Gas chromatography with atomic emission detection for dimethylselenide and dimethyldiselenide determination in waters and plant materials using a purge-and-trap preconcentration system

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Abstract

Dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) were determined in plant and water samples by capillary gas chromatography using microwave induced-plasma atomic emission spectrometry for detection. The analytes were leached from the solid samples into methanol by using an ultrasonic probe, and a portion of the extract was preconcentrated by means of a purge-and-trap system before being chromatographed. The analytes were directly purged from the water samples in the presence of 6% (v/v) methanol. Element-specific detection and quantification was carried out by monitoring the selenium (196 nm) emission line. Calibration curves were obtained by plotting peak area versus concentration and the correlation coefficients for linear calibration were 0.9999 for both analytes. Detection limits of 0.8 and 1.1 ng l^{-1} were obtained for DMSe and DMDSe, respectively, for water samples. For plant materials, the detection limits calculated for 0.5 g samples were 0.3 and 0.4 ng g^{-1} for DMSe and DMDSe, respectively. Concentration levels of DMSe ranging from 1.2 to 4.2 ng g^{-1} were found in some of the plant materials analyzed. No DMDSe was found in any of the samples. The accuracy of the method was checked by analyzing different spiked water and plant samples.
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1. Introduction

The growth of certain industrial sectors has increased the release of selenium into the environment. Also, organoselenium compounds are used as herbicides, fungicides, and bactericides in agriculture. Moreover, these volatile compounds are produced by biomethylation processes of inorganic selenium as well as from the conversion of selenocystine and selenomethionine by various organisms. These biological processes constitute the major mechanism for selenium detoxification [1]. This work focus on dimethylselenide and dimethyldiselenide determination, which are the most abundant organic species in environmental and biological samples [2].

The speciation of selenium has been reviewed by various authors [2–7]. The volatility of DMSe and DMDSe makes gas chromatography a frequently used technique for their determination. The bibliography reports a wide variety of detection methods used after GC separation, such as mass spectrometry (MS) [8–11], inductively coupled plasma mass spectrometry (ICP-MS) [11–15], atomic absorption spectrometry (AAS) [16,17], atomic fluorescence spectrometry (AFS) [18,19], flame photometric detection (FPD) [17] and photoionization detection (PID) [20]. Microwave-induced plasma with atomic emission spectrometry (MIP-AES) is an established tool for element-specific detection, which has also been used for the purpose here presented [7,19,21–25]. Selectivity and sensitivity are major advantages of this

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detection system, MIP-AED is even more sensitive than ICP-MS and AFS [19].

The literature reports different preconcentration techniques for DMSe and DMDSe before GC separation. The most common approach involves cryogenic trapping followed by thermal desorption [12,13,15,17,21,23,24], although solid-phase extraction (SPE) [9] and solid-phase microextraction (SPME) have also been used [11,14,19,25]. Purge-and-trap (PT) preconcentration has been proposed for the determination of volatile organoselenium compounds [17,21,22,24] in water samples, but all the procedures reported are based on cold trapping. However, the procedure discussed here yields very good detection limits without the need of a cryogenic module. No previous reports describing the use of PT for the preconcentration of DMSe and DMDSe in plant materials have been found. The data and discussion here given show that by combining an ultrasounds-assisted leaching process [26] and a PT device, a sensitive, reliable procedure for the extraction and measurement of these organoselenium compounds results.

2. Experimental

2.1. Instrumentation

The volatile selenium compounds were injected into the capillary column by means of a purge-and-trap sample enrichment system (Tekmar Dohrmann 3100 model, Agilent) which was controlled by Teklink (2.02 Version). The purging vessel was a 5 ml glass U-tube with frit sparger 0.5 in. top fit, which was thermostated at 35 °C using a lab-made system. A typical PT operating process was applied, including the three main steps: sample purging, analyte desorption and baking. Analytes were purged by passing a helium-flow of 40 ml min^{-1} for 6 min through the aqueous solution which was maintained at 35 °C. During the purging step the analytes were trapped on a column (30.5 cm × 0.312 cm o.d. × 0.259 cm i.d.) coated with Tenax GC, silica gel and activated carbon, maintained at a temperature of 40 °C. Once concentrated, the volatile selenium compounds were desorbed by heating the trap to 210 °C and opening the valves for 3.5 min. The trap was finally cleaned at 230 °C for 10 min. The PT system was directly coupled to the gas chromatograph in a direct split interface (DSI) configuration, set a 250 °C to avoid analyte condensation during analysis. The end of the transfer line was directly inserted into the split injector of the GC.

Gas chromatography was carried out using an Agilent 6890 gas chromatograph directly coupled by a transfer line to a G2350A microwave-induced plasma atomic emission detector (Agilent, Waldbronn, Germany). Updated G2070AA ChemStation application with the G2360AA GC-AED software was used to control and automate many features on the GC and AED systems. The injection temperature was set at 250 °C, in the split mode (ratio 4:1). Peak

Table 1
Experimental conditions of the PT-GC-AED system

PT conditions	Sample volume	5 ml
	Gas flow	40 ml min^{-1} He
	Purge vessel	35 °C
	Purge cycle	6 min at 40 °C
	Desorb cycle	3.5 min at 210 °C (preheat 200 °C)
	Cleaning cycle	10 min at 230 °C
	Trapping material	Tenax-silica gel/charcoal
GC conditions	Injection port	250 °C, split ratio (4:1)
	Capillary column	DB-624 (30 m × 0.32 mm i.d. × 1.8 μm)
	Carrier gas	Helium, 4 ml min^{-1}
	Oven program	40 °C (2 min) 150 °C at 20 °C min^{-1} (0.5 min)
GC-AED interface parameters	Transfer line	DB-624
	Transfer line temperature	250 °C
AED conditions	Reagent gas	H$_2$ at 10 psi
	Spectrometer purge flow	Nitrogen, 2.5 l min^{-1}
	Helium make-up flow	60 ml min^{-1}
	Cavity temperature	250 °C
	Se wavelength	196.018 nm
	Solvent vent-off time	0–3 min

separation was achieved on a 30 m × 0.32 mm i.d. DB-624 capillary column from Agilent with a 1.8 μm film thickness. A 30 m × 0.32 mm i.d. HP-5, 5% phenylmethylpolysiloxane (0.17 μm film thickness) and a 25 m × 0.32 mm i.d. HP-1, 100% dimethylpolysiloxane (0.25 μm film thickness) capillary columns were also tested. The experimental conditions for the chromatographic separation and the detection system are summarized in Table 1. Filter and backamount (base-line correction parameter) adjustment in the AED were set according to Agilent default specifications. Each chromatographic run took 13 min including the purging time. Retention times were 3.37 and 6.07 min for DMSe and DMDSe, respectively.

An ultrasonic probe processor UP 200H with an effective output of 150 W in liquid media (Dr. Hielscher, Germany) was used for leaching of the analytes from the plant matrices.

2.2. Chemicals

Dimethylselenide [(CH$_3$)$_2$Se, DMSe; 99% purity] and dimethyldiselenide [(CH$_3$)$_2$Se$_2$, DMDSe; 98% purity] were obtained from Fluka (Buchs, Switzerland) and Aldrich (Steinhem, Germany), respectively. Stock solutions of the organoselenium species of 2000 mg l^{-1} were prepared by appropriate dilution with hexane and stored at 4 °C. Lower concentration stock solutions (20 mg l^{-1}) were prepared daily in methanol and were stored in the refrigerator. Working standard solutions were prepared immediately before use by diluting the methanolic standards with water obtained from a Milli-Q water purification system (Millipore, Bedford, MA,

USA). Analytical-reagent grade hexane and methanol were purchased from Lab-Scan (Dublin, Ireland). Gases (helium, nitrogen and hydrogen) were supplied by Air Liquid (Madrid, Spain).

It should be noted that DMSe and DMDSe have the following risk (R) [27] and safety (S) [28] notes: R23/25-33-50;S20/21-28-45-60-61, and should be handled with the appropriate caution.

2.3. Samples

Some of the plant samples were collected directly in irrigated and cultivated gardens and others were obtained from a local supermarket. These samples were washed repeatedly with pure water and manually crushed by using an agate mortar. Crushed samples were stored in the dark at 4 °C in polycarbonate flasks that were tightly closed with a screw cap until analysis. A total of 21 natural water samples of different origin (sea, river, lake and tap) were obtained in the Southeast of Spain. Two hundred-milliliter volumes of water were collected in polycarbonate flasks and care was taken to ensure that all the recipients were completely filled with the samples to avoid the presence of a gaseous phase. Samples were stored in the dark at 4 °C until analysis. No filtration was performed on the water samples, minimising the sample handling [18]. Samples were normally analyzed within 48 h of arrival at the laboratory. All the flasks were previously washed using a 1% (v/v) nitric acid solution and rinsed carefully with pure water. Laboratory tests showed no residual contamination in the flasks and no adsorption on their inner surfaces.

2.4. Sample treatment and recovery assays

A 0.5 g portion of plant material was weighed into a capped 50 ml polycarbonate centrifuge tube and 8 ml of methanol were added for extraction. The mixture was sonicated at ambient temperature for 30 s by means of a probe directly immersed in the solution (60% of amplitude) and then centrifuged for 3 min at $1000 \times g$. The resulting supernatant fluid was made up to 10 ml volume with methanol. An aliquot of the extract (600 µl) was diluted to 10 ml with water and a 5 ml volume (the maximum volume permitted in the purging vessel) was submitted to the optimized PT-GC-AED procedure. In the case of the water samples, the addition of methanol at the 6% (v/v) concentration level was the only treatment required before being submitted to the optimized purging step.

Since the retention time of the most retained compound was 6.07 min, the analysis of DMSe and DMDSe in water samples can be performed within 13 min, including the sample purge time. The analyses of the plant samples required no more than 20 min including the sample treatment.

As no reference materials for volatile organic selenium species are currently available, recovery studies were carried out by spiking the samples at four different concentration levels. Four different water samples, each one corresponding to one of the types of water under analysis, were fortified by adding 1.6 ml of methanol containing a known amount of each analyte to 25 ml of sample, the final concentrations of both analytes ranged from 20 to 60 ng l^{-1}. The water sample thus prepared contained 6% (v/v) methanol. For the plant samples, 0.5 g of the sample (onion, garlic and grass) were fortified by adding 100 µl of the methanolic standard solutions, the spiked concentration levels for both analytes ranged between 10 and 25 ng g^{-1}. The mixtures were crushed in the mortar before being extracted by the procedure described above. Three replicates were analyzed at each fortification level.

3. Results and discussion

3.1. Optimization of the purge-and-trap conditions

The optimization of the PT step was made by using 0.2 and 0.4 ng ml^{-1} DMSe and DMDSe standard aqueous solutions, respectively, under different experimental conditions. All experiments were carried out in triplicate. The purge gas flow-rate was set at 40 ml min^{-1} in accordance with the manufacturer's recommendations. The time necessary to purge the compounds out of the sample solution was studied between 5 and 8 min, with a desorption cycle of 4 min at 230 °C and a purge temperature of 30 °C. A value of 6 min was chosen as optimal, since purge times higher than 6 min led to a slight decrease in the peak area for DMDSe, this effect being more pronounced at times higher than 7 min for DMSe, as can be seen in Fig. 1A, where the influence of the purge time on the extraction yield is expressed as peak area for the two analytes. Indeed, very long purging times decreased the signal because the helium itself causes stripping of the trapped analytes. The effect of the desorption time was studied between 3 and 5 min, being finally fixed at 3.5 min, which as shown in Fig. 1B provided the best sensitivity for both analytes. As regards desorption temperature, it was varied between 190 and 230 °C, finally being fixed at 210 °C, because the maximum sensitivity attained for DMDSe was at this temperature value (Fig. 1C). The trap temperature during the adsorption step was varied between 30 and 50 °C, the best sensitivity being attained at 40 °C for both analytes (Fig. 1D). The transfer line temperature was varied between 100 and 250 °C. Temperatures higher than 150 °C decreased the signal for DMDSe, and since no influence of this parameter was observed for DMSe, 150 °C was the value adopted. Finally, when the purging vessel temperature was varied between 25 and 55 °C, the more efficient purge of both analytes was observed at 35 °C. The chosen conditions for the PT system are summarized in Table 1.

3.2. Chromatographic and AED parameters

Since DMSe and DMDSe have a low-polarity, non-polar stationary phases, such as HP-1 or HP-5, should provide an
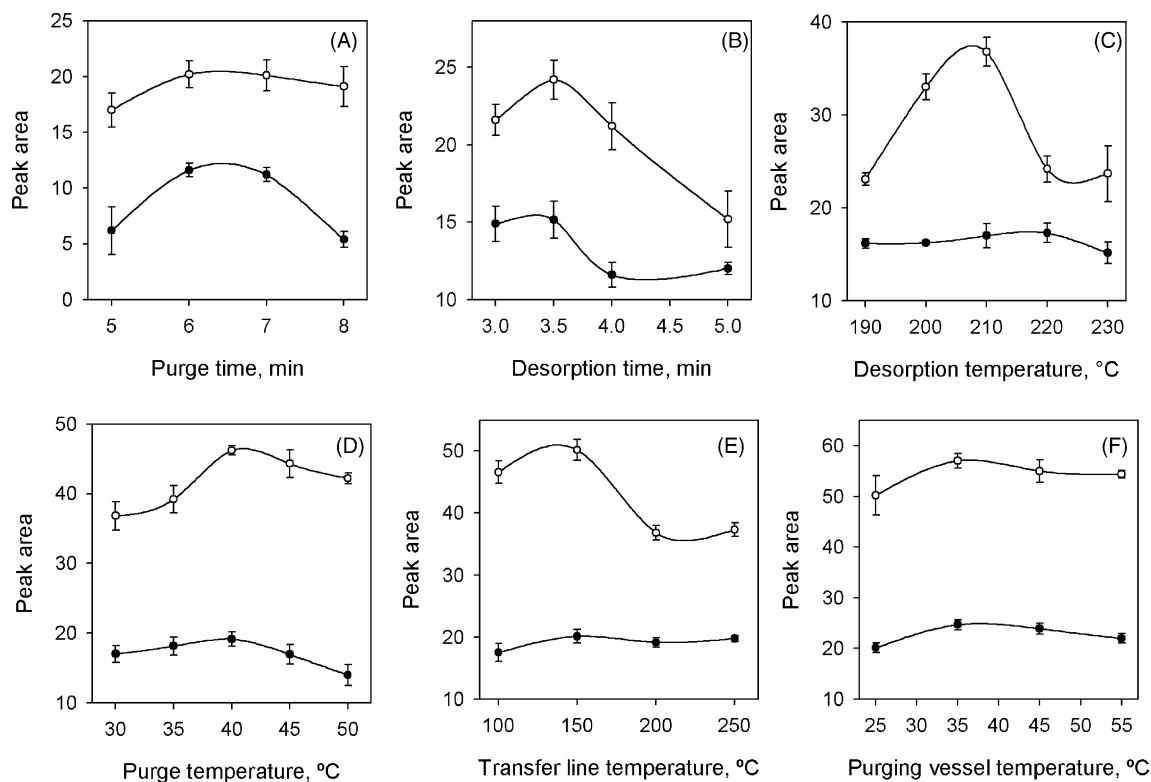
Fig. 1. Effect of (A) purge time; (B) desorption time; (C) desorption temperature; (D) purge temperature; (E) transfer line temperature and (F) purging vessel temperature on the purging of dimethylselenide (●) and dimethyldiselenide (○).

adequate separation. But after comparison of the retention times obtained with these two non-polar phases and those obtained with the DB-624 of medium polarity [25], it was established that the latter provided better results. The major polarity of DB-624 joined with its larger film thickness, a factor that increases the retention time [23], allowed DMSe to be eluted after the solvent vent-off time (time during which the column effluent is not directed towards the detector). With the selected program temperature and using a 4 ml min^{-1} carrier gas flow-rate, the two analytes eluted from the DB-624 column, well separated from the solvent peak, at 3.37 and 6.07 min for DMSe and DMDSe, respectively. It is noteworthy that the most volatile compound was eluted practically at the end of the desorption time.

The injection temperature, i.e. the temperature of the compounds entering the analytical column after passing through the transfer line between the purge-and-trap system and the GC, was varied between 150 and 300 °C. A maximum signal was obtained at 250 °C for both compounds, so this was the value selected.

The detector parameters optimised were the make-up gas flow rate and reagent gases pressure. The influence of the total make-up flow rate (the sum of the column and auxiliary plasma flows), was studied in the range 40–200 ml min^{-1}. Lower flow-rates produced instability in the plasma and were not assayed, and for values higher than 200 ml min^{-1} the signals were lost for the two analytes. Finally, 60 ml min^{-1} was adopted as a compromise value.

To monitor the selenium emission line, the manufacturer recommends the use of both hydrogen and oxygen as reagent gases when low make up flow rates are to be applied. The influence of the hydrogen pressure was studied between 6.4 and 30 psi, with the oxygen valve off, the maximum sensitivity was attained at 10 psi. The sensitivity worsened when oxygen was also present, thus hydrogen was the only scavenger gas used.

The elution profile for a standard mixture under the selected conditions is shown in Fig. 2A. The rise in the baseline level at 3 min in the chromatograms corresponds to the switching off of the solvent venting.

3.3. Optimization of the extraction procedures

3.3.1. Plant samples

Optimization of the sample treatment for plants was carried out using fortified samples at the 20 ng g^{-1} concentration level for both DMSe and DMDSe. The direct extraction by purging a suspension containing the solid sample was not possible with the instrumentation available, and so a previous extraction step was required. In this way the extract obtained was submitted to preconcentration with the PT system. Preliminary experiments were carried out in order to extract the two organoselenides directly into water. Nevertheless, when 2 g of sample were manually shaken with 8 ml water for 5 min, and the supernatant obtained after centrifugation submitted to the purging stage, no signal was obtained
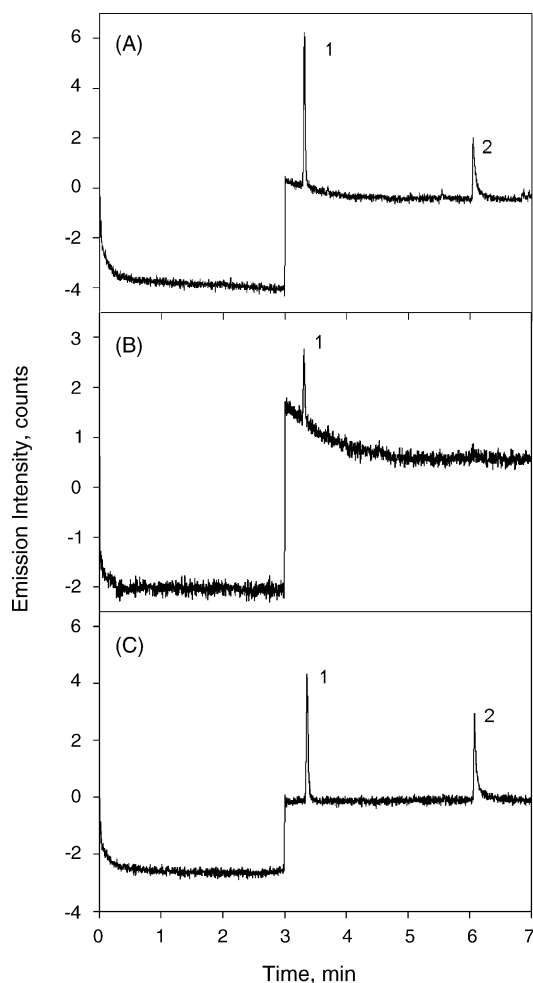
Fig. 2. PT-GC-AED chromatograms obtained from (A) a standard mixture (40 ng l^{-1} of each analyte); (B) Mint 1 sample and (C) a spiked lake water sample at 30 and 50 ng l^{-1} of DMSe and DMDSe, respectively: (1) DMSe and (2) DMDSe.

for DMDSe, and the recovery value for DMSe was around 20%. When the sample mass was diminished to 0.5 g, the recovery value for DMSe increased to 40% and a 10% recovery was attained for DMDSe. No improvement was attained when sonication was applied by means of a probe directly immersed in the aqueous mixture and maintaining the extraction vessel in an icebath in order to avoid volatilization of the analytes.

Since both organoselenium compounds are soluble in methanol, this solvent was tried as the extractant. By sonicating 0.5 g of sample in the presence of 8 ml of methanol for 30 s (60% amplitude) and making up to 10 ml the supernatant obtained by centrifugation, recovery values around 100% were attained for both analytes. When manual shaking for 5 min rather than sonication was used, recovery values decreased approximately 10% for both analytes, confirming the importance of the sonicating step. Sonication not only improves the recovery values but also decreases the sample treatment time. It is important to note that the methanolic extract could not be directly submitted to the purging step,

because the alcohol would block the trap. Moreover, the possibility of concentrating the extract using a rotatory vacuum evaporator, in order to be reconstituted in an aqueous solution which could be directly purged in the PT system, was discarded because the analytes were lost during the evaporation step. Therefore, an aliquot of the extract was diluted with water to be purged with helium gas and concentrated in the trap. The maximum volume of the methanolic extract submitted to preconcentration would increase the sensitivity of the procedure, although methanol:water ratios higher than 0.6:9.4 affect the signal of the more volatile compound, DMSe, so this ratio was selected.

To check the performance of the procedure, plant samples of 0.5–2 g were submitted to the optimized extraction procedure. Because poor homogenization resulted when sample masses higher than 2 g (8 ml the organic solvent), higher masses were not assayed. Recovery values were very close to 100% for 0.5 g samples, but they significantly decreased when the mass of sample used was increased. The loss in recovery could not be avoided by increasing the sonication time. Therefore, a sample mass of 0.5 g was selected with 30 s of sonication time, in this way providing very good detection limits without the need of using an ice-bath.

3.3.2. Water samples

Although both analytes could be determined in waters by submitting the sample directly to the purging step, 6% (v/v) methanol was incorporated to the samples in order to use the same procedure as used for plant samples and to take advantage of the considerable improvement in sensitivity. It is important to point out that when methanol was present in the purging medium, the slopes of the calibration graphs were 70 and 40% higher for DMSe and DMDSe, respectively, than in its absence. Therefore, the incorporation of 6% (v/v) methanol to the water samples is recommended. It should also be noted that in the absence of methanol the sensitivity of DMDSe was better than that of DMSe, as expected for their molecular formulae and the detection system used, but in the presence of the alcohol, the purge efficiency of DMSe increased in such an extent that made it more sensitive than DMDSe, as shown by the calibration slopes (Table 2).

Table 2
Analytical data for the target compounds (as the entire compounds)

Parameter	DMSe	DMDSe
Slope[a] (l ng^{-1})	0.285 ± 0.002	0.230 ± 0.002
Ordinate[a]	0.80 ± 0.08	-1.28 ± 0.09
Correlation coefficient	0.9999	0.9999
Linearity (ng l^{-1})	5–100	10–80
Detection limit (ng l^{-1})	0.8	1.1
Quantification limit (ng l^{-1})	2.7	3.8
Detection limit (ng g^{-1})	0.3	0.4
Quantification limit (ng g^{-1})	0.9	1.3

[a] Mean ± standard deviation ($n = 3$).

3.4. Calibration, precision and detection limits

For calibration, aqueous standard solutions prepared in 6% (v/v) methanol at six concentration levels were analyzed by the optimised procedure. Two replicates for each calibration level were made and peak areas were used for calibration purposes. Table 2 shows the characteristics of the calibration graphs used to quantify each compound. The correlation coefficients showed a high degree of correlation between concentration and peak area, as shown in Table 2. The detection limits were calculated using a signal-to-noise ratio of 3 and since 5 ml aliquots were submitted to the PT stage, absolute detection limits of 4 pg (37 fmol) for DMSe and 5.5 pg (29 fmol) for DMDSe were obtained. The detection limits obtained for 0.5 g plant samples submitted to the optimized extraction and preconcentration procedure are also included in Table 2. The quantification limits were calculated using a signal-to-noise ratio of 10. The repeatability was calculated using the relative standard deviation for 10 successive injections of a standard mixture prepared at five-fold the quantification limits, being 5 and 6.9% (RSD) for DMSe and DMDSe, respectively. Ten different aliquots of a spiked plant sample at a concentration level of five-fold the quantification limits were analyzed and the RSD values obtained for DMSe and DMDSe being 5.5 and 7.2%, respectively.

3.5. Analysis of samples and recovery study

The optimized method for the analysis of plant samples was applied to 12 different unspiked types of vegetables and

Table 3
Results for DMSe in vegetables and waters using the proposed procedure

Sample	DMSe content[a] (ng g^{-1})
Cauliflower	1.23 ± 0.20
Cauliflower leaves	1.37 ± 0.03
Carrot leaves	2.40 ± 0.13
Carrot stem	1.80 ± 0.32
Chive roots	2.15 ± 0.16
Mint 1	4.12 ± 0.01
Mint 2	1.70 ± 0.32
Broccoli	1.30 ± 0.28
Cabbage	2.13 ± 0.50
Tap[b] water	5.0 ± 0.9
River[b] water	3.9 ± 0.8

[a] Mean ± standard deviation ($n = 3$).
[b] Concentrations in ng l^{-1}.

plant tissues (roots, leaves). It is worth nothing that DMDSe was not found in any of the samples analyzed. DMSe was detected in grass, cloves of garlic, leeks, onions and in the edible parts of carrots and chives, but below the quantification limit (0.9 ng g^{-1}). As can be seen in Table 3, DMSe was detected in some plant samples in the concentration range 1.2–4.1 ng g^{-1}. DMSe was detected only in 2 of the 21 water samples analyzed, in both cases the concentration levels being near the quantification limit (Table 3). The results obtained were in accordance with the fact that DMSe is the most common volatile organic selenium species produced by microorganisms [20].

The recoveries from spiked waters and plants varied from 86.4 to 105.8% for DMSe and from 85 to 98.7% for DMDSe,

Table 4
Mean recovery efficiencies and SD obtained in fortified samples using the proposed procedures

Sample	Spike level[a]	Found level[a,b]		Recovery[c] (%)	
		DMSe	DMDSe	DMSe	DMDSe
Grass	10	9.86 ± 0.70	8.55 ± 0.90	98.6 (7.1)	85.5 (10.5)
	15	14.46 ± 0.78	12.75 ± 1.25	96.4 (5.4)	85.0 (9.8)
	20	21.16 ± 0.91	18.72 ± 1.48	105.8 (4.2)	93.6 (7.9)
	25	24.0 ± 0.96	22.67 ± 1.74	96.0 (4.0)	90.7 (7.7)
Onion	10	8.96 ± 0.72	9.80 ± 0.62	89.6 (8.0)	98.0 (6.3)
	15	12.96 ± 1.18	14.7 ± 1.04	86.4 (9.1)	98.0 (7.1)
	20	19.5 ± 0.78	19.17 ± 1.02	97.5 (4.0)	95.9 (5.3)
	25	24.47 ± 1.25	24.42 ± 1.61	97.9 (5.1)	97.7 (6.6)
Garlic	10	9.34 ± 0.87	9.2 ± 0.94	93.4 (9.3)	92.0 (10.2)
	15	15.12 ± 1.34	13.03 ± 1.38	100.8 (8.9)	86.9 (10.6)
	20	20.12 ± 1.35	18.58 ± 1.69	100.6 (6.7)	92.9 (9.1)
	25	25.82 ± 1.14	22.92 ± 2.15	103.3 (4.4)	91.7 (9.4)
River water	20	19.08 ± 1.32	18.24 ± 1.55	95.4 (6.9)	91.2 (8.5)
	40	38.68 ± 1.93	40.99 ± 2.50	96.7 (5.0)	98.7 (6.1)
	60	60.84 ± 1.95	55.92 ± 3.52	101.4 (3.2)	93.2 (6.3)
Seawater	20	18.96 ± 1.40	17.96 ± 1.60	94.8 (7.4)	89.8 (8.9)
	40	41.04 ± 2.46	36.16 ± 3.22	102.6 (6.0)	90.4 (4.3)
	60	58.44 ± 2.40	57.66 ± 3.0	97.4 (4.1)	96.1 (5.2)

Values in parentheses are RSD values.
[a] ng g^{-1} for plants and ng l^{-1} for waters.
[b] Mean ± standard deviation ($n = 3$).
[c] Mean value ($n = 3$).

the average recovery $\pm$ SD ($n = 36$) being $95.1 \pm 5.1\%$, as can be seen from Table 4. Fig. 2B and C shows the chromatograms obtained for Mint 1 sample and a spiked lake water sample, respectively.

4. Conclusion

The high concentration effect achieved by means of the purge-and-trap device joined with the excellent selectivity and sensitivity provided by the atomic emission detector, allow a rapid and sensitive procedure to be presented. The use of an ultrasound probe was shown to be a suitable way of leaching dimethylselenide and dimethyldiselenide from plant samples, which reduces considerably the treatment time. The presence of a low proportion of methanol in the solution to be purged leads to a large increase in sensitivity. The analytical characteristics and the excellent recovery data prove the reliability of the procedure for water and plant samples.

Acknowledgements

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