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Solid phase extraction – Multisyringe flow injection system for the spectrophotometric determination of selenium with 2,3-diaminonaphthalene

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ABSTRACT

In the present work, a solid phase extraction (SPE) is hyphenated with an automatic MSFIA system to improve the selenite determination based on the reaction of selenite with aromatic o-diamines (such as 2,3-diaminonaphthalene (DAN)) to form the piazselenol complex. This reaction is greatly influenced by acid concentration, temperature, the time needed for colour development, and presence of foreign ions. For these reasons a thermostatic bath, glycine, and Na_2-EDTA are used as heater, buffer, and masking agent, respectively. The principle of the determination is based on the sorption of the piazselenol onto a C_{18} membrane disk, followed by its elution by acetonitrile. The piazselenol can then be detected by absorptiometry or fluorometry, both detection techniques being tested in our system. The best detection limit (1.7 $\mu g\,L^{-1}$) and RSD (3.04%) are obtained by absorptiometry at 380 nm. Environmental samples were spiked and analyzed, with recoveries close to 100%.

1. Introduction

Selenium is an essential element for human and animals health. Humans require selenium for the function of a number of selenium dependent enzymes, that so-called selenoproteins which are antioxidant enzymes. Selenium deficiency has been associated with impaired immune system of the iodine metabolism [1]. The biological function of selenium shows a dual character because the selenium content range between toxic and deficient concentration in animals is rather narrow [2]. Due to this double role of selenium, during the last years, several methodologies have been developed to analyze it in different kinds of samples [3–5].

Spectrometric techniques, such as atomic absorption and atomic fluorescence, are the most widely used detection ones to selenium analyses. These techniques are based on the hydride generation to obtain a high selectivity and sensitivity [6,7]. The main disadvantages of these techniques are the complexity and the instrumental costs [8].

Both absorptiometry and fluorometry are very attractive alternatives, because they are cheaper, easier to operate, and can be used in the construction of portable analyzer. The 2,3-diaminonaphthalene (DAN) reacts with selenite and permits the determination of selenite at trace amounts [9]. The 4,5-benzopiazselenol formed in the reaction of selenium with DAN can be detected by absorptiometry or fluorometry.

Flow techniques improve routine analysis, since they provide precise, accurate and rapid measurements with minimal sample handling. Furthermore, sample volume and reagent consumption are decreased with regard to batch methods. Multisyringe flow injection analysis (MSFIA) combines the multi-channel operation and high injection throughput of FIA with the robustness and the versatility of SIA [10].

Worth special note among recent trends in SPE is the use of membrane disks, which afford greater processing expeditiousness and reduces clogging by suspended particles and matrix components; also, due to a lower void volume and a higher surface area associated with small particles, as compared to resin packaged into cartridges, partitioning of the analytes is favoured and channelling is minimized [11]. Moreover, unlike conventional resins, SPE disks can be easily used by unskilled operators [12].

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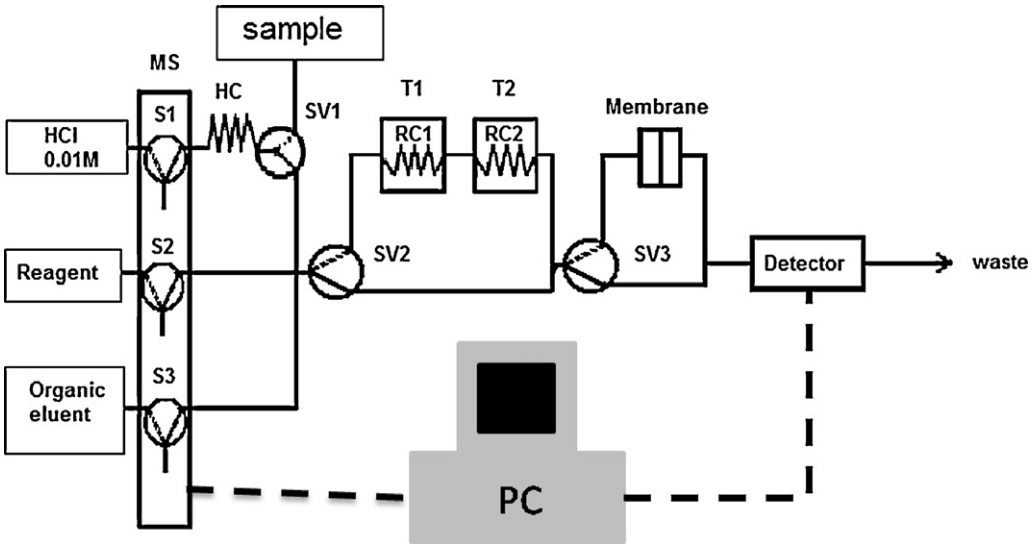

Fig. 1. MS (multisyringe), S (syringe solenoid) valve, SV (additional solenoid valve), HC (holding coil), T (thermostatic bath; T1 = 80 °C, T2 = 20 °C).

In the present work a multisyringe system is combined with the use of a membrane disk to improve the selenite determination with DAN.

2. Experimental

2.1. Reagents

The reagent solution was prepared by dissolving 50 mg of DAN in 20 mL of 0.25 M HCl. Then 10 mL of a solution containing 0.1 g of hydroxylamine and 0.05 g of Na_2-EDTA was merged with the reagent solution. Finally, 5 mL of 0.5 M glycine solution was added. The resulting solution was diluted to a final volume of 50 mL. This solution was extracted three times with 5 mL of cyclohexane to remove impurities. After the last extraction, the solution was filtered through a paper filter, thus obtaining a transparent solution. A 0.01 M HCl solution was employed as a carrier. All solutions were prepared with ultrapure water from Millipore equipment.

Organic solvents (methanol, ethanol, acetonitrile, and cyclohexane) HPLC reagent grade were purchased from Scharlau (Sentmenat, Barcelona, Spain). DAN was purchased from Acros (New Jersey, USA). HCl 37% puriss. p.a., was purchased from Riedel-de Haën (Sigma–Aldrich, Seelze, Germany). Glycine and ethylenediaminetetraacetic disodium salt (Na_2-EDTA) were purchased from Scharlau (Sentmenat, Barcelona, Spain), both being reagent grade, ACS quality. Hydroxylamine 99% was purchased from Carlo Erba (Milano, Italy).

Two kinds of 3 M Empore membrane disks (C_{18} and SDB-XC) were tested to preconcentrate the piazselenol complex. The C_{18} membrane disk was constituted by a silica sorbents where octadecyl groups had been grafted to provide non-polar interactions, while SDB-XC was a poly(styrenedivinylbenzene) copolymer, embedded in a PTFE filter disk, with a high hydrophobic character and no ion-exchange capacity [13]. In addition to the hydrophobic interaction that also occurs with C_{18}-silica, such sorbents allow π–π interactions with aromatic analytes. Bare C_{18}-silica can retain a fraction of inorganic trace elements, probably due to the presence of silanol groups on its surface. However, in practice, due to its hydrophobic character, C_{18}-silica is not well suited for retention of trace element species, as the latter are often polar or ionic. Retention on C_{18}-silica may be improved by the addition of a ligand reagent to the sample before its percolation through the sorbent [14]. In our case, we have chosen to improve selectivity of these supports by using them as extraction supports of benzopiazselenol for selenite determination.

A stock solution containing 1000 mg L^{-1} selenium (IV) was prepared from Na_2SeO_3 according to standard methods (APHA–AWWA–WPCF). A 10 mg L^{-1} stock solution was weakly prepared. Working standard solutions were daily prepared by appropriate dilution of this stock solution.

2.2. Apparatus

In the present system the main device is a multisyringe burette module with programmable speed (Multiburette 4S, Crison, Alella, Barcelona). It allows the simultaneous movement of four syringes (analogous to those used in SIA assemblies), which are connected to an iron rod moved by a stepper motor. Three-way isolation valves are placed on the head of each syringe with the aim of increasing the versatility of the technique and reducing reagent consumption.

In the proposed system (Fig. 1), only three syringes were used S1 (5 mL), S2 (1 mL), and S3 (5 mL). The multisyringe was equipped with three additional independent solenoid valves (SV) (Takasago Electric, Nagoya, Japan). Valve SV1 is connected to syringe S1 with a sample coil, which is used for sample pick up. In its normally closed position (NC), it is connected to the sample input, and in its normally open position (NO) to the manifold. Valve SV2 in its NO position is connected to a reaction coil, and its NC position is connected to a bypass reaction coil in order to facilitate injection of carrier and the eluting solutions while avoiding passage through the thermostatic bath. Finally, valve SV3 in its NO position is connected to the extracting membrane; this affording a higher operating pressure than its NC position, where it is connected to the membrane bypass.

The manifold was constructed using 0.8 mm of i.d. PTFE tube. For holding coil, sample and reagents pick up a PTFE tube of 1.5 mm of i.d. was used in order to allow a faster liquid pick up than a 0.8 mm of i.d. tube.

To control temperature of the reaction coil a thermostatic bath from Bioblock scientific model Polystat 86633 was employed.

A four channels connector was used to join the three syringes with. Two additional T connectors were employed to join reaction coil and membrane with its respective bypass. All these connectors were made from Delrine plastic, which resists to organic solvents better than typical methacrylate connectors.

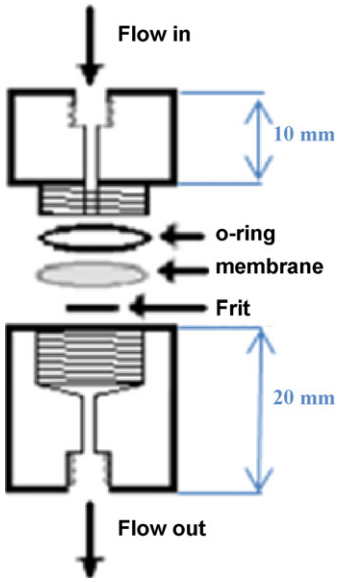

Fig. 2. Membrane disk holder.

The device containing the membrane (Fig. 2) consisted of two Delrine cylinders (SCIWARE, Palma de Mallorca, Spain). The membrane was placed in a 8 mm i.d. gap as can be seen in Fig. 1. This gap has a conical section where a polyethylene frit with an average pore diameter of 10 μm may be attached in order to avoid distortion of the membrane. A membrane of 8 mm i.d. was used in this device.

An USB2000 Ocean Optics spectrophotometer was used as a photometric detector. An UV–VIS–NIR light source DH-2000 from Mikropack was employed. An optical fibre with a 450 μm core diameter (Ocean Optics model QP450-1-XSR) was used to connect light source with spectrophotometer. A LS-55 PerkinElmer spectrofluorimeter was used for the fluorometric detection of the piazselenol complex. System control, data acquisition and processing were performed using the Autoanalysis 5.0 software package [15] (Sciware, Palma de Mallorca, Spain).

2.3. Procedure

In our system the sample is picked up in the holding coil HC through SV1. Then the sample slug and reagent are merged just before SV2. The mixture is impelled throughout the reaction coil (RC1 and RC2) at 1.5 mL min^{-1}. This reaction coil RC1 is submerged in a thermostatic bath at 80 °C in order to increase the reaction yield and decrease the reaction time. A cold bath is employed to cold down the solution. The use of the cold bath T2 allows obtaining a better RSD, and to increase the life time of the extracting membrane. The reaction coil output is connected to SV3, which allows the mixture to flow through the extracting membrane or to a bypass. When mixture flows through the membrane, the piazselenol complex is retained, while the reagent excess flows freely through it with negligible retention. Then 2.5 mL of carrier solution is dispensed to the reaction coil at 1.5 mL min^{-1} to ensure that all mixture flows through the membrane. After this, 0.5 mL of carrier is dispensed to the reaction coil bypass to let the membrane to cool, avoiding the membrane to be in contact with hot solutions. Then 0.5 mL of acetonitrile is dispensed at 4 mL min^{-1} in the same way. 1.5 mL of carrier is delivered to the system to propel the acetonitrile slug to detector, where its absorbance or fluorescence signal is quantified by a photometer or fluorimeter detector, respectively. The membrane is thus ready for next injection. After this SV2 and SV3 are switched to reaction coil and membrane bypass, respectively. A 0.25 mL slug of acetonitrile is propelled by carrier at 8 mL min^{-1} to remove any small amount of Se–DAN complex remaining in the reaction coil.

3. Results and discussion

A multisyringe burette can support relative higher backpressure than the peristaltic pumps and solenoid micropumps. It also combines the multi-channel operation and high injection throughput of a FIA system. For these reasons, a multisyringe was selected as a liquid driver to carry out the preconcentration onto the membrane disk. A 1 mL syringe was selected to dispense reagent solution, thus the dilution of sample in large volume of reagent is avoided.

The piazselenol can be retained by membrane disk such as C_{18}, and SDB-XC. Then it can be eluted by organic solvents, such as acetonitrile, methanol, or cyclohexane. Organic solvents enhance the fluorescence signal of piazselenol in aqueous medium due to changes in viscosity and micropolarity. In this way, water quenching is minimized [16]. Therefore, both fluorescence and absorbance signal can be measured in organic phases.

3.1. Study of piazselenol reaction

The mechanism and kinetics of the reaction between selenium and DAN were widely studied in 1960s [17]. The reaction is greatly influenced by pH, temperature, time needed for colour development and presence of foreign ions. In the literature, the best pH range for the reaction in an aqueous medium lies between 1.8 and 2.0 [9,17,18]. Fluctuations of pH may occur as a result of incubation temperature and time variation. The pH 2.0 was buffered preparing the DAN solution with glycine 0.05 M. In order to avoid the oxidation of DAN and the interference of foreign ions, 0.1 g of hydroxylamine and 0.05 g Na_2-EDTA were added to each 50 mL of DAN solution. Higher concentrations of Na_2-EDTA produce a white precipitate several hours after solution preparation.

Heating reduces the time of reaction, but working at temperatures close to 100 °C produces bubbles in flow system. High

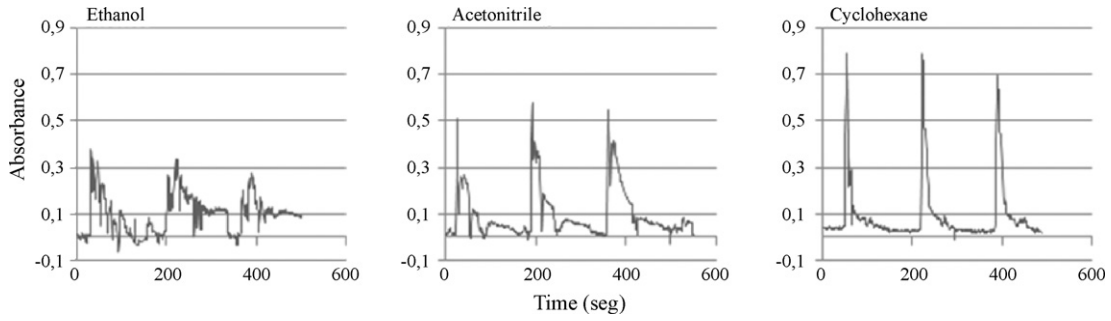

Fig. 3. Obtained signals from 1 mL of standard solution containing 1 mg L^{-1} Se(IV) was reacted with DAN and preconcentrated onto the C_{18} membrane. The piazselenol was eluted by 2 mL of different organic solvents at 2 mL min^{-1}.

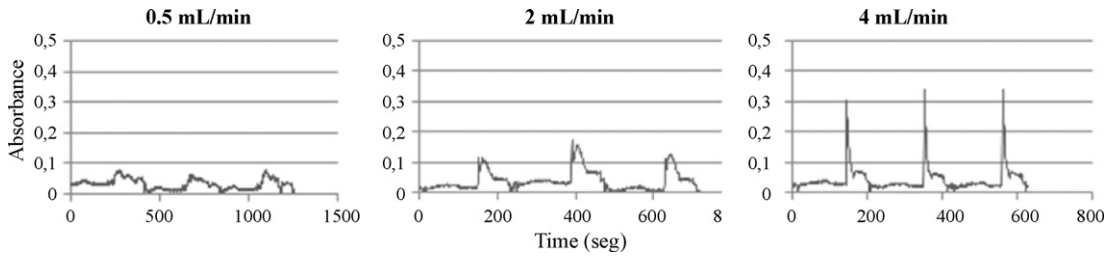

Fig. 4. Obtained signals from 1 mL of standard solution containing 0.25 mg L^{-1} Se(IV) was reacted with DAN and preconcentrated onto the C_{18} membrane. The piazselenol was eluted by 2 mL of acetonitrile at different flow rates.

temperatures provide a shorter reaction time but also a faster degradation of reaction product. A temperature of 80 °C was tested and good signal and reproducibility were obtained. Thus 80 °C was selected for further experiences.

The influence of the reagent concentration onto the signal intensity of 1 mg L^{-1} of Se(IV) was evaluated for concentrations of DAN varying between 0.01 and 0.1% (m v^{-1}). In order to ensure an excess of reagent to obtain a high reaction yield and a short reaction time, 0.1% of DAN was selected for further experiments.

The reaction time is one of the most important parameters to obtain a high analytical signal. In a first approach, stopped flow experiments were made in the reaction coil in order to determine the optimal reaction time. For this purpose, 1 mL of 1 mg L^{-1} of Se(IV) was merged with 0.2 mL of 0.1% DAN inside the reaction coil of 1.5 mL of volume. Then the flow was stopped during warm-up times varying between 25 and 500 s. An increase of the signal was observed up to 100 s. For longer times the signal remains constant. For this approach a large reaction coil volume was needed for larger sample volume, as a consequence a large carrier volume was needed to clean it and therefore the waste generation increased.

In flow experiments, the warm-up time depends on the flow rate and the length of reaction coil. A reaction coil of 1.5 mL was used to test the influence of flow rate on the signal intensity. This effect in reaction coil was studied between 0.3 and 2 mL min^{-1} for 1 mg L^{-1} Se(IV). This was equivalent to warm-up times between 300 to 45 s, respectively. From 0.3 to 1.5 mL min^{-1} any significant decrease of signal was observed, and 1.5 mL min^{-1} was selected. A flow rate of 1.5 mL min^{-1} is equivalent to a warm-up time of 60 s, which is lower than suitable value obtained in stopped flow experiences.

The sample volume was evaluated from 2 to 12 mL. When the sample volume was increased the signal height increased too. For larger sample volumes, a worse RSD was obtained and injection throughput was reduced. As a compromise between sensitivity and injection throughput, 4 mL of sample was selected for further experiences.

3.2. Study of the solid phase extraction step

The piazselenol complex preconcentration was tested onto SDB-XC and C_{18} membrane disks. For this purpose 1 mL of 1 mg L^{-1} Se(IV) was reacted with DAN solution and the complex was preconcentrated onto the membrane.

SDB-XC is a poly(styrenedivinylbenzene) copolymer used as a reversed phase sorbent for solid phase extraction. SDB-XC is not bonded to silica, like C_{18}, but it is a 100% cross-linked porous copolymeric particle with spherical shape. It does not exhibit the secondary cationic (silanol) interactions and pH limitations common to bonded silica sorbents, which shows pH stability in the range from 2 to 12. So SDB-XC offers more predictable and reproducible reversed phase interaction. However the pore size of C_{18} is lower (60 Å) than SDB-XC (80 Å).

It was observed that C_{18} membrane allows a better separation between the reagent (DAN) and the reaction product (4,5-benzopiazselenol); whereas polymeric membrane (SDB-XC) retains a little amount of reagent that produces a higher blank signal. For this reason the C_{18} membrane disk was selected for further experiences.

Different organic solvents, such as methanol, ethanol, acetonitrile, and cyclohexane were tested to elute the piazselenol complex (Fig. 3). When absolute methanol and ethanol are merged with water into the system, bubbles formation was observed. In order to avoid this drawback, 80% (v v^{-1}) methanol and ethanol were used. Ethanol elutes piazselenol better than methanol, but ethanol produces high blank signal due to the change in the refraction index. Cyclohexane is proposed by standard methods (APHA–AWWA–WPCF) for the piazselenol extraction. A very good elution of Se–DAN complex was obtained using 0.3 mL of cyclohexane. But after 10 or 12 injections a higher backpressure was observed when carrier was injected through the membrane. In order to minimize this effect, a fourth syringe was added to dispense ethanol through the membrane to elute the retained cyclohexane. Since larger volumes of ethanol were required, the injection throughput was reduced and waste generation volume increased.

Acetonitrile has proven to be the best option to elute the piazselenol complex, since it is soluble in water, and avoid the need of a fourth syringe. Furthermore, it does not produce bubbles or changes of refraction index when it is mixed with water.

The elution flow rate was tested between 0.5 and 6 mL min^{-1}, as a function of shape and signal intensity of the detected peaks (Fig. 4). For flow rates lower than 2 mL min^{-1}, the signal height of benzopiazselenol was low, and a broaden peak was obtained. For flow rates between 2 and 4 mL min^{-1}, the shape of the peak was modified with the appearance of an artefact: two peaks were obtained (one being high and thin and the other being low and large). Beyond 4 mL min^{-1}, the signal presented only one peak and for higher flow rates, the residence time in the detection cell was reduced and a worse reproducibility was obtained. Therefore, 4 mL min^{-1} was selected as the best compromise for elution flow rate.

The effect of the eluent volume onto the signal was also tested. For this purpose 4 mL of 1 mg L^{-1} Se(IV) was preconcentrated onto the membrane and was eluted by acetonitrile between 0.1 and 2 mL. For lower volumes than 0.5 mL the elution was incomplete, and for higher volume than 0.5 mL the signal remains constant. Thus 0.5 mL was selected as the suitable volume.

3.3. Analytical figures of merit

The analytical parameters of the proposed method were determined under previously established optimum operating conditions. Absorptiometry and fluorometry were compared as detection technique for the piazselenol complex. The absorbance of piazselenol in an acetonitrile slug was quantified at 380 nm. A wavelength of 400 nm was chosen as the reference wavelength, because the complex do not absorb at this wavelength.

Table 1
Analytical figures of merit of the proposed methods.

Detection technique	Absorptiometry	Fluorometry
Slope	0.734	1057.97
Intercept	0.051	104.81
r^2	0.9995	0.9998
Blank signal	0.044 ± 0.005	82.48 ± 10.46
RSD (%)	3.04	5.61
LOD ($\mu g\,L^{-1}$)	1.7	29.6
Injection throughput ($inj\,h^{-1}$)	8	8
Linear range ($\mu g\,L^{-1}$)	5.7–1290	10–850

The fluorimetric detection of the piazselenol was carried out at $\lambda_{excitation} = 378$ nm and $\lambda_{emission} = 595$ nm, with 5:20 slits configuration. Table 1 shows the results obtained.

The limit of detection (LOD) was calculated as three times the standard deviation of 10 blank lectures divided by the slope of the calibration curve ($3\sigma\ S^{-1}$). The relative standard deviation (RSD) was evaluated from 10 successive injections of a solution containing 0.5 mg L^{-1} of Se(IV). A preconcentration factor of 13.8 was obtained. The preconcentration factor was calculated comparing the peak heights with and without preconcentration of 4 mL of 1 mg L^{-1} solution of Se(IV).

Usually, fluorometry is more sensitive than absorptiometry. But in our case, fluorometry showed a worse reproducibility probably due to quenching effects of little amounts of water. Therefore, and in order to validate the method, absorptiometry was selected since it showed better results in terms of RSD and detection limits.

3.4. Interferences

The effect of the presence of most common anions in water such as nitrates, sulphates, chlorides and phosphates were tested. Concentrations up to 500 mg L^{-1} of these anions had no effect on the detection of 0.5 mg L^{-1} Se(IV). Nitrites produced a positive interference, being its highest tolerable amount of 15 $\mu g\,L^{-1}$. The nitrite interferences can be avoided by weakly boiling of sample for 2 min.

A number of cations such as Ca^{2+}, Na^{+}, K^{+} and Mg^{2+} were also tested, and no interfering effect was observed for concentrations up to 500 mg L^{-1}. The reaction between copper and DAN produced a positive interference, while Fe^{2+} has reduced DAN, preventing the reaction with Se(IV). Both interferences were avoided by adding EDTA. The maximum tolerated concentrations of Cu^{2+} and Fe^{2+} were 50 and 10 mg L^{-1}, respectively.

3.5. Validation of the proposed method and environmental samples analysis

Our SPE–MSFIA system was compared versus the standard method 3500-Se D (APHA–AWWA–WPCF method for selenium determination with DAN by absorptiometry). For this purpose, a freshwater sample was analyzed. Since the content of selenium in this sample was under the detection limit of both techniques, it was spiked with 30 $\mu g\,L^{-1}$ Se(IV). Results were $32.9 \pm 6.9\ \mu g\,L^{-1}$ Se(IV) for the standard method, and $34.3 \pm 1.5\ \mu g\,L^{-1}$ Se(IV) for the new proposed SPE–MSFIA system.

Table 2 shows the analytical figures of merits of both methods. The main disadvantage of standard method is the evaporation of cyclohexane. Cyclohexane vapors are toxic for humans. With the SPE–MSFIA system this trouble is avoided, because all the procedure is being carried out inside the manifold. From this point of view SPE–MSFIA system is healthier for workers.

In order to test the usefulness of our SPE–MSFIA system, tap water and seawater were analyzed. As both samples were under the detection limit, they were spiked with 0.1 mg L^{-1} Se(IV) and analyzed again. The percentages of recovery were 104.5 and 95.2% for tap water and seawater, respectively.

Table 2
SPE–MSFIA system versus the 3500-Se D standard method (APHA–AWWA–WPCF).

Parameter	Standard method	SPE–MSFIA system
Sample volume (mL)	10	4
Thermostatic bath temperature (°C)	50	80
Heating time (min)	30	4
Organic phases	Cyclohexane	Acetonitrile
Organic phase volume (mL)	2	0.5
Detection limit ($\mu g\,L^{-1}$)	10	1.7
DAN consumption ($mg\,sample^{-1}$)	5	0.8
Na_2-EDTA consumption ($mg\,sample^{-1}$)	18	0.8
Hydroxylamine consumption ($mg\,sample^{-1}$)	50	1.6

4. Conclusions

An automatic SPE–MSFIA system was developed successfully. The C_{18} membrane disk allows a better separation between DAN and the piazselenol than poly(styrenedivinylbenzene) copolymer disk. Acetonitrile is the best eluent option because it is soluble in water and no refraction index changes were observed. C_{18} membrane disks required a flow rate beyond 4 mL min^{-1} to obtain a good elution of Se–DAN complex. Due to a better RSD, absorptiometry was selected as the detection technique. The SPE–MSFIA system is applied to spiked environmental samples with recoveries close to 100%.

In comparison with standard methods 3500-Se D (APHA–AWWA–WPCF), the developed system allows better detection limit and standard deviation, lower sample handling, lower sample and reagent consumption, and it is healthier for workers because organics solvent evaporation is avoided.

Although the proposed system does not show the same sensibility and selectivity than HG-AAS or HG-AFS, the detection limit of the new SPE–MSFIA system is under the maximum amount of selenite allowed in drinking waters. Moreover the proposed system is cheaper and easier to operate than others mentioned above. In addition it can also be used to develop portable analyzers.

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