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Determination of volatile halogenated organic compounds in soils by purge-and-trap capillary gas chromatography with atomic emission detection

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Abstract

Nine volatile halogenated organic compounds (VHOCs), including four trihalomethanes (THMs), were determined in soils by capillary gas chromatography with microwave induced-plasma atomic emission spectrometry (GC-AED), using a purge-and-trap system (PT) for sample preconcentration. Analytes were previously extracted from the soil sample in methanol and the extract was preconcentrated before being chromatographed. Element-specific detection and quantification were carried out monitoring two wavelength emission lines, corresponding to chlorine (479 nm) and bromine (478 nm). Each chromatographic run took 21 min, including the purge step. The method showed a precision of 1.1–7.2% (R.S.D.) depending on the compound. Detection limits ranged from 0.05 to 0.55 ng ml^{-1}, for chloroform and dichloromethane, respectively, corresponding to 3.3 and 36.0 ng g^{-1} in the soil samples. The chromatographic profiles obtained showed no interference from co-extracted compounds. Low levels of dichloromethane and chloroform ranging from 0.04 to 1.13 μg g^{-1} were found in samples obtained from small gardens irrigated with tap water. The method is reliable and can be used for routine monitoring in soil samples.

Keywords: Volatile halogenated organic compounds; Trihalomethanes; Soils; Purge-and-trap; Gas chromatography-atomic emission detection

1. Introduction

Volatile halogenated organic compounds (VHOCs) are widely used as coolants in refrigerators, as propellants and as cleaning solvents in industry [1]. They also appear in the environment as products resulting from the treatment of potable water and wastewater for disinfection purposes [2]. The presence of this group of chemicals in soils, sediments, waters, and the atmosphere is therefore widespread. VHOCs present specific environmental and health risks [3] and are suspected of being carcinogenic, a toxicity that has led to increasing interest in their determination in the environment.

Although the bibliography for the determination of volatile organic compounds in water samples is extensive, the methods used for quantifying these compounds in soil samples are less numerous. The effectiveness of the extraction procedure is a critical step in the whole method. Purge-and-trap [4–8], supercritical fluid extraction [9], and solid-phase extraction [10] have been the most frequently proposed extraction methods. The method recommended by US EPA (EPA/SW-846-5030A and 8260A) for the measurement of volatile organic compounds in soils is purge-and-trap followed by gas chromatography–mass spectrometry [11]. Problems derived from the effectiveness of the extraction step and the lack of reference materials add importance to the development of new methods for VHOC determination in soil samples.

Atomic emission spectrometry for the detection of gas chromatographed VHOCs provides selective information [12,13], which cannot be obtained with other commonly used element-selective detectors, such as flame ionization detector (FID) [6–10] or electron capture detector (ECD). We have found no publications reporting the use of atomic emission (AED) for the detection of VHOCs in soil samples.

In this study, a procedure for the determination of nine VHOCs, including four trihalomethanes, in soil samples, using AED as detection method for PT-GC is discussed.

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Table 1
Volatile halogenated organic compounds chromatographed

Compound	Molecular formula	Boiling point (°C)	Monitored emission line (nm)	Retention time (min)
Dichloromethane	CH_2Cl_2	40	Cl 479	6.27
Chloroform	$CHCl_3$	68	Cl 479	7.74
Tetrachloromethane	CCl_4	76	Cl 479	8.11
1,2-Dichloroethane	$C_2H_4Cl_2$	83	Cl 479	8.25
Bromodichloromethane	$CHBrCl_2$	87	Br 478	9.13
Tetrachloroethene	C_2Cl_4	121	Cl 479	10.20
Dibromochloromethane	$CHBr_2Cl$	117	Br 478	10.36
Bromoform	$CHBr_3$	149	Br 478	11.45
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	146	Cl 479	11.74

2. Experimental

2.1. Chemicals

The studied VHOC standards came from Lab-Scan (Dublin, Ireland) and Supelco (Bellefonte, PA, USA), and their purity was, in every case, greater than 98.3%. As can be seen in Table 1, their boiling points ranged between 40 and 150 °C. Standard solutions of 3000 μg ml^{-1} of each compound were prepared by dissolving the standards in methanol of analytical-reagent grade (Merck, Barcelona, Spain) and stored in the dark at 4 °C. Working standard solutions were prepared daily by diluting the methanolic standards with high quality water obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) and also stored at 4 °C in the refrigerator.

Helium, nitrogen, and oxygen (99.9999%) were purchased from Air Liquide (Madrid, Spain).

2.2. Instrumentation

The purge-and-trap sample enrichment system was a Tekmar Dohrmann 3100 model (Agilent, Waldbronn, Germany), which was controlled by Teklink (2.02 Version) software. The purging vessel was a 5 ml glass U-tube with 1/2″ frit sparger top fit. The vessel was rinsed three times with the sample before each experiment, and further rinsed three times with deionized Milli-Q water after each analysis. It was thermostated at 25 °C using a lab-made system. Analytes were purged out from 5 ml of aqueous solution with a helium flow-rate of 40 ml min^{-1} for 9 min and maintaining the trap temperature at 30 °C, the analytes being carried in this way to a trap column (30.5 cm × 0.312 cm o.d. × 0.259 cm i.d.) coated with a Tenax GC, silica gel, and activated carbon layer, as recommended by the US EPA method [14], which prevents the adsorption of purged water vapor. The purge-and-trap system includes a moisture control module (MCM). Once confined in the trap, the volatile organic compounds were desorbed by opening the vents at 260 °C for 4 min. During this desorption step, the carrier gas is drawn through the trap in the opposite direction of the purge flow in the column, in order to minimize band broadening at the beginning of the chromatographic column. Once the analytes have been desorbed, a bake step is programmed at 270 °C for 8 min, to avoid possible memory effects of the tailing compounds. The purge-and-trap system was directly coupled to the gas chromatograph in a direct split interface (DSI) configuration, by means of a transfer line set at 200 °C, in order to avoid analyte condensation during analysis.

An Agilent 6890 gas chromatograph was directly coupled to a G2350A microwave-induced plasma atomic emission detector (Agilent). Updated G2070AA ChemStation application with the G2360AA GC-AED software was used to control and automate many features of the GC and AED systems, and for data acquisition and treatment. The chromatograph was fitted with a 30 m × 0.32 mm i.d. DB-624 capillary column with 1.80 μm film thickness from Agilent. The oven temperature was programmed as follows: 40 °C for 3 min, rising to 100 °C at 30 °C min^{-1} and holding for 2 min, and finally to 200 °C at 25 °C min^{-1} and holding for 1.6 min. Helium was used as the carrier gas at 1 ml min^{-1}, in the constant-flow mode. The helium make-up flow-rate was set at 40 ml min^{-1}, being measured with the window purge gas flow on. Solvent venting was switched on immediately after starting the desorption step in the purge-and-trap system and switched off 4 min later. The spectrometer was purged with nitrogen at a flow-rate of 2.5 l min^{-1}. Oxygen at 25 psi was used as reagent. Filter and backamount adjustment in the AED were set according to Agilent default specifications. The elements analyzed and their emission lines, in nanometers, were: chlorine 479.45 nm and bromine 478.55 nm.

An IKAKS 130 basic shaker (IKA, Staufen, Germany) was used for automatic shaking. An S.P. Selecta centrifuge (Selecta, Spain) was used for phase separation.

2.3. Sample collection and storage

Six soil samples were obtained from private gardens used for domestic purposes, which were normally irrigated with tap water. Four soil samples from large agricultural areas were also sampled. Special care was taken in the sampling step because of the effect on subsequent results of sample collection, size and handling, together with their storage and holding time. Samples of soil (100 g) were collected in plastic (polypropylene) bottles, ensuring that all the recipients were completely filled with the sample, to avoid the

presence of a gaseous phase, and stored at 4 °C on arrival. Sub-samples were ground by using a mortar before their analysis (which was normally performed within 48 h of arrival at the laboratory).

2.4. Extraction procedure and recovery assays

A 5-g portion of ground soil was weighed into a 50 ml capped polycarbonate tube and 10 ml of methanol were added for extraction. The mixture was horizontally shaken for 20 min (800 rpm) at room temperature, after which the liquid phase was separated from the solid residue by centrifugation at 3000 rpm for 5 min and decanted into a reservoir. A second extraction was performed and the two liquid phases combined and made up to 25 ml with methanol. Aliquot of the extract (750 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. If dichloromethane and chloroform are not being analyzed, the second extraction would be omitted, hence decreasing the analysis time.

Spiked samples were prepared by adding 1 ml of methanol containing a known amount of each analyte to 5 g of ground soil previously weighed in a centrifuge tube. The tube was immediately sealed and vigorously shaken in order to homogenize the mixture, then stored for 24 h at 4 °C. Three replicates were analyzed at each fortification level, which ranged from 0.09 to 1.8 $\mu g\,g^{-1}$, depending on the volatile organic compound in question.

3. Results and discussion

3.1. Separation and detection parameters

A detailed explanation of the purge-and-trap optimization conditions was provided in previous studies [15]. Experiments were conducted to choose the oven program that allowed the best separation of the nine volatile organic compounds in the lowest possible time. From this study, the selected program temperature enabled the nine compounds to be eluted between 6 and 12 min, as shown by their respective retention times in Table 1. Separation was carried out using a constant helium flow-rate of 1 $ml\,min^{-1}$, since higher flow-rates produced overlapping peaks while lower flow-rates increased peak widths and hence analysis time.

Since atomic emission spectrometry provides element-specific detection, higher selectivity can be obtained monitoring chlorine and bromine emission lines compared to common elements such as carbon. Simultaneous multi-element detection can be applied to Cl-479 and Br-478 because their analytical lines are not separated from each other by more than 40 nm and the same scavenger gas is required, oxygen. The presence of oxygen prevents carbonaceous deposition on the wall of the discharge tube. The influence of oxygen pressure was studied between 20 and 35 psi, because pressures under 20 psi do not prevent accumulation of elemental carbon in the AED discharge tube [16]. Sensitivity decreased at pressures higher than 25 psi for all the studied compounds, and this was the value adopted [15].

Two different patterns were observed when the helium make-up flow-rate was varied. A standard solution of 10 $ng\,ml^{-1}$ preconcentrated in the purge-and-trap system and injected into the chromatograph was used to optimize this parameter. The helium make-up gas flow-rate was varied from 30 to 45 $ml\,min^{-1}$. No signals were obtained at 30 $ml\,min^{-1}$, while maximum sensitivity was obtained at 35 $ml\,min^{-1}$ flow-rate for the four most retained compounds. In the case of the other compounds, peak area slightly increased up to 40 $ml\,min^{-1}$and then remained constant. The helium make-up gas flow was finally adjusted to 40 $ml\,min^{-1}$, where the sensitivity was markedly higher for four of the analytes.

Elution profiles for the standard mixture under the optimized conditions at the two monitored channels are shown in Fig. 1A and B.

3.2. Calibration, precision and detection limits

For calibration, aqueous standards at five concentration levels were prepared and 5 ml aliquots of each standard were purged and analyzed. Two replicates were made for each calibration level. Linear calibration curves were obtained by plotting peak areas versus concentrations and the linear relationships for the studied compounds are shown in Table 2. Correlation coefficients were better than 0.9975, demonstrating the high degree of correlation between concentration and peak area for the studied compounds. The repeatability of the method was calculated using the relative standard deviation for 10 successive injections of an extract of a spiked soil sample under the optimized procedure, ranging between 1.1% for tetrachloromethane and 7.2% for both dichloromethane and chloroform. Furthermore, the optimized procedure was applied to 10 aliquots of the same fortified soil sample, the R.S.D. ranging between 5.0 and 15% for dibromochloromethane and tetrachloromethane, respectively. Detection limits were calculated using a signal-to-noise ratio of three for all investigated compounds and values are also given in Table 3. Values for the detection limits are also given in Table 3 for soil samples when using the optimized extraction procedure.

3.3. Optimization of the extraction procedure

The extraction procedure was optimized using a laboratory-prepared soil sample as indicated in Section 2.4. The direct extraction [3] by purging a solution containing the soil sample was not possible with the instrumentation available, and so a previous extraction step was required. The extract obtained was submitted to preconcentration with the PT system. In this way, organic contaminants readily desorbable from the soil pore spaces and external

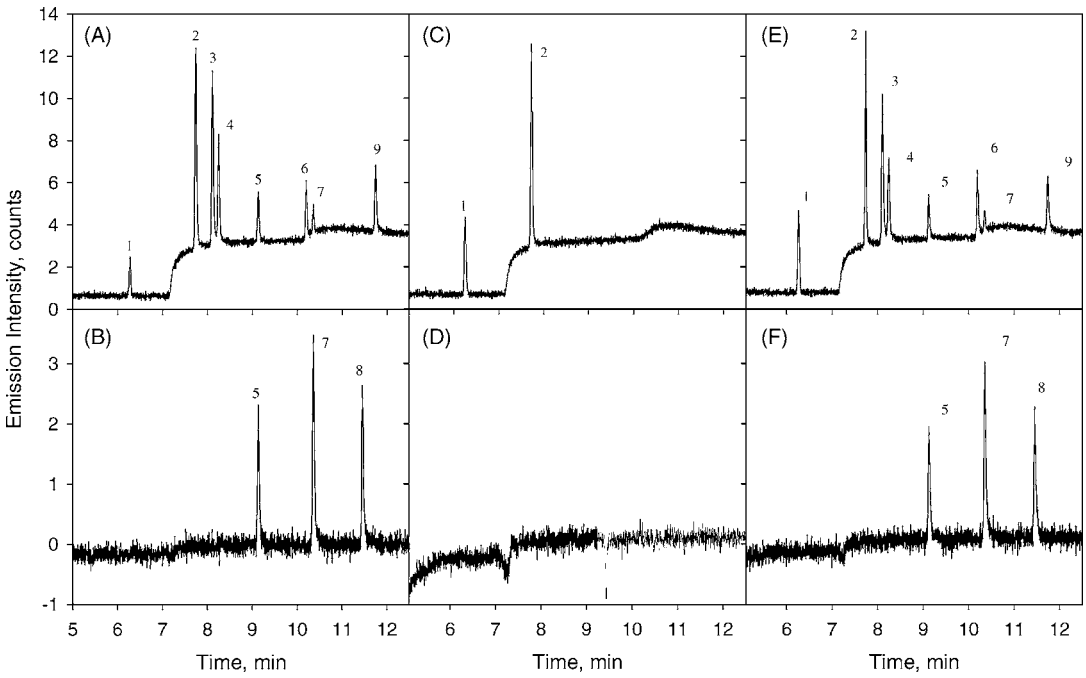

Fig. 1. PT-GC-AED chromatograms obtained from a standard mixture of the volatile halogenated organic compounds (A, B), soil sample 3 (C, D) and fortified soil sample 3 (E, F). (A, C, E) Cl 479 nm, and (B, D, F) Br 478 nm. Concentrations of the standard mixture: (1) dichloromethane, 11 ng ml^{-1}; (2) chloroform, 1.9 ng ml^{-1}; (3) tetrachloromethane, 18 ng ml^{-1}; (4) 1,2-dichloroethane, 4 ng ml^{-1}; (5) bromodichloromethane, 4 ng ml^{-1}; (6) tetrachloroethene, 6.4 ng ml^{-1}; (7) dibromochloromethane, 4 ng ml^{-1}; (8) bromoform, 3.7 ng ml^{-1}; and (9) 1,1,2,2-tetrachloroethane, 3.8 ng ml^{-1}.

Table 2
Calibration data for the target compounds

Compound	Sensitivity[a] (cts ng^{-1})	Linearity range (ng ml^{-1})	Detection limit[b] (ng ml^{-1})	Detection limit[c] (ng g^{-1})
Dichloromethane	0.15	2.5–25.0	0.55	36.7
Chloroform	1.42	0.4–5.0	0.05	3.3
Tetrachloromethane	0.36	2.5–30.0	0.23	15.3
1,2-Dichloroethane	1.55	0.5–10.0	0.09	6.0
Bromodichloromethane	1.19 (1.15)	1.0–10.0	0.24	16.0
Tetrachloroethene	0.66	2.0–10.0	0.28	18.7
Dibromochloromethane	1.18 (1.43)	0.5–10.0	0.15	10.0
Bromoform	0.70	0.5–10.0	0.14	9.3
1,1,2,2-Tetrachloroethane	0.69	0.5–10.0	0.13	8.1

[a] Calculated for the element used for quantification purposes. Values into parenthesis correspond to chlorine data.
[b] Corresponding to S/N=3.
[c] Calculated for 5 g of soil, according to the optimized procedure.

soil surfaces, and those which have diffused into internal micropores of the soil matrix can be measured [6].

Preliminary experiments were carried out to increase the extraction efficiency by shaking 5 g of a spiked soil with 5 ml of methanol at 800 rpm for times ranging between 5 and 30 min. Although different patterns were observed with different shaking times, maximum sensitivity was observed for each of the nine monitored compounds with 20 min of shaking, as observed in Fig. 2A. Volumes of 2.5, 5, 10, and 15 ml of the organic solvent were assayed with 5 g of the soil shaken for 20 min. As can be seen from Fig. 2B, peak areas increased for all analytes up to 10 ml and then practically remained constant, so a 10 ml volume was used. Under the selected conditions (i.e. 5 g of soil horizontally shaken with

Table 3
Concentrations of the volatile halogenated organic compounds in soil samples (μg g^{-1})[a]

Soil sample	Dichloromethane	Chloroform
1	ND	0.04 ± 0.01
2	0.86 ± 0.06	0.13 ± 0.04
3	1.13 ± 0.08	0.16 ± 0.01
4	0.79 ± 0.13	0.11 ± 0.01
5	0.66 ± 0.10	1.10 ± 0.22
6	0.51 ± 0.06	0.14 ± 0.01

ND means non detected.
[a] Mean ± standard deviation ($n = 3$).

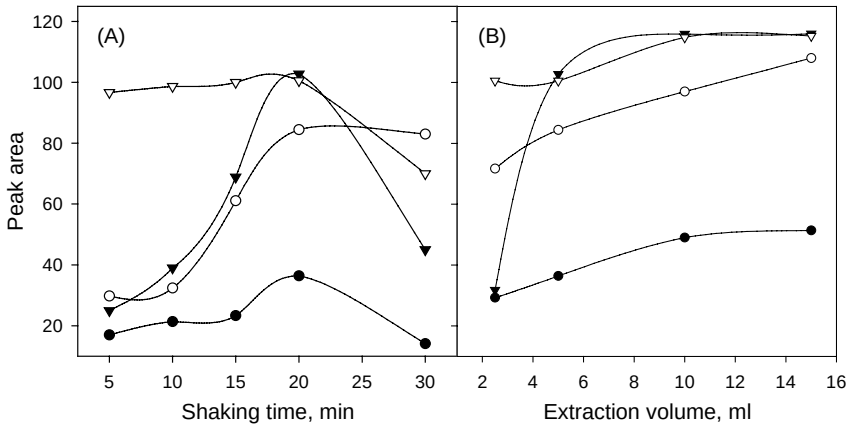

Fig. 2. Effect of (A) the extraction time and (B) the methanol volume on the peak area for dichloromethane (●), chloroform (○), tetrachloroethene (▼) and 1,1,2,2-tetrachloroethane (▽), for a spiked soil sample.

10 ml of methanol for 20 min), the extraction percentages were nearly 100% for all the studied VHOCs, except for dichloromethane and chloroform, which showed recoveries of 70 and 50%, respectively. The total extraction of these two compounds was achieved by extracting twice in methanol. Therefore, if the determination of dichloromethane and chloroform is not required, a simple extraction is sufficient to provide very good extraction percentages for the other analytes.

To check the performance of the procedure, soil samples of 1–5 g were submitted to the optimized extraction procedure. Because poor homogenization for sample masses higher than 5 g was achieved with 10 ml of the organic solvent, a sample mass of 5 g was selected.

The obtained methanolic extract is diluted in water to be purged with helium gas and concentrated in the Tenax trap. The maximum volume of the extract submitted to preconcentration would increase the sensitivity of the procedure, although methanol:water ratios higher than 0.75:9.25 produce blocking of the trap, so this ratio was selected.

The possible salting out effect of the extracted analytes in the purge step was checked by adding 750 μl of the methanolic extract to 9.25 ml of a 4.3 M sodium chloride solution. No differences were observed by diluting the extract in water or in sodium chloride solution, so the extract was diluted with water under the optimized procedure, thus preventing salt accumulation in the purging vessel.

3.4. Analysis of soil samples and recovery study

Ten soil samples were used to test the extraction procedure. Table 3 shows the results obtained, dichloromethane and chloroform being the two volatile halogenated organic compounds found in the samples obtained from private gardens. No VHOCs were found in the soils obtained from large agricultural areas probably because they are normally irrigated with subterranean waters, which have not been exposed to chlorination reactions. All samples were analyzed in triplicate. Fig. 1 shows the chromatograms obtained for a soil (C, D) and a spiked soil sample (E, F).

The standard addition method was used to investigate the possibility of a matrix effect. Each graph was constructed from four points, and each point represents the mean of two injections. The slopes of the calibration graphs with the standards directly prepared in water and the standard addition calibration graphs obtained from the soil samples were similar, confirming the absence of any matrix effect.

A persistence study was carried out by spiking 50 g of a blank soil (free of the VHOCs under analysis) with concentration levels ranging between 0.4 and 2.5 $\mu g\,g^{-1}$,

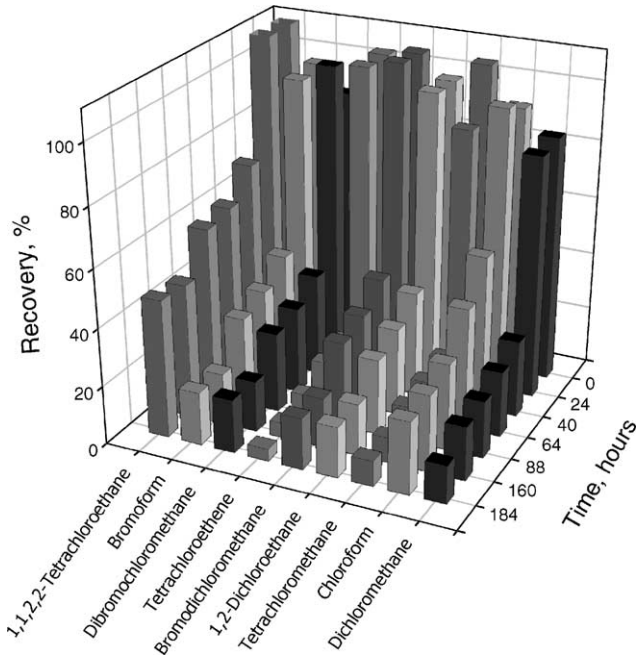

Fig. 3. Variation of the concentration of the nine volatile halogenated organic compounds with time for a spiked soil.

depending on the compound. The spiked sample was extended on a filter paper and exposed to atmosphere at room temperature. Aliquots of 5 g were sampled at given intervals and analyzed. The results obtained are shown in Fig. 3. Note that the greatest decrease for all compounds was observed 40 h after spiking.

A capability study [17] which provides information for estimating the inherent, common cause (inherently random) variation of a process and to compare that variation to requirements was carried out. To this purpose, 10 samples (5.0 g) of soil 2 were fortified for the nine VHOCs under study and measured 10 times. Nine mean recoveries with its corresponding standard deviations were obtained, from these data a mean overall recovery and a mean overall standard deviation were calculated. Twice the overall standard deviation value was chosen as lower and upper specification limits. In all cases, data follow a normal distribution. For 1,1,2,2-tetrachloroethane, chloroform, and bromodichloromethane, the means of the process (ranged between 93 and 97.5%) fall short on the target and the left tail of the distribution falls outside the lower specification limits. For tetrachloromethane and 1,2-dichloroethane, the means of the process (ranged between 103 and 112%) fall high on the target and the right tail of the distribution falls outside the higher specification limits. Potential capability indexes (C_{pk}) for these five analytes ranged from 0.55 to 0.70. For the rest of the compounds C_{pk} values were higher than 0.97. In all cases, high C_{pk} values were obtained, indicating that the process produced values within the tolerance limits.

4. Conclusion

The use of GC-AED allows nine volatile halogenated organic compounds in soils to be reliably determined. The special characteristics of AED together with the high concentration effect achieved by means of a purge-and-trap device permits a sensitive procedure that can be considered as an alternative choice to the use of mass spectrometry as the detection system for the same purpose, involved in the standard procedure used by the US EPA.

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