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Determination of volatile organic compounds in water by purge-and-trap gas chromatography coupled to atomic emission detection

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Abstract

In this study, the potential of the combination of atomic emission detection (AED) with conventional purge-and-trap gas chromatography for the determination of 16 volatile organic compounds (VOCs) in water was investigated. The advantages of element-specific detection that are proprietary to GC–AED were shown, i.e. differentiation between the halogens, substance independent calibration and calculation of empirical formulas. For element-specific detection, four wavelengths were monitored, corresponding to carbon (495.72 nm), hydrogen (486.13 nm), chlorine (479.45 nm) and bromine (478.55 nm) emission. Calibration standards were prepared following a special protocol developed in our laboratory in order to avoid sample losses due to the high volatility of most of the VOCs. The reproducibility within batch falls generally within a range of 5% relative standard deviation (R.S.D.). Only the highly volatile analytes showed values up to 25% R.S.D. The method was validated by analyzing standards at different concentration levels.

Keywords: Water analysis; Detection, GC; Atomic emission detection; Purge-and-trap methods; Volatile organic compounds; Halogenated compounds

1. Introduction

Volatile organic compounds (VOCs) like benzene, dichloromethane, haloforms and others represent a very diverse group of chemicals. Their use as solvents, cleaning agents, propellants and fuels in a large number of industrial and commercial applications has led to their ubiquitous presence as water pollutants. They can be found in virtually all homes and workplaces in our modern technological society. The consumer items we use, the energy sources we require, and the water we drink (via the formation of chlorinated compounds by the chlorination of drinking water that contains organic matter) all increase

our exposure to these compounds. Numerous health effects may be linked with exposure to VOCs. Especially the halogenated compounds are suspected carcinogens [1].

Due to these facts monitoring of VOCs is mandatory. Their analysis has always been a major challenge to environmental chemists. Several authorities, such as the US Environmental Protection Agency (EPA), the European Union (EU) and national agencies, have included VOCs in their priority pollutants list, and methods have been established for analyzing them in water samples of various origins [2–6]. While in the USA the EPA demands specific analytical methods to be used, there are no promulgated methods for the analysis of VOCs in Western Europe. However, the DIN (Deutsches Institut für

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Normung) methods serve as models throughout Europe and are widely followed. This has obviously led to the use of different analytical tools for the same purposes in the USA and European countries [7].

Purge-and-trap gas chromatography (PT-GC) as described first by Swinnerton and Linnenbom [8] and developed by Bellar and Lichtenberg [9] has become a valuable and widely accepted method for the analysis of VOCs in water and was adopted by the EPA in various methods [10,11].

However, till now these methods are based on GC with the non-specific flame ionization detection (FID) or on GC with element-selective (electron-capture detection, ECD) or molecular-specific detection methods (mass spectrometry, MS) [12,13]. FID is indeed highly sensitive, but it monitors all compounds containing carbon without any selectivity. Thus, a major part of the relevant information is lost, as heteroatoms cannot be detected, which would be necessary to distinguish the halogenated from the non-halogenated VOCs, as they are particularly important because of their toxicity. ECD offers this possibility. However, the problems here are its restricted selectivity and, above all, a limited linear range, particularly for the compounds containing only few halogen atoms, which causes problems with the detection and the quantitation: the system must be calibrated for each substance and for a rather narrow concentration range. The use of MS would certainly improve the analysis, but a calibration for every detected compound will be unavoidable as well.

A relatively new type of detection is atomic emission detection (AED). The power of this detection method lies in its sensitivity and supreme selectivity. In AED, the solutes eluting from the GC column are atomized in a microwave induced plasma (MIP) and the resulting atoms and ions, in the excited state, emit light of a characteristic wavelength as they return to the ground state. The polychromatic light is dispersed in a spectrometer and the emission of the characteristic wavelengths is measured using a photodiode array [14].

The use of AED coupled to PT-GC has the following potential advantages:

(1) The sensitive measurement of carbon with simultaneous element specific detection of relevant

heteroatoms such as the halogens. For the environmental analysis most relevant halogens, bromine and chlorine, halogenated and non-halogenated compounds can be detected even in one run with a single detector.

(2) Differentiation between the different halogens (I, Br, Cl, F) is possible, as it is possible to distinguish between the different halogens according to their characteristic emission wavelength. As mentioned above Br and Cl can be analyzed within the same run, whereas for I and F additional runs are necessary.

(3) The quantitation is greatly simplified in comparison to the use of ECD or MS as calibration with the authentic analyte is not necessary. A substance-independent calibration can be used instead, as pronounced structural influences for the compounds of interest are not to be expected.

(4) Purgable compounds are highly volatile and have a low molecular mass which makes the determination of their empirical formulas with AED more straightforward and successful than for higher-molecular-mass compounds, where the measurement uncertainty of the elemental ratios does not allow reliable calculation of the exact ratio of atoms in the molecule. The calculated elemental ratios allow, in conjunction with the retention times, the tentative identification of unknown analytes.

Until now there are only a few publications dealing with AED as a detection method for PT-GC. A study about trihalomethanes was carried out by Quimby et al. [15], but no systematic investigation of a broader range of VOCs followed. Two recent papers deal with the analysis of organic sulphur compounds [16] and organic selenium compounds [17] using PT-GC in combination with AED.

Thus, the goal of this work was to carry out a systematic study of the analysis of VOCs using AED as detection method for PT-GC in order to seek out its potential in this field of environmental trace analysis.

2. Experimental

All analyses were performed on an OI 4460A sample concentrator from OI Analytical (College Station, TX, USA), coupled to a HP 5890 Series II

gas chromatograph equipped with a HP 5921A atomic emission detector, both from Hewlett–Packard (Avondale, PA, USA). The instrumental conditions are summarized in Table 1.

2.1. Chemicals and materials

Fifteen representative analytes covering a boiling point range from 40–213°C from EPA 524.2 rev. 4.0 method list were chosen and 1-bromo-2-chloroethane was used as internal standard (see Table 2). The most volatile compounds, such as vinylchloride, were not considered in this work, since the PT-GC system used did not offer the possibility of cryotrapping and cryofocusing. All of the analytes were analytical-reagent grade from Merck (Darmstadt, Germany). Methanol (analytical-reagent grade) from Merck was used as solvent. For the preparation of

Table 2
List of analytes

Compounds	B.p. (°C)	M_r
Methylene chloride	40	85.0
1,1-Dichloroethane	57	99.0
Chloroform	61	119.5
1,1,1-Trichloroethane	74	133.5
Carbon tetrachloride	76	154.0
1,2-Dichloroethane	83	99.0
Trichloroethene	87	131.5
1,2-Dichloropropane	96	113.0
1-Bromo-2-chloroethane ^a	106–107	143.5
Toluene	111	92.0
Tetrachloroethene	121	166.0
Chlorobenzene	132	112.5
Bromobenzene	156	157.0
1,3-Dichlorobenzene	173	147.0
1,2-Dichlorobenzene	180	147.0
1,2,4-Trichlorobenzene	213	181.5

^a Internal standard.

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

<i>PT conditions</i>	Sample volume	5 ml
	Purge cycle	11 min at ambient temp.
	Desorb cycle	4 min at 180°C
	Bake cycle	20 min at 180°C
	Purge gas	Helium 5.0 at 40 ml min ⁻¹
	Desorb flow	60 ml min ⁻¹
	Trap	Tenax/silica-gel/charcoal
<i>GC conditions</i>	Oven program	30°C (7 min) 100°C at 5° min ⁻¹ (1 min) 200°C at 15° min ⁻¹ (2 min)
	Injector temperature	200°C
	Flow-rate	6 ml min ⁻¹ constant flow
	Carrier gas	Helium 5.0
	Split ratio	10:1
	Column	HP 624 30 m × 0.32 mm I.D., 1.8 μm film thickness
<i>AED conditions</i>	Transfer line temperature	220°C
	Cavity temperature	220°C
	Reagent gas	O ₂ at 0.7 bar
	Make-up gas	He at 10 ± 0.2 ml min ⁻¹
	Wavelengths	C 496 (495.72 nm), H 486 (486.13 nm), Cl 479 (479.45 nm), Br 478 (478.55 nm)

the water standards distilled water from our laboratory was used. Glassware was purchased from Supelco.

2.2. Preparation of standards

Because of the high volatility of the VOCs a special protocol for the preparation of standards was developed. Standards were prepared by volume and calculated to mass by density. The analytes were transferred via graduated gas-tight glass syringes of 10 and 100 μl into the solvent, kept at minimum headspace in a 40-ml glass vial with a Mininert push-button valve. In a second dilution step, carried out in the same way, working solutions were prepared, from which aliquots were taken to prepare the water standards. All solutions were stored at 4°C in the refrigerator. Thus, good reproducibility was obtained, falling within a range of 5–10% R.S.D.

2.3. Removal of water vapor from the purge gas

A crucial problem for AED was the high amount of water vapor carried over from the PT unit by the purge gas, as it destabilized the plasma and made the detection of early eluting compounds impossible due to high interferences on all elemental traces moni-

tored. The problem could be overcome by using a dryer. Two types of dryer were tested, a Perma Pure dryer model MD-110-12 S purchased from Perma Pure Products (Oceanport, NJ, USA), which consists of a Nafion membrane tubing sealed in a stainless steel tubing, and a dryer from International Science Consultants (Ringwood, UK), where a Nafion membrane tubing of 1 m length \times 1.14 mm I.D. and 0.13 mm wall thickness is enclosed in a plastic container with removable nylon end caps, which was filled with molecular sieve as desiccant. In the former, the wet gas stream which flows through the Nafion tubing was dried by a countercurrent stream of dry nitrogen at a flow-rate of 400 ml min^{-1} , in the latter it was dried by adsorption on the molecular sieve.

3. Results and discussion

3.1. Comparison of the performance of the two dryers

The effectiveness of the two dryers was determined by purging a sample of distilled water and observing the signal on the H trace.

In Fig. 1 the H traces are shown when using the two dryers. As it can be seen, the Perma Pure dryer

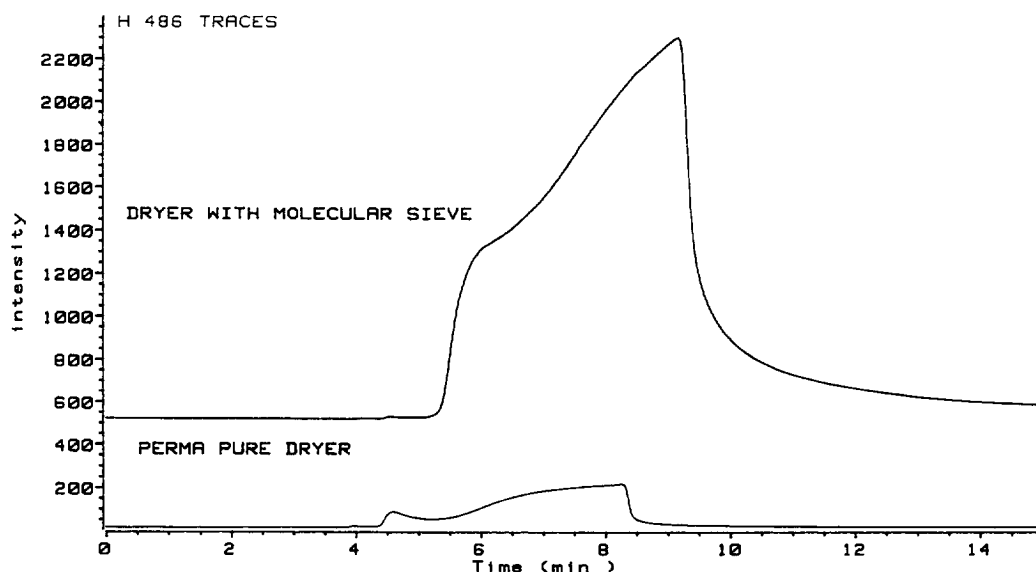


Fig. 1. Comparison of the effectiveness in the removal of water vapor of the dryer with the molecular sieve (top) and the Perma Pure dryer (bottom) on the H 486 traces.

performed better than the dryer with a molecular sieve. The bump on the H trace recorded with the molecular sieve dryer corresponded to a 90% removal of the water vapor from the purge gas, whereas with the Perma Pure dryer 99% of the water could be removed. However, the H trace was still highly affected by the remaining amount of water vapor and could therefore not be used for analysis.

Other positive effects by using a Nafion membrane dryer are the elimination of interferences on the C trace due to the water carry-over and the removal of the methanol used as a mediator for the preparation of primary standards as shown in Fig. 2. Although only small amounts of these primary standards are used for the preparation of secondary standards and water samples, the methanol concentration is still very high. Even if the methanol is only partially purged, as can be expected due to its high affinity towards the water matrix, it will destabilize the plasma.

It seems more reasonable to remove the water vapor by a drying gas, if it can be easily supplied, as a desiccant needs to be regenerated from time to time. Furthermore, if losses of some analytes occur, they will be accumulated on the desiccant with the water and may produce memory effects by back diffusion through the membrane.

The effect of the flow of the drying gas was investigated by employing flow-rates of 40 ml min⁻¹, 400 ml min⁻¹ (specified by the manufacturer, corresponding to 10 times as much as the purge gas flow in the PT) and 800 ml min⁻¹. With 40 ml min⁻¹ flow the water was not as completely removed as with the two higher flow-rates. With 800 ml min⁻¹ the effects were the same as with 400 ml min⁻¹. Thus, a flow-rate of 400 ml min⁻¹ of drying gas was chosen.

Under these experimental conditions good chromatographic separation of the compounds could be obtained as shown in Fig. 3.

3.2. Purge efficiency tests

The purge efficiency P was determined by subsequently purging the same sample and is expressed in percent by using the formula:

$$P(\%) = \frac{A_1}{\sum A_i} \cdot 100$$

where A_1 is the peak area of a compound in the first purge cycle and A_i is the peak area of the same compound in cycle i .

Five replicates of a standard at 0.5 µg l⁻¹ level

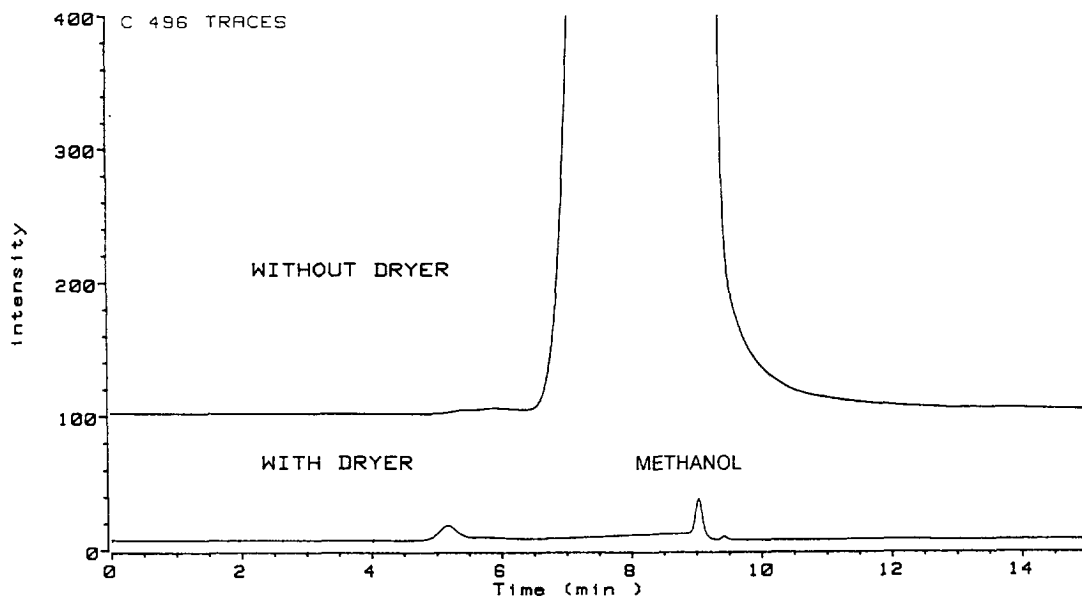


Fig. 2. Elimination of the interference due to the water carry-over and of the methanol signal on the C trace by the Perma Pure dryer.

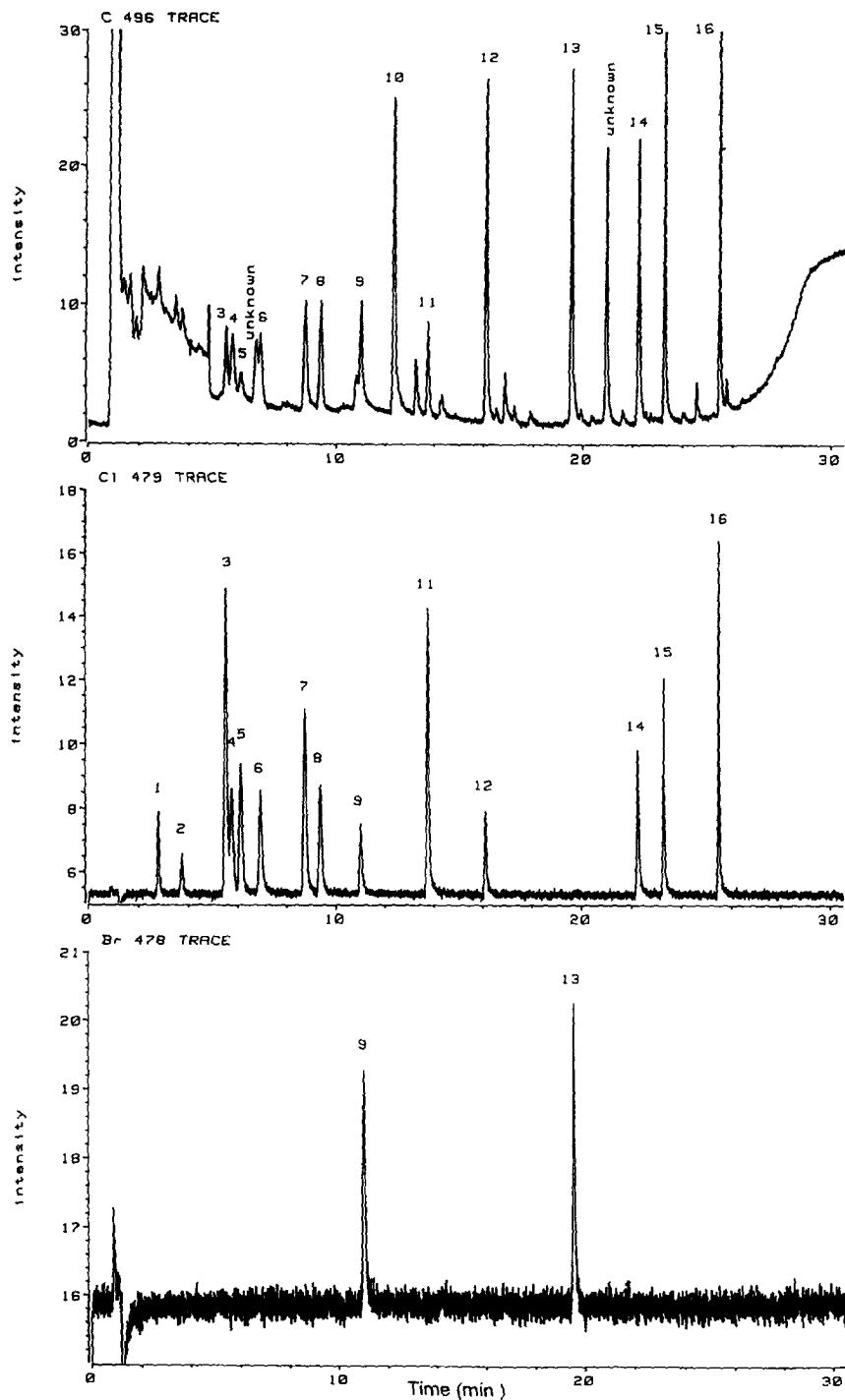


Fig. 3. GC separation of the compounds detected on the C 496 trace (top), Cl 479 trace (middle) and the Br 478 trace (bottom) ($c \approx 3 \mu\text{g l}^{-1}$ each compound): (1) dichloromethane, (2) 1,1-dichloroethane, (3) chloroform, (4) 1,1,1-trichloroethane, (5) tetrachloromethane, (6) 1,2-dichloroethane, (7) trichloroethene, (8) 1,2-dichloropropane, (9) 1-bromo-2-chloroethane, (10) toluene, (11) tetrachloroethene, (12) chlorobenzene, (13) bromobenzene, (14) 1,3-dichlorobenzene, (15) 1,2-dichlorobenzene, (16) 1,2,4-trichlorobenzene. Experimental conditions see Table 1. Emission intensity is given in arbitrary units.

were purged twice. The second run did not show any responses for the compounds in the sample except for 1,2,4-trichlorobenzene, which is the least volatile compound used in the calibration mixture. However, the purge efficiency for this compound of 94.1% (0.5% R.S.D.) calculated on the C trace and of 94.7% (1% R.S.D.) calculated on the Cl trace is still satisfactory. Thus, it could be stated that all analytes investigated are quantitatively purged.

3.3. Calibration for substances

For calibration, water samples at 5 concentration levels (from ca. $0.5 \mu\text{g l}^{-1}$ up to $4 \mu\text{g l}^{-1}$ for each analyte) were prepared and 5 ml aliquots of each standard were purged and analyzed.

Before the analysis of the standards 5 ml of distilled water were purged in order to get a method blank.

Several impurities on the C trace were noted. On the Cl trace a chloroform peak was detected, which was probably due to contamination from the laboratory atmosphere, as chloroform is a commonly used solvent in our laboratory. Even taking maximum care in sample preparation it was impossible to overcome these problems, and neither the chloroform nor the impurities on the carbon trace could be eliminated

(Fig. 4). However, the peaks on the carbon trace did not interfere with the analyte peaks, and the chloroform was not considered in quantitation.

Three replicates for each calibration level were done.

Quantitative evaluation was carried out not only on the C trace, but (where applicable) also on the Br and Cl trace. For all the elemental traces of the analytes linear regression could be applied within the concentration range investigated. The regression was better for the less volatile compounds, e.g. trichlorobenzene or the dichlorobenzenes, which showed reproducibilities of 5–10% R.S.D. within replicates, than for the highly volatile compounds such as carbon tetrachloride or 1,1-dichloroethane.

Calibration parameters of a volatile compound (1,1,1-trichloroethane) and a less volatile compound (1,2-dichlorobenzene) are shown in Table 3 for the C and the Cl trace.

For the C trace of 1,1,1-trichloroethane, reproducibilities were of up to 25% R.S.D. The calibration for chlorine in 1,1,1-trichloroethane fits better than the C trace calibration, which is due to the fact, that peaks were better shaped and the Cl trace was free from interferences. From these results, a major advantage of AED compared to other detection methods can be seen, i.e. the possibility to calibrate

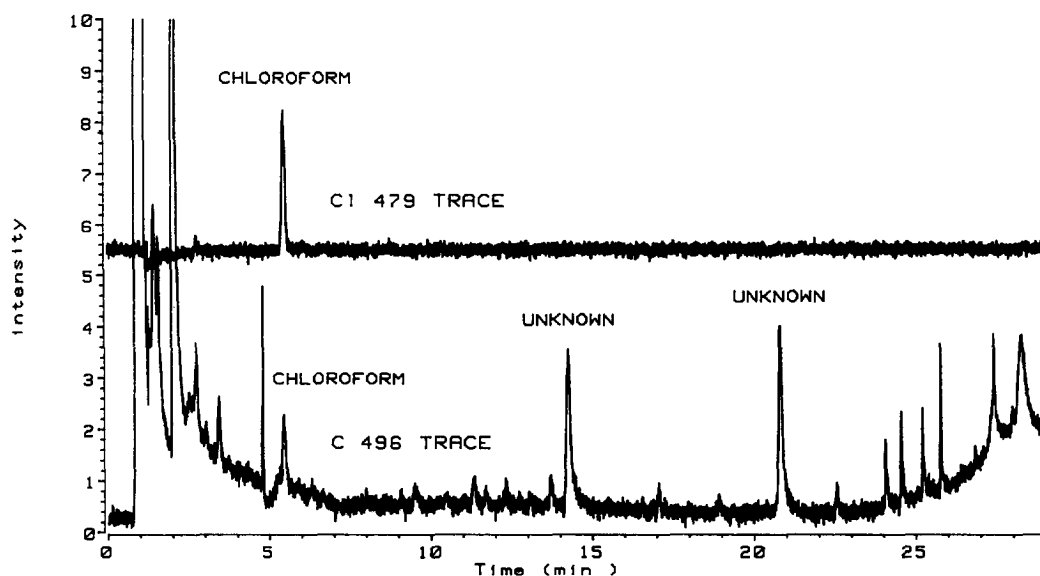


Fig. 4. Cl 479 (top) and C 496 trace (bottom) of a blank with distilled water. Emission intensity is given in arbitrary units.

Table 3
Calibration data for the carbon trace and the chlorine trace of 1,1,1-trichloroethane and 1,2-dichlorobenzene

Compound	Slope (area counts ng ⁻¹)	Intercept (area counts)	r ²
<i>C 496 trace</i>			
1,1,1-Trichloroethane	923	3.3	0.9801
1,2-Dichlorobenzene	1013	-15.2	0.9980
<i>Cl 479 trace</i>			
1,1,1-Trichloroethane	136	6.7	0.9985
1,2-Dichlorobenzene	228	-0.5	0.9997

using the heteroelement traces, which are generally not affected by interferences as strongly as the C trace.

The calibration of 1,2-dichlorobenzene had a correlation coefficient of 0.9980 and the calibration for chlorine in 1,2-dichlorobenzene showed reproducibilities within replicates between 5–10% R.S.D., which was achieved for all the analytes investigated with boiling points higher than 100°C. It could generally be observed, that on the one hand calibration curves plotted using the single elemental traces fitted better for the less volatile analytes than for the highly volatile compounds, a fact which can be explained by compound losses due to the high volatility. On the other hand better regression data could be obtained by calibrating on the heteroelement traces rather than on the C trace, as they were free from interferences. However, at this point it should be mentioned that the elimination of interferences is also possible with other detection methods such as ECD and MS.

3.4. Substance independent calibration

An advantage of the use of AED is that the compounds entering the plasma are completely atomized and the structure of the analyte does not affect the elemental response. Thus, response factors for each element are constant within the linear range of the detector. They can be calculated and used for substance independent calibration.

Fig. 5 shows that within the same sample less volatile compounds such as substituted benzenes, have the same response factor for carbon, i.e. ca.

1850 area counts ng⁻¹. Highly volatile analytes, e.g. carbon tetrachloride and 1,2-dichloroethane have a lower response, a fact which is rather due to their volatility than actually due to the differences in elemental response among different compounds. It was probably the 1–2 days storage time, which is necessary to allow all solutions and standards to homogenize, that already led to evaporation losses of the highly volatile analytes.

Although other authors [18,19] reported structural dependence of the response, such as the increase of carbon and hydrogen response with the number of halogens or higher responses for alkanes and alkenes than for aromatics, this was not systematically observed in this work. As shown in Table 4, e.g. the C sensitivity of carbon tetrachloride, a highly chlorinated alkane, is much lower than for e.g. toluene.

Nevertheless, substance independent calibration could be applied by analyzing a single standard spiked with analytes at different concentration levels within the same chromatographic run as shown in Fig. 6 for chlorine.

3.5. Validation

The method was validated for the individual components by using different calibration curves in order to be able to compare the data with those obtained with other detectors. This means, that the method detection limit (MDL) may differ for the same analyte depending on which elemental trace the method has been evaluated. The precision of the method was estimated for each substance by de-

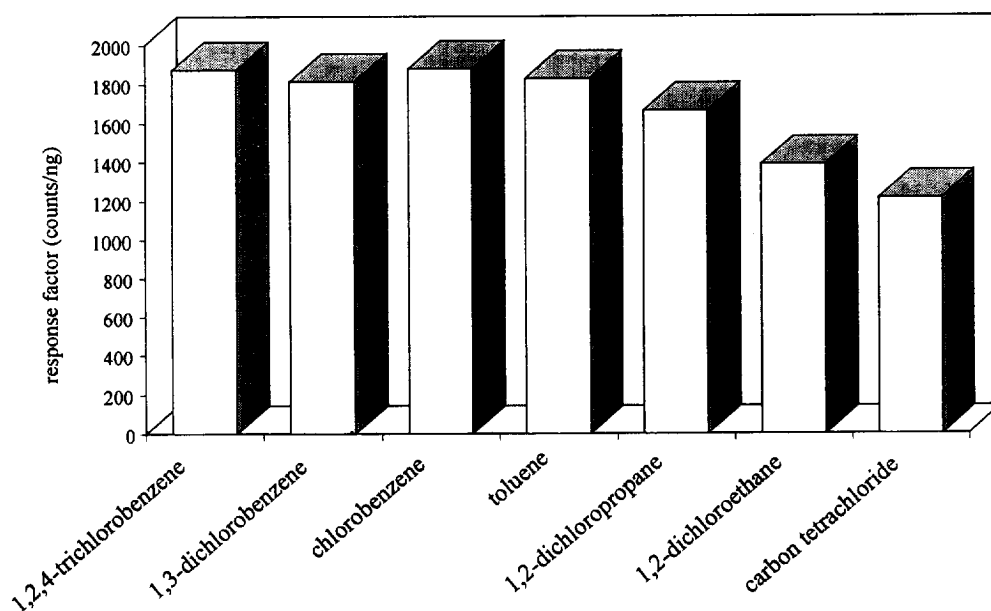


Fig. 5. Response factors for C 496 of selected analytes in the same sample.

Table 4
Validation parameters of the method

Compounds	MDL ($\mu\text{g l}^{-1}$ substance)			S.D. of the method %			Sensitivity (counts/ $(\mu\text{g l}^{-1})$)		
	C	Br	Cl	C	Br	Cl	C	Br	Cl
Methylene chloride	nd	nd	0.13	–	–	44	–	–	47
1,1-Dichloroethane	nd	nd	0.17	–	–	58	–	–	51
Chloroform	nd	nd	nd	–	–	21	–	–	154
1,1,1-Trichloroethane	0.12	nd	0.13	11	–	18	923	–	136
Carbon tetrachloride	0.36	nd	0.13	7	–	35	741	–	129
1,2-Dichloroethane	0.12	nd	0.18	6	–	24	740	–	189
Trichloroethene	0.11	nd	0.23	4	–	14	1280	–	201
1,2-Dichloropropane	0.07	nd	0.06	5	–	19	849	–	190
1-Bromo-2-chloroethane ^a	0.12	0.28	0.22	7	26	12	943	113	194
Toluene	0.02	nd	nd	10	–	5	935	–	183
Tetrachloroethene	0.13	nd	0.09	5	–	12	926	–	199
Chlorobenzene	0.02	nd	0.14	4	–	5	923	–	227
Bromobenzene	0.04	0.318	nd	7	11	–	1000	139	–
1,3-Dichlorobenzene	0.04	nd	0.14	6	–	5	917	–	214
1,2-Dichlorobenzene	0.03	nd	0.10	8	–	4	1013	–	228
1,2,4-Trichlorobenzene	0.03	nd	0.06	3	–	17	934	–	218

nd = not detectable on this trace.

^a Used as internal standard.

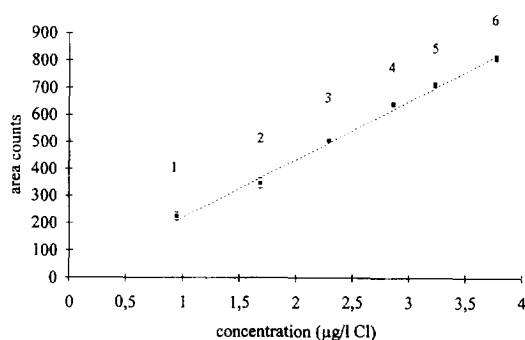


Fig. 6. Calibration plot (regression coefficient $r^2=0.9977$) for chlorine within the same sample; compounds taken for calibration: (1) chlorobenzene, (2) 1,3-dichlorobenzene, (3) 1,1-dichloroethane, (4) 1,1,1-trichloroethane, (5) trichloroethene, (6) tetrachloroethene. The symbols mark mean (■) and mean \pm R.S.D. (○).

termining the residual standard deviation s_y according to the following formula:

$$s_y = \sqrt{\frac{1}{n-2} \sum_j \sum_i (y_{i,j} - \hat{y}_i)^2}$$

with $y_{i,j}$ the value of a measurement, \hat{y}_i the estimate of this value from the calibration line and n the number of the calibration levels. This was used to calculate the standard deviation of the method s_{x_0} by using the equation:

$$s_{x_0} = \frac{s_y}{b}$$

with s_y the standard deviation of the residuals and b the slope of the calibration plot, which is a measure for its sensitivity.

The method detection limits were calculated by employing the 3σ criterium on each elemental trace

for the individual analytes. This led of course to differences between the MDL calculated from the different elemental traces, expressed in terms of the total concentration of a compound in the sample. Table 4 shows the validation parameters of the method.

The useful range (linearity) of the method has been examined up to a concentration range of $2.15 \mu\text{g l}^{-1}$ C (as toluene), $3.99 \mu\text{g l}^{-1}$ Cl (as carbon tetrachloride) and $2.62 \mu\text{g l}^{-1}$ Br (as 1-bromo-2-chloroethane). Within this range linearity can be assumed.

The highly volatile analytes as expected show the worst precision, whereas for analytes with a higher boiling point than 90°C the standard deviation of the method did not exceed 20% on the Cl trace and remained below 10% on the C trace.

MDLs fall within a range from 0.03 – $0.4 \mu\text{g l}^{-1}$, and compare well to values generally obtained with other detectors. PT-GC-AED thus exhibits a sufficient detection power for regulatory monitoring of halocarbons in drinking, ground and surface water where the threshold limits for individual compounds are $>1 \mu\text{g l}^{-1}$.

3.6. Determination of empirical formulas

As outlined above a major benefit of AED is the possibility of a compound independent calibration, a fact which can be used for determining empirical formulas. The formulas were calculated by a software macro of the AED system. The results of the formula determination of a standard containing 7 analytes are shown in Table 5. The large deviation of

Table 5
Determination of empirical formulas with AED

Compounds	Formulae	Element ratio calculated				Formula determined			
		C	H	Cl	Br	C	H	Cl	Br
Toluene	C_7H_8	1	1.10	0.01	–	7	7.7	0	0
Tetrachloroethene	C_2Cl_4	1	0.75	1.95	–	2	1.5	3.9	0
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	Calibration peak				6	5	1	0
Bromobenzene	$\text{C}_6\text{H}_5\text{Br}$	1	0.58	0.01	?	6	3.2	0	1
1,3-Dichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$	1	0.66	0.33	–	6	3.9	2.0	0
1,2-Dichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$	1	0.65	0.33	–	6	3.9	2.0	0
1,2,4-Trichlorobenzene	$\text{C}_6\text{H}_3\text{Cl}_3$	1	0.64	0.47	–	6	3.9	2.8	0

C/H ratios is due to the fact that the H trace was still highly affected by the remaining water vapor.

The results show the possibility of the reliable calculation of empirical formulas. In combination with the information from the retention times, unknown compounds can thus often be tentatively identified by their elemental composition. This can be an important issue both in screening analysis and also in quality assurance where this additional information can help to more reliably assign the peaks to the analytes.

4. Conclusions

In this work a method was established and evaluated for the determination of VOCs in water with PT-GC using AED. It was shown that in this combination the AED is a useful tool in environmental trace analysis. The main advantages of this detector are its sensitivity, the possibility of a substance independent calibration and of determining empirical formulas. Furthermore, AED allows differentiation between the different elements of an analyte, e.g. it will even be possible to distinguish the halogens, which is very important in the analysis of priority pollutants and not possible with either of the existing element-selective detectors.

AED marks a compromise, offering extremely high sensitivity for carbon and good sensitivity for chlorine and bromine on the one hand and excellent selectivity on the other hand. On the base of simultaneous multi-element detection in combination with the possibility of compound independent calibration, AED has the advantage of providing empirical formula information, which, together with the retention time allows identification. Considering these factors, AED may be applied in routine environmental analysis, as the ease and expedience of the compound independent calibration may be an interesting and economically important argument. Its great potential for screening analysis should be emphasised, as no other detector allows such reliable and selective detection of halogenated compounds and, in some cases, tentative identification of compounds by their empirical formulas.

The method we have established in this work may be improved, e.g. by a more efficient removal of the

water vapor, e.g. by cryogenic techniques, thus making possible a quantitation on the hydrogen trace, too, or the use of cryotrapping methods, by which the whole amount of analytes is transferred on to the column, rendering the method still more sensitive by a factor of 10.

Further efforts have to be made to improve the validation of the method, as the preparation of the standards for calibration seems to be the major source of errors, not only in this application of GC-AED.

References

- [1] WHO, IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, 20 (1979) 491.
- [2] US Environmental Protection Agency, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, 1982.
- [3] US Environmental Protection Agency, Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88-039, 1988.
- [4] Deutsches Institut für Normung. Deutsche Einheitsverfahren zur Wasser-, Abwasser-, und Schlammuntersuchung; Gemeinsam erfassbare Stoffgruppen (Gruppe F), DIN 38 407 Teil 4, 5 und 9.
- [5] C.J. Koester and R.E. Clement, *CRC Crit. Rev. Anal. Chem.*, 24 (1993) 263.
- [6] J. Namiešnik, T. Górecki, M. Biziuk and L. Torres, *Anal. Chim. Acta*, 237 (1990), 1.
- [7] T.C. Voice and B. Kolb, *J. Chromatogr. Sci.*, 32 (1994) 306.
- [8] J.W. Swinnerton and V.J. Linnenbom, *J. Gas Chromatogr.*, 5 (1967) 70.
- [9] T. Bellar and J.J. Lichtenberg, *J. Am. Water Works Assoc.*, 66 (1974) 739.
- [10] The Determination of Halogenated Chemicals in Water by the P&T method, Method 502.1, US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.
- [11] Volatile Aromatic and Unsaturated Organic Compounds in Water by P&T GC, Method 503.1, US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.
- [12] US Environmental Protection Agency, Method 524.2, VOCs in water by P&T Capillary GC/MS, EPA 600/4-88-039, 1988.
- [13] J.W. Munch and J.W. Eichelberger, *J. Chromatogr. Sci.*, 30 (1992) 471.
- [14] P.C. Uden (Editor), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy* (ACS Symposium Series), American Chemical Society, Washington, DC, 1992.
- [15] B.D. Quimby, M.F. Delaney, P.C. Uden and R.C. Barnes, *Anal. Chem.*, 51 (1979) 875.

- [16] C. Gerbersmann, R. Lobinski and F.C. Adams, *Anal. Chim. Acta*, 316 (1995) 93.
- [17] M.B. de la Calle Guntinas, R. Lobinski and F.C. Adams, *J. Anal. At. Spectrom.*, 10 (1995) 111.
- [18] S. Pedersen-Bjergaard, T.N. Asp, J. Vedde and T. Greibrokk, *J. Microsep.*, 4 (1992) 163.
- [19] H. Yieru, O. Qingyu and Y. Weile, *J. Chromatogr. Sci.*, 28 (1990) 584.