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## SENSITIVITY AND LINEARITY OF HEADSPACE AND LIQUID-LIQUID EXTRACTION TECHNIQUES FOR GAS CHROMATOGRAPHIC ANALYSIS OF HALOCARBONS IN WATER

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### SUMMARY

The headspace and the liquid-liquid extraction methods for the analysis of trihalomethanes and other halocarbons in water were compared by using mixed column gas chromatography.

The sensitivity and linearity of the nickel-63 asymmetric type electron-capture detector were evaluated for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ ,  $\text{CHBr}_3$ ,  $\text{CHCl}_2\text{-CH}_3$ ,  $\text{CH}_2\text{Cl-CH}_2\text{Cl}$ ,  $\text{CCl}_3\text{-CH}_3$ ,  $\text{CHCl=CCl}_2$  and  $\text{CCl}_2=\text{CCl}_2$ , using the two extraction methods. In both instances, the linearity extends over several orders of magnitude, thus simplifying the use of calibration techniques for the quantitative analysis and facilitating the use of integrators and data systems.

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### INTRODUCTION

The gas chromatographic (GC) analysis of trihalomethanes (THMs) and other haloalkanes in drinking water supplies requires the use of extraction and concentration methods in order to bring the actual concentration in the injected sample to a level high enough to permit the detection and quantitative evaluation with electron-capture detection (ECD). Many analytical methods which use the headspace technique or liquid-liquid extraction have been suggested<sup>1-12</sup>. In these methods a widely used quantitative procedure is the external standard calibration method, which requires the preparation of many standard samples over a wide range of concentrations, in order to take into account the possible non-linearity of the ECD response, mainly when tritium electron-capture detectors are used, or the variable efficiency of the extraction procedures as a function of the concentration of the compounds.

In a previous paper<sup>13</sup> the static headspace method was used in conjunction with a mixed column GC separation, which allows the complete resolution of THMs and other halocarbons from the solvents (pentane, hexane and isooctane) used for liquid-liquid extraction. This GC technique is therefore suitable for the evaluation

of different extraction methods and was used to investigate the linearity and the sensitivity of headspace and liquid-liquid extraction. At the same time, the sensitivity and the linearity of the nickel-63 electron-capture detector were tested with many light halocarbons, in order to establish whether the external standard calibration procedure can be simplified by the determination of absolute or relative calibration factors that remain constant over the whole range of concentration investigated and permit therefore a quick quantitative calculation by electronic integrators and data systems.

## EXPERIMENTAL

Three series of calibrations were made by using a Varian nickel-63 (8 mCi) electron-capture detector, installed in a Series 3700 gas chromatograph with two columns connected in series (30 cm of 10% SP-1000 and 350 cm of 10% OV-1). The temperature program was as follows: isothermal at 78°C for 9 min, then raised at 5°C/min to 110°C and finally held at 110°C for 15 min.

The calibrations used all of the haloalkanes listed in Table I and were carried out in order to study: (a) the sensitivity and linearity of the detector; (b) the linearity and detection limits of the static headspace technique and (c) the linearity and detection limits of the *n*-pentane liquid-liquid extraction technique.

They were made as follows:

### ECD calibration

The nickel-63 pulsed electron-capture detector (Varian) was used for calibration, in the constant-current pulse-modulated mode, by using pure nitrogen as the carrier gas. The cell comprised displaced coaxial cylinders, 0.3 ml in volume. Pulse amplitude: 50 V nominal; Pulse width: 0.64  $\mu$ s nominal. Detector temperature: 250°C. Under these conditions the correlation between the pulse frequency in kHz and the

TABLE I

WEIGHT AND MOLAR RESPONSES OF THE NICKEL-63 ELECTRON-CAPTURE DETECTOR TO VARIOUS HALOCARBONS

F.U. = Frequency units: see text.

Compound	MW	Counts	Counts	F.U.	Hz
		$g \cdot 10^{-16}$	$mol \cdot 10^{-16}$	$mol \cdot 10^{-13}$	$mol \cdot 10^{-13}$
CH <sub>2</sub> Cl <sub>2</sub>	84.93	0.0097	0.82	0.164	0.019
CHCl <sub>3</sub>	119.38	2.1	250.7	50.1	6.0
CCl <sub>4</sub>	153.82	36.7	5645.2	1129.0	134.3
CHCl <sub>2</sub> Br	163.83	16.3	2670.4	534.1	63.5
CHClBr <sub>2</sub>	208.29	12.9	2686.9	537.4	63.9
CHBr <sub>3</sub>	252.75	4.33	1094.4	218.9	26.0
CHCl <sub>2</sub> -CH <sub>3</sub>	98.96	0.0024	0.237	0.047	0.005
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	98.96	0.013	1.28	0.256	0.030
CCl <sub>3</sub> -CH <sub>3</sub>	133.41	4.68	624.3	124.9	14.86
CHCl=CCl <sub>2</sub>	131.39	2.86	375.8	75.16	8.9
CCl <sub>2</sub> =CCl <sub>2</sub>	165.83	14.67	2432.7	486.5	57.9

detector response in frequency units (F.U.) is given by

$$\text{Pulse frequency} = \text{F.U.} \times 0.119 + 1.57$$

and is linear in the range 2–18 kHz<sup>14</sup>.

The quantitative analysis was carried out by using a Varian CDS 111-C digital integrator; five integration counts correspond to a signal amplitude of  $1 \mu\text{V} \cdot \text{s}$  which, at range  $\times 1$  and attenuation  $\times 1$ , is equivalent to 1 F.U. The samples of halocarbons were diluted in methanol and directly injected into the GC column by means of a 10- $\mu\text{l}$  microsyringe; from 2 to 5  $\mu\text{l}$  were injected in order to permit the evaluation of the actual sample amount, by measuring the residual liquid in the syringe needle after injection and reducing therefore the errors due to injection of very small amounts.

The methanol used contained small amounts of halocarbons which could not be removed by distillation. The amount of contaminants was measured during the calibration experiments and taken into account in the following quantitative calculations. A typical composition was (values in  $\mu\text{g/l}$ ): chloroform, 3; bromodichloromethane, 1; tetrachloromethane, 0.76; tetrachloroethylene, 1.5; 1,1,1-trichloroethane, 1.3; 1,1,2-trichloroethylene, 0.8.

#### *Headspace calibration*

In the headspace gas analysis a single sample is quickly taken from the gas over the condensed phase in a closed static system that has been thermostatted in order for equilibrium to be reached between the two phases. Therefore, for quantitative analysis it is necessary to take into account only the distribution of the components between the liquid and gas phases at equilibrium.

The calibration was carried out with the technique previously described<sup>13</sup>: screw-capped vials of volume 40 ml with PTFE-faced septa, washed with distilled water and methanol and dried overnight at 200°C, were used; the caps and septa were washed with light petroleum ether and dried overnight at 80°C. The vials were completely filled with single or multiple component primary aqueous standards prepared by dissolving suitable volumes of the stock methanol solutions used for calibration of the detector (see above) in doubly distilled water; 1% (w/w) of sodium chloride was added as salting-out reagent. It was found previously<sup>15–17</sup> that sodium chloride concentrations smaller than 1% do not significantly increase the chromatographic response by changing the halocarbon activity coefficients; this amount of salt was added in the previous method<sup>14</sup> in order to equalize the salt contents of the various water samples analyzed. The same amount was therefore also used in this calibration. Before GC analysis, 5 ml of water were removed from each vial in order to create the headspace volume, and the samples were thermostatted at 30°C in a water-bath for 1 h. The injections (150  $\mu\text{l}$ ) were made by using 250- $\mu\text{l}$  Hamilton gas-tight syringes.

#### *n-Pentane liquid-liquid extraction*

The liquid-liquid extraction is mainly determined by the temperature-dependent partition coefficients between the aqueous and organic layers, but is also influenced by the volume ratio and by the duration of shaking and of the phase-separation steps. After several preliminary experiments, and by taking into account previous literature data<sup>2,12,18–20</sup>, the following method was applied: 10 ml of sample (prepared as described above) were extracted with 2 ml of *n*-pentane, by shaking vigorously for 2 min and waiting until complete phase separation was achieved; 5  $\mu\text{l}$  of the *n*-pentane extract were then injected in the gas chromatograph.

## RESULTS AND DISCUSSION

*ECD calibration*

Figs. 1 and 2 show the linear dynamic range for the analyzed halocarbons. The observed deviation at low concentrations is due to the effect of the impurities in the methanol and can be corrected for by subtracting from the area counts of the various peaks the blank value measured by injecting the pure solvent. This procedure is of course essential when performing trace analysis, but is not necessary when studying the ECD linearity, because deviations from linearity at low concentrations cannot be due to detector failure, and are only related to impurities in the sample (positive deviation) or in the carrier gas (negative deviation due to vacancy phenomena). The linearity limits of the detector are indicated by the deviation at high concentrations.

The sensitivities of the detector to various halocarbons were calculated from the experimental data by least squares regression analysis using the points within the linear portions of the graphs of Figs. 1 and 2. Table I shows the values of counts/weight and counts/mol of the halocarbons. The first parameter is currently used in the determination of these compounds in the environment and is employed in the graphs shown, therefore permitting a rapid evaluation of the practical linearity range. On the other hand, the weight concentration values may be misleading when the total amount of halocarbons is considered, owing to the large range in molecular weights of these compounds. Consideration of the relative responses have therefore to be made by using molar concentration values. The responses in terms of frequency units and of the pulse frequency per mol are also shown.

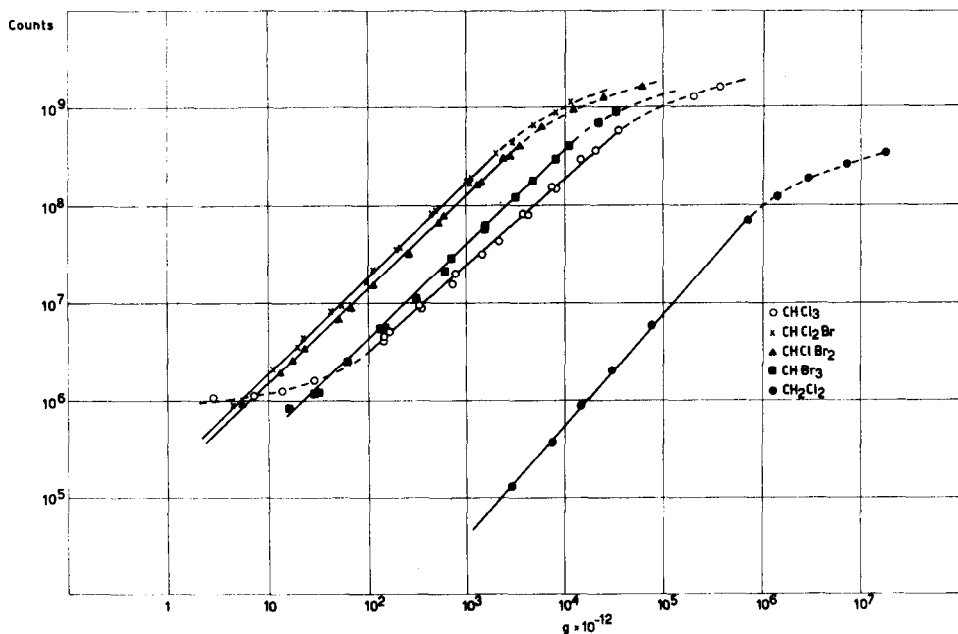


Fig. 1. Sensitivity and linear dynamic range of the nickel-63 concentric type pulsed electron-capture detector to trihalomethanes and dichloromethane.

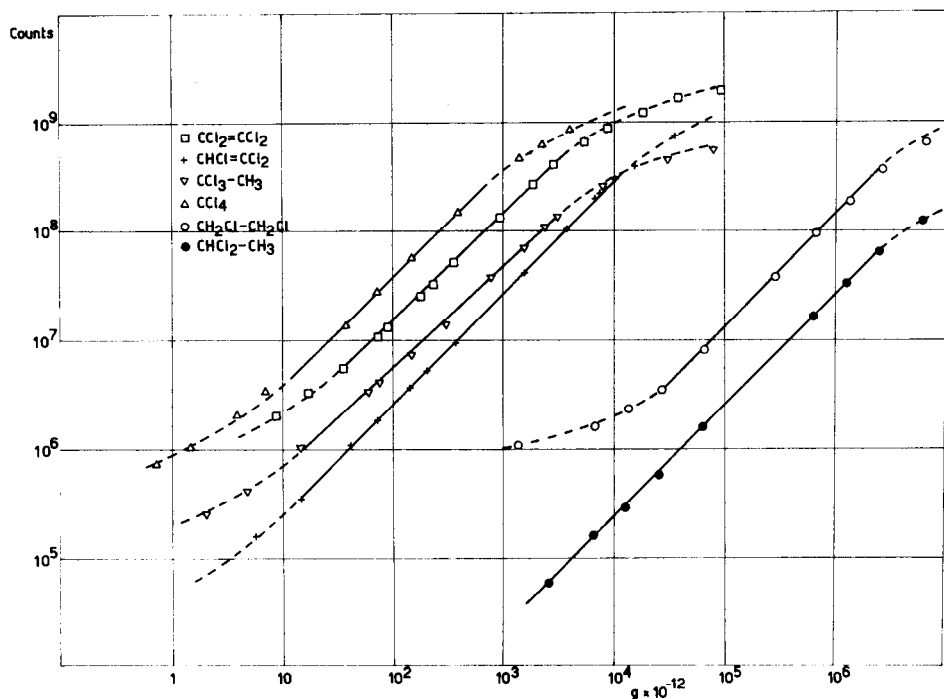


Fig. 2. Sensitivity and linear dynamic range as in Fig. 1, but for some chlorinated ethanes and ethenes.

Table II shows that the relative molar response obtained in this work are in good agreement with literature values, taking into account the different columns used, the type of ECD, temperature, flow-rate, etc. The relative responses of the various halocarbons are largely dependent on their molecular structure, number and type of halogen atoms, as shown previously<sup>21</sup> but still subject to uncertainty. In this

TABLE II

ECD MOLAR RESPONSES (RELATIVE TO CHLOROFORM) CALCULATED IN THIS WORK AND THOSE TAKEN FROM THE LITERATURE

ECD temperature: 250°C.

Compound	This work	Ref. 22	Ref. 11
CH <sub>2</sub> Cl <sub>2</sub>	0.003	0.0082	0.017
CHCl <sub>3</sub>	1	1	1
CCl <sub>4</sub>	22.51	19.82	9.41
CHCl <sub>2</sub> Br	10.65	—	4.70
CHClBr <sub>2</sub>	10.71	—	2.70
CHBr <sub>3</sub>	4.36	—	0.88
CHCl <sub>2</sub> -CH <sub>3</sub>	0.001	—	—
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.005	0.0043	0.017
CCl <sub>3</sub> -CH <sub>3</sub>	2.49	—	3.29
CHCl=CCl <sub>2</sub>	1.50	1.10	1.17
CCl <sub>2</sub> =CCl <sub>2</sub>	9.70	8.71	5.29

instance, the response of the various THMs should theoretically increase by replacing the chlorine atoms of chloroform with bromine. The first substitution ( $\text{CHCl}_2\text{Br}$ ) does result in an increase in response, but the addition of other bromine atoms does not lead to a further increase in sensitivity. The correlation between structure and ECD response therefore requires further investigation.

### Headspace extraction

Figs. 3 and 4 show the linearity range of the headspace extraction method described, by plotting the peak area counts for the various halocarbons as a function of the initial concentration in the standard aqueous samples. The results are therefore dependent on many parameters influencing the phase distribution and are correlated with the particular extraction method used and with the choice of experimental conditions. Table III shows the values of the overall sensitivity of the headspace extraction method to the various halocarbons. The values in counts per concentration unit, expressed both as  $\mu\text{g l}^{-1}$  and  $\text{mol l}^{-1}$ , are given.

The distribution of a compound between two phases depends on the temperature, ratio of headspace to liquid volume, vapour pressure and interaction of the compound on the liquid matrix. The partition coefficient,  $K$ , is given by

$$K = \frac{[A]_v}{[A]_w} \text{ when } \frac{\gamma_v}{\gamma_w} \rightarrow 1 \text{ at equilibrium}$$

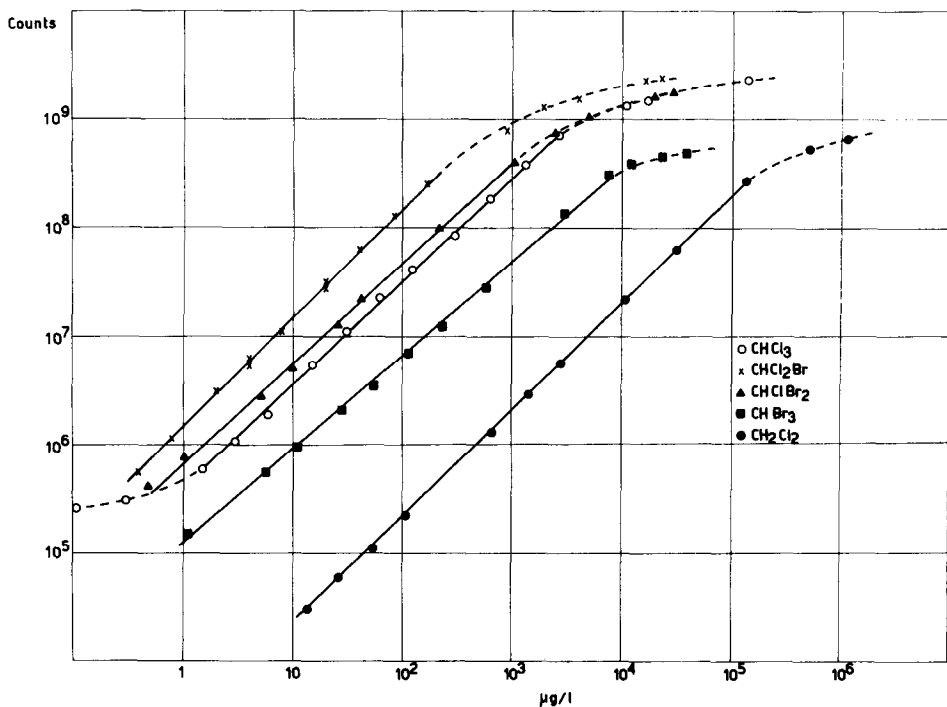


Fig. 3. Overall sensitivity and linearity of the headspace extraction method (see text) for trihalomethanes and dichloromethane.

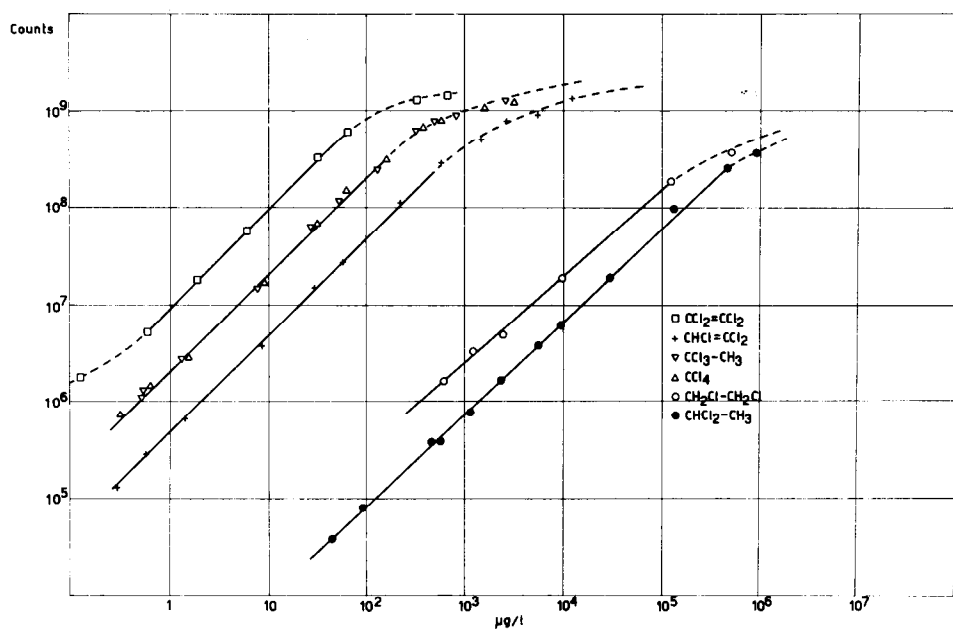


Fig. 4. Overall sensitivity and linearity of the headspace extraction method for some chlorinated ethanes and ethenes.

TABLE III

OVERALL SENSITIVITY TO VARIOUS HALOCARBONS OF THE STATIC HEADSPACE EXTRACTION METHOD, PARTITION COEFFICIENT,  $K$ , CALCULATED VAPOUR PRESSURE,  $P_v$ , AVAILABLE SOLUBILITY DATA AND  $P_v/K$  RATIO (SEE TEXT)

Compound	Sensitivity		$K$	$P_v$ at 30°C (Torr)	Solubility in 100 parts of water <sup>24</sup>	$\frac{P_v}{K}$
	Counts	Counts				
	$10^{-4} \cdot \mu\text{g l}^{-1}$	$10^{-10} \cdot \text{mol l}^{-1}$				
$\text{CH}_2\text{Cl}_2$	0.18	15.3	0.125	524.1	2 (20°C)	4192
$\text{CHCl}_3$	32.7	3 903.7	0.12	209.7	0.82 (20°C)	1750
$\text{CCl}_4$	1044	160 588.1	0.19	121.7	0.08 (20°C)	642
$\text{CHCl}_2\text{Br}$	145.1	23 771.7	0.059	—	—	—
$\text{CHClBr}_2$	46.0	9 581.3	0.023	—	—	—
$\text{CHBr}_3$	4.51	1 139.9	0.0071	7.9	0.1	1113
$\text{CHCl}_2\text{-CH}_3$	0.064	6.33	0.17	236.8	—	1394
$\text{CH}_2\text{Cl-CH}_2\text{Cl}$	0.13	12.86	0.06	94.3	0.9 (0°C)	1572
$\text{CCl}_3\text{-CH}_3$	184.4	24 600.8	0.26	148.5	—	562
$\text{CHCl=CCl}_2$	51.3	6 740.3	0.12	91.2	0.1 (25°C)	760
$\text{CCl}_2=\text{CCl}_2$	219.4	36 383.1	0.10	23.0	0.02 (20°C)	239

where  $[A]_v$  and  $[A]_w$  are the equilibrium vapour and aqueous phase concentrations of solute A and  $\gamma_v$  and  $\gamma_w$  are the corresponding activity coefficients<sup>16</sup>. In this instance, the equation for  $K$  can be rewritten as

$$K = \frac{V_w W_v}{V_v (W_T - W_v)}$$

where  $W_v$  and  $W_w$  are the equilibrium weights of A in the vapour and aqueous phases,  $V_v$  and  $V_w$  are the volumes of the two phases and  $W_T$  is the total weight of A in the system. The parameter  $W_v$  can then be calculated

$$W_v = \frac{(\text{Resp})_{\text{HS}} C_w}{(\text{Resp})_S} \cdot \frac{V_v}{V_I}$$

where  $(\text{Resp})_S$  is the ECD response (counts  $\text{g}^{-1}$ ) obtained from the standard sample,  $(\text{Resp})_{\text{HS}}$  is the ECD response (counts  $\text{g}^{-1}$  l) obtained from the analysis of the headspace sample,  $C_w$  is the initial concentration ( $\text{g l}^{-1}$ ) of the solute in the aqueous phase and  $V_I$  is the volume sampled from the headspace volume and injected.

The  $K$  values are shown in Table III. The calculated vapour pressures of the pure liquids at 30°C and the available values of the solubility are also shown<sup>23,24</sup>. The concentration in the headspace volume depends both on the vapour pressure

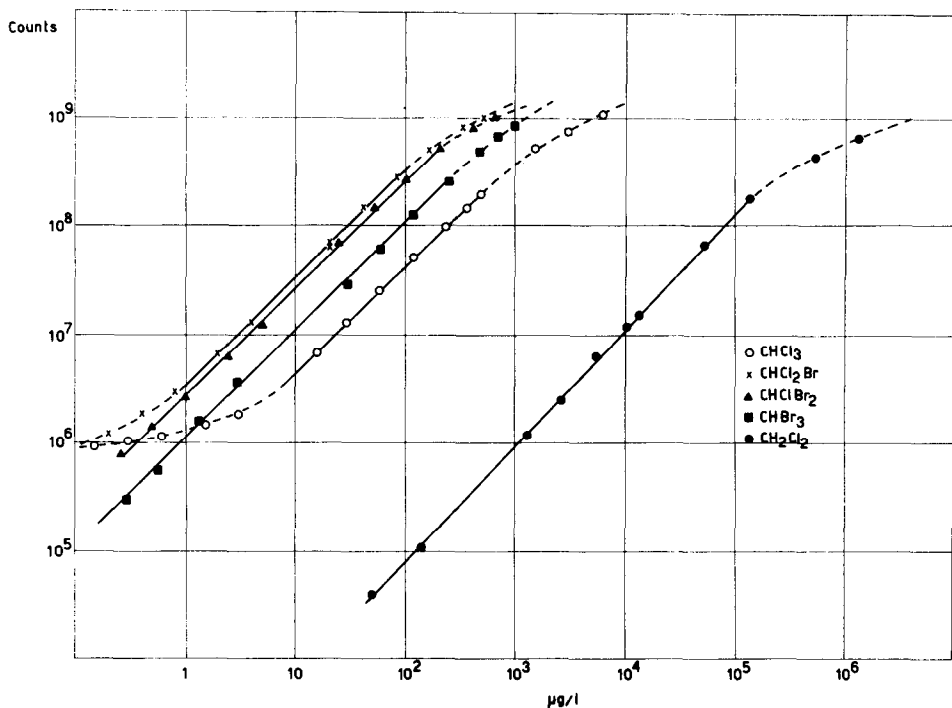


Fig. 5. Overall sensitivity and linearity of the *n*-pentane liquid-liquid extraction of trihalomethanes and dichloromethane.



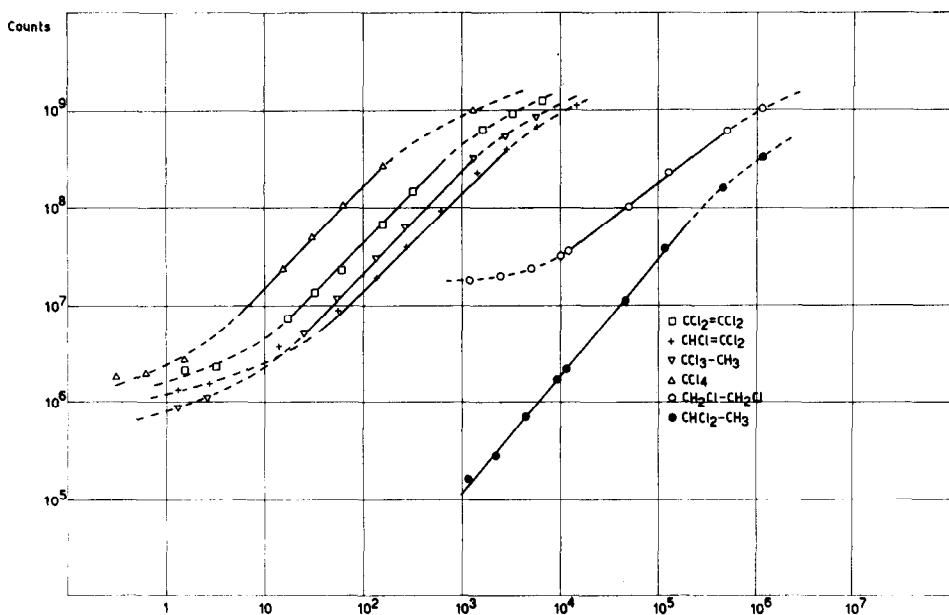


Fig. 6. Overall sensitivity and linearity of the *n*-pentane liquid-liquid extraction of some chlorinated ethanes and ethenes.

and on the solubility of the substances in water; these two parameters exert opposite effects on the phase transfer. If the evaporation of the compounds from the liquid phase to the headspace were to depend only on the vapour pressure,  $P_v$ , the ratio  $P_v/K$  would have a constant value. On the contrary, Table III shows that this ratio increases with the capacity of the halocarbons to form hydrogen bonds with water, owing to the presence of active hydrogen atoms<sup>25-27</sup>.

#### *n*-Pentane extraction

Figs. 5 and 6 show the linearity range of the liquid-liquid extraction method using *n*-pentane, expressed as shown previously. Table IV shows the values of the overall sensitivity of this method and the extraction efficiency (%) calculated by comparing the values obtained for the extracted halocarbons with those expected for 100% recovery<sup>12,19</sup>. Previously reported extraction efficiencies for THMs with *n*-pentane and isooctane are also compared with our values. Reliable data for halocarbons other than THMs are not available. A correlation of the extraction efficiency with literature solubility data is not possible because generally these compounds are reported to be soluble in all proportions with pentane or other hydrocarbons. In this instance the extraction efficiency is not correlated to the solubility of THM in pure organic solvents only, but to the partition between organic and aqueous layer of very small amounts of halogenated compounds. It is seen that the extraction efficiency is proportional to the reciprocal of the molecular volume of the halocarbon.

TABLE IV

OVERALL SENSITIVITY TO VARIOUS HALOCARBONS OF THE LIQUID-LIQUID EXTRACTION METHOD AND EXTRACTION EFFICIENCY

Compound	Sensitivity		Extraction efficiency (%)				Molecular volume
	Counts	Counts	This work	Ref. 12 (pentane)	Ref. 19 (pentane)	Ref. 19 (isooctane)	
	$10^{-4} \cdot \mu\text{g l}^{-1}$	$10^{-10} \cdot \text{mol l}^{-1}$					
CH <sub>2</sub> Cl <sub>2</sub>	0.124	10.53	98				69.04
CHCl <sub>3</sub>	38.9	4 643.8	70	83.6	80	78	80.66
CCl <sub>4</sub>	154.6	23 780.5	32.3				96.62
CHCl <sub>2</sub> Br	340.6	55 800.4	76	87.4	88	83	82.49
CHClBr <sub>2</sub>	290.1	60 424.9	81.8	89.4	90	88	85.01
CHBr <sub>3</sub>	106.7	26 968.4	89.6	91	94	90	89.62
CHCl <sub>2</sub> -CH <sub>3</sub>	0.112	11.08	66.3				74.58
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.038	3.76	98.7				78.53
CCl <sub>3</sub> -CH <sub>3</sub>	22.65	3 021.7	37.2				99.63
CHCl=CCl <sub>2</sub>	14.75	1 938.0	39.7				89.68
CCl <sub>2</sub> =CCl <sub>2</sub>	42.42	7 034.5	22.2				102.23

## CONCLUSIONS

The experiments confirmed the wide linearity range of the nickel-63 electron-capture detector and showed that this is true also of the overall response of the headspace and liquid-liquid extraction methods, providing they are carried out with a sufficient reproducibility of the volume ratios, temperature, equilibration time, etc.

As a consequence, the quantitative analysis can be accomplished by the external standard technique, without the need for interpolation of calibration factors from a non-linear calibration plot as a function of the peak area, prepared by injection of many samples of different concentrations, but using response factors calculated at the beginning of the analysis series and tested only to verify the scarcely probable, but possible, change in the overall detector response due to contamination, leaks, etc. This facilitates the use of automatic sampling systems and calculation programs.

In addition, when the response factors relative to a few standard halocarbons are known, the initial calibration or its periodical verification can be simplified because it is necessary only to verify the response of these standard substances to ensure that all the other compounds have the same calibration factor previously measured, within their linearity ranges. When several compounds having different ECD sensitivities have to be measured in the same sample, reference standards having different sensitivities should also be selected.

The deviations from linearity at high sample amounts, due to detector overcharge, are seldom observed in trace analysis, while the deviations at low concentration (due to blank values, impurities in solvents, water, etc., used for standard preparation), can greatly influence the accuracy of the results if the calibration factors are calculated for low concentration standards. The relative response factors have therefore to be calculated from the slope of the linear portion of the response curve, in order to minimize the effect of different amounts of contaminants in the various

ingredients used for the preparation of the calibration samples. Furthermore, extrapolation of the linear portion toward low counts permits the measurement in the actual samples of amounts of halocarbons well below these sometimes found as the blank values of the calibration procedure, mainly in liquid-liquid extraction techniques, where the concentration of the sample increases through appropriate selection of the volume ratio.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 *The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method*, Method 501.1, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1979.
- 2 *The Analysis of Trihalomethanes in Drinking Water by Liquid-Liquid Extraction*, Method 501.2, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1979.
- 3 H. Binder, *J. Chromatogr.*, 25 (1966) 189.
- 4 F. Drawert, W. Heimann, R. Emberger and R. Tressl, *Chromatographia*, 2 (1969) 77.
- 5 B. Kolb, *J. Chromatogr.*, 122 (1976) 553.
- 6 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis*, Heyden, London, New York, Rheine, 1977.
- 7 R. Olson, D. T. Williams and P. D. Bothwell, *Environ. Sci. Technol.*, 13 (1979) 936.
- 8 E. A. Dietz and K. F. Singley, *Anal. Chem.*, 51 (1979) 1609.
- 9 L. Lukačovič, M. Mikuláš, A. Vanko and G. Kiss, *J. Chromatogr.*, 207 (1981) 373.
- 10 A. Cavallaro and P. Grassi, *Boll. Lab. Chim. Prov.*, 27 (1976) 337.
- 11 G. Ziglio and G. Beltrametti, *Quad. Ist. Igiene, Univ. Milano*, No. 2, July 1980.
- 12 A. Kirshen, *Varian Instrum. Appl.*, 5 (1981) 2.
- 13 G. Castello, T. C. Gerbino and S. Kanitz, *J. Chromatogr.*, 247 (1982) 263.
- 14 *Aerograph <sup>63</sup>Ni ECD manual*, Publ. No. 85-001139-21, Varian, Walnut Creek, CA, 1977.
- 15 E. A. Dietz, Jr. and K. F. Singley, *Anal. Chem.*, 51 (1979) 1809.
- 16 S. L. Friant and I. H. Suffet, *Anal. Chem.*, 51 (1979) 2167.
- 17 J. Drozd and J. Novák, *J. Chromatogr.*, 165 (1979) 141.
- 18 J. P. Mieure, *J. Am. Water Works Assoc.*, 69 (1977) 60.
- 19 J. J. Richard and G. A. Junk, *J. Am. Water Works Assoc.*, 69 (1977) 62.
- 20 H. Norin and L. Ronberg, *Water Res.*, 14 (1980) 1397.
- 21 E. D. Pellizzari, *J. Chromatogr.*, 98 (1974) 323.
- 22 D. A. Miller and E. P. Grimsrud, *Anal. Chem.*, 51 (1979) 851.
- 23 R. C. Weast, *CRC Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, OH, 51st ed., 1970.
- 24 R. H. Perry and C. H. Chilton, *Chemical Engineers Handbook*, McGraw-Hill, New York, 5th ed., 1953.
- 25 R. H. Ewell, J. M. Harrison and L. Berg, *Ind. Eng. Chem.*, 36 (1944) 871.
- 26 G. C. Pimentel and A. McClellan, *The Hydrogen bond*, Freeman, San Francisco, CA, 1960.
- 27 R. C. Nelson, R. W. Hemwall and G. D. Edwards, *J. Paint Technol.*, 42 (1970) 636.