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METHODS FOR THE QUANTITATIVE ANALYSIS OF VOLATILE HALOCARBONS FROM AQUEOUS SAMPLES BY EQUILIBRIUM HEADSPACE GAS CHROMATOGRAPHY WITH CAPILLARY COLUMNS

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SUMMARY

Volatile halogenated hydrocarbons (halocarbons) from aqueous solutions are analysed by headspace gas chromatography with fused-silica capillary columns and an electron-capture detector with detection limits below the parts per billion level. Special emphasis is placed on quantitative determination. Calibration by the internal and external standard techniques and by the method of standard additions is discussed and compared with the multiple headspace extraction procedure, which is based on a repeated headspace extraction of the sample.

INTRODUCTION

Three procedures are mainly recommended and in practical use for the analysis of volatile halocarbons in water samples, and all begin with an extraction by using either a liquid or a gas to separate the volatile halocarbons from the water.

Solvent extraction is simple and needs no specialized equipment. Particular problems arise only with foaming water samples or if difficult emulsions are obtained, as sometimes occurs with sewage sludge samples. However, if a large number of samples are to be processed, preferably automatically, other procedures, which are easier to automate than a solvent extraction and which make use of a gas for extracting the volatile halocarbons from the water, become more attractive.

Gas extraction by purge and trap[1] needs the most complicated instrumentation, because the volatiles are first stripped from the water sample by a continuous flow of an inert gas and are adsorbed in a short trapping column that is kept at ambient temperature. The trapped components are thermally desorbed and back-flushed on to the analytical column. It is obvious that the desorption must be carried out as fast as possible to start with a small concentration profile in the analytical column, particularly if this is a capillary column.

Dietz and Singley[2] have found with purge and trap that the chromatograms are of much poorer quality than those observed with the headspace technique with regard to peak tailing and detector noise. This might be caused by the troublesome sample transfer from an adsorption tube on to a gas chromatographic (GC) column, which, in principle requires a cold trap in between, particularly in view of the rigorous demands of capillary GC.

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All three methods combine the extraction of the halocarbons with their enrichment in the resulting extract. Such an enrichment effect is immediately apparent with the solvent extraction and also with the purge and trap technique, but is less obvious with the headspace procedure, unless the small partition coefficients are known, as shown by the following considerations.

Table I lists some partition coefficients of halocarbons from aqueous solutions. If, for the sake of simplicity, a partition coefficient of $K=1$ is assumed, the gas phase concentration equals that of the aqueous phase. In general, it is not difficult to inject a 1-ml gas sample on to a GC column, but even a 1-μl sample from the aqueous phase will cause problems, if injeced at high sensitivity. In this example, an enrichment factor of 1000 has apparently been achieved by using headspace gas chromatography (HSGC). With smaller partition coefficients, the results will even be better.

SAMPLE HANDLING

Particular care is necessary in handling the samples and standard solutions, considering the high volatility of these halocarbons in aqueous solutions. It is the inherent advantage of HSGC that aqueous samples can be filled into vials at the place of sample collection where the vials can immediately be sealed, thus preventing any losses due to evaporation.

The preparation of standard solutions, however, is prone to systematic errors as a result of the high volatility of these compounds, if the following rules are not strictly observed. First, stock solutions must be prepared and stored in flasks that are filled completely, with no gas volume remaining above the liquid phase, where the volatiles can accumulate. Second, the use of pipettes is prohibited and any sample transfer should be performed with syringes only, and even in syringes the sample should be drawn in slowly to avoid the build-up of gas bubbles. The need to observe these two rules is a consequence of the low partition coefficients of these compounds (Table I).

HEADSPACE LINEARITY

"Headspace linearity" is the linear relationship between the concentration of a compound in the sample and its partial vapour pressure above it. This results in a linear

TABLE I

VOLATILITY OF HALOCARBONS FROM AQUEOUS SOLUTIONS AT 65.4°C

Compound	*B.p. (°C)*	*Partition coefficient, K**
Dichloromethane	40.1	2.6
Chloroform	61.0	2.3
Trichloroethylene	87.0	0.3
Tetrachloroethylene	121.0	0.8
Chlorobenzene	132.0	2.8
Dibromochloromethane	120.0	5.4
Bromoform	149.5	12.8

* K = concentration in aqueous phase/concentration in gas phase. Determined by the multiple headspace extraction procedure[3].

relationship between concentration and peak area up to a certain limit, thus covering the so-called range of an "ideal dilute solution" with a constant activity coefficient[4]. This linear range is usually found with concentrations up to at least 0.1 % and often up to 10 % and even higher, depending on the solubility, polarity and, in general, on the activity coefficient, but cannot be predicted and must be determined experimentally.

However, most headspace applications must deal with concentrations much lower than 0.1 % and therefore the upper end of the linear range seldom causes problems. Even non-polar compounds such as halocarbons, being poorly soluble in water, have been found to give linear relationships up to concentrations of 0.1 %. However, for trace analysis electron-capture detection (ECD) is usually applied, and it is the smaller linear range of this detector that limits the usable concentration range rather than the headspace linearity.

ANALYTICAL SYSTEM

All investigations discussed in this paper were carried out with a Perkin-Elmer headspace sampling system[4]. Owing to the complex composition of halogenated hydrocarbon mixtures from water samples, the application of capillary columns is mandatory. However, these columns have a smaller capacity than packed columns. An electron-capture detector is therefore needed, but its sensitivity is only enhanced for compounds with more than two halogen atoms. In addition to the high separation efficiency with fused-silica capillary columns, the selectivity of a slightly polar liquid phase, such as SE-54, has been found necessary to separate certain pairs of compounds, *e.g.*, trichloroethylene and dichlorobromomethane, which otherwise cannot be resolved on non-polar methylsilicones.

Johansen[5] demonstrated the advantages of using highly loaded capillary columns for compounds of high volatility to increase both the retention at lower temperatures and the column capacity. Therefore, for this particular application, a 50 m × 0.32 mm fused-silica capillary with a film thickness of 1 μm was used. A chromatogram is shown in Fig. 1. For the same reason, Piet *et al.*[6] used a wide-bore capillary of I.D. 0.5 mm.

QUANTITATIVE METHODS FOR HEADSPACE ANALYSIS OF HALOCARBONS IN WATER

Reproducibility of headspace sampling at the trace concentration levels

In principle, all methods for quantitative analysis that are common in GC can also be applied in headspace GC with the exception of peak area normalization. External standard techniques are most convenient, particularly for the trace analysis of volatile compounds, but require good sampling reproducibility, as the chromatograms of two independent injections are compared. The precision of the pneumatic sampling device used here fulfills this requirement sufficiently well, as the instrumental reproducibility of injection is described by a coefficient of variation of about 1 %, although in a practical trace analysis some additional problems during sample handling and preparation of standards may considerably affect this figure. The overall figure for reproducibility in trace analysis is generally not as good, reflecting the skill of the operator as well as the precision of the instrumentation. Any kind of automation will, of course, help to improve the precision of the analysis.

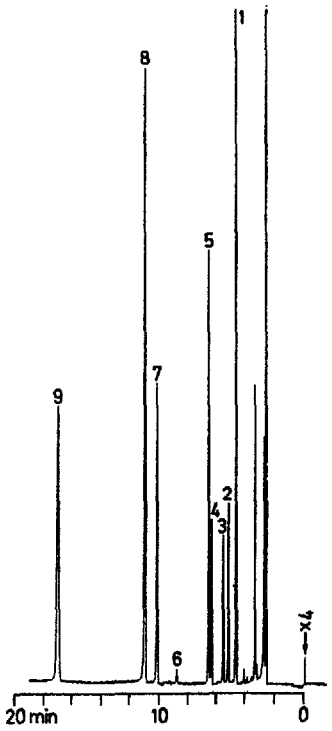

Fig. 1. Headspace analysis of halocarbons from aqueous solution. Instrument: Sigma 2B; headspace injector HS-6; 50 m × 0.32 mm fused-silica capillary with SE-54 (thick film) at 80°C isothermal; sample, 1 ml of aqueous solution at 80°C; carrier gas, nitrogen at 1.9 bar, split 1:25; scavenger gas, argon–methane at 50 ml/min; detection, ^{63}Ni; ECD, 3.5 nA, ×4. Peaks: 1 = chloroform, 37 μg/l; 2 = 1,1,1-trichloroethane, 2.3 μg/l; 3 = carbon tetrachloride, 0.3 μg/l; 4 = trichloroethylene, 8.9 μg/l; 5 = dichlorobromomethane, 4.3 μg/l; 6 = 1,1,2-trichloroethane, 3.0 μg/l; 7 = dibromochloromethane, 5.2 μg/l; 8 = tetrachloroethylene, 2.3 μg/l; 9 = bromoform, 31 μg/l.

The results for reproducibility from four repetitive headspace analyses of an aqueous halocarbon sample, similar to that shown in Fig. 1, are listed in Table II. The values for the relative standard deviation (RSD) of the absolute peak areas are fairly good and allow the use of external standard techniques for quantitation, as discussed below in more detail.

The fundamentals of quantitative analysis have already been discussed[4] with particular emphasis on the influence of the activity coefficient and thus of the sample matrix on the volatility.

TABLE II

PRECISION OF HSGC (n = 4)

Compound	*Concentration (μg/l)*	*RSD (peak area) (%)*
1,1,1-Trichloroethane	3.0	5.5
Carbon tetrachloride	0.5	5.9
Trichloroethylene	4.0	5.5
Tetrachloroethylene	2.0	7.1

Internal standard method

The method of using an internal standard is applied mainly if the reproducibility of sample injection is not sufficiently good and is often recommended when a manually operated gas syringe is used for headspace injection, although it has the inherent drawback that the internal standard must be added to each sample. Particularly for a series of samples this additional sample handling step is time-consuming and inconvenient; moreover, there is the risk of introducing more errors than it was intended to avoid. This applies mainly to compounds of high volatility at trace concentrations.

With an internal standard, response factors must be determined which, however, include not only the detector response of the various compounds, but also their specific partition coefficients. More precisely, they are called headspace response factors[7]. The determination of these headspace response factors requires the pure sample matrix to be available for preparing calibration standards. This requirement may cause problems when the pure matrix is not available.

External standard method

The use of an external standard is the simplest and most convenient calibration method, particularly with a sampling device of sufficiently great precision. The calibration is carried out with the identical compound and no response factor needs to be determined, but the pure matrix is also required for preparing a calibration standard; this has already been found disadvantageous for the internal standard method discussed above. The difficulties caused by this requirement depend strongly on the type of analysis. No problems will occur if drinking water is to be analysed for halocarbons, while the same analysis of a sewage sludge sample with its undefined matrix will vitiate both the internal and external standard methods, and would strongly indicate the method of standard additions or for the multiple headspace extraction procedure (MHE).

Method of standard additions

This procedure has the inherent advantage that the influence of the sample matrix on the volatility of a compound is included in the calibration procedure and no response factors need be determined. However, each sample has to be analysed twice, with and without an added amount of the volatile sample constituent. The original concentration of the volatile compound is derived from the difference in the peak sizes on the two chromatograms.

The method of standard additions is the most universal calibration procedure in the headspace analysis of liquid samples or solutions, because the calibration is carried out with each individual compound in the identical matrix. It is good practice in headspace analysis to begin with this procedure if new and unknown samples have to be analysed before any further simplification, *e.g.*, by using the external standard technique, is considered. For routine analysis of a large series of similar samples with an identical matrix, calibration by an external standard is preferred.

Method of multiple headspace extraction (MHE)

This procedure was originally developed for the analysis of volatile compounds in solid sampless[8], but has been found useful for liquid samples also, provided the volatile compounds show a low partition coefficient, as do the halocarbons in aqueous solutions. A similar stepwise approach has been used by McAuliffe[9].

The MHE procedure is based on a stepwise gas extraction with intermediate headspace analysis by which the remaining concentration of the volatile compound in the sample is monitored after each extraction step. After each headspace analysis the vials remain pressurized with the head pressure of the column, and an efficient extraction yield can be achieved if the internal pressure in the vial is vented to atmosphere, *e.g.*, by piercing the septum of the headspace vial with a needle. If the pressure is *e.g.*, 1 bar, half of the gas phase from the vial will be vented together with the volatiles in it. The phase equilibrium is thus disturbed and needs some time before it is re-established. The pressure release should be performed immediately after each injection, because the analysis time is used simultaneously to re-equilibrate the sample. The next headspace analysis will show a chromatogram where the peaks are smaller. If the whole procedure is repeated several times, it is possible to strip off all volatiles completely. Apparently, a continuous stripping procedure is simulated by such a stepwise approach.

If carried out until exhaustive extraction, it would only be necessary to sum all peaks areas obtained from a compound from all consecutive chromatograms to obtain an area total corresponding to the total amount of that compound in the headspace vial and–this is the essential feature of this method—which is independent of its phase distribution. Thus, any influence of the sample matrix is eliminated.

The same result can also be obtained by mathematical extrapolation, as the stepwise extraction at equal time intervals proceeds exactly acording to an exponential function and exhaustive extraction can thus be avoided. The area total ΣA is derived as the sum of a geometric progression, and only a few such determinations are needed to apply regression calculation. In practice, two determinations have been found sufficient for calculating this area total according to the equation

$$\Sigma A = \frac{A_1^2}{A_1 - A_2}$$

where A_1 and A_2 are the peak areas from the first and second headspace analyses, respectively.

A more detailed theoretical treatment has been published elsewhere[8,10]. This area total, which has been obtained either by linear regression or by the simple two-step procedure, remains to be calibrated as any peak area in GC analyses. This necessary calibration includes only the detector response and not the matrix effect, which has been eliminated by extrapolation. Any other sample with a completely different matrix can be used for this purpose. It is possible, therefore, to prepare a calibration standard for the analysis of volatile halocarbons from pure water and to apply it to the determination in a different sample, such as a sewage sludge sample. Even a homogeneous vapour mixture containing no matrix can be used as an external standard, and such a sample is conveniently prepared if a few microlitres of the pure compound or of a dilute solution of it are injected through the septum of an already sealed but empty headspace vial in which this calibration sample is vaporized completely at the prevailing temperature of sample thermostating. The resulting homogeneous vapour mixture is thus used to determine the detector response, but in order to include the instrumental conditions in the calibration procedure, this calibration standard must be carried through the multiple extraction procedure as well.

The gas volume transferred from the vial by the pneumatic sampling system is

slightly dependent on the volume of the gas space and thus on the phase ratio and it may become necessary to simulate the missing sample volume in the calibration vial by the addition of some inert material, such as glass beads, to achieve the same free gas space in the sample and the calibration vial.

The calibration standard is processed in the same way, and an area total is again calculated for each sample component; however, in this instance the corresponding amount is known, and from this result the concentration of that compound in any sample can be derived. It is important to note that in this instance, the sample matrix no longer has any influence, and that such a calibration standard can be applied to any type of sample containing this particular compound.

The procedure of multiple headspace extraction allows the use of an internal standard as well. As a result, two area totals are obtained both from the volatile sample constituent and the added internal standard, which require the determination of a detector response factor for comparison. This factor compensates only for different detector responses; it can be determined by injection of a test mixture as usual and not necessarily by headspace technique; even tabulated values can be applied.

The MHE procedure has been found very convenient for practical applications and compares favourably with the method of standard additions. The expenditure is the same, because two repeated determinations must be made on each sample.

Practical examples of the MHE procedure

Fig. 2 gives the chromatograms from a three-step MHE analyis of halocarbons from aqueous solution, showing the exponential decrease in peak heights.

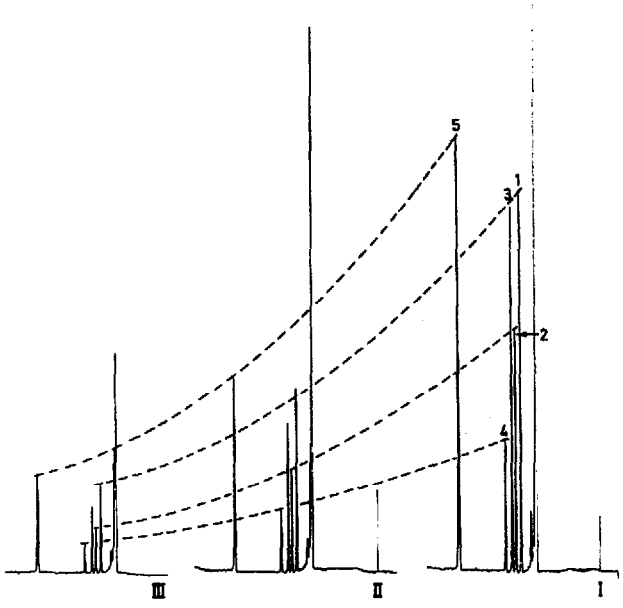

Fig. 2. Multiple headspace extraction of halocarbons from aqueous solutions. Instrument: Sigma 2B; headspace injector HS-6; 50 m × 0.23 mm fused-silica capillary with OV-101 (thick film) at 45°C isothermal; carrier gas nitrogen at 1 ml/min, split 1:25; scavenger gas argon–methane at 10 ml/min; sample, 1 ml, 30 min at 80°C; detection, ^{63}Ni; ECD 3.5 nA, ×4. Peaks (chromatogram I): 1 = chloroform, 25 μg/l; 2 = 1,1,1-trichloroethane, 5 μg/l; 3 = carbon tetrachloride, 0.5 μg/l; 4 = trichloroethylene, 4 μg/l; 5 = tetrachloroethylene, 2 μg/l.

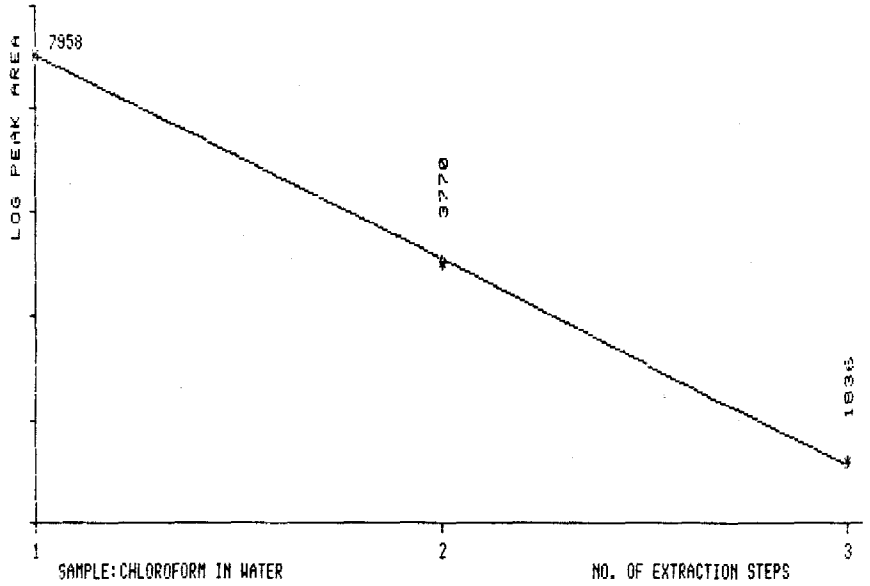

Fig. 3. Calculation of the area total of chloroform from the three-step MHE analysis of the water sample shown in Fig. 2. Exp. (—K) = 0.480325. Extrapolated final area = 15,243.1.

If the resulting peak areas are plotted on a semilogarithmic scale *versus* the number of analyses, a linear relationship is obtained with a correlation coefficient of – 0.9999, as shown for chloroform as an example in Fig. 3.

An area total of 15,243 is obained by linear regression calculation from these three area values, and a virtually identical result of 15,121 is obtained, if only the first two area values are used and calculated from the above equation. This good agreement clearly shows that the simple two-step procedure is adequate for practical applications.

REFERENCES

1 *Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method*, Method 501.1, United States EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, November 6, 1979.
2 E. A. Dietz, Jr. and K. F. Singley, *Anal. Chem.*, 51 (1979) 1809–1814.
3 P. Pospisil and B. Kolb, in preparation.
4 B. Kolb, *J. Chromatogr.*, 112 (1975) 287–295.
5 N. G. Johansen, *Chromatogr. Newsl.*, 7 (1979) 18–21.
6 G. J. Piet, P. Slingerland, F. E. de Grunt, M. P. M. v.d.Heuvel and B. C. J. Zoeteman, *Anal. Lett.*, A11 (1978) 437–448.
7 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis*, Heyden, London, 1977, p. 10
8 B. Kolb, M. Auer and P. Pospisil, *Angewandte Chromatographie – Applied Chromatography, No. 35E.* Perkin-Elmer, Überlingen, 1981.
9 C. D. McAuliffe, *U. S. Pat.*, 3.759.086 (1973).
10 B. Kolb, *Chromatographia*, 15 (1982) 587–594.