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Determination of selenium by gas chromatography–electron-capture detection using a rapid derivatization procedure

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Abstract

A rapid method of determination of selenium by gas chromatography with electron-capture detection using 3-bromo-5-trifluoromethyl-1,2-diaminobenzene as complexing ligand was investigated. The temperature-dependent reaction was kinetically evaluated and at 100°C the time for the quantitative formation of piazselenol can be reduced to less than 5 min without any discrepancies in the quantitative determination of selenium. The method was applied to the determination of the organoselenium compounds evolved from incubated sediments. The compounds were separated and identified as dimethylselenide and dimethyldiselenide using GC–MS.

1. Introduction

Selenium is often present in the environment in many forms as a result of microbiological transformation of the inorganic forms to organoselenium species. The concentration of the selenium is of particular concern as there is a narrow range between the essential and toxic concentrations of the element to living organisms. The transformation of inorganic selenium forms to the more volatile but less toxic organoselenium species is an important link in the global cycling of the element [1]. The toxicity of certain inorganic selenium species to some living organisms is some three orders of magnitude greater than alkyl selenides [2]. Toxic levels of selenium can be easily introduced into the food chain through green plants as a result of high plant uptake from contaminated soils, sediments and agricultural drainage water [3]. In recent years, gas chromatography (GC) has been extensively used for the detection and determination of ultra-trace amounts of selenium in such environmental samples. The method is based on the selective complexation of the selenium with the 1,2-diaminobenzene ligand in acidic media to form the piazselenol (**I**). Nakashima and Tôei [4] were the first to demonstrate the unique sensitivity of electron-capture detection (ECD) to the introduction of electron-withdrawing groups substitution into the diaminobenzene ligand (**II**). Since then, various substituted 1,2-diaminobenzenes [4–10] have been examined to increase the ECD sensitivity. Shimoishi [5] synthesized and tested the chromatographic properties of thirteen piazselenol derivatives. He reported that 4,6-dibromopiazselenol had the best sensitivity and distribution ratio. In 1988, Al-Attar and Nickless [10] prepared and demonstrated the supremacy of the 3-bromo-5-trifluoromethyl-1,2-diamino-

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benzene with respect to the sensitivity, shorter retention time and chromatographic peak shape which made GC–ECD an attractive procedure among the various methods [13–16] used to determine selenium.

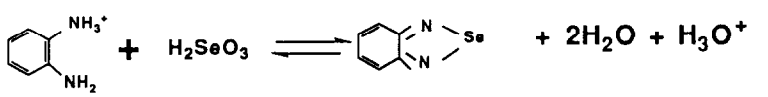
Choice of the diamine reagent depends mainly upon the chromatographic properties of the formed piazselenol and the electron-withdrawing groups present. The retention time determines the resolution of the selenium peak from among other peaks of co-extracted materials. The levels of selenium present in environmental samples is likely to be very low, probably at the pg/g level. Therefore, of vital importance is a capability of detecting and determining such levels likely to be present. Any reduction in the time necessary for the quantitative formation of the piazselenol would substantially increase the advantages of the GC–ECD method.

The abbreviations CF_3/Br-PDA and Br_2-PDA refer to the 3-bromo-5-trifluoromethyl-1,2-diaminobenzene and 3,5-dibromo-1,2-diaminobenzene ligands, respectively. Similarly, CF_3/Br-PDSe and Br_2-PDSe refer to the respective piazselenols.

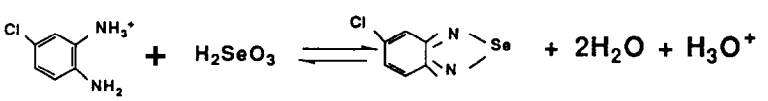
The quantitative formation of piazselenol at room temperature is, however, a time consuming process but the reaction rate is temperature dependent. Therefore, the concept of high-temperature derivatization is a novel and desirable trend. Thus, in 1992. Johansson and Olin [11] successfully derivatized Se(IV) using 3,5-dibromo-1,2-diaminobenzene at 100°C, the quantitative formation of piazselenol being completed in 5 min. In addition, they reported a small loss when extraction of piazselenol was made from large volumes (over 100 ml). However, a standard solution of Se(IV), treated as the sample is recommended for accurate analysis of real samples.

The objectives of the present study were (i) to investigate the possibility of using a high-temperature (≤ 100°C) derivatization step based on the reaction between the Se(IV) and CF_3/Br-PDA as a ligand for the quantitative determination of selenium and (ii) to apply the method to the determination of selenium in the volatilization products resulting from microbiological action on selenium containing sediments.

The CF_3/Br-PDA was preferred to the others ligands proposed in the literature because (a) the limit of detection is in the low pg level of concentration, (b) the piazselenol so formed is stable to an acid-washing procedure required to remove the excess ligand, (c) the reagent is commercially available in fair state of purity, (d) the retention time of the piazselenol is short at reasonable isothermal column temperatures, so minimizing column bleed and consequent contamination of the electron-capture detector and (e) the distribution ratio of the formed piazselenol is high and was verified using standard reference materials producing good results [10]. Quantitative piazselenol extraction is obtainable by a single extraction as will be proved by the present study.



(I)



(II)

2. Experimental

2.1. Instrumentation

GC was carried out using a Carlo Erba 4160 gas chromatograph equipped with a nickel-63 electron-capture detector and Hewlett-Packard electronic integrator Model 3390 A.

The piazselenol extracts were separated on 10 m × 0.53 mm fused-silica (film thickness 2.65 μm) HP-1 cross-linked methylsilicone capillary column. Typical separation conditions were: oven temperature, 120°C; injector temperature, 260°C; injection was performed in splitless mode using 1-μl injections. The nickel-63 pulsed electron capture (Carlo Erba HF-25) was used in the constant-current pulse-modulation mode with a pulse voltage of 50 mV, 0.1-μs pulse and reference current of 10 nA. Detector temperature, 250°C; hydrogen was used as a carrier gas at a flow-rate of 10 ml/min and make-up gas was nitrogen at 50 ml/min. The kinetic studies were performed in 1-cm quartz cuvettes using a Pye-Unicam SP-1700 UV spectrophotometer equipped with a thermostatted cell holder.

2.2. Materials

All glassware was washed with detergent solution (Micro-liquid laboratory cleaner), rinsed with tap water, then distilled water and placed in 40% (v/v) nitric acid for at least 48 h. The glassware was finally rinsed with double-distilled water and oven dried at 60°C before use.

All-glass double-distilled water was used for preparing standards and dilutions. AnalaR (BDH, Poole, UK) hydrochloric, perchloric, nitric and formic acids were used without further purification. Reagent-grade elemental selenium, sodium selenite and selenium dioxide were obtained from BDH, 3-bromo-5-trifluoromethyl-1,2-diaminobenzene purchased from Maybridge (Trevillett, Tintagel, UK) was purified and converted to the chloride form by recrystallization from hydrochloric acid [10], 1,2-diamino-3,5-dibromobenzene hydrochloride was obtained from Aldrich, UK.

Solutions of 8.83 m*M* of each of the diamine reagents were prepared by dissolving 0.257 g of CF_3/Br-PDA and 0.267 g of Br_2-PDA in 100 ml of 0.25 *M* HCl and 0.5 *M* $HClO_4$, respectively. The solutions were purified by extraction with 25 ml toluene (AnalaR) and were kept in the dark at 4°C. Further working solutions of both reagents were prepared by appropriate dilution with 0.25 *M* hydrochloric acid.

Selenium(IV) stock solution of 1 mg/ml was prepared from sodium selenite (0.219 g) in 0.25 *M* hydrochloric acid.

A solution of 1 μg/ml Se(IV) was first prepared from selenium stock solution, and from this solution 0.01 μg/ml Se was prepared by serial dilution with 0.25 *M* HCl.

The standard working solutions used for the calibration were prepared as follows: in a series of 10-ml volumetric flasks containing 0.25 *M* HCl, a volume of 100, 200, 300, 400 or 500 μl of 0.01 μg/ml Se standard was added and the volumes were made up with 0.25 *M* HCl.

2.3. Internal standard: lindane

A stock solution of 0.0418 g of 99% lindane obtained from Pan Britannica (Waltham Abbey, UK), was dissolved in AnalaR toluene (100 ml). A series of working standard solutions containing 25 ng/ml of lindane was prepared by serial dilution of the stock standard solution.

2.4. Kinetic experiments

The rate of reaction was followed by adding 0.1 ml of 126.6 μ*M* Se(IV) into a quartz cuvette containing 3 ml of 0.3 m*M* CF_3/Br-PDA preheated to the desired temperature in a thermostatted cell holder. Absorbance measurements of the piazselenol was immediately started and measured every 60 s. The reaction of the selenium(IV) and the CF_3/Br-PDA was followed at the characteristic wavelength 334 nm for the CF_3/Br-PDSe maximum absorbance as indicated by Fig. 1, using temperatures of 20, 40, 60 and 80°C for the kinetic study. The data were collected and printed by automatic recording of

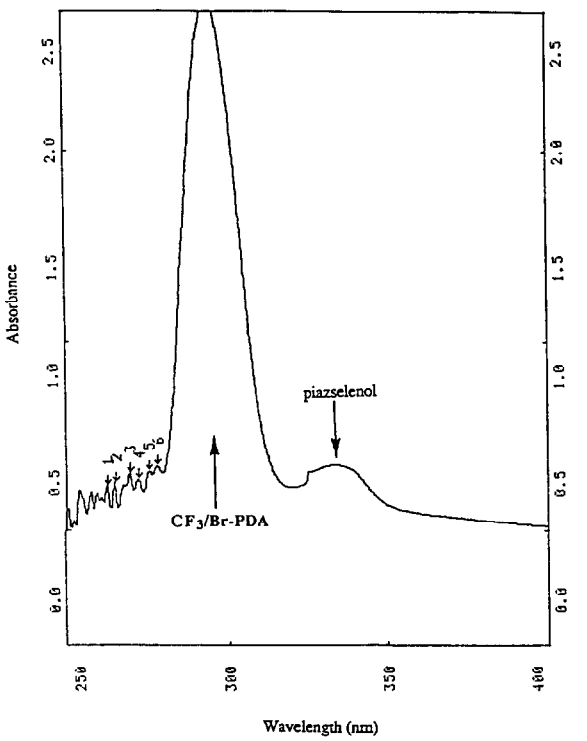


Fig. 1. UV absorption spectrum of 4-bromo-6-trifluoromethylpiazselenol. Maximum absorbance at the analytical wavelength (334 nm).

the absorbance A_{max} of the formed piazselenol using a Philips printer. A non-linear least-squares calculation was implemented. The SAS. NLIN program was used to fit the model to the experimental data [17].

2.5. Derivatization at elevated temperature

A 100 ng/l Se(IV) solution (10 ml) in 0.25 *M* HCl was heated in 20-ml screw-capped vials [18] in a thermostatted water bath at the desired temperature (20–100°C). When the required temperature had stabilized, 0.1 ml of 8.83 m*M* CF_3/Br-PDA was added and the vials were recapped and heated. After $5t_{1/2}$ (where $t_{1/2}$ is the half-life of the CF_3/Br-PDSe reaction), the vials were removed and cooled to room temperature in a cold water bath. The piazselenol formed was extracted as in the general procedure.

2.6. General procedure for extraction of piazselenol

The piazselenol was transferred quantitatively together with 5 ml double-distilled water to a 50-ml separating funnel and 5 ml of toluene (AnalaR) containing 25 ng/ml lindane as an internal standard was added. The mixture was vigorously shaken for 5 min and the aqueous phase discarded. The toluene extracts were washed twice with 3 ml of 50% (v/v) perchloric acid (sp.gr. 1.7 g/ml) and once with double-distilled water, then dried over anhydrous sodium sulphate prior to injection into the GC–ECD.

2.7. Extraction efficiency

The efficiency of a single extraction of the piazselenol was assessed. Thus, a series of piazselenol solutions of volume 20 ml containing varying concentrations of selenium were prepared at 100°C for 5 min, ranging from 0.0, 1.0, 2.0, 3.0, 4.0, to 5.0 ng of Se(IV). Each solution was extracted by the general procedure, and the aqueous solution retained. To this residual aqueous solution were added 0.2 ml of 8.83 m*M* CF_3/Br-PDA solution. The derivatization procedure was carried out at room temperature for the calculated $5t_{1/2}$ for piazselenol formation. The resultant solutions were extracted with 1 ml toluene as in the general procedure, 1 μl was injected for GC–ECD.

In order to test the extraction at successively lower concentrations of selenium, the procedure was repeated twice more. A similar concentration series based either on 100- or 250-ml sample volumes containing up to 5.0 ng of Se(IV) were treated in an exactly similar manner.

2.8. Sediments incubation experiments

The organoselenium compounds were generated from incubated (50 g dry mass) batches of three different sediments collected from River Avon. The sediments were placed in 250-ml Erlenmeyer flasks. A solution mixture of 20 ml containing 5 mg Se(IV) [19], and nutrient broth

(0.5%), D-Glucose (0.1%), yeast extract (0.05%) was added to promote microorganism growth. The flasks were connected to an air flow system at 20 ml/min. The generated organoselenium compounds were trapped in 15 ml nitric acid (AnalaR). The traps were sampled and analysed every 4 to 6 days for Se content using GC–ECD.

2.9. Determination of the evolved organoselenium compounds trapped in nitric acid

The nitric acid sample (1 ml) was mixed with 20 μl of 30% (w/v) hydrogen peroxide in a closed quartz tube and irradiated with a 700-W UV lamp for 3 h to decompose the organoselenium compounds [20]. An aliquot of between 0.25 to 0.5 ml depending on the selenium concentration of the decomposed sample solution together with 1 ml of formic acid [21] (sp.gr. 1.2 g/ml) was transferred to a 150-ml beaker and the nitrate expelled by heating on a boiling water bath until the disappearance of the nitrous fumes. The residue was transferred quantitatively with 4 ml double-distilled water into a 20-ml screw-capped vial. Hydrochloric acid (5 ml), hydrobromic acid (0.5 ml) and 3% (v/v) bromine water (0.05 ml) were added and the vial tightly screw capped. The mixture was heated for 30 min at 100°C to reduce Se(VI) and to oxidize Se(0) and Se(−II) to Se(IV). The vial was removed and hydroxyammonium chloride ($NH_2OH \cdot HCl$, 1 ml of 1 *M* aqueous solution) [22] added to reduce any excess bromine, then 0.5 ml of 8.83 m*M* CF_3/Br-PDA were added and the vial returned to the boiling water bath for a further 5 min. It was then removed, cooled to room temperature in a cold-water bath and the piazselenol was extracted as in the general procedure.

2.10. GC–mass spectrometry (MS)

GC–MS was performed on a Varian 3400 GC system interfaced with a Finnigan ITS 40 ion-trap mass spectrometer. The volatiles were separated on a capillary column, 50 m CP Sil 13, 5 μm film thickness coupled to a 50 m CP Sil 13, 2.5 μm column. Helium was used as carrier gas at 1 ml/min. Temperature programming, 50°C (1 min) increased to 100°C at 10°C/min. The sample was injected through a modified gas loop injector using a gas-tight syringe 50 ml from which only 50 μl were injected through the injector loop. Spectra were acquired in the electron impact (EI) mode, 70 eV, Auto Ion control in Finnigan MAT ion trap; with mass resolution 1 u; electron emission 11 mA; multiplier voltage 1600 V; acquire time 90 min; scanning continuously over a mass range 50–250 u at a rate of 0.599 s/scan; peak threshold 10 counts. Retention times: $(CH_3)_2Se$, 11.4 min (*m/z* 110) and $(CH3)_2Se_2$, 36.5 min (*m/z* 190).

3. Results and discussion

3.1. Rate of reaction

The abbreviations within square brackets, including Se(IV), denote concentrations. In general, diamines which are ionized to a greater extent at low pH should have a faster reaction rate [5]. In the acid concentration 0.01–6 *M* for the high-temperature derivatization the reaction rate is very dependent on (i) the form of the electronegative group attached to the benzene ring and (ii) the concentration ratio of the CF_3/Br-PDA and selenious acid in the reactant mixture.

Comparing Br_2-PDSe and CF_3/Br-PDSe, the CF_3 group is of greater electron-withdrawing ability than Br, so resulting in a more favourable electron density on the N atoms to allow ready reaction with the selenious acid.

In the following section, as will be confirmed by the kinetic results, the expected rate (*r*) equation of piazselenol (Piaz) formation was:

$$r = d[\text{Piaz}]/dt = -d[\text{Se(IV)}]/dt$$
$$= K_2'[\text{Se(IV)}][CF_3/\text{Br-PDA}] \quad (1)$$

where K_2' is the rate constant.

Under the experimental conditions, and using Ostwald's isolation method, Eq. 1 was experimentally tested using excess reagent. How-

ever, in order to confirm the proposed rate equation, the experimental data were fitted to the integrated second-order rate equation:

$$\ln [Se(IV)] = \ln [Se(IV)]_0 - K_2[CF_3/Br\text{-}PDA]t \quad (2)$$

Eq. 2 is more conveniently expressed as

$$\ln [Se(IV)] = \ln [Se(IV)]_0 - kt \quad (3)$$

where $k = K_2[CF_3/Br\text{-}PDA]$ and $[Se(IV)]_0$ represents the initial selenium concentration; K_2 is the second order rate constant. In a series of experiments at 20°C, firstly the initial concentration of selenium was varied at constant ligand concentration (Fig. 2). The slopes of the resultant lines are equal. Next the reagent concentration was varied at constant selenium concentration. The k values of the three lines are different depending on the ligand concentration but the K_2 values are the same (Fig. 3). However, the proposed rate equation is confirmed. The second-order rate constants for different temperatures were determined by fitting the experimental results obtained from a series of temperature dependent piazselenol formation curves (Fig. 4) to the negative exponential equation, by non-linear least squares,

$$A_t = A_{max} - b\,e^{-kt} \quad (4)$$

where A_t = absorbance of the piazselenol at time t and A_{max} = absorbance of the piazselenol at time infinity.

The results are presented in Table 1.

The activation energy in J mol^{-1} was calculated from the slope of the Arrhenius plot, ln K_2 *vs.* $1/T$ in the temperature-dependent second-order reaction:

$$\ln K_2 = 27.75 - 57\,600/RT \quad (5)$$

Comparison of the CF_3/Br-PDA with the previously evaluated Br_2-PDA ligand [11] shows

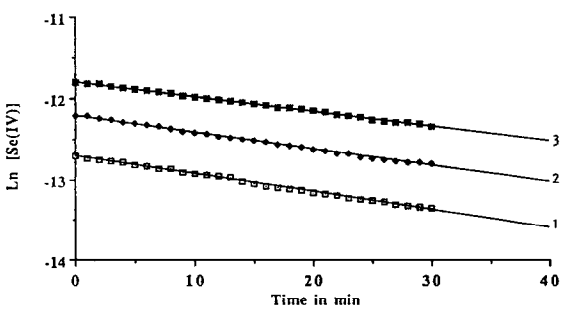


Fig. 2. Determination of the rate constant of CF_3/Br-PDSe formation. The [CF_3/Br-PDA] was kept at 0.29 mM and the [Se(IV)] was varied: 1 = 3.056 μM, 2 = 4.98 μM and 3 = 7.47 μM.

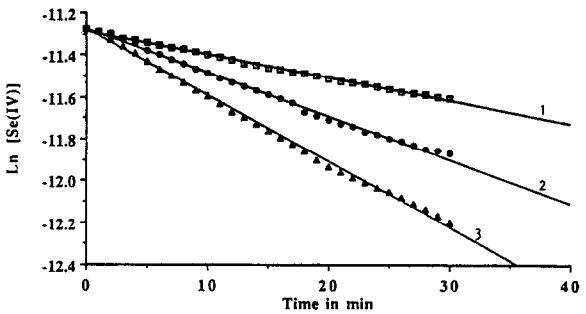


Fig. 3. Determination of the rate constant of CF_3/Br-PDSe formation. The total [Se(IV)] was kept at 12.7 μM and the [CF_3/Br-PDA] was varied: 1 = 0.206 mM, 2 = 0.309 mM and 3 = 0.463 mM.

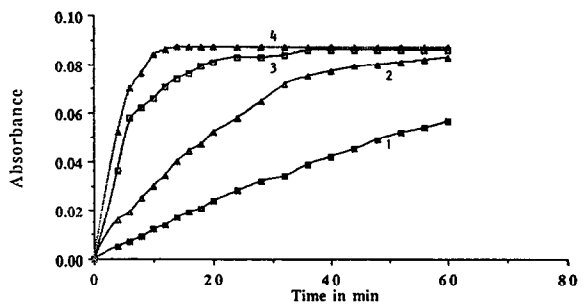


Fig. 4. Determination of the temperature dependence of piazselenol formation, The rate constant was calculated at the following temperatures: 1 = 20°C, 2 = 40°C, 3 = 60°C and 4 = 80°C.

Table 1
The second-order rate constants for varying temperatures

Temperature (°C)	Average K_2(l/mol · min)
20	61 (2)
40	277 (5)
60	1048 (11)
80	3405 (32)

Determined three times with 0.3 mM CF3/Br-PDA and 4.22 μM Se(IV) using absorbance at 334.0 nm.
Values in parentheses are the estimated standard deviations.

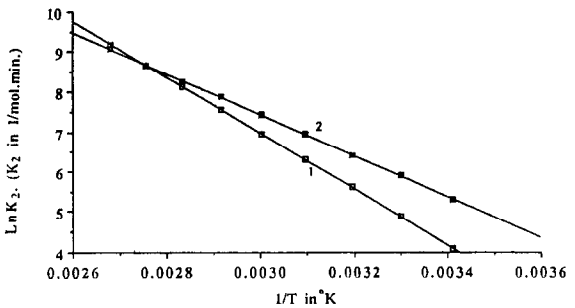


Fig. 5. Determination of Arrhenius activation energy (EA) for CF_3/Br-PDSe by plotting the ln K_2 *vs.* $1/T$. K_2 for Br_2-PDA from ref. 11 for comparison: 1 = CF_3/Br-PDA and 2 = Br_2-PDA.

that the activation energy of the CF_3/Br-PDA is greater, and hence the rate of the reaction is slower as a function of temperature until a temperature of 90°C is reached as indicated in Fig. 5. The determination of the $5t_{1/2}$ value, with 0.1 m*M* CF_3/Br-PDA at 20 to 100°C is presented in Table 2 which indicates that quantitative formation of piazselenol is completed in less than 4 min at 100°C.

3.2. The efficiency of the extraction

An investigation to provide information of the efficiency of a single extraction of the piazselenol was carried out by varying the concentrations of selenium and differing concentration-to-volume ratios. A second extraction of the residual aqueous phase (originally treated at 100°C) with excess ligand at room temperature was carried out. In all cases, no selenium was detected in the analysis of the second toluene extract, even though it was only one fifth of the original volume of toluene used in the general procedure.

So providing an adequate test for both the efficiency of extraction and the quantitative formation of the piazselenol after high-temperature derivatization. Therefore, providing clear evidence that the distribution coefficient for CF_3/Br-PDSe at least as great as that for Br_2-PDSe [11]. Moreover, the room temperature derivatization method previously described [10] provides entirely satisfactory results.

Table 2
The time required for quantitative piazselenol formation

Temperature (°C)	$5t_{1/2}$ (min)
20	564
30	260
40	125
50	63
60	33
70	18
80	10
90	6
100	3.6

Estimated times of 5 half times ($5t_{1/2}$) calculated at 0.1 m*M* CF3/Br-PDA.

3.3. Calibration

In order to evaluate the efficacy of the high temperature derivatization of the CF_3/Br-PDSe method, analyses were performed for known concentrations of Se(IV) contained in the synthesized piazselenol (CF_3/Br-PDSe). The results obtained were compared with those obtained for the identical concentrations of Se derivatized at 100°C for 5 min.

The results obtained are shown in Fig. 6, which indicate quantitative piazselenol formation.

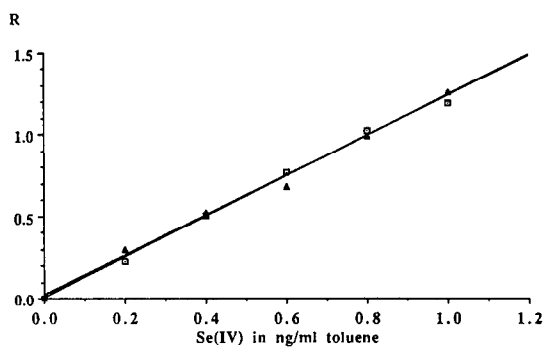


Fig. 6. Calibration plot for piazselenol. Comparison of synthesized piazselenol and 100°C for 5 min derivatized Se(IV). *R* is the area ratio between piazselenol and the internal standard: ▲ = synthesized piazselenol and □ = high-temperature derivatization. $y = 0.0183 + 0.978x$; $r^2 = 0.983$.

3.4. The evolved organoselenium compounds as total selenium

The use of CF_3/Br-PDA reagent facilitates the quantitative detection of the selenium evolved during the course of a few days of incubation. The determination was carried out in a manner in which three possible interferents were considered:

(i) The organoselenium compounds were decomposed for 3 h with UV-irradiation after addition of hydrogen peroxide. However, all the selenium was transferred into inorganic selenium form which forms the basis of the reaction of the diaminobenzene reagent with the selenium.

(ii) The nitrate was expelled to avoid interference [20] with both the reduction of Se(VI) to Se(IV) and oxidation of the diaminobenzene ligand. Any traces were eliminated by addition of hydroxyammonium hydrochloride [22], so allowing all the ligand present to provide quantitative complexation of selenium without loss of any reagent by oxidation.

(iii) The reduction, oxidation of the selenium species to Se(IV) and the high-temperature derivatization were carried out in screw-capped vials to prevent any discrepancies in quantitative selenium determination due to volatilization during the heating process [18]. The digestion method is, however, a collective demonstration of the previously established work, which provided an adequate digestion and suitable reaction media for both reactants. Fig. 7 illustrates a typical GC–ECD chromatogram obtained by the method described in the text.

Quantitation of selenium was carried out using the peak area data obtained from integration. The calibration graph was generated by plotting the peak area ratio *versus* the concentration of the standards. The area ratio of the unknown sample concentration was determined by comparison with the calibration graph using the programmed regression analysis method. The 4-bromo-6-trifluoromethylpiazselenol with capillary GC–ECD gives a linear calibration relationship. The detection limit, 0.083 ng Se/ml was calculated from the calibration graph using the method described by Liteanu and Rica [23].

The results are presented in Table 3.

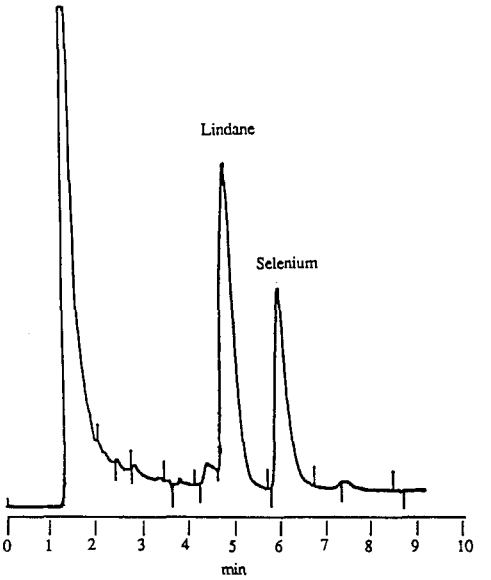


Fig. 7. Chromatogram of toluene extracts of 1 ng Se(IV)/10 ml sample solution with 0.1 m*M* CF_3/Br-PDA at 100°C for 5 min. The piazselenol was extracted with 5 ml toluene containing the internal standard, washed twice with 3 ml of 50% $HClO_4$ and once with double distilled water. The volume of 1 μl was injected in the GC–ECD system.

3.5. Separation and identification of organoselenium compounds

The volatiles above the incubated sediments were separated by withdrawing a 500-μl gas

Table 3
The evolved selenium at selected time intervals

Incubation period in days	Total evolved selenium in μg/kg sediment		
	Raybridge	Staverton	Keynsham
4	143	35	5
6	436	40	7
10	564	56	15
14	572	71	20
20	647	119	23
24	905	ND[a]	ND[a]
28	1125	187	32

Replicate determinations were carried out.
[a] Not determined.

sample with a gas-tight Hamilton 1750 pressure-lock gas syringe and injecting it directly into the GC–flame ionization detection system. The result obtained (Fig. 8) indicates the prominent two peaks at retention times 4 and 9 min. The peaks were identified later as dimethyl selenide and dimethyl diselenide, respectively, using GC–MS. The selenium-containing fragments are often easily recognized in mass spectra from the very characteristic groups of peaks resulting from the typical distribution of the six natural selenium isotopes. However, the peak arising from the most abundant ^{80}Se isotope is in general chosen to represent the selenium-containing fragments. Low-molecular-mass organoselenium compounds are labile towards heat and initial vaporization of the sample gives rise to decomposition before ionization, resulting in separation of the elemental selenium. In such cases the resultant mass spectra shows either no molecular ion or one with very low abundance [24], so explaining the relatively low parent peak of the dimethyl selenide $(CH_3)_2Se$ (reaction 6) obtained from the GC–MS analyses of the volatiles Fig. 9A.

The mass spectra for the dimethyl diselenide $(CH_3)_2Se_2$ shows three fragmentation patterns presented in Fig. 9B, which gives a clear picture of the prominent ^{80}Se isotope indicated by the presence of the appropriate metastable peaks as a result of elimination of a methyl radical from the molecular ion as a dominant process (reaction 7a), forming the fragments at m/z 175 and at m/z 160.

The more complex spectra observed are consequences of the alternative losses of other

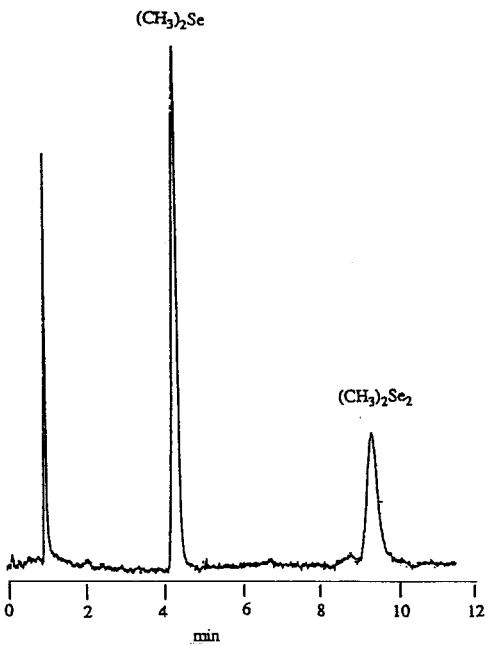


Fig. 8. Chromatogram of the separated organoselenium compounds volatilized from selenium amended sediment. Headspace 500 ml was injected into 20% SE-30 column. Temperature programmed 50°C (2 min) increased by 30°C/min to 120°C, nitrogen flow-rate 30 ml/min using flame ionization detection.

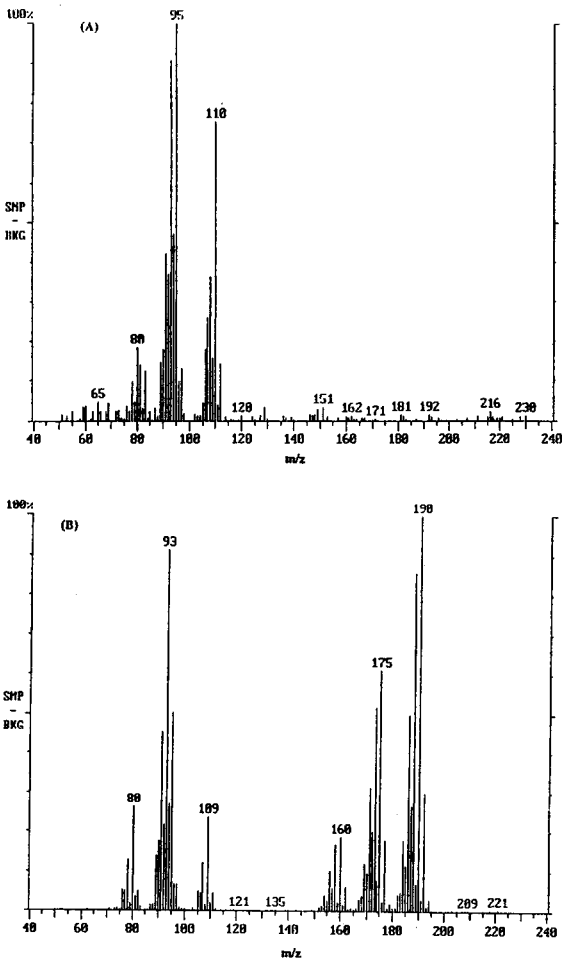


Fig. 9. GC–MS of (A) dimethylselenide and (B) dimethyldiselenide. Y-axis represent relative abundance.

$$[CH_3\text{–}Se\text{–}CH_3]^+ \xrightarrow{-CH_3} [CH_3\text{–}Se]^+ \xrightarrow{-CH_3} [Se]^+ \quad (6)$$
m/z 110 m/z 95 m/z 80

$$[CH_3\text{–}Se\text{–}Se\text{–}CH_3]^+ \xrightarrow{-CH_3} [CH_3\text{–}Se\text{–}Se]^+ \xrightarrow{-CH_3} [Se\text{–}Se]^+ \quad (7a)$$
m/z 190 m/z 175 m/z 160

$$[CH_3\text{–}Se\text{–}Se\text{–}CH_3]^+ \xrightarrow{-HSe} [CH_3\text{–}Se\text{–}CH_2]^+ \xrightarrow{-CH_4} [Se\text{–}CH]^+ \xrightarrow{-CH} [Se] \quad (7b)$$
m/z 190 m/z 109 m/z 93 m/z 80

$$[CH_3\text{–}Se\text{–}Se\text{–}CH_3]^+ \xrightarrow{-CH_3\text{–}Se} [CH_3\text{–}Se]^+ \xrightarrow{-CH_3} [Se]^+ \quad (7c)$$
m/z 190 m/z 95 m/z 80

different groups attached to the selenium atom (reaction 7b), which results in fragmentation at m/z 109 from loss of HSe followed by elimination of CH_4 group at m/z 93. The alternative pattern is the cleavage of the Se–Se bond resulting in fission of the molecule into two halves giving rise to fragment at m/z 95 (reaction 7c).

The clear interpretation from the spectra is the evidence of reactions 7b and 7c proved by the abundance of the prominent peak at m/z 93 from the addition of fragmentation CH–Se at m/z 93 (reaction 7b), of ^{80}Se isotope and the fragmentation of CH_3–Se at m/z 93 (reaction 7c), of isotope ^{78}Se.

4. Conclusions

The proposed procedure for high-temperature derivatization of low levels of selenium with 3-bromo-5-trifluoromethyl-1,2-diaminobenzene has been shown to be simple, rapid, sensitive and precise. The method has obvious advantages over other substituted diaminobenzene ligands, which involves the comparison of the sensitivity, retention time and clean chromatograms.

The method, which has been applied to assess the released organoselenium compounds from sediments should be applicable to the environmental, biological and geological samples.

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