected to port 2 to aspirate 2 mL of 8 mol L^{-1} HNO_3 into the HC. Then it moves to port 3 and the HNO_3 is propelled toward the column at a flow rate of 2 mL min^{-1}. V is deactivated (V-off, to waste).
3. Sample loading: once the column is ready, *X* mL of standard or sample (port 1) is dispensed toward the column (port 3) at a flow rate of 0.6 mL min^{-1}.
4. Elimination of interferences: the CC is connected to port 2 to aspirate 0.5 mL of 8 mol L^{-1} HNO_3 into the HC. Then it moves to port 3 and the HNO_3 is propelled toward the column at a flow rate of 2 mL min^{-1}.
5. Elution of Sr: at this point all the strontium retained on the column is eluted. 5.125 mL of 0.01 mol L^{-1} HNO_3 (port 4) are loaded into the HC and V is activated (V-on) to propel the eluent (5.125 mL of 0.01 mol L^{-1} HNO_3) through the column (port 3) at a flow rate of 2 mL min^{-1}.
6. Change of sample: in order to avoid memory effects, 1 mL of the new sample is aspirated (port 1), and 2 mL are discarded toward waste (port 10).
7. Change of the resin: applicable when required depending on the sample matrix. The column is regenerated by replacing the resin automatically. First, the old resin is loaded into the HC and sent to waste (port 10), then new resin is loaded into the HC from the resin reservoir (port 6) which contains a saturated solution of the resin and dispensed at port 3 with V-off (to waste) to fill the column.

3. Results and discussion

3.1. Flow system set-up

Some advantages of this “lab-on-valve” system are compactness and the permanent rigid position of the sample processing channels that ensure repeatability of microfluidic manipulations. The LOV system has a glass syringe for driving fluids. A three-way solenoid valve is placed at the head of the syringe, allowing load and dispense of solutions due to its bidirectional operation. The external solenoid valve directs the liquid to the collector (on position) or to the waste bottle (off position), with great precision and reproducibility. This allows drastic reduction of reagents consumption, waste generation, reduction of resin consumption and time saving in relation to manual methodologies, whose operations can last days against an

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[1] The software used in this work can be obtained on request. http://www.sciware-sl.com/.

injection frequency of 3–5 injection h^{-1}, depending on the sample volume. Besides, the proposed LOV system is able to renew the solid phase extraction at will in a fully automated way, without requiring the analyst intervention, resulting in higher reproducibility and repeatability.

Regarding detectors, on the one hand, in this work, the ICP-OES is used as an screening tool for total Sr determination in environmental samples, which allows to find out quickly the existence and content of total Sr, avoiding unnecessary and time consuming operations when not required. On the other hand, in order to obtain specifically the activity of ^{90}Sr a low background proportional counter is used after the separation procedure, the eluted fraction is evaporated over a stainless-steel planchet, for further determination of ^{90}Sr beta activity.

3.2. *Optimal working conditions*

In order to find the best operational conditions for separation and preconcentration of ultra-trace levels of strontium with the proposed LOV system, optimization steps were performed using multivariate techniques.

The optimization was carried out with the statistical software Minitab® 15. All measurements in the experimental design were made for total strontium by ICP-OES.

The optimization methodology started with a screening to study the independent variables and their possible interactions by a full factorial design [17]. In all cases, three center points were included, to identify any irregularities, such as loss of linearity in the center of the interval. The independent factors studied were: eluent volume (1–6 mL), eluent concentration (0.01–0.05 mol L^{-1}) and elution flow rate (0.6–2 mL min^{-1}). Results showed that the curvature and two of the three variables studied, volume and concentration of the eluent, were significant.

Then, these significant variables were optimized with a response surface design [18], using a face centered central composite design. A total of 11 experimental runs were conducted to optimize the experimental conditions. Critical values were obtained for these two variables, eluent concentration – 0.01 mol L^{-1} and eluent volume – 5.125 mL, which were used for further assays.

3.3. *Analytical parameters*

A mass calibration curve for total strontium (absolute intensity versus mass in ng Sr), with a statistically satisfactory fit was obtained ($y = 3484x + 17{,}294$, $R^2 = 0.9987$, $n = 10$). Under the optimum conditions described above the mass calibration curve is linear over the range 0–500 ng Sr.

The limit of detection achieved is 1.8 ng for total Sr, calculated from three times the standard deviation of ten replicates of the blank divided by the slope of the calibration curve [19,20]. So with this method, the Agency for Toxic Substances and Disease Registry (ATSDR) [6] reference value for total strontium could be easily measured. The minimum detectable activity (MDA) of 0.008 Bq for ^{90}Sr was calculated according to the recommendations of ISO 11929 [21] for a confidence level of 95%. So the World Health Organization (WHO) reference value of ^{90}Sr can be also easily measured [22].

The proposed method is effective even for a sample volume of 8 mL having a recovery above 90%. Thus, the present system is able to work in a wide range of concentrations, since the loaded sample volume can vary from 0.1 to 8 mL, allowing the analysis of samples with Sr content between 0.2 and 5000 μg L^{-1}.

The preconcentration factor for the low background proportional counter is 8, and for ICP-OES is 1.6. Despite not being very high, is an added advantage to the isolation of Sr. Table 2 shows the analytical figures of merit of the present work.

Table 2
Analytical parameters of the proposed method.

Analytical parameters	
Detection limit	1.8 ng
Regression coefficient ($n = 10$)	0.9987
Repeatability ($n = 10$)	1.2%
Reproducibility ($n = 5$)	2.6%
Resin durability	30 injections
Sample volume	0.1–8 mL
Sensitivity	3484 IU ng^{-1}
Linear working range	0–500 ng
Sample concentration range	0.2–5000 μg L^{-1}
Injection throughput	3–5 h^{-1}

Table 3
Analysis of water samples by ICP-OES (total strontium).

Sample	Added Sr (μg L^{-1})	Found Sr (μg L^{-1})	Recovery (%)
Tap water 1	0	708 ± 17	
	50	755 ± 14	94
Tap water 2	0	416 ± 22	
	50	461 ± 16	92
Mineral water	0	33.3 ± 0.8	
	50	87.3 ± 2.0	105
Groundwater	0	305 ± 8	
	50	351 ± 6	90

Results are expressed as the mean value ± standard deviation ($n = 3$). Samples are prepared in nitric acid 8 mol L^{-1}.

The functional lifetime of the column depends on the repeatability of the methodology, i.e. the number of tests or injections that can be done with the same resin present in the column without affecting its functionality. Results obtained in more than 100 analyses revealed an analyte recovery higher than 90% over the first 30 injections with a RSD of 4%. Therefore, replacing the resin after 30 injections is recommended to prevent a deficiency in its functionality.

The proposed LOV system is able to renew the solid phase extraction at will in a fully automated way, without requiring the analyst intervention, resulting in a high reproducibility and repeatability. The reproducibility of the method, RSD 2.6%, was determined from results obtained on different working days, changing the packing of the resin column and using a solution which contained 50 ng of total strontium, so the resin replacement effect is included in the RSD given.

3.4. *Interferences*

The interfering elements studied were selected taking into account a previous work [16] and the characteristics of the resin, since active sites of the resin can be affected and retention can be reduced [15]. Thus, Ca (0–400 mg L^{-1}), Mg (0–50 mg L^{-1}), K

Table 4
Analysis of water samples by low background proportional counter for ^{90}Sr.

Sample	Added ^{90}Sr (Bq)	Found ^{90}Sr (Bq)	Recovery (%)
Tap water	0	<MDA	
	0.050	0.047 ± 0.006	94
Groundwater	0	<MDA	
	0.050	0.050 ± 0.006	100
Seawater	0	<MDA	
	0.050	0.046 ± 0.006	94

Results are expressed as the activity ± uncertainty. Water samples are prepared in nitric acid 8 mol L^{-1}.

Table 5
Comparison with previous works based on flow analysis-SPE.

Flow technique	Injection throughput (h^{-1})	Resin used[c] (g)	Resin durability (injections)	Sample used (mL)	MDA^{90}Sr (Bq)	LODSr ($\mu g L^{-1}$)	Refs.
SIA	1.5	0.1155	15	0.1[b]	2.62	NA	[27]
SIA	2.7	0.2739	30	0.1[b]	4.17	NA	[28]
MSFIA	2	0.1000	30	2	0.01	10	[16]
LOV	3–5[a]	0.1100	30	0.1–8[a]	0.008	1.8	Proposed method

[a] Depending on sample volume to preconcentrate.
[b] Nuclear power plant waste.
[c] Sr-Resin by Triskem International, France.

(0–400 $\mu g L^{-1}$), Ba (0–100 $\mu g L^{-1}$) and Pb (0–100 $\mu g L^{-1}$) were considered, as they are common metallic cations found in environmental samples. Interferences are considered significant when the analytical signal variation is greater than ±10%.

Results showed no significant interference in the ranges of concentration studied for K, Ba and Pb, while Mg and Ca cause interference above 20 mg L^{-1} and 30 mg L^{-1}, respectively.

3.5. Application to natural samples

The developed method was evaluated by analyzing different water matrices. Results of analysis for three replicates ($n=3$) for total Sr by ICP-OES are shown in Table 3, while the results of ^{90}Sr using a low background proportional counter are shown in Table 4.

In the case of total Sr, water samples were prepared in 8 mol L^{-1} HNO_3, and a known concentration of strontium (50 $\mu g L^{-1}$), obtained from the corresponding standard, was added. Results reveal a positive recovery, over 90% in all cases. Results obtained of total Sr in water matrices agree with the values normally found, up to 1 mg L^{-1} in drinking water [6] and ppm (mg L^{-1}) levels in groundwater [23,24]. Seawater sample showed significant interferences when determining total Sr by ICP-OES. These interferences could be caused by the proximity between the wavelengths of Ca and Sr.

In order to validate the proposed method, water samples prepared in 8 mol L^{-1} HNO_3 were also spiked with the certified ^{90}Sr standard with an activity of 0.05 Bq ^{90}Sr. Recoveries were satisfactory, over 90% in all cases. The Bateman equation was used at two different times for calculation of ^{90}Sr activity. That is to say, total beta activity (^{90}Sr activity and its daughter ^{90}Y) was measured at two different times: one along the first day after the separation process and another a week later; the solution of the Bateman equations allow to obtain the initial ^{90}Sr–^{90}Y activities [25]. Results are expressed as activity ± uncertainty. The uncertainty (95% confidence level, $k=2$) was calculated according to the recommendations of ISO [26]. In the case of ^{90}Sr, seawater sample could be satisfactorily analyzed, indicating the good performance of the SPE and that the interference problem cited above was due to the detector (ICP-OES).

3.6. Comparison with previous works based on flow analysis-SPE

A comparison of the main figures of merit of various representative works is presented in Table 5.

There are a few methods developed in a flow-based approach exploiting SPE for strontium determination, and only one was designed to perform both determinations, total and radioactive strontium, with the same system [16] like the proposed method.

The amount of resin consumed is similar to the SIA [27] and MSFIA methods and 2.5 times lower than in the other SIA method [28]. The resin can also be reused 30 times. The most prominent feature of the proposed method, inherent to the LOV technique, is the automated renewal of the resin, which is not present in previous works.

The injection throughput is up to two times higher than in previous flow-based works, and of course, much higher than in manual approaches for Sr separation.

The detection limit for total strontium is five times lower than the obtained in a previous MSFIA method [16]. The MDA for ^{90}Sr is similar to the one obtained in this MSFIA system and between 330 [27] and 500 [28] times smaller than in the remaining methods. It is also worth to highlight that the volume of sample required is quite low, and similar to the volume used at the methods applied to nuclear power plant waste.

4. Conclusions

The proposed procedure was successfully applied to total strontium determination at trace levels by ICP-OES and to ^{90}Sr activities by a low background proportional counter. The method has been applied to different water samples of environmental interest. Besides, with the proposed method it is possible to analyze total and radioactive Sr in drinking waters achieving the reference levels established by the ATSDR and the WHO.

The main achievements of the proposed method are the improved LOD and MDA with respect to previous works for total and radioactive strontium determination, the automation of the column replacement provided by the BI and the cost reduction per analysis due to the long durability of such small amount of resin.

Furthermore, among others advantages the proposed method offers high precision and reproducibility, reduction of the time spent, minimization of sample and reagents required in the analysis, and above all the improvement in the safety, what is of high relevance when manipulating radioactive isotopes.

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