Determination of Volatile Organic Compounds by Headspace Trap

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Abstract

A new analytical method for the determination of halogenated and aromatic volatile organic compounds in groundwater, mineral water, and drinking water at concentrations ranging between 1–10000 ng/L is developed. A new type of headspace sampler that combines static headspace sampling with a trap is used, yielding very low detection limits and good repeatability without carryover effects. An unexpected transformation of 1,1,2,2-tetrachloroethane into trichloroethene is observed and explained.

Introduction

Over the last 10 years, analytical techniques for the determination of halogenated and aromatic volatiles have improved, leading to better limits of detection (LOD) and reproducibilities. The three main historical techniques are static headspace (1–7), dynamic headspace (purge and trap) (1,3,4,8,9), and solid-phase microextraction (SPME) (10).

Repeatability, detection limit, and elimination of water before the chromatographic run are the three principal variables. Static headspace has an excellent repeatability [coefficients of variation (CV) < 5%], with no interference by water, but sometimes the achieved LOD is not enough to comply with some environmental regulation. For example, it cannot be used to measure concentrations of benzene below 0.5–1 µg/L. SPME has a good LOD (below 0.5 µg/L), but a worse repeatability (CV > 10 %) when using an autosampler (10). The purge and trap technique has a better LOD than static headspace, but the elimination of water may be difficult, and the system is prone to carry-over effects. This makes it is necessary to clean the system using reagent water between every sample. The device must be washed, purged with detergent solution, rinsed with distilled water, and dried for analyses of samples containing large amounts of water-soluble materials, suspended solids, high boiling point compounds, or high levels of volatile compounds. Moreover the trap and other parts of the system must be baked and purged (9).

A new type of headspace sampler, the PerkinElmer Turbomatrix HS40 Trap, which combines headspace sampling with a trap (PerkinElmer, Wellesley, MA), was used in this study, as it had a good LOD (like purge and trap systems), a very good repeatability (similar to static headspace), and allowed the elimination of water before the chromatographic run. Carry-over effects were not observed in our range of concentration (1–10000 ng/L) so it was not necessary to extensively bake and purge the trap after every sample was analyzed.

The Turbomatrix HS 40 Trap instrument is an autosampler for up to 40 vials that can be used to determine volatile organic compounds present in several matrices.

It works with the pulsed-pressure approach, combining a slight modification of the balanced pressure principle with the use of an on-board cold and packed trap to extend its detection limits. The analysis is performed through the following steps:

Equilibration
The vial is warmed at a fixed temperature, defined by the sample characteristics, for a set constant time in order to reach equilibrium conditions.

Pressurization
The needle pierces the septum, and carrier gas (at a pre-set pressure) is allowed to enter the vial to set the internal pressure to a particular value. Simultaneously, a valve isolates the gas chromatography (GC) column, avoiding any column pressure change. This column isolation flow is manually set by the operator 10 mL/min higher than the column flow.

Trap load
During this step, the headspace of the vial is sent to the cold packed trap, allowing a flow of the headspace through the trap. This trap load step can be repeated up to four times for each vial (Figure 1).

Trap dry-purge
The cold packed trap is purged with carrier gas to eliminate water. Even if the adsorbent material is mostly hydrophobic and

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the vial equilibration temperature is kept low, a certain amount of water will remain in the trap. This would damage the capillary column and worsen the detection limits by increasing the baseline. Therefore, water vapor must be eliminated.

Trap desorb and trap hold

During these steps, the trap temperature is increased to the desired high value at a rate of 400°C/min to release the trapped

Figure 1. Turbomatrix HSTrap during trap load: column isolation flow is on.
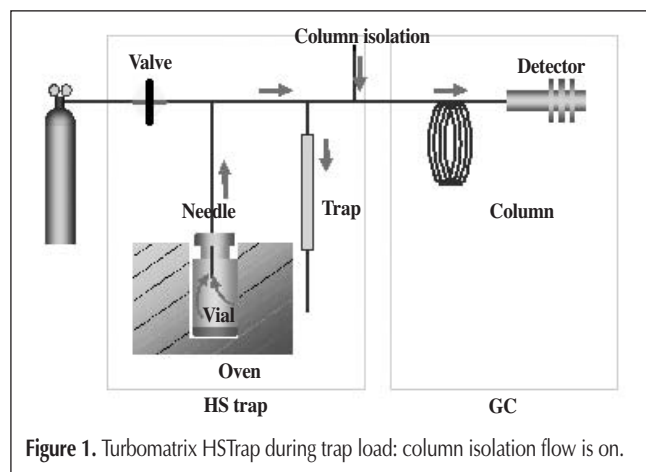
analytes. It is then kept at that value for a specified time to clean it, avoiding any possible carry-over.

As soon as the trap is heated, the isolation of the column from the carrier gas flow is stopped and the GC run begins. The trap is desorbed in the backflush mode, and the analyst decides whether or not to activate the split line present at the end of the trap.

During these studies several instrumental parameters were optimized to reach LODs and performances required by the Italian law. Moreover, the instability of some halogenated volatiles, especially 1,1,2,2-tetrachloroethane, were observed and explained.

Experimental

The instrument used was the PerkinElmer Turbomatrix Headspace 40 Trap connected by an inert heated transfer line to a PerkinElmer Clarus 500 GC with a duel channel flame ionization detector (FID) and electron capture detector (ECD) or to a PerkinElmer Clarus 500 GC–MS.

The analyses performed in the first part of this study were done with a PerkinElmer Elite Volatiles column 60 m × 0.32-mm i.d. (1.8-µm film thickness) that was connected to the headspace trap by an inert column (1.5 m × 0.32 mm) and to the FID and ECD by an inert universal Y splitter. Helium was the carrier gas.

GC conditions were: Ar–CH$_4$ flow, 30 mL/min (as make-up gas for the ECD); air flow, 450 mL/min (for the FID); H$_2$, 45 mL/min (for the FID); injector temperature, 150°C; ECD temperature, 370°C; FID temperature, 300°C; oven, 35°C for 12.00 min, then programmed at 5.0°C/min to 60°C, after 1 min, programmed at 17.0°C/min to 220°C for 0.0 min, and finally at 30°C/min to 240°C.

Optimal headspace parameters used were: vial temperature, 70°C; needle temperature, 100°C; transfer line temperature, 130°C; trap material, air toxics; trap load temperature, 40°C; trap desorption temperature, 320°C; thermostatation time, 20 min; cycles number, 3; pressurization time, 1.5 min; decay time, 1.5 min; desorption time, 0.3 min; trap hold, 0.6 min; dry purge time, 12 min; cycle time, 54 min; column pressure, 33 psi; vial pressure, 33 psi; desorption pressure, 50 psi; purge, on; shaker, on; outlet split, on or off according to the actual concentration range (low or high concentration, as specified below, in Table I).

The following reagents were used: ultrapure water produced by Millipore (Billerica, MA); Elix 3-MilliQ was boiled for at least 90 min, cooled, and preserved under a nitrogen atmosphere; Suprapure hydrochloric acid (30%) was supplied by Merck (Darmstadt, Germany).

Custom Standard CUS-6068 was from (Ultrascientific, Kingstown, RI). For its composi-

Table I. Composition of Standard CUS-6068, Calibration Range and t_R of Halogenated and Aromatic VOCs Analyzed

Analyte	Conc. µg/L	Bias µg/L	Low concentration calibration range (µg/L)	High concentration calibration range (µg/L)	t_R min	Detector
Hexachlorobutadiene	501	0.3	0.003–0.050	0.03–0.50	29.45	ECD
o-Xylene	1504	8	0.075–1.500	0.75–15.00	24.56	FID
m-Xylene	1503	8	0.075–1.500	0.75–15.00	24.06	FID
p-Xylene	1504	8	0.075–1.500	0.75–15.00	24.06	FID
Styrene	1506	8	0.075–1.500	0.75–15.00	24.43	FID
Ethylbenzene	1504	8	0.075–1.500	0.75–15.00	23.76	FID
Toluene	1503	8	0.075–1.500	0.75–15.00	21.10	FID
Benzene	1505	8	0.075–1.500	0.75–15.00	14.57	FID
Bromoform	300.2	1.5	0.015–0.300	0.15–3.00	24.11	ECD
Bromodichloromethane	50.2	0.3	0.003–0.050	0.03–0.50	17.40	ECD
Dibromochloromethane	200.6	1	0.010–0.200	0.10–2.00	21.67	ECD
Tetrachloroethene	50.1	0.3	0.003–0.050	0.03–0.50	22.43	ECD
1,1,2,2-Tetracloroethane	1003	5	0.065–1.300	0.65–13.00	24.68	ECD
1,2-Dibromoethane	10	0.1	0.0005–0.010	0.005–0.10	22.09	ECD
1,1,1-Trichloroethane	300.8	1.5	0.015–0.300	0.15–3.00	13.43	ECD
1,2,3-Trichloropropane	1001	5	0.050–1.000	0.50–10.00	24.76	ECD
Trichloroethene	100.4	0.5	0.005–0.100	0.05–1.00	17.28	ECD
1,1,2-Trichloroethane	1505	8	0.075–1.500	0.75–15.00	20.86	ECD
1,2-Dichloropropane	502	2.5	0.025–0.500	0.25–5.00	17.07	ECD
Trichlomethane	300.2	1.5	0.015–0.300	0.15–3.00	10.59	ECD
1,2-Dichloroethane	300.6	1.5	0.015–0.300	0.15–3.00	13.14	ECD
1,1-Dichloroethane	1504	8	0.075–1.500	0.75–15.00	8.17	ECD
cis-1,2-Dichloroethene	1504	8	0.075–1.500	0.75–15.00	9.77	ECD
trans-1,2-Dichloroethene	1504	8	0.075–1.500	0.75–15.00	7.52	ECD
1,1-Dichloroethene	300.1	1.5	0.015–0.300	0.15–3.00	5.73	ECD

tion, see Table I. Standard solution A was freshly prepared by diluting 10 µL of custom standard in 1 mL of ultrapure water. Standard solution B was freshly prepared by diluting 100 µL of standard solution A in 1 mL of ultrapure water. Sodium sulfate anhydrous, volatiles free, was obtained by heating commercial prepared sodium sulfate (Baker, Deventer, Holland) at 400°C for 24 h.

Two calibration curves were prepared by using standard solutions A and B, dissolved, respectively, in 0.5, 1.0, 2.0, 5.0, 7.0, and 10.0 µL of solution A (low concentration curve) and of solution B (high concentration curve) in 10 mL of ultrapure water. Then 30 µL of HCl and 100 mg of sodium sulfate under a nitrogen atmosphere was added.

All samples were processed by adding 30 µL of acid (sufficient to eliminate 700 mg/L of carbonate) and 100 mg of sodium sulfate to 10 mL of sample. The HCl addition must be superior if the carbonate concentration was greater than 700 mg/L to adjust pH to less than four. This precaution was indispensable to avoid any problem with 1,1,2,2-tetrachloroethane, as better specified during the following discussion.

The "high curve" was obtained by opening the outlet split, and the "low curve" was obtained by closing it.

The analysis performed in the second part of this study was done working with a PerkinElmer Clarus 500 GC–MS, using the

following conditions: the chromatographic column was a PerkinElmer Elite Volatiles (60 m × 0.25-mm i.d., 1.4 µm) connected to the headspace trap by an inert column (1.5 m × 0.32 mm).

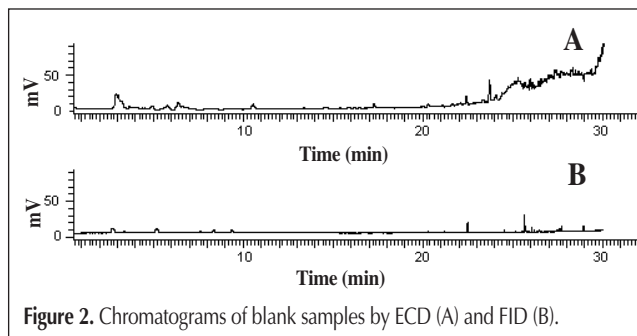The carrier gas was He. The temperatures were: injector, 150°C; oven, 40°C for 12.00 min, then programmed at 5.0°C/min

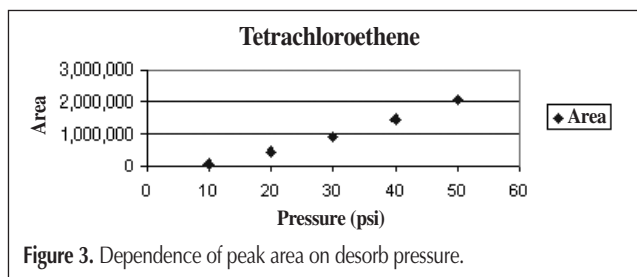**Figure 2.** Chromatograms of blank samples by ECD (A) and FID (B).

Figure 3. Dependence of peak area on desorb pressure.

Table II. Halogenated and Aromatics VOCs Analyzed with Selected Ion Recording GC–MS, in the Concentration Range from 0.100 to 2.000 µg/L. Target Ion and Qualifiers Used to Quantify and Correlation Coefficient Obtained Are Shown

| Analyte	Target Ion (m/z)	Qualifier 1 (m/z)	Qualifier 2 (m/z)	r^2
Hexachlorobutadiene	225	227	260	0.9968
o-Xylene	91	106	105	0.9979
m-Xylene	91	106	105	0.9993
p-Xylene	91	106	105	0.9989
Styrene	104	103	78	0.9972
Ethylbenzene	91	106	65	0.9962
Toluene	91	92	–	0.9994
Benzene	78	77	51	0.9932
Bromoform	173	171	252	0.9975
Bromodichloromethane	83	85	129	0.9984
Dibromochloromethane	129	127	131	0.9991
Tetrachloroethene	166	164	131	0.9986
1,1,2,2-Tetracloroethane	83	85	168	0.9995
1,2-Dibromoethane	107	109	–	0.9934
1,1,1-Trichloroethane	97	99	119	0.9992
1,2,3-Trichloropropane	75	110	77	0.9989
Trichloroethene	95	130	132	0.9987
1,1,2-Trichloroethane	97	83	99	0.9979
1,2-Dichloropropane	63	62	65	0.9996
Trichlomethane	83	85	87	0.9994
1,2-Dichloroethane	62	64	–	0.9989
1,1-Dichloroethane	63	65	–	0.9990
cis-1,2-Dichloroethene	61	96	98	0.9987
trans-1,2-Dichloroethene	61	96	98	0.9992
1,1-Dichloroethene	61	96	98	0.9978
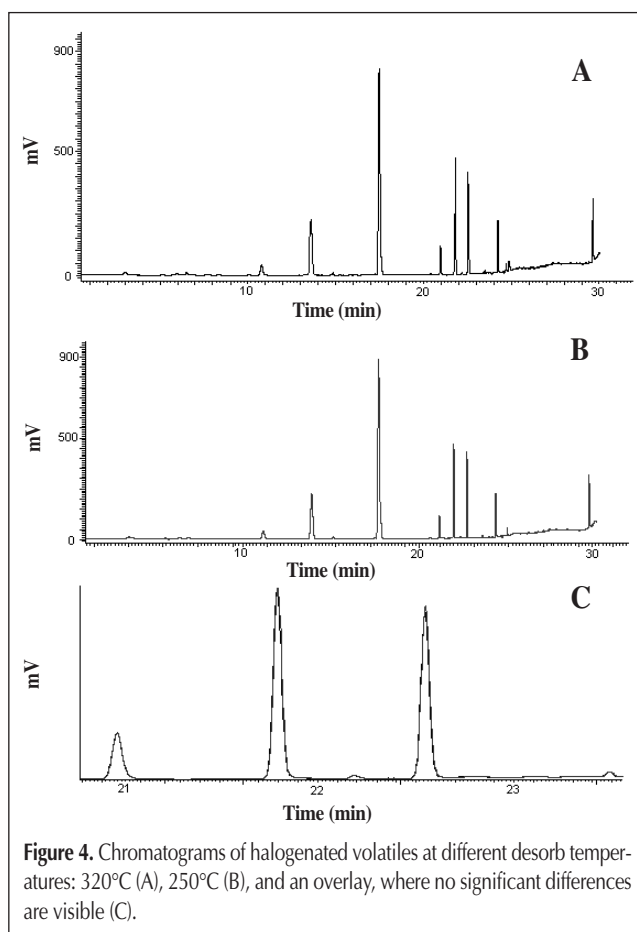
Figure 4. Chromatograms of halogenated volatiles at different desorb temperatures: 320°C (A), 250°C (B), and an overlay, where no significant differences are visible (C).

to 60°C, after 1 min programmed at 20.0°C/min to 220°C.

The MS was operated in the single ion mode, acquiring for each analyte the ions specified in Table II. For each ion, a 0.05 s dwell time was used with a 0.001 s delay between them.

Headspace parameters used were the same as previously reported.

Discussion

The first problem that occurred during the optimization process of the analytical technique was obtaining blank water, which does not contain contaminants invalidating the analysis.

The normal ultrapure water produced by Millipore Elix 3–Milli Q may sometimes still contain organohalides, such as trichloromethane, trichloroethene, bromoform, etc., which are present in common Italian drinking water. Therefore, the water was boiled for 90 min to eliminate the majority of these organohalides.

This boiled water was preserved under a nitrogen atmosphere in order to prevent any further contamination of organohalides, such as chloroform or dichloromethane, which can usually be found in standard laboratories.
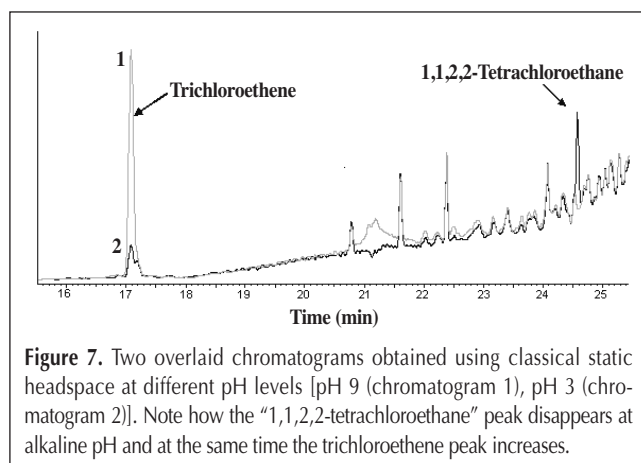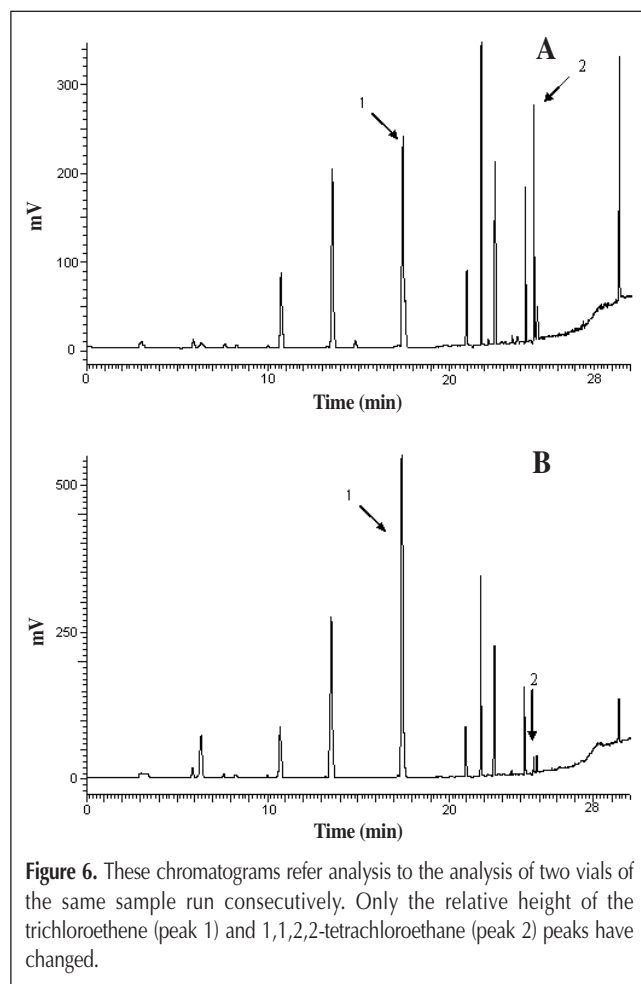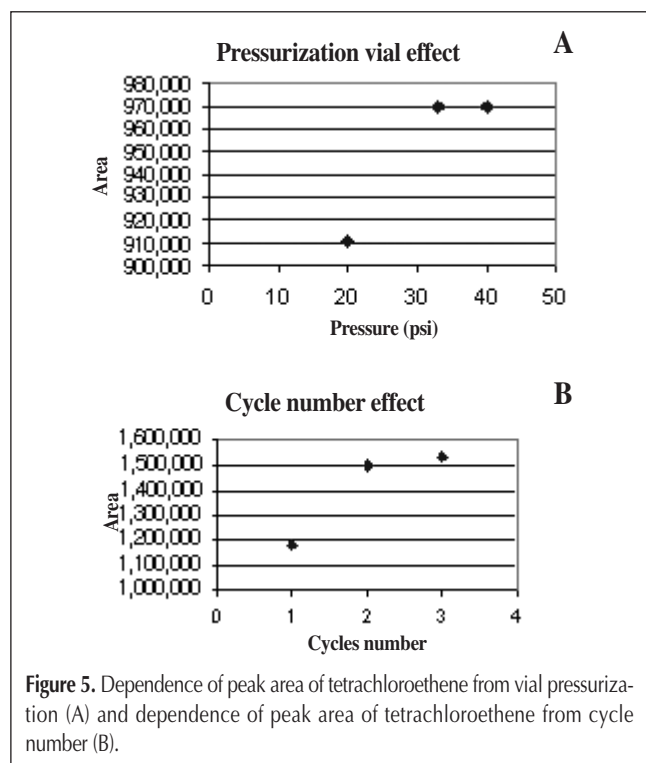
Before analysis, the vials were heated for 2 h at 180°C and then stored in a dessicator. Because of the lack of a clean room, it was not possible to analyze dichloromethane. A blank chromatogram is shown in Figure 2.

Several tests were done to find the best possible pressure settings to reduce the amount of water vapor that otherwise may interfere with the normal functionality of the detectors. Different pressure levels were also tested to reduce the dry-purge time. However, the lower pressures can shorten the time, and the LOD

values were worse. Figure 3 shows how high pressure increases the signal.

The best desorption temperature was 320°C. However, this was not a critical variable (Figure 4). Even though 250°C was enough to desorb all the analytes without any difficulty, it was still recommended to use higher temperatures in order to clean the trap from other possible interferences.

To increase sensitivity without excessively increasing analysis time, the trap load step can be repeated. Figure 5B shows the importance of this parameter and the three cycles that gave good results. The vial pressure was not a critical parameter. Figure 5A

Figure 6. These chromatograms refer analysis to the analysis of two vials of the same sample run consecutively. Only the relative height of the trichloroethene (peak 1) and 1,1,2,2-tetrachloroethane (peak 2) peaks have changed.

Figure 5. Dependence of peak area of tetrachloroethene from vial pressurization (A) and dependence of peak area of tetrachloroethene from cycle number (B).

Figure 7. Two overlaid chromatograms obtained using classical static headspace at different pH levels [pH 9 (chromatogram 1), pH 3 (chromatogram 2)]. Note how the "1,1,2,2-tetrachloroethane" peak disappears at alkaline pH and at the same time the trichloroethene peak increases.

does not show any signal increase above 30 psi.

Finally, a serious problem with 1,1,2,2-tetrachloroethane was observed. The determination of 1,1,2,2-tetrachloroethane was often impossible because it partially or totally disappeared during the chromatographic run. Meanwhile, an increase in trichloroethene's signal is observed. All official methods (1,2,4,8) describe procedures that can be applied to 1,1,2,2-tetrachloroethane, without reporting data concerning the validation for this analyte.

Only Environmental Protection Agency (EPA) 5030C (8) describes a generic interference during purge and trap analysis, if the system is contaminated.

This phenomenon was first observed (as shown in Figure 6) when working with HSTrap, and the use of a lower desorption temperature did not solve the matter. The same happened with classical headspace analysis (without trap), as shown in Figure 7 and with "syringe-type" headspace.

Though it is well known, 1,1,2,2-tetrachloroethane is not a stable compound, and it decomposes to trichloroethene at high temperatures (11). 1,1,2,2-Tetrachloroethane, in a water solution, was stable at room temperature for one month, at acid/neutral pH, but it decomposed to trichloroethene by E2 elimination at basic pH.

The study demonstrated that the previously mentioned phenomenon may appear during thermostating at 70°C using neutral water. Therefore, it was necessary to acidify all solutions to pH < 4 because under these conditions the relative height of the two peaks remained constant (as shown in Figure 8). The data clearly demonstrated that the observed reaction took place during thermostatation of the vials in the water phase and was not because of active sites present in the trap, as stated in EPA method 5030C (8). It was also noted that 1,1,2,2-tetrachloroethane completely disappeared and degraded into trichloroethene by adding Na_2CO_3 to the solution [as suggested by the ISS 00/14 method (1)] in order to eliminate CO_2 from sparkling water (Figure 9).

The conditions of acidification eliminate any problem with a carbonate concentration below 700 mg/L. A variation of the pH did not cause problems of repeatability or anomalous increasing of other signals. It was also possible to determine repeatability, linearity, LOD, roughness, and accuracy using a natural mineral water with a concentration of approximately 180 mg/L or carbonate.

Table III lists LODs (International Union of Pure and Applied Chemistry definition), repeatability, correlation coefficients of the calibration curves, and recovery using samples of the same mineral with 7.0 μL of solutions A and B, respectively.

Linearity was calculated with the analysis of the residues, and no particular deviation was observed.

Robustness was estimated at the confidence level of 99%; thus, it was very interesting to observe that changing the following parameters: operator, desorption pressure, dry purge time,
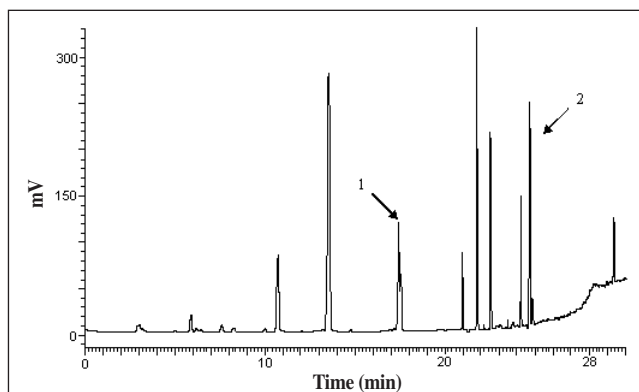

Figure 8. Chromatogram obtained with acidification of the sample with 30 μL HCl.
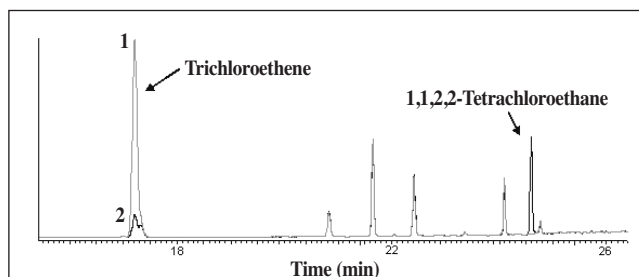

Figure 9. Two overlaid chromatograms of the same sample obtained using a headspace trap. Na_2CO_3 is added to the sample (chromatogram 1). An unspiked sample (chromatogram 2).

Table III. Concentrations are the Mean of 10 Replicates. Data Obtained Splitting the Sample at the End of the Column to an ECD and an FID

| Analyte | High concentration | | | Low concentration | | | LOD | Recovery |
| | Concentration | | | Concentration | | | | |
	μg/L	CV%	r^2	μg/L	CV%	r^2	μg/L	(%)
Hexachlorobutadiene	0.23	7.1	0.9962	0.030	20.2	0.9916	0.0005	121
o-Xilene	7.36	2.3	0.9953	0.639	4.5	0.9982	0.0496	85
m+p-Xilene	14.56	2.4	0.9955	1.263	5.1	0.9981	0.0425	84
Stirene	7.39	2.1	0.9955	0.617	7.6	0.9937	0.0276	82
Ethylbenzene	7.33	2.2	0.9960	0.662	3.2	0.9986	0.0056	88
Toluene	7.35	1.7	0.9967	0.654	3.1	0.9991	0.0362	87
Benzene	7.20	2.5	0.9948	0.708	1.8	0.9976	0.0326	94
Bromoform	1.58	1.8	0.9982	0.140	3.4	0.9985	0.0106	93
Bromodichloromethane	0.25	2.7	0.9909	0.021	4.8	0.9974	0.0010	84
Dibromochloromethane	1.06	1.4	0.9983	0.088	2.3	0.9991	0.0008	88
Tetrachloroethene	0.25	3.1	0.9908	0.031	2.7	0.9959	0.0007	122
1,1,2,2-Tetracloroethane	7.05	1.2	0.9962	0.722	1.3	0.9994	0.0026	111
1,2-Dibromoethane	0.05	1.5	0.9987	0.004	1.7	0.9991	0.0006	81
1,1,1-Trichloroethane	1.50	2.1	0.9915	0.155	4.4	0.9959	0.0002	103
1,2,3-Trichloropropane	6.20	4.9	0.9985	0.536	2.6	0.9916	0.0083	107
Trichloroethene	0.51	2.0	0.9972	0.056	2.9	0.9983	0.0025	112
1,1,2-Trichloroethane	7.95	1.4	0.9987	0.693	4.2	0.9995	0.0060	92
1,2-Dichloropropane	2.37	8.4	0.9987	0.259	5.0	0.9958	0.0180	103
Trichloromethane	1.73	2.0	0.9989	0.174	5.7	0.9919	0.0152	116
1,2-Dichloroethane	1.54	3.1	0.9936	0.123	4.7	0.9914	0.0010	82
1,1-Dicloroethane	8.67	2.5	0.9918	0.775	3.0	0.9975	0.0213	103
cis-1,2-Dicloroethene	7.52	2.9	0.9959	0.880	4.4	0.9951	0.0839	117
trans-1,2-Dicloroethene	7.59	2.4	0.9978	0.729	2.1	0.9912	0.0909	97
1,1-Dicloroethene	1.39	2.6	0.9974	0.183	5.2	0.9969	0.0049	121
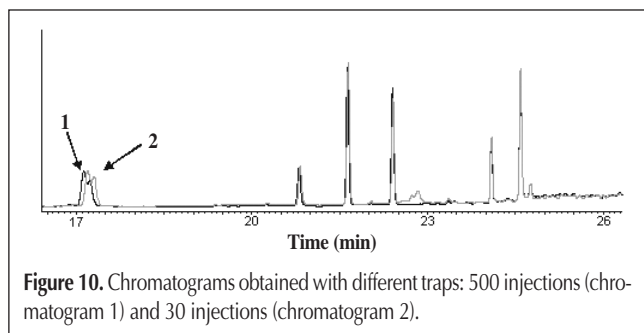
Figure 10. Chromatograms obtained with different traps: 500 injections (chromatogram 1) and 30 injections (chromatogram 2).

trap, vial pressure, desorption temperature of the trap, and desorption time did not influence the method. Even by changing the trap (one with about 500 injection and one with 30 injection), no significant change was noted, as shown in Figure 10.

Conclusion

A new method was developed for the determination of halogenated and aromatic volatiles. The method was very precise and accurate.

All parameters were established according to the Italian laws on drinking, mineral water, and groundwater, except for the LOD of 1,2,3-trichloropropane, which had a limit of 1 ng/L, but only 8 ng/L was reached. One nanogram per liter could not be reached because of elevated noise at the retention time of 1,2,3-trichloropropane, which was caused by high column bleeding.

The effect of pH on the analysis, which is usually underestimated in the standard methods [EPA 5030B (7) or UNI EN ISO 10301 (2)], was observed and described.

It was demonstrated that the transformation of 1,1,2,2-tetrachloroethane into trichloroethene must be inhibited using an acidic pH by adding hydrochloric acid to every sample. Other recent studies have noted that a high pH (> 11 to 12) also influenced other halogenated volatiles.

The determination of very volatiles halogenated substances (e.g., vinyl chloride and chloromethane) involving different instrumental parameters is in progress.

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