

Automation of ^{99}Tc extraction by LOV prior ICP-MS detection: Application to environmental samples

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Abstract

A new, fast, automated and inexpensive sample pre-treatment method for ^{99}Tc determination by inductively coupled plasma-mass spectrometry (ICP-MS) detection is presented. The miniaturized approach is based on a lab-on-valve (LOV) system, allowing automatic separation and preconcentration of ^{99}Tc . Selectivity is provided by the solid phase extraction system used (TEVA resin) which retains selectively pertechnetate ion in diluted nitric acid solution. The proposed system has some advantages such as minimization of sample handling, reduction of reagents volume, improvement of intermediate precision and sample throughput, offering a significant decrease of both time and cost per analysis in comparison to other flow techniques and batch methods. The proposed LOV system has been successfully applied to different samples of environmental interest (water and soil) with satisfactory recoveries, between 94% and 98%. The detection limit (LOD) of the developed method is 0.005 ng. The high durability of the resin and its low amount (32 mg), its good intermediate precision (RSD 3.8%) and repeatability (RSD 2%) and its high extraction frequency (up to 5 h^{-1}) makes this method an inexpensive, high precision and fast tool for monitoring ^{99}Tc in environmental samples.

1. Introduction

Technetium was the first radioactive element produced artificially. ^{99}Tc is one of the Tc isotopes with a long half-life ($T_{1/2}=2.1\times 10^5$ y). Large amounts of ^{99}Tc have been produced and released to the environment from human nuclear activities such as nuclear weapons testing, nuclear fuel cycle, nuclear accidents and nuclear medicine activities including a wide variety of diagnostic tests (e.g., renal, thyroid, cardiac gammagraphy, and detection of internal infectious process), making ^{99}Tc the only environmentally significant Tc isotope [1] ; [2]. The predominant chemical form of ^{99}Tc is the pertechnetate ion (TcO_4^-) in oxidizing environments, being very stable. The pertechnetate ion is hardly complexed with organic compounds in aerobic environments. Moreover the high water solubility and environmental mobility of Tc (in the form of TcO_4^-) as well as its long half-life, makes ^{99}Tc a radionuclide of high environmental interest. Thus, becoming its accurate determination in various types of samples mandatory [1] ; [3].

Due to the extremely low concentration of ^{99}Tc in environmental matrices, the sample preparation, preconcentration, chemical separation and purification for removal of potential interferences for ^{99}Tc detection are the most important issues governing the accurate determination of this analyte.

The long half-life and therefore low specific activity of ^{99}Tc (0.64 Bq ng^{-1}), makes mass spectrometry (MS) techniques potentially sensitive tools for measurement of ^{99}Tc [4]; [5]; [6] ; [7]. ICP-MS is the most widely and frequently used mass spectrometric technique for measurement of ^{99}Tc in many types of environmental samples, due to its high sensitivity and rapidity [8] ; [9]. However, one

of the main limitations of this technique is that high concentration of dissolved solids should be avoided in order to enlarge the good performance of the instrument, making necessary matrix and interferences removal prior introduction into the ICP-MS. Therefore, a sample clean-up prior to analysis is mandatory. Another challenge in ^{99}Tc measurement by ICP-MS is to overcome isobaric and molecular interferences. Chemical separation techniques used for radiometric methods can also be applied in the mass spectrometric determination of ^{99}Tc . The main difference is that the separation methods used for mass spectrometric measurement are focused on the removal of stable isotopic interferences with the mass of 99 AMU [10] ; [11]. Main interferences are isobaric from the stable isotope ^{99}Ru and the molecular ion $^{98}\text{Mo}^1\text{H}$.

Solid phase extraction (SPE) separates the analytes of interest from the matrix, being 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 [12]. TEVA-Resin was used as solid phase extraction material in the present work, since it is a high selective material for Tc.

Hence, ICP-MS detection requires isolation and preconcentration of ^{99}Tc . These operations are conventionally carried out through a large number of analytical steps, high consumption of sample and reagents, an elevated investment of time and money as well as a high risk associated to radionuclide manipulation. In order to solve the mentioned inconveniences, flow-analysis techniques have been widely and successfully applied to determine radioactive elements [13]. In particular, lab-on-valve (LOV) [14] ; [15] 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 allowing bead injection (BI).

Thus, the main aim of this work was the development of a rapid, selective and sensitive method for the separation and preconcentration of ^{99}Tc , applied to several types of sample matrices, in order to reduce the number of analytical steps, save time and money, and especially to avoid the intervention of the analyst in samples potentially contaminated with ^{99}Tc . Thus, a LOV system using TEVA-Resin and ICP-MS as detector for environmental monitoring of ^{99}Tc at trace levels is presented.

2. Experimental

2.1. Reagents and standard solutions

All solutions were prepared from analytical grade reagents with Millipore water. All ^{99}Tc standard solutions were obtained by appropriate dilution of the standard with $0.1 \text{ mol L}^{-1}\text{HNO}_3$.

The ^{99}Tc standard was obtained from decay of $^{99\text{m}}\text{Tc}$ radionuclide. The nuclear medicine area of the International Center of Medicine (CIMA) generates $^{99\text{m}}\text{Tc}$ from Elumatic III-Techneium $^{99\text{m}}\text{Tc}$ Generator, which provides each day enough activity for the programmed explorations. Weekly, when the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator arrived, a vial of 5 mL with an average activity of 20 GBq, was kept aside during a month to ensure that all $^{99\text{m}}\text{Tc}$ had decayed into its daughter ^{99}Tc . After that, the calculation of the ^{99}Tc activity was carried out with a low background proportional counter (Canberra LB4100) at 1600 V and a counting time of 1000 min. This information together with the specific activity of ^{99}Tc (0.64 Bq ng^{-1}), allow the calculation of ^{99}Tc

concentration in the aliquot. This aliquot was taken as working standard solution.

0.4 $\mu\text{g L}^{-1}$ of ^{106}Pd solution (High-Purity Standards, 1000 mg L^{-1} , USA) was added as internal standard for ^{99}Tc detection by ICP-MS, to correct possible instrumental drifts.

Reagents and materials included HNO_3 65% (J.T. Baker, USA), TEVA-Resin, particle size 50–100 μm (Triskem Industries, France) and glass fiber prefilters (Millipore, USA).

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

2.2. Samples

All water samples (mineral water, dam water, tap water and well water) were prepared in a final concentration of 0.1 mol L^{-1} HNO_3 . Dam water and well water were filtered through a membrane of 0.45 μm . Analytical determination of all water samples was carried out directly with the proposed system.

The soil sample was subjected to a microwave digestion, following the SW 846-3051 procedure recommended by the Environmental Protection Agency (EPA, USA) [16]. 0.5 g of soil sample was weighted and 10 ml of HNO_3 65% was added. The mixture was exposed to a microwave digestion (350 psi, 175 $^\circ\text{C}$, and 400 W) during 5 min. The digested extract was evaporated to dryness and dissolved up to 25 mL in a solution of 0.1 mol L^{-1} HNO_3 . Finally, the sample was filtered with a 0.2 μm membrane.

2.3. Manifold and software

The constructed LOV system is shown in [Fig. 1](#). The LOV microconduit

(Sciware Systems, Mallorca, Spain), fabricated from methacrylate, encompassing eight integrated microchannels (1.5 mm i.d./16.0 mm length, excepting the bead column channel of 3.2 mm i.d.), was mounted atop of a eight-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 constituted of a column located at the channel 1 of the LOV, packed with 32 mg of TEVA-Resin, achieving an adequate compaction grade to avoid overpressures in the system [17]. To contain the sorbent within the cavity of the LOV module and prevent it from escaping, the outlet of the column was

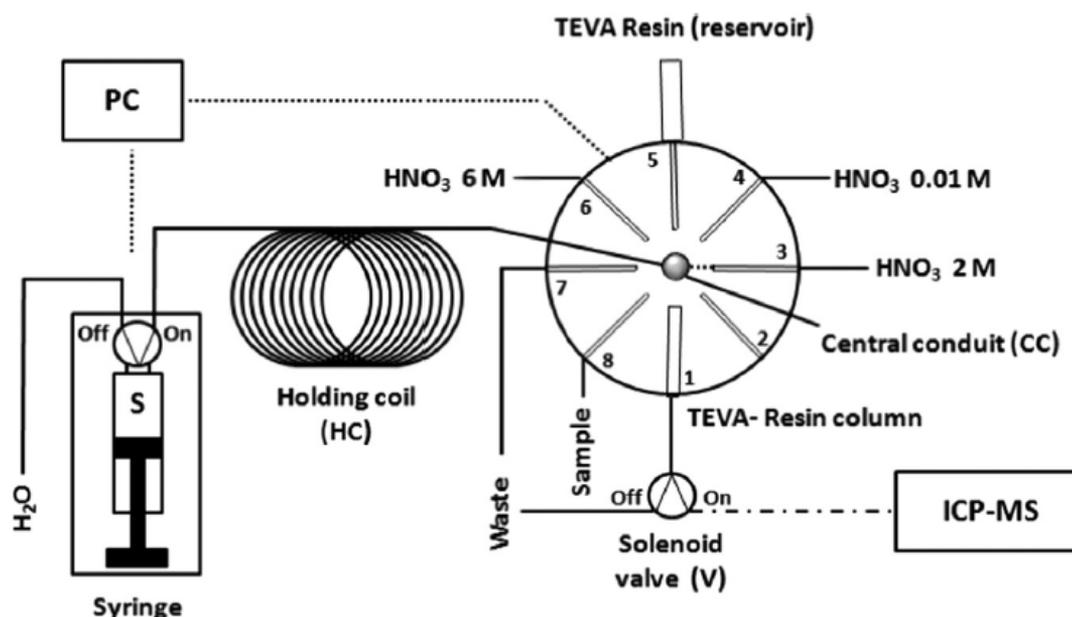


Fig. 1. LOV system for ^{99m}Tc isolation and preconcentration.

Furnished with a glass fiber prefilter (Millipore) which retains the beads while allows solutions to flow freely. The resin was prepared as a suspension and contained in a 5 mL plastic syringe, which was mounted vertically on port 5 of the

integrated microsystem. Thus, peripheral ports configuration was: port 1 (column), port 3 ($2 \text{ mol L}^{-1} \text{HNO}_3$), port 4 ($0.01 \text{ mol L}^{-1} \text{HNO}_3$), port 5 (resin reservoir), port 6 ($6 \text{ mol L}^{-1} \text{HNO}_3$), port 7 (waste) and port 8 (sample).

Outlet of port 1 is connected to an additional external solenoid commutation valve (V) (MTV-3-N 1/4 UKG; Takasago, Japan) which helps driving the flow in the desired way (on: in line flow to sample collector; off: to waste).

A glass syringe mounted in a multisyringe buret (BU4S; Crison Instruments) with programmable flow rates is used as liquid driver. 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 reservoirs).

The flow network is constructed with 0.8 mm i.d. PTFE tubing. The holding coil is constructed with 1.5 mm diameter i.d. PTFE tubing, corresponding to a volume of 8 mL. All connections are made by means of PVDF connectors.

The analytical procedure and all instruments used to perform the sample pretreatment are automatically controlled by the software package AutoAnalysis 5.0 (Sciware Systems, Palma de Mallorca, Spain) [\[18\]](#). 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 needed. It involves a basic protocol which allows the implementation of specific and individual DLLs, addressing the configuration of the assembled flow analyzer.

Determination of ^{99}Tc was carried out by an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific XSERIES II) equipped with a multichannel

peristaltic pump, a cross-flow nebulizer (Thermo Scientific) and a Scott spray chamber. Instrument settings are shown in Table 1. All measurements were performed in triplicate.

2.4. Analytical procedure

The complete automated sequence for technetium isolation and preconcentration is listed in Table 2, and summarized as follows:

1. Conditioning of TEVA-Resin: the central conduit (CC) is connected to port 4 for aspirating 2 mL of 0.1 mol L⁻¹ HNO₃ into the holding coil (HC). Then it moves to port 1 and the HNO₃ is propelled towards the column at a flow rate of 2 mL min⁻¹. V is deactivated (V-off, to waste).

Table 1
Instrumental settings for the ICP-MS.

Radio frequency power gas flow	Forward	1100 W
	Plasma	15 L min ⁻¹
	Auxiliary	1.2 L min ⁻¹
	Nebulizer	0.95 L min ⁻¹
Acquisition parameters (all analysis)	Dwell time	0.05 s
	Scan mode	Peak-hop transient
	Sweeps per reading	20
	MCA channels per spectral-peak	1
	Resolution/AMU 10% peak maximum signal processing	0.7
	Signal processing	Steady state: average
	Reading per replicate	1
	Replicates	3
	Baseline readings	0
	Isotopes measured	⁹⁹ Tc
	Internal standards	¹⁰⁶ Pd
	Cones	Xt
	Spray chamber	Quartz impact bead
Chamber temperature	3 °C	

2. Sample loading: once the column is ready, X mL of standard or sample (port 8) is dispensed toward the column (port 1) at a flow rate of 0.6 mL min⁻¹. V is deactivated (V-off, to waste).

3. Elimination of interferences: the CC is connected to port 3 to aspirate 1 mL of 2 mol L⁻¹ HNO₃ into the HC. Then it moves to port 1 and the HNO₃ is propelled towards the column at a flow rate of 2 mL min⁻¹. V is deactivated (V-off, to waste).
4. Elution of ⁹⁹Tc: 6 mL of 6.5 mol L⁻¹ HNO₃ (port 6) is loaded into the HC and V is activated (V-on) to propel the eluent (6 mL of 6.5 mol L⁻¹ HNO₃) through the column (port 1) at a flow rate of 2 mL min⁻¹ to the fraction collector.
5. Column rinse: in order to reduce the high acid concentration of the previous step, 5 mL of water is passed towards the column (port 1).
6. Change of sample: 1 ml of new sample (port 8) is aspirated and discarded toward waste (port 7), to eliminate the possible presence of previous sample.
7. Change of the resin: the column is regenerated by replacing the resin automatically. First, the old resin is loaded into the holding coil (HC) and sent to waste (port 7), then new resin is loaded into the HC from the resin reservoir (port 5) which contains a saturated solution of the resin and dispensed at port 1 with V-off (to waste) to fill the column. This step is only carried out when required depending on the sample matrix.

Table 2
Automated procedure for technetium separation and preconcentration.

Step	Flow rate (mL min ⁻¹)	LOV position	V
Conditioning of TEVA-Resin			
(a) Loading 2 mL of 0.1 mol L ⁻¹ HNO ₃ into HC	5	4	Off
(b) Rinsing 2 mL on the column	2	1	Off
Sample loading			
(a) Loading X mL sample into HC	5	8	Off
(b) Rinsing X mL on the column	0.6	1	Off
Elimination of interferences			
(a) Loading 1 mL of 2 mol L ⁻¹ HNO ₃ into HC	5	7	Off
(b) Rinsing on the column	2	1	Off
Elution of technetium			
(a) Loading 6 mL of 6.5 mol L ⁻¹ into HC	5	5	Off
(b) Rinsing on the column	2	1	On
Change of sample			
(a) Loading 1 mL of new sample into HC	5	8	Off
(b) Discarding 2 mL to the waste	5	3	Off
Beads replacing			
(a) Loading old beads into HC	5	1	Off
(b) Discarding old beads	5	3	Off
(c) Loading new beads into HC	5	2	Off
(d) Filling the column	2	1	Off

Prior to the detection by ICP-MS, the obtained eluates were evaporated almost to dryness at 80±5 °C. The remaining volume (around 1 mL) was dissolved with nitric acid at 2%, up to 25 mL.

3. Results and discussion

3.1. Flow system set-up

The developed system allows drastic reduction of reagents consumption and hence waste generation, reduction of resin consumption and time saving in relation to manual methodologies, whose operations can last days against an injection frequency of 0.3–5 injection h⁻¹, depending on the sample volume by this flow approach. Besides, the proposed LOV system is able to renew the solid phase extraction in a fully automated way, without requiring the analyst intervention,

resulting in higher intermediate precision and repeatability.

With the developed system described above, the isolation and preconcentration of ^{99}Tc are accomplished, removing interferents and other matrix components, ensuring the correct ^{99}Tc determination. The use of an ICP-MS as detector provides high sensitivity and good precision to determine long-lived natural and artificial radioisotopes at trace and ultra-trace levels in environmental samples, being an excellent tool for control in environmental radiological monitoring.

3.2. Optimal working conditions

In order to find the best operational conditions for the separation and preconcentration of ultra-trace levels of ^{99}Tc with the proposed LOV system, the optimization was performed using multivariate techniques. The optimization was carried out with the statistical software Statistica 7.0.

The optimal values of the factors that have significant influence in ^{99}Tc extraction using the TEVA resin were obtained by a response surface design [19]. The sample loading flow rate was fixed in 0.6 mL min^{-1} to ensure enough contact time between the sample and the resin. Significant factors studied were eluent volume (3–6 mL) and eluent concentration ($6\text{--}10 \text{ mol L}^{-1}$), using a face centered central composite design. A total of 11 experimental runs were conducted to optimize the experimental conditions, including central points. All experimental responses were statistically analyzed, showing satisfactory results (i.e. ANOVA table, adjust coefficient for 2-way interaction model, curvature, normal distribution of the residuals histogram and the fit between observed vs. predicted values). In this manner 6 mL of eluent and 6.5 mol L^{-1} of eluent concentration were found as critical

values, and these were used in further assays.

3.3. Column properties

TEVA-Resin provides high selectivity extracting technetium in form of pertechnetate in diluted nitric solutions, due to its active functional groups [17]. The active component of the TEVA-Resin, an aliphatic quaternary amine, works like a typical strong base anion exchange resin [20]. Pertechnetate ions are absorbed with a high efficiency at lower acid concentrations solutions, hence sample was prepared in 0.1 mol L⁻¹ nitric acid [21] ; [22].

Once the resin has been conditioned with nitric acid of the same concentration as the samples, the nitrate ion is bound to the quaternary amine and acts as a counter ion in the anionic interchange with the pertechnetate. The high retention of Tc (VII) on the TEVA resin at very low concentrations of nitric acid is due to the high selectivity of the quaternary ammonium salt to the pertechnetate anion over the acid anion [23].

So, the resin is contained in a syringe mounted as a bead reservoir in port 5 of the LOV with 0.1 mol L⁻¹ HNO₃ solution. Once the resin is charged on the column, on-line extraction and isolation of the ⁹⁹Tc are carried out automatically, ensuring high repeatability between replicates.

3.4. Analytical parameters

The fit statistics for a ⁹⁹Tc mass calibration curve (counts vs. mass in ng ⁹⁹Tc) were satisfactory ($y=1394.3\pm 19.2 x+14.8\pm 0.4$, $n=6$). Using the optimal conditions described above, the mass calibration curve is linear over the range 0.016–108 ng ⁹⁹Tc (Limit of quantification (LOQ)-maximum mass assayed).

The limit of detection was estimated from three times the standard deviation of 10 replicates of the blank divided by the slope of the calibration curve [24] ; [25], achieving a LOD of 0.005 ng for ^{99}Tc . This LOD, equivalent to $4.9 \times 10^{-8} \text{ mg L}^{-1}$ expressed as concentration, reaches the required limit of detection proposed by EPA for drinking water ($5.3 \times 10^{-6} \text{ mg L}^{-1}$) [26].

The proposed method can be applied to samples with a wide range of concentrations, since the sample volume can vary from 0.1 to 100 mL allowing the analysis of samples with ^{99}Tc content between 0.16 and $1.08 \times 10^6 \text{ ng L}^{-1}$. Thus, the ^{99}Tc maximum contaminant level for drinking water proposed by EPA ($5.3 \times 10^{-5} \text{ mg L}^{-1}$) [26] can be also easily measured. In order to quantify a sample with this concentration, a minimum volume of 0.35 mL is suggested.

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

Furthermore, as stated before the proposed LOV system is able to renew the solid phase extraction in a fully automated way, without requiring the analyst intervention, resulting in high intermediate precision and repeatability. The intermediate precision of the method, RSD 3.8%, was determined from results obtained on different working days, changing the packing of the resin column and using a solution which contained 40.6 ng of ^{99}Tc , so the resin replacement effect is

included in the given RSD. The repeatability of the method, RSD 2% ($n=10$), was determined from

Table 3
Analytical parameters of the proposed method.

Analytical parameters	
Detection limit	0.005 ng
Quantification limit	0.016 ng
Regression coefficient	0.9998
Repeatability ($n=10$)	2%
Intermediate precision ($n=5$)	3.8%
Resin durability	> 100 injections
Preconcentration volume	> 100 mL
Sensitivity	1394.3 counts ng^{-1}
Linear working range	0.016–108 ng
Injection throughput	0.3–5 h^{-1}

Results obtained in one working day, without changing the packing of the resin column and using a solution which contained 25.4 ng of ^{99}Tc .

Table 3 summarizes the analytical parameters of the proposed system.

3.5. Interferences

The interfering elements studied in this work were defined according to previous works for the ^{99}Tc measurement by ICP-MS [9] ; [27]. Main interferences are isobaric interferences from the stable isotope ^{99}Ru and the molecular ion $^{98}\text{Mo}^1\text{H}$ [10] ; [11]. Thus, for a standard solution of $1.08 \mu\text{g L}^{-1}$ of ^{99}Tc , the influence of Ru (up to 1:100, Tc:Ru) and Mo (up to 1:1000, Tc:Mo) on the analytical signal of ^{99}Tc was evaluated. Interferences were considered significant when these cause differences in the analytical signal greater than $\pm 10\%$.

Results showed no significant interference for Mo, while Ru caused interference above the relation 1:25. However, it should be taken into account that in

soil samples the Ru levels vary between 0.1 and 13 ng g⁻¹[28], existing a low possibility of Ru interference with the levels of Tc encountered in these kind of environmental sample. Furthermore, no interference was found when analyzing natural environmental samples.

3.6. Application to environmental samples

The developed method was evaluated by analyzing different water matrices and a soil sample. Results of ⁹⁹Tc analysis for three replicates by ICP-MS are shown in Table 4. Water samples were analyzed adding a known concentration of ⁹⁹Tc (4.1 ng L⁻¹). Results reveal a satisfactory recovery, ranging from 94% to 98% in all cases. A soil sample was also analyzed using technetium standard addition (4.3 ng L⁻¹), obtaining a recovery of 98%.

Table 4
Analysis of environmental samples by ICP-MS.

Sample	Added ⁹⁹ Tc (ng L ⁻¹)	Found ⁹⁹ Tc (ng L ⁻¹)	Recovery (%)
Dam water	0	< LOD	
	4.09	3.83 ± 0.06	94
Tap water	0	< LOD	
	4.09	3.87 ± 0.02	95
Mineral water	0	< LOD	
	4.09	3.89 ± 0.05	95
Well water	0	< LOD	
	4.09	4.00 ± 0.12	98
Soil	0	< LOD	
	4.3	4.1 ± 0.2	96

Results are expressed as the mean value ± standard deviation ($n=3$). Samples were prepared in nitric acid 0.1 mol L⁻¹. LOD=0.05 ng L⁻¹. 100 mL of water samples was analyzed.

Table 5
Comparison with previous works based on sample pretreatment with SPE (TEVA-Resin).

Analytical procedure	Sample	Sample size	Analytical steps	Analytical sample time (h)	SPE: TEVA Resin ^a			LOD (ng L ⁻¹)	Ref.
					Resin used (g)	Durability	HNO ₃ per sample (g)		
Manual	Seaweed	10 g	13	25	0.3	10	7.7	2	[29]
Manual	Water	50–300 mL	13	23	0.7	4	10.7	0.8	[9]
Automated by FIA	Soil	3–6 g	5	^b 3–5.5	0.322	–	4.8	0.085	[30]
Automated by FIA	Ground water	250 mL	2	1.5	1.4	–	16.5	0.2	[31]
Automated by LOV	Soil	0.5 g	5	5.5	0.032	> 100	2.6	0.05	This work
Automated by LOV	Environmental water	0.1–100 mL	2	^b 2.2–5	0.032	> 100	2.6	0.05	This work

^a TEVA-Resin by Triskem International, France.

^b Depending on sample volume.

3.7. Comparison with manual methods and automated systems based on flow analysis

In order to highlight the benefits of the proposed method, we critically compare our work with those exploiting solid phase extraction in particular using TEVA-Resin and ICP-MS detection, including both manual and flow based methodologies.

In [Table 5](#) can be seen the elevated number of analytical steps used in manual methods, which are drastically reduced in automated approaches. On the one hand, for soil samples the analytical steps include microwave digestion, extraction and dilution to low acid concentration for the ⁹⁹Tc detection in the ICP-MS. On the other hand, for water samples only the steps regarding extraction of the analyte up to its detection are included. Thus, manual methods require about one day of work, while with automated methods based on flow analysis, this time can be reduced to 2–5 h. In addition, the consumption of reagents and sample substantially

decreases in automated methods, resulting in considerable savings (up to 3 times less sample volume and up to 4 times less reagent consumption).

The comparison between FIA approaches and our work shows that FIA methods have a higher consumption of sample and reagents due to their continuous operation mode. Contrarily, the proposed system allows a drastic reduction of reagents consumption (up to 7 times less) and so waste generation, and also a decrease of the resin consumption (up to 44 times less). In addition, the resin can be reused up to 100 injections. Furthermore the LOV technique allows the fully automated column replacement. Another drawback of FIA systems is the need of a more frequent recalibration because of the aging of Tygon tubing.

Finally, the reached detection limit is up to 40 times lower than those obtained in previous manual methods and up to 16 times lower than those obtained in previous FIA methods.

4. Conclusions

An automated LOV method for extraction and preconcentration of ^{99}Tc prior ICP-MS detection has been developed. The proposed procedure was successfully applied to the determination of trace levels of ^{99}Tc in soil and water samples, achieving the reference levels established by the EPA for drinking water.

Main features of the developed method are the fully automation of the isolation/preconcentration procedure, including the on-line replacement of the column; the improved LOD respect to previous works; the drastic shortening of analysis time; and the reduced sample and reagents consumption. Furthermore, the long durability (more than 100 times) of such small amount of resin (0.032 g)

contributes to reduce the cost per analysis. In addition, with the proposed automated system ICP-MS limitations to analyze ^{99}Tc are overcome, enlarging the good performance of the ICP-MS and improving its selectivity and sensitivity.

Moreover, the proposed method offers accuracy, high precision and improvement of the analyst safety, which is of high relevance when manipulating radioactive isotopes. All these characteristics make of the present LOV-system a useful tool for ^{99}Tc environmental monitoring, allowing rapid responses.

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