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Combined solvent extraction–purge and trap method for the determination of volatile organic compounds in sediments[☆]

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Abstract

A method involving methanol solvent extraction (SE) and purge and trap (PT) was evaluated for the determination of chlorinated volatile organic compounds (VOC) in sediments. The method was tested by means of standard solutions encompassing twenty chlorinated compounds with boiling points ranging between 24 and 150°C (at 1 atm = 101 325 Pa). Detection limits (0.05–0.4 µg/g), linearity ranges and recoveries (only 1% average losses by glassware manipulation and 7.5% losses after water sediment suspension with standards and methanol extraction) show the suitability of the method for the determination of chlorinated VOC in environmental samples. A specific advantage of this method is the possibility of storage of the VOC methanol extracts for long periods of time at –20°C without significant alteration of the quantitative results. In the conditions of the study, the average recovery of individual VOCs after storage for 50 days was 89%.

1. Introduction

Man has traditionally disposed of wastes in the most expedient and economic way possible. Residues have been stored in sites of marginal commercial value or near the industrial facilities where they have been generated. Soil, sediment and groundwater pollution are the main problems resulting from these activities. In this respect, the widespread use of volatile organic compounds (VOCs) for industrial applications has very often resulted in this type of compound appearing to be associated with waste lixiviation problems, producing adverse effects on the environment and human health [1].

Accurate mass balances of the VOCs present in polluted sediments are essential for reliable environmental impact studies and feasible remedial programmes. Unfortunately, VOC determination in soils and sediments has not been completely mastered [1]. The efficient extraction (purging) of volatile chemical species from solid matrices is far more difficult than from waters and no specific method is generally accepted in the literature. Thus, methods involving soil extraction with organic solvents (*i.e.*, *n*-hexane [2], *n*-pentane [3] and *n*-pentane–propan-2-ol [3]) and subsequent analysis by gas chromatography (GC) have been proposed. Other methods are based on headspace GC analysis of soil samples heated within capped vials after addition of water [4–8] or methyl glycol (propylene glycol) [9]. In other cases the samples are introduced within canisters or Tedlar bags and the outgassed

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compounds are introduced into a GC system by means of a gas sample valve [10].

Other approaches take advantage of the purge and trap (PT) methods developed for the routine determination of VOCs in water [11,12]. In general, the range of application of these methods has been extended to solid matrices by thermal vaporization of soil or sediment samples (sometimes after addition of water or methanol) and VOC trapping in adsorption tubes packed with Tenax resins [13–18]. An important advantage of these modified procedures is their applicability to the analysis of large series of samples with relatively simple handling when the tubes are submitted to GC analysis in combination with automated thermal desorbers (ATDs).

Unfortunately, this type of approach has recently been reported to give significantly poorer quantitative results, in terms of analytical precision and recovery, than the procedures based on the headspace method [7,8]. This drawback appears to be particularly important for low-boiling organochlorinated solvents such as methylene chloride, trichloroethane, trichloroethylene and tetrachloroethylene. Volatilization losses occurring during sample transfer from the storage vial to the purging vessel seem to be at the origin of this problem [8]. Attempts to minimize these volatilization effects by reduction of soil, water and glassware temperature have been unsuccessful in preventing these losses [8].

In view of these results, an alternative approach to be investigated concerns the combination of solvent extraction and PT methods, that is, sample extraction with a hydrophilic solvent, dilution within a large volume of water and PT analysis by the usual method, a combination that avoids any soil or sediment transfer between different vials. On the other hand, solvent transfer from the extraction to the purge containers can be performed with gas-tight syringes, which avoids volatilization losses. This type of solvent extraction–PT (SE–PT) application has been successfully developed for the determination of gasoline hydrocarbons in soils [19] and, in addition, avoids the need for immediate instrumental analysis of the soils or sediments after sampling. In this study, the possibilities for the analysis of

organochlorinated hydrocarbons were investigated. Recoveries, detection limits and linearity ranges for 20 compounds encompassing a boiling temperature range between 24 and 150°C (1 atm), from trichlorofluoromethane to bromoform, were evaluated.

2. Experimental

2.1. Materials

Samples were stored in 40-ml screw-capped vials sealed with 0.010-in. thick 0.25-mm diameter Teflon-faced silicone-rubber septa (Model 2-3285; Supelco, Bellefonte, PA, USA). Methanol extracts were stored in 2-ml crimp-topped vials (Model 5181-3375; Hewlett-packard, Palo Alto, CA, USA) and kept at –20°C until analysis. PT was performed with a Supelco Model 6-4713 modified purging device containing a glass frit of medium porosity (10–15 μm). Water and methanol solutions were transferred with 10- μl and 5-ml PTFE Luer Lock (150-mm needle) syringes (Models 701N and 1005TLL, respectively; Hamilton, Bonaduz, Switzerland).

All standards were obtained from Supelco (Environmental Analytical Standard Series). Residue analysis methanol was purchased from Merck (Darmstadt, Germany). Tenax TA (60–80 mesh) was obtained from Perkin-Elmer (Norwalk, CT, USA). About 180 mg of this adsorbent were packed in 8.8 cm \times 4 mm I.D. stainless-steel tubes (Model L4270123; Perkin-Elmer) and plugged between silanized glass-wool inserts (Model 54120790; Perkin-Elmer). Ultra-pure helium (Quality 5.3; Abello Linde, Barcelona, Spain) was used as the carrier and purge gas. This gas was additionally purified with two serially connected hydrocarbon (Model 7971; Chrompack, Middelburg, Netherlands) and oxygen (Model 7970; Chrompack) filters.

2.2. Conditioning of the adsorption tubes

The tubes were cleaned by passage of 100 ml/min of helium while heating at 250, 300, 325 and 350°C for successive periods of 30 min each.

They were then tested by GC analysis using the ATD injector. Blank requirements were that no chromatographic peaks under the electron-capture or flame ionization detectors equivalent to 10 pg should be observed.

2.3. Sampling

About 1–3-g sediment sample aliquots were obtained from a water reservoir receiving the discharges from an organochlorinated solvent factory (Flix, Spain) and from an estuary contaminated with spillages from a chemical chlorine complex where organochlorine solvents were produced (Alagoas, Brazil). The samples were introduced into pre-weighed 40-ml screw-capped vials containing 5 ml of methanol. After closing the vial, the sediment suspension was shaken vigorously for 5 min and stored at 4°C in a freezer free from organic solvent vapours and let to settle. In the laboratory, 2 ml of the supernatant methanol extracts were taken with a syringe and introduced into 2-ml vials without leaving a headspace. These vials were sealed with an aluminum seal holding an 11-mm PTFE-faced septum and stored at –20°C.

2.4. Purge and trap

A 200- μ l volume of the methanolic extracts was diluted in 100 ml of Milli-Q-purified water and 5 ml of this water were introduced into the PT device by means of a 5-ml syringe. This water aliquot was purged with helium at a flow-rate of 40 ml/min for 11 min. All the purging gas was passed through a Tenax TA tube fitted to the system by means of Model 404-1 PTFE ferrules held with 1/4-in. Swagelock connections. The tubes were subsequently introduced into the ATD system.

2.5. Instrumental analysis

A Perkin-Elmer ATD Model 400A coupled to a Perkin-Elmer Autosystem gas chromatograph equipped with flame ionization and electron-capture detectors connected in parallel were used in all analyses. The adsorption tubes were heated at

300°C for 5 min while passing helium through at a flow-rate of 260 ml/min. About 20% of the desorbed compounds were collected in a cryofocusing trap cooled to –30°C. This percentage was controlled by an inlet split which diverted 210 ml/min of the desorption gas to a vent and 50 ml/min to the cold trap. After the tube desorption period, the cryofocusing trap was heated to 300°C at 40°C/s with a holding time of 10 ml. A helium flow-rate of 16 ml/min was used to purge the cold trap during this period. When leaving the trap, the vaporized compounds were divided further by a second split which vented 8 ml/min to the outlet and directed 8 ml/min (about 50%) towards the GC instrument. Thus, only about 10% of the initial amounts of compounds present in the adsorption tubes were allowed to enter the GC column. At the outlet of the column a Y-type glass tight connection diverted about half of the eluting flow to each detector. The transfer line between the ATD instrument and the gas chromatograph was heated at 225°C.

All analyses were performed with a 75 m \times 0.53 mm I.D. DB-624 (film thickness 3 μ m) megabore capillary column (catalogue No. 125-1374; J&W Scientific, Folsom, CA, USA). Helium (8 ml/min) was used as the carrier gas. The column was heated from 40°C (holding time 5 min) to 160°C (holding time 1 min) at 5°C/min and then to 210°C (holding time 5 min) at 10°C/min. The electron-capture detector was heated at 290°C and nitrogen (34 ml/min) was used as the make-up gas. The flame ionization detector was heated at 250°C. Hydrogen (45 ml/min) and air (430 ml/min) were used to keep the flame at the operative chromatographic conditions.

2.6. Quantification

Two standard mixtures were used for quantification. One was prepared with trichlorofluoromethane, 1,1-dichloroethylene, dichloromethane, 1,1-dichloroethane, chloroform, carbon tetrachloride, trichloroethylene, 1,2-dichloropropane, 2-chloroethyl vinyl ether, 1,1,2-trichloroethane, tetrachloroethylene and dibromochloromethane. The other contained *trans*-

1,2-dichloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethane, bromodichloromethane, *trans*-1,3-dichloropropene, *cis*-1,3-dichloropropene, bromoform and 1,1,2,2-tetrachloroethane. Various methanol solutions of each compound at concentrations between 0.4 and 10 $\mu\text{g}/\text{ml}$ were prepared with these mixtures. Reference solutions for 1,2,3-trichloropropane and hexachlorobutadiene were prepared separately. These solutions were stored in the above-mentioned aluminium-sealed vials and kept at -20°C . After 2 weeks of storage they were always discarded and new series of diluted standards were prepared.

Aliquots of 4 μl of all these solutions were introduced into volumetric flasks containing 10 ml of Milli-Q-purified water. The flasks were capped and shaken vigorously and 5 ml of the water were introduced into the PT device. The standard volatile compounds were trapped in adsorption tubes and these were analysed in the ATD–GC system. Peak-area integration of the chromatograms corresponding to these tubes resulted into 22 reference straight lines allowing the individual calibration of the compounds identified in the samples.

2.7. Recovery tests

About 1–3 g of sediment were introduced into a 40-ml vial together with 5 ml of methanol and 20 μl of the above-mentioned two standard mixtures containing each compound at a concentration of 200 $\mu\text{g}/\text{ml}$. The vials were capped, shaken and left to equilibrate for 24 h at 4°C . Then, 2 ml of the supernatant methanol were introduced into aluminum-sealed vials and an aliquot (200 μl) of this solution was diluted in 100 ml of Milli-Q-purified water and analysed by the PT method following the above-indicated procedure. Alternatively, the methanol solutions were stored at -20°C for 50 days and analysed by the PT method after dilution of a 200- μl aliquot in 100 ml of Milli-Q-purified water. Leak tests not including the introduction of sediment into the 40-ml vials were also performed. In these tests, the methanol solutions were only stored at -20°C in the aluminum-capped vials for 24 h.

3. Results and discussion

Representative chromatograms of the two standard mixtures used for quantification and the recovery tests are shown in Fig. 1. The DB-624 column used affords baseline resolution of all peaks. This column, under the above-indicated operating conditions, also provides a baseline-resolved chromatogram when the two standard mixtures are analysed jointly. However, these operating conditions are critical to achieve the separation of chloroform, 1,1,1-trichloromethane, carbon tetrachloride and 1,2-dichloroethane and also for the separation of 2-chloroethyl vinyl ether and *trans*-1,3-dichloropropene. Two other compounds that are difficult to separate, 1,1,2,2-tetrachloroethane and 1,2,3-trichloropropane (not included in these standard mixtures), were also resolved with this DB-624 column.

3.1. Response factors, limits of detection and range of linearity

The different peak areas in the chromatograms of the standard mixtures shown in Fig. 1 illustrate the wide diversity of the electron-capture detection (ECD) response factors for each compound. These factors (area units per μg of compound) are listed in Table 1, where they are expressed by reference to that of 1,1-dichloroethylene. As expected, they are essentially dependent on the number and type (*i.e.*, fluorine, chlorine, bromine) of halogen atoms in each compound. The relative differences may be higher than three orders of magnitude.

These different response factors give rise to significant differences in detection limits and linear concentration ranges for each VOC. Thus, the observed limits of detection and ranges of linearity on analysis with this SE-PT method are also given in Table 1. In general, there is a good correspondence between response factors and limits of detection. However, it must be noted that the values shown in Table 1 are only guidelines, not necessarily absolute minimum values. The SE-PT method used in this study has been designed for the analysis of VOC

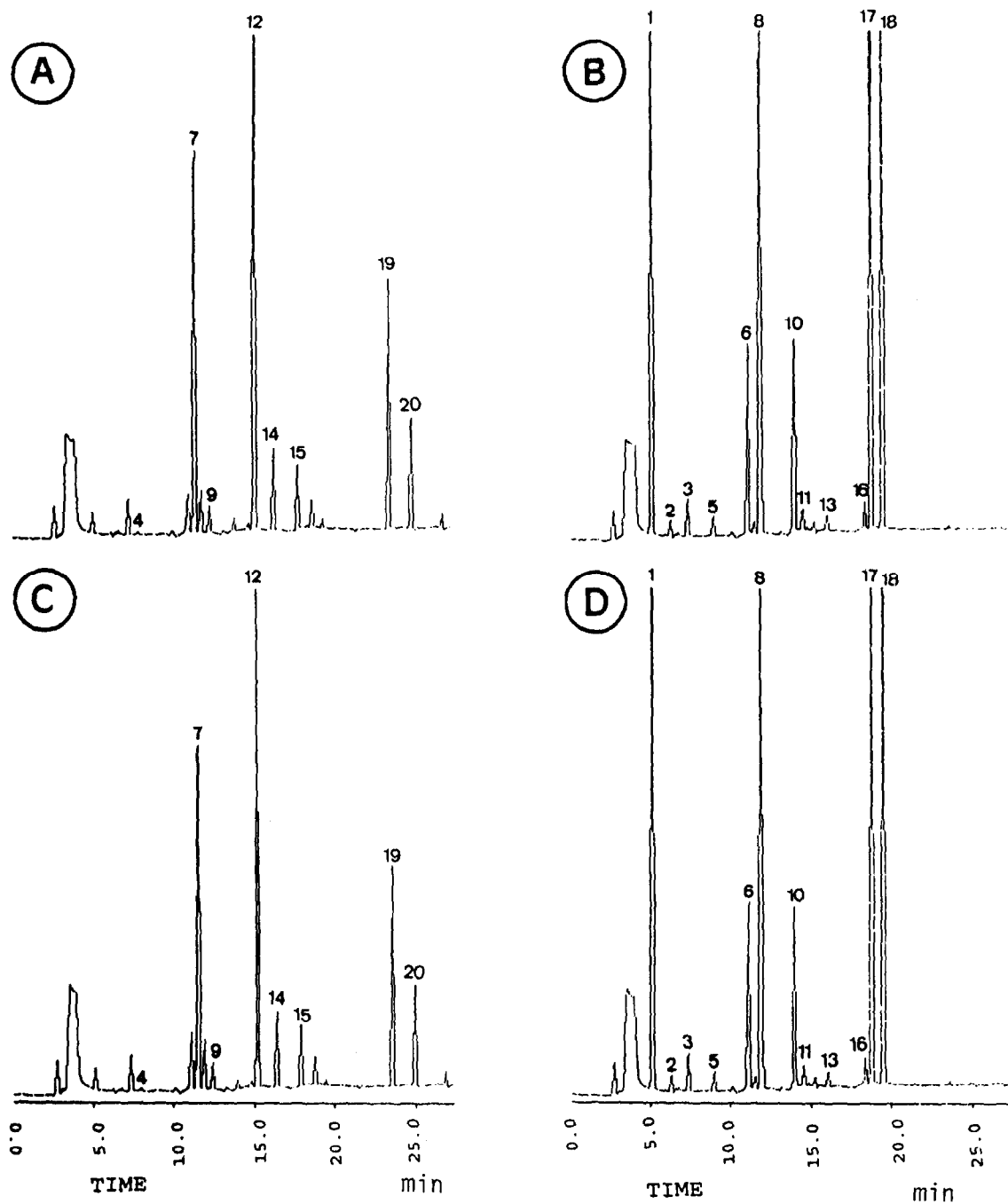


Fig. 1. Chromatograms of the standard mixtures used in the evaluation of the SE-PT method. (A and B) original mixtures; (C and D) recovered methanol extracts after water suspension with sediment and storage at -20°C for 24 h. Peak numbers refer to compound identification in Table 1.

Table 1

Detection limits, ranges of linearity and response factors (relative to 1,1-dichloroethylene) for 22 volatile organic compounds commonly encountered in sediments

No.	Compound	Detection limit ($\mu\text{g/g}$)	Linearity range (ng)		Response factor ($\text{area}/\mu\text{g}$)
			Lower	Upper	
1	Trichlorofluoromethane	0.05	0.04	40	1600
2	1,1-Dichloroethylene	0.40	0.20	400	1
3	Dichloromethane	0.10	0.10	200	100
4	<i>trans</i> -1,2-Dichloroethylene	0.10	0.05	400	13
5	1,1-Dichloroethane	0.10	0.10	100	90
6	Chloroform	0.10	0.04	40	52
7	1,1,1-Trichloroethane	0.05	0.04	40	1300
8	Carbon tetrachloride	0.05	0.02	20	2900
9	1,2-Dichloroethane	0.05	0.4	40	140
10	Trichloroethylene	0.10	0.08	20	790
11	1,2-dichloropropane	0.50	0.20	200	81
12	Bromodichloromethane	0.05	0.02	40	1600
13	2-Chloroethyl vinyl ether	0.10	0.10	200	57
14	<i>trans</i> -1,3-Dichloropropene	0.10	0.10	200	180
15	<i>cis</i> -1,3-Dichloropropene	0.10	0.10	200	160
16	1,1,2-Trichloroethane	0.10	0.40	200	110
17	Tetrachloroethylene	0.20	0.10	20	2300
18	Dibromochloromethane	0.05	0.05	20	1800
19	Bromoform	0.20	0.10	200	240
20	1,1,2,2-Tetrachloroethane	0.05	0.02	200	250
21	1,2,3-Trichloropropane	0.10	0.10	100	140
22	Hexachlorobutadiene	0.05	0.02	40	5500

mixtures, not for single compounds. Therefore, the working conditions and general evaluation were established following this criterion. Lower detection limits would be achieved if the method only involved the analysis of compounds having the highest response factors. In comparison with detection limits reported in the literature, those in Table 1 are lower than for methods such as those involving solvent extraction and GC [2], but higher than for PT methods with the direct vaporization of soil or sediment samples [16,18].

The ranges of linearity for the individual VOCs are also reported in Table 1. These values are expressed as the absolute amount in nanograms introduced into the PT device. According to the split flows of the ATD-GC system, the VOC amounts effectively arriving at the electron-capture detector represent only about 5% of the tabulated values. Again, the amounts indicated in Table 1 do not correspond to the

detailed study of each compound but to the differences between compounds observed in the general evaluation of the method for the analysis of the standard mixtures shown in Fig. 1. According to these linearity ranges, a suitable working interval for all compounds is 0.4–20 ng. This interval has found to be adequate for the analysis of all field samples considered.

3.2. Recoveries

The performance of the SE-PT method (Table 2) was evaluated by means of diverse recovery tests. The leak tests (see Experimental) resulted in recoveries of 94–105% with an average value of 99%. The most volatile compound, trichlorofluoromethane, shows the lowest recovery, 94%, and the highest standard deviation, 17% ($n = 3$). The recoveries higher than 100% may correspond to slight contamination due to

Table 2

Results corresponding to the recovery experiments of the 20 compounds included in the two reference mixtures used for quantification (units in $\mu\text{g/ml}$ of methanol; 100% recovery corresponds to 0.8 $\mu\text{g/ml}$)

No.	Compound	Leak test, only glassware ($n = 3$)		Sand, 24 h (mean, $n = 2$)	Silt, 24 h (mean, $n = 2$)	Sediment, 24 h ($n = 4$)		Sediment, 50 days ($n = 4$)	
		Mean	S.D.			Mean	S.D.	Mean	S.D.
1	Trichlorofluoromethane	0.75	0.14	0.87	0.89	0.88	0.032	0.66	0.087
2	1,1-Dichloroethylene	0.79	0.050	0.84	0.80	0.83	0.030	0.72	0.022
3	Dichloromethane	0.84	0.040	0.88	0.92	0.90	0.087	0.74	0.033
4	<i>trans</i> -1,2-Dichloroethylene	0.80	0.021	0.65	0.70	0.67	0.078	0.69	0.045
5	1,1-Dichloroethane	0.83	0.060	0.81	0.77	0.79	0.051	0.76	0.038
6	Chloroform	0.82	0.025	0.80	0.78	0.79	0.032	0.76	0.048
7	1,1,1-Trichloroethane	0.79	0.010	0.70	0.66	0.68	0.037	0.66	0.072
8	Carbon tetrachloride	0.79	0.0	0.78	0.76	0.77	0.014	0.72	0.017
9	1,2-Dichloroethane	0.80	0.0058	0.73	0.73	0.73	0.028	0.70	0.045
10	Trichloroethylene	0.77	0.010	0.72	0.68	0.70	0.029	0.72	0.029
11	1,2-Dichloropropane	0.79	0.012	0.77	0.74	0.76	0.025	0.73	0.029
12	Bromodichloromethane	0.79	0.0058	0.75	0.74	0.75	0.015	0.75	0.024
13	2-Chloroethyl vinyl ether	0.76	0.12	0.67	0.87	0.73	0.13	0.65	0.11
14	<i>trans</i> -1,3-Dichloropropene	0.79	0.020	0.69	0.67	0.68	0.025	1.07	0.051
15	<i>cis</i> -1,3-Dichloropropene	0.79	0.017	0.70	0.68	0.69	0.022	0.38	0.021
16	1,1,2-Trichloroethane	0.76	0.11	0.65	0.70	0.68	0.13	0.64	0.041
17	Tetrachloroethylene	0.78	0.012	0.76	0.76	0.76	0.0096	0.73	0.024
18	Dibromochloromethane	0.77	0.070	0.69	0.82	0.73	0.10	0.74	0.028
19	Bromoform	0.78	0.020	0.71	0.69	0.70	0.017	0.69	0.033
20	1,1,2,2-Tetrachloroethane	0.76	0.040	0.70	0.64	0.67	0.048	0.69	0.047
	All compounds	0.79		0.74	0.75	0.74		0.71	

the presence of VOCs in the atmosphere of the laboratory.

Two types of solid matrices, a sand (20% water content, 0.27% organic carbon) and a silt (17% water content, 0.64% organic carbon), were used for the tests involving a suspension of the standard solution with sediments. The results are illustrated in Fig. 1, where the chromatograms corresponding to the standard mixtures and to the recovered methanol extracts after suspension in silt are shown. In the two series of experiments the recoveries ranged between 81 and 110% (average 92.5%) and between 80 and 115% (average 94%) for sand and silt, respectively (Table 2). The Student's *t*-test evaluation of the average values obtained with the two types of sediments showed no significant difference for any of the VOCs included in the study. For this reason, the results corresponding to both series of sediments were grouped together,

averaged and used for comparison with other tests.

These average results are also given in Table 2. Their comparison with the leak test described above indicates a general trend to lower VOC recoveries in the presence of sediments. Thus, the total average recoveries of the experiments with and without sediments are 92.5% and 99%, respectively. Conversely, in the case of the most volatile compounds, trichlorofluoromethane, 1,1-dichloroethylene, dichloromethane [boiling points at 1 atm (101 325 Pa) = 24, 37 and 40°C, respectively], the average recoveries of the sediment suspension tests do not show any further decrease, which points to a very limited interaction between these VOCs and the sedimentary matrices. In this respect, none of the average recoveries of these three compounds show significant differences between the two experiments when evaluated with the Student's *t*-test.

The general trend to lower recoveries in the presence of sediments is influenced by the amount of sediment used for suspension. This is shown in Fig. 2, where the results of diverse recovery tests in the presence of various amounts of sediments are represented for selected VOCs. A slight decrease in recoveries with increasing amounts of sediment is observed. In principle, sample amounts of the order of 1 g are preferred although limits of detection (and hence VOC concentrations in the sediments under study) will also have to be taken into account.

One of the main advantages sought by this combined SE-PT method concerns the lack of dependence between the sampling and analytical operations. The methanol extracts can be stored at -20°C in the aluminium-sealed vials for extended periods of time, which allows large numbers of samples to be taken without the need for immediate instrumental analysis. In order to test the effectiveness of this approach, VOC losses after long periods of storage were tested. For this purpose, the methanol extracts obtained after the sediment suspension experiments were stored at -20°C in the aluminium-sealed vials for 50 days and analysed again after this period. The results are also given in Table 2. The recoveries range between 80 and 95% (results for *trans*- and *cis*-1,3-dichloropropene not included) with an

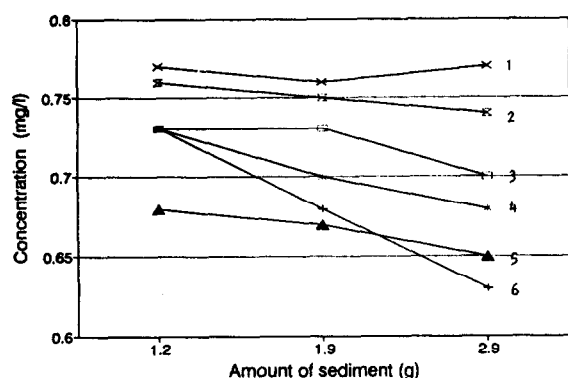


Fig. 2. Recovered concentrations of selected VOC on water suspension with increasing amounts of sediment. 1 = CCl_4 ; 2 = tetrachloroethylene; 3 = dibromochloroethane; 4 = 1,2-dichloroethane; 5 = 1,1,2-trichloroethane; 6 = 2-chloroethyl vinyl ether.

average value of 89%. That is, the losses after this long period of storage only represent an additional VOC loss of 4% in relation to the initial recovery values. This small loss indicates that the differences are not significant for most VOCs when evaluated with the Student's *t*-test.

However, with the most volatile compounds, trichlorofluoromethane, 1,1-dichloroethylene and dichloromethane, the Student's *t*-test shows that the average recovery differences, -14 , -8 and -6% , respectively, are significant (confidence levels 99.5, 99.5 and 97.5%, respectively). This is probably due to vapour losses during the long period of 50 days despite storage at -20°C . Significant differences were also observed with the two perchlorinated compounds, carbon tetrachloride and tetrachloroethylene (-6 and -4% , Student's *t*-test confidence levels of 99.5 and 95%, respectively). It is known that these two solvents may undergo oxidation in humid conditions [20–22] and the decrease in concentration seems more likely to be due to this type of process occurring during the long storage period than to evaporation losses that are not observed with other more volatile compounds.

Another interesting aspect concerns *trans*- and *cis*-1,3-dichloropropene, with significant differences in average values at the 99.95% confidence level. Nevertheless, the concentrations of these two compounds are decreased for the *cis* isomer, $0.38 \mu\text{g}/\text{ml}$, and increased for the *trans* isomer, $1.07 \mu\text{g}/\text{ml}$. If the concentrations of both species are averaged, $0.72 \mu\text{g}/\text{ml}$ (S.D. $0.37 \mu\text{g}/\text{ml}$), there is no significant decrease in the total amount of 1,3-dichloropropene which corresponds to a conversion of the *cis* into the *trans* isomer during the 50 days of storage at -20°C .

3.3. Real case studies

Several chromatograms corresponding to sediments collected in aquatic systems situated in the area of influence of two organochlorinated solvent factories are shown in Fig. 3. The concentrations are given in Table 3. Fig. 3A corresponds to sediments collected near a chemical factory situated in Flix and Fig. 3B and C correspond to chromatograms from sediments

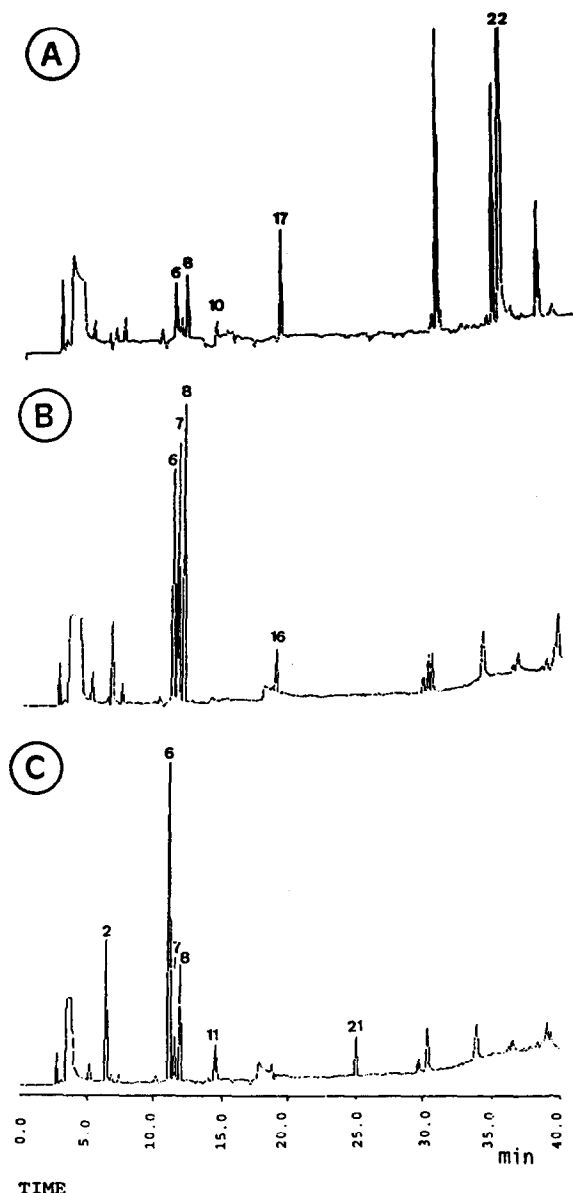


Fig. 3. Chromatograms showing the VOC extracts from sediments collected in (A) Flix and (B and C) Alagoas (see Table 3). Peak numbers refer to Table 2.

sampled in the chlorochemical complex of Alagoas (Brazil). These chromatograms are generated from the analysis of 1–3 g of sediment and, after the dilution steps determined in the GC-PT method, correspond to the effective

injection of the extract equivalent to a sample amount of 2–6 mg. This procedure allowed the determination of all trace VOCs present in the samples. However, further dilution (fivefold) was required for quantification of one major compound, hexachlorobutadiene (No. 22 in Fig. 3A).

Three compounds are common to all three samples, chloroform, 1,1,1-trichloroethane and carbon tetrachloride, which correspond to solvents usually synthesized in these types of factories. Carbon tetrachloride may also be a side-product generated in the synthesis of other organochlorinated solvents. As indicated above, the operating conditions selected for the DB-624 column used in this study allow the baseline resolution of these three compounds. Other VOCs, *i.e.*, trichloroethylene, 1,2-dichloropropane, 1,1,2-trichloroethane, tetrachloroethylene, 1,2,3-trichloropropane and hexachlorobutadiene, only occur in some of the samples. In this respect, hexachlorobutadiene ($71 \mu\text{g/g}$) is a characteristic compound of the air, waters and sediments surrounding the Flix factory and 1,2-di- and 1,2,3-trichloropropane (26 and $10 \mu\text{g/g}$, respectively) were used as raw materials in the Alagoas complex.

4. Conclusions

The limits of detection and linearity ranges of the combined SE-PT method considered in this study were tested for a group of 20 standard halogenated VOCs. The results showed that the method provides suitable parameters for the determination of volatile organochlorinated compounds in sediments. These standards were also used for diverse recovery calculations showing that, on average, only 1% of the individual amounts is lost in the glassware manipulations. Further, recovery experiments involving water sediment suspensions with the standards and storage of the methanol extracts for 1 and 50 days resulted in average losses of 7.5 and 11%, respectively. These relatively small values show the usefulness of the method and confirm that, with the system and conditions of storage select-

Table 3

VOC concentrations ($\mu\text{g/g}$) in sediments from aquatic systems receiving discharges from organochlorinated solvent factories

No.	Compound	Flix (A)	Alagoas (B)	Alagoas (C)
2	1,1-Dichloroethylene	n.d. ^a	n.d.	22
6	Chloroform	0.2	0.3	0.6
7	1,1,1-Trichloroethane	n.d.	1.0	0.4
8	Carbon tetrachloride	0.1	0.2	0.1
10	Trichloroethylene	0.1	n.d.	n.d.
11	1,2-Dichloropropane	n.d.	n.d.	26
16	1,1,2-Trichloroethane	n.d.	0.2	n.d.
17	Tetrachloroethylene	0.3	n.d.	n.d.
21	1,2,3-Trichloropropane	n.d.	n.d.	10
22	Hexachlorobutadiene	71	n.d.	n.d.

^a n.d. = Not detected.

ed in this study, the concentration measurements are not significantly affected by long delay periods between sampling and analysis. Hence the present SE-PT method appears to be particularly useful in applications where the long distances between the area of study and the instrumental equipment do not allow the immediate determination of the VOC species. In fact, after 50 days of storage no significant decrease in VOC concentration was observed except for the more volatile compounds such as trichlorofluoromethane, 1,1-dichloroethylene and dichloromethane (boiling points at 1 atm lower than 40°C), two perchlorinated compounds, carbon tetrachloride and tetrachloroethylene, and the 1,3-dichloropropenes, among which a conversion from the *cis* to the *trans* isomer is observed.

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