Journal of Chromatography, 186 (1979) 785–794

CHROM. 12,198

DIRECT AQUEOUS INJECTION GAS CHROMATOGRAPHY FOR THE ANALYSIS OF TRACE ORGANICS IN WATER

P. G. SIMMONDS

International Science Consultants, The Pines, The Chase, Hurn Road, Ringwood, Hants. (Great Britain)

and

EDWARD KERNS

U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (U.S.A.)

SUMMARY

A novel and simple method of direct aqueous injection gas chromatography is described, whereby water is selectively removed by diffusion across a permaselective membrane prior to the sample entering the chromatographic column. The technique is demonstrated using electron-capture gas chromatography to determine trace halocarbons in drinking water samples using direct injection of 1–20-μl aliquots.

INTRODUCTION

Current interest in environmental contamination has stimulated the development of various analytical methods for determining organic compounds in water samples. Generally, where the concentration of individual compounds is less than 1 μg/l (10^{-3} ppm) some preconcentration or enrichment of the sample is required. Concentration procedures include, head space analysis[1–3], liquid–solid adsorption[4,5], solvent extraction[6–8] and gas-phase stripping followed by adsorption[9–17]. Many of these methods while achieving the desired sensitivity are often laborious, difficult to calibrate, and not easily automated.

The direct analysis of water samples by gas chromatography (GC)[18–23] is attractive because it avoids many of these difficulties, but has not attained widespread use because of limited sensitivity. However, high sensitivity is possible for certain halocarbons when electron-capture detectors (ECD) are used, either with head space analysis[24], or by a direct aqueous injection (DAI) method. Nicholson and coworkers[25,26] were able to demonstrate sensitivities in the 0.1–500 μg/l range for the principal halocarbons found in drinking water by direct injection of 9-μl water samples onto a Chromosorb 101 column. Hammerstrand[27] achieved detection limits of 0.9 μg/l for chloroform in water using a similar method. An alternative DAI method using GC–mass spectrometry (MS) was proposed by Harris *et al.*[28], although for injection volumes larger than 1 μl it was necessary to remove the mass spectrometer electron multiplier and source potentials during elution of the water peak.

Detection limits of about 1 mg/l were reported. The determination of organohalides in water at concentrations below 1 μg/l has been described by Fujii[29] using a gas chromatograph–mass spectrometer equipped with multiple-ion detection. Volumes of 100 μl were injected onto a glycerol coated column so that the water eluted long after the halocarbons of interest. A venting valve was necessary to prevent water from entering the mass spectrometer.

The limitation of these DAI methods is that they are restricted to special chromatographic columns, with either low (porous polymer) or high (glycerol) retention volumes for water. Furthermore there is some danger that concentrations of organic compounds below 1 ppm may be adsorbed by certain porous polymer columns[30].

In this study, we describe a novel and simple method of direct aqueous injection whereby water is selectively removed by diffusion across a permaselective membrane of DuPont Nafion® tubing. Nafion tubing has been used successfully for continuous drying of sample process streams for a number of years[31]. Since water is removed before the sample enters the chromatographic column, any appropriate column can be used. Furthermore there is no longer any possibility of altering column performance through interaction or removal of the liquid phase by large volumes of injected water. The practical advantages of this method are demonstrated in the direct electron-capture GC analysis of drinking water samples.

EXPERIMENTAL

Nafion, is a perfluorosulfonic acid polymeric material with strong adsorption properties for water (E.I. DuPont de Nemours, Plastics Division, Wilmington, Del., U.S.A.). In these experiments the polymer was used in the form of tubing either type 811 (I.D. 0.635 mm, wall thickness 0.127 mm) or type 815 (I.D. 1.14 mm, wall thickness 0.127 mm). Fig. 1 illustrates the construction method and experimental arrangement for employing Nafion tubing in direct aqueous injection GC. The essential feature of this technique is that water is selectively removed from aqueous samples injected into a length of Nafion tubing positioned ahead of the chromato-

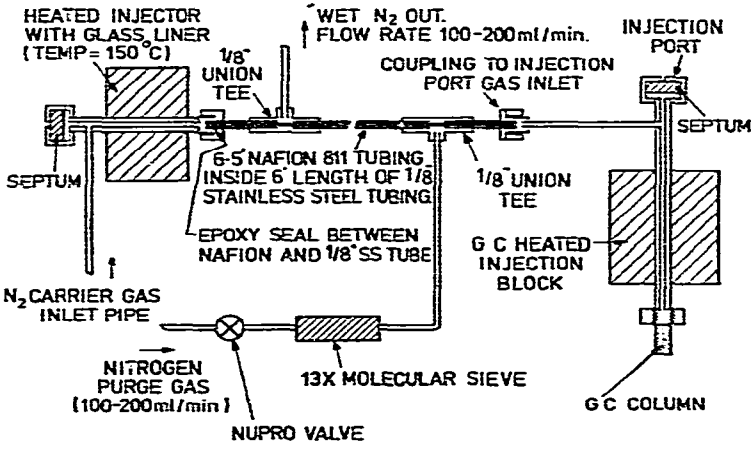


Fig. 1. Experimental arrangement for DAI GC using Nafion tubing.

graphic column. In Fig. 1, the water sample (1–20 μl) is first vapourized in a separate heated injection port (150–200°) and then passes into the Nafion tubing which is enclosed within a stainless-steel tube. As the water vapour is adsorbed and permeates through the walls of the Nafion tubing it is removed by a counter-current flow of dry nitrogen gas sweeping the outer surface of the tubing. Any trace organics continue onto the head of the column and are chromatographed in the usual way. Since the Nafion tubing terminates at the ordinary injection port of the gas chromatograph, other samples may still be injected onto the column in the conventional manner.

Two separate gas chromatographs were used in this investigation. A Pye 104 (Pye Instruments, Cambridge, Great Britain) equipped with a ^{63}Ni ECD and operated at a temperature of 250° was used for most of the preliminary experiments. Constant pulse conditions were employed with amplitude 50 V, pulse width 1 μsec, and pulse period 500 μsec. The column was made from 5 ft. × 1/4 in. O.D. aluminium tubing packed with 100–120 mesh Carbowax 400/Porasil C, Low K (Waters Assoc., Milford, Mass., U.S.A.) and maintained isothermally at 60°. The second chromatograph used was a Varian 2100 fitted with a ^{3}H–Sc ECD operated at 200°. The glass column was 6 ft. × 2 mm I.D. and packed with 3% Carbowax 20 M coated on Carbopack B, 60–80 mesh (Supelco, Bellefonte, Pa., U.S.A.) and maintained isothermally at 75°. The carrier gas used in both instruments was oxygen-free nitrogen at a flow-rate of 30 ml/min. The same nitrogen was also used as a sweep gas to flush the outer surface of the Nafion tubing. Typical flow-rates were in the range 100–200 ml/min, and the nitrogen was always dried by passage over freshly activated 13 X molecular sieve.

Calibration standards were prepared by a two stage dilution technique. Standard solutions of chloroform, bromoform, bromodichloromethane, chlorodibromomethane, trichloroethylene, methyl chloroform and carbon tetrachloride were prepared by carefully adding 1–5 μl of the pure compounds to halocarbon-free methanol in 50- or 100-ml precision volumetric flasks. Purified water was placed into 40-ml septum sealed glass vials so as to leave no head space, and then spiked with appropriate volumes (nominally 1–10 μl) of the standard solution to give aqueous halocarbon standards in the range 0.1–100 ng/ml. The septa used to seal the vials were PTFE-faced to minimize contamination. The aqueous standards were always shaken thoroughly for about 15 min to ensure uniform mixing and prepared as required from the methanol stock solutions, since extended storage of the aqueous standards was found to yield poor precision.

Water samples for analysis were collected in 5-ml glass reactor vials (Pierce, Rockford, Ill., U.S.A.) also sealed with PTFE-faced septa. Samples were analysed by injecting from 5–20-μl aliquots directly into the apparatus within 24 h of collection.

Head space analysis

A comparison of the DAI method with a simple direct head space technique was investigated using the procedure illustrated in Fig. 2. A 30-ml precision glass syringe was flushed several times and then filled with the water sample to the 10-ml mark (A). A 10-ml volume of purified nitrogen was then introduced into the syringe through a three-way miniature PTFE valve (B) (Hamilton, Reno, Nev., U.S.A.). The equal volumes of water and gas were then shaken vigorously for 5 min to establish equilibrium between phases according to the method of McAuliffe[32]. The nitrogen was then transferred to a 10-ml glass syringe fitted with a two-way

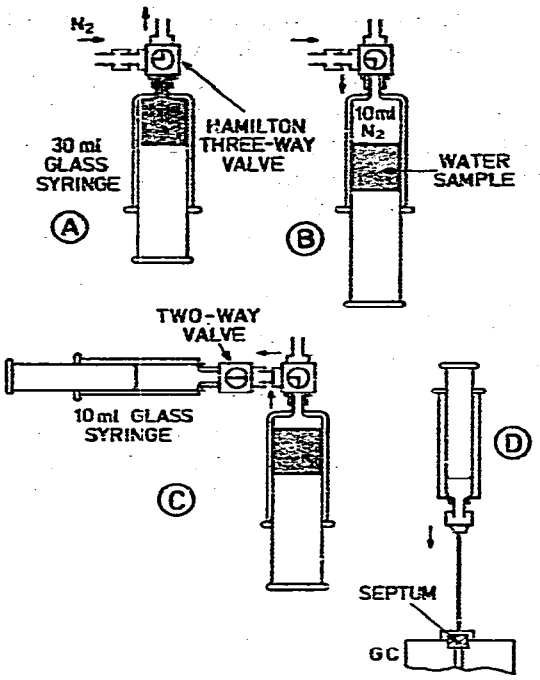


Fig. 2. Direct head space technique using nitrogen equilibration gas.

PTFE valve (C). From 1–5 ml of this sample was then injected directly into the chromatograph (D). Or, alternatively, the 10-ml gas sample could be used to fill the sample loop of a gas sampling valve.

The head space method is a very useful and complementary technique to DAI with at least an order of magnitude greater sensitivity towards the more volatile halocarbons. This is because in addition to their shorter retention times, they have a more favourable distribution coefficient between the gas and water phases. Since the head space sample is saturated with water vapour we have found it useful to also inject these samples through the Nafion tubing thereby preventing a peak for water on the chromatogram. The principal disadvantage of both the head space and gas sparging methods is that greater manipulation of the sample is required and hence these methods are less easily automated.

RESULTS AND DISCUSSION

Typical chromatograms obtained from the direct aqueous analyses of 10-μl samples from two different tap water supplies are illustrated in Fig. 3. The two samples have quite different amounts of individual halocarbons. For example, the sample represented by Fig. 3A contains a large concentration of chloroform but relatively little dibromochloromethane and no bromoform. Whereas Fig. 3B is low in chloroform but has moderate amounts of dibromochloromethane and bromoform. The analyses of additional tap water samples collected from four Southern counties in the British Isles are listed in Table I. Clearly there is considerable variation in the concen-

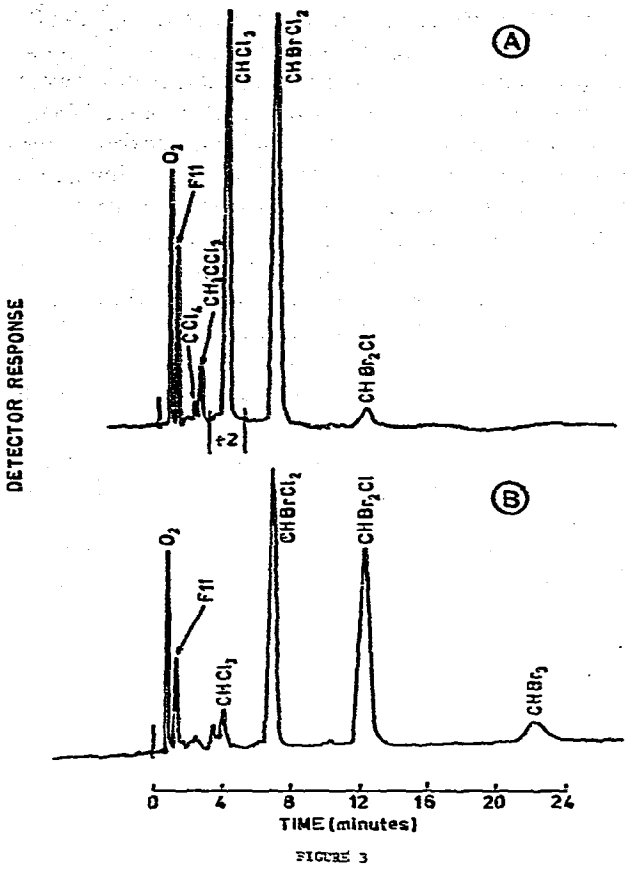


FIGURE 3

Fig. 3. Analysis of 10-μl aliquots of two different drinking water samples: (A) collected Launceston, Cornwall; (B) collected Ringwood, Hampshire (F11 = trichlorofluoromethane).

TABLE I

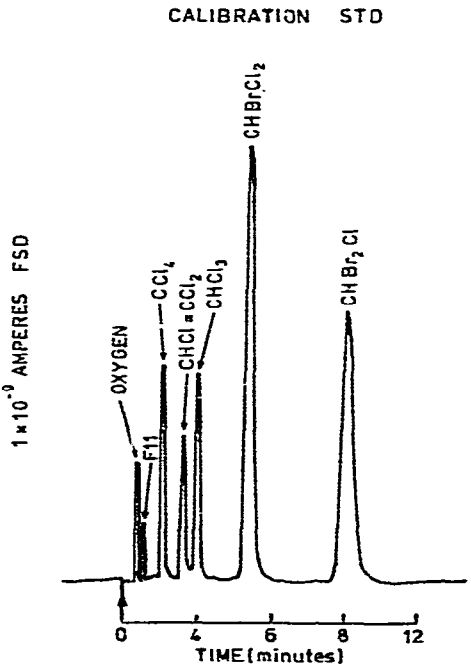
HALOCARBON CONCENTRATIONS IN DRINKING WATER SAMPLES FROM FOUR SOUTHERN COUNTIES IN THE BRITISH ISLES (JANUARY 1979)

Halocarbon	*Concentration (µg/l)*			
	Salisbury, Wiltshire	*Wareham, Dorset*	*Ringwood, Hampshire*	*Launceston, Cornwall*
Carbon tetrachloride	0.15	0.1	0.1	0.53
1,1,1-Trichloroethane	0.4	—	0.32	3.6
Trichloroethylene	0.1	—	0.25	0.1
Chloroform	0.4	0.3	1.3	34.5
Bromodichloromethane	1.3	0.56	3.2	4.8
Dibromochloromethane	2.7	2.4	4.3	0.4
Bromoform	0.4	0.84	0.3	—

trations of the different halocarbons found in these samples. There is from 10–100 times more chloroform in the Cornwall sample compared with drinking water from the other three counties. Similar large differences in halocarbon concentrations were observed by Fugii[29] in water samples collected from different areas of Tokyo, Japan.

Since it is firmly established that many of the principal halocarbons are actually formed during the chlorination process[2,9], the variations in halocarbon concentrations from different regions nust reflect quite large differences in the levels of precursor compounds in the prechlorination water. It has recently been proposed that halomethanes found in natural waters are formed biologically from peroxidase catalysed halogenation reactions[33]. Therefore it seems reasonable to expect that where chlorobromomethanes are found in chlorinated waters they could be formed from the direct chlorination of indigenous mono-and dibromomethanes. Certainly, methyl halides including methyl bromide are common constituents of marine environments[3,34].

The analysis of a calibration standard and calibration curves for the principal halocarbons found in drinking water are shown in Figs. 4 and 5, respectively. The change in response with concentration (Fig. 5) is essentially non-linear for most compounds at concentrations exceeding about 10 μg/l. However, it should be remembered that the ECD has a relatively limited dynamic range when operated in the constant pulse mode as was the case in these experiments.



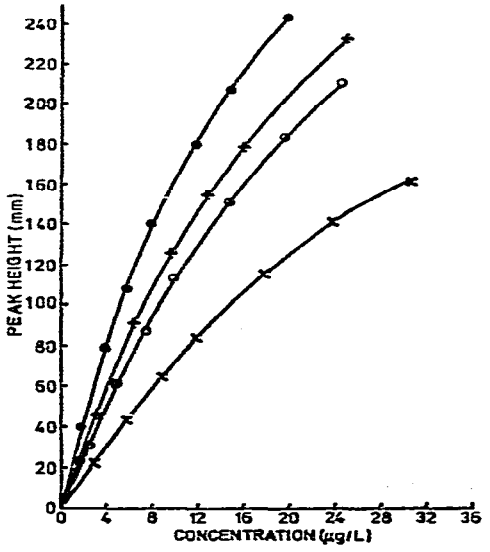


Fig. 4. Analysis of calibration standard by DAI. Sample size = 10 μl.

Fig. 5. Calibration curves for principal halocarbons found in drinking water. × = Chloroform, ○ = dibromochloromethane, ● = dichlorobromomethane, + = trichloroethylene.

It might be expected that the concentrations of different halocarbons within the water distribution system could be subject to diurnal variations. This effect is demonstrated in Fig. 6, where the concentrations of the principal halocarbons in tap water from the Hampshire area were monitored every 2 h throughout a 24-h period. This experiment also demonstrates the practical advantage of the DAI method in that the 2-h analyses were automated with an electronic timer and a solenoid driven sampling valve fitted with a 10-μl sample loop. Chloroform and bromodichloromethane show only modest changes throughout this limited period while dibromochloromethane is surprisingly stable. These relatively small fluctuations may reflect varying concentrations of precursor compounds or minor changes in the chlorination efficiency, but they could not account for the large regional differences which have been observed.

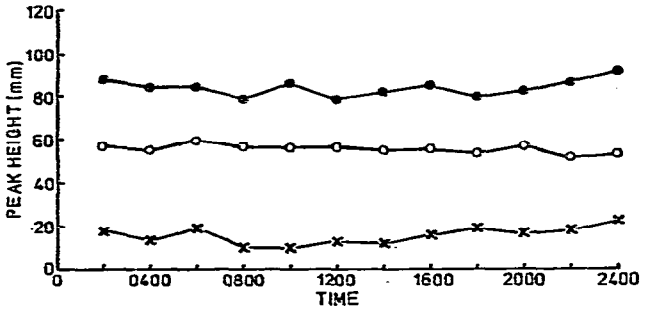


Fig. 6. Change of concentration of principal halocarbons found in Hampshire drinking water throughout a 24-h period. ○ = Dibromochloromethane, × = chloroform, ● = dichlorobromomethane.

Nicholson *et al.*[26] have reported that concentrations of halocarbons determined by DAI are generally higher than those found by gas sparging methods. We have compared our DAI method with a simple direct head space technique (Table II), and find that DAI does give higher values at least for the chlorobromomethanes. However, the concentration of chloroform determined by the two methods is similar, whereas the values of trichloroethylene, carbon tetrachloride and 1,1,1-trichloroethane are all

TABLE II

COMPARISON OF ANALYSIS OF HALOCARBONS IN HAMPSHIRE WATER BY HEAD SPACE AND DAI METHODS

Halocarbon	*Concentration (μg/l)*	
	Head space	*DAI*
Carbon tetrachloride	0.57	0.1
1,1,1-Trichloroethane	0.6	0.32
Trichloroethylene	0.28	0.25
Chloroform	1.38	1.3 –
Bromodichloromethane	1.22	3.2
Dibromochloromethane	2.18	4.3
Bromoform	0.2	0.3

higher by the head space method. Thus for some compounds our results do differ from those observed by Nicholson *et al.* Some of these differences can most probably be attributed to the relatively low purging efficiency obtained with the single equilibration head space technique compared to complete gas sparging. It has also been recognised that certain compounds which are precursors of the halocarbons are thermally labile and can therefore be expected to react in the hot injection block. Furthermore, each precursor is likely to have a different optimum temperature for conversion to the corresponding halocarbon. The fact that we operate our injector at a lower temperature ($\approx$ 150°) than the 250° used by Nicholson, may moderate the more temperature-sensitive reactions. To test this possibility water samples were injected over a range of injector temperatures as shown in Table III. The results are interesting in that there is very little change in the concentrations of the principal

TABLE III
EFFECT OF INJECTOR TEMPERATURE ON DAI ANALYSIS

Injection block temperature (°C)	*Halocarbon concentration (μg/l)*			
	Chloroform	*Bromodichloromethane*	*Dibromochloromethane*	*Bromoform*
150	1.3	3.2	4.3	0.3
175	1.3	3.2	4.3	0.3
200	1.3	3.23	4.35	0.3
225	1.31	3.58	4.78	0.35
250	1.45	3.72	4.94	0.35

halocarbons until the injector temperature exceeds 200° and then there is a small increase in all components. This would suggest that 150° (the lowest practical injector temperature) is sufficient to convert most of the precursor compounds to their corresponding halocarbons. Nevertheless these observations do stress the need to carefully monitor the injection temperature in DAI analysis and confirm the conclusion drawn by Nicholson that the DAI technique represents the total potential haloforms present in the water sample. It is also recommended that frequent calibrations be employed if high precision is required. The precision achieved with DAI in these experiments for nine consecutive 10-μl injections of a standard solution (each halocarbon = 2 μg/l) was quite good and within the experimental error of microliter syringes. Relative standard deviations were chloroform (1.7%), trichloroethylene (4.2%), carbon tetrachloride (2.4%), 1,1,1-trichloroethane (3.8%), bromodichloromethane (1.2%), dibromochloromethane (2.0%) and bromoform (2.5%). Detection limits for these compounds and several halocarbons which are of interest as primary pollutants are summarised in Table IV.

Because of the specificity of the ECD, other compounds and in particular weak electron absorbers, such as dichloromethane and 1,3-dichloropropane, were not detected in the drinking water samples analysed. Detection limits for these compounds were therefore determined independantly using calibration mixtures. Since large quantities of water do not reach the detector in our system, other types of detector could be used where the effect of water would ordinarily be detrimental. An attractive possibility is the use of DAI–GC–MS; especially with mass fragmentography to achieve specific and sensitive detection of compounds of interest.

TABLE IV

DETECTION LIMITS FOR VARIOUS HALOCARBONS BY DAI ELECTRON-CAPTURE GC

Halocarbon	*Detection limits (μg/l)*
Chloroform	0.3
Carbon tetrachloride	0.05
Trichloroethylene	0.1
1,1,1-Trichloroethane	0.1
Bromodichloromethane	0.2
Dibromochloromethane	0.5
Bromoform	0.2
Chlorobenzene	1500.0
1,2-Dichlorobenzene	35.0
1,3-Dichlorobenzene	35.0
Dichloromethane	100.0
1,3-Dichloropropane	200.0

* Sample size, 10-μl aqueous injection.

In this and other work[35], halocarbons were not affected by passage through the Nafion tubing as is also the case for many other organic compounds and most inorganic gases. Baker[36] has investigated the permeability of Nafion tubing to a broad range of compounds. Hydrocarbons, most aldehydes, esters and ethers are not removed, although highly polar compounds, such as alcohols, amines and certain ketones, are partially or wholly removed along with the water. Therefore tests should be performed for any proposed investigation to test the suitability of the Nafion water removal system for any particular group of compounds. In addition to its obvious application in determining halocarbons in drinking water supplies the DAI technique should prove generally useful in monitoring primary pollutants in a variety of water systems particularly where environmental contamination might be suspected as a problem. The ease with which the technique can be automated should make it attractive for large scale surveys and for those investigations where continuous monitoring is of interest.

ACKNOWLEDGEMENT

We wish to thank Dr. Paul Fahrenthold for his advice and continuous encouragement during the course of this work.

REFERENCES

1 J. J. Rook, *Water Treat. Exam.*, 21 (1972) 259.
2 J. J. Rook, *Water Treat. Exam.*, 23 (1974) 234.
3 J. E. Lovelock, *Nature (London)*, 256 (1975) 193.
4 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Agguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
5 R. D. Kloepfer and B. J. Fairless, *Environ. Sci. Technol.*, 6 (1972) 1036.
6 F. Dietz and J. Traud, *Vom Wasser.*, 41 (1973) 137.
7 K. Grob, K. Grob Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
8 M. C. Goldberg, L. Delong and M. Sinclair, *Anal. Chem.*, 45 (1973) 89.
9 T. A. Bellar and J. J. Lichtenberg, *J. Amer. Water. Works. Assoc.*, 66 (1974) 739.

10 J. Novák, J. Žlutický, V. Kubelka and J. Mostecký, *J. Chromatogr.*, 76 (1973) 45.
11 K. Kaiser, *J. Chromatogr. Sci.*, 9 (1971) 227.
12 A. Zlatkis, A. Lichtenstein and A. Tishbee, *Chromatographia*, 6 (1973) 67.
13 B. Dowty and J. L. Laseter, *Anal. Lett.*, 8 (1975) 25.
14 A. J. Murray and J. P. Riley, *Anal. Chim. Acta*, 65 (1973) 261.
15 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
16 K. Grob and G. Grob, *J. Chromatogr.*, 90 (1974) 303.
17 J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.*, 11 (1973) 559.
18 R. C. Dressman, *J. Chromatogr. Sci.*, 8 (1970) 265.
19 F. I. Onuska, *Water. Res.*, 7 (1973) 835.
20 M. E. Fox, *Environ. Sci. Technol.*, 7 (1973) 838.
21 *Annual book of ASTM standards*, ASTM, Philadelphia, Pa., 1972, Part 23, pp. 706, 819.
22 A. DiCorcia and R. Samperi, *Anal. Chem.*, 46 (1974) 140.
23 J. W. Sugar and R. A. Conway, *J. Water Pollut. Contr. Fed*, 40 (1968) 1622.
24 G. J. Piet, P. Sligerland, F. E. de Grunt, M. P. M. van de Heuvel and B. C. J. Zoeteman, *Anal. Lett.*, 5 (1978) 437.
25 A. A. Nicholson and O. Meresz, *Bull. Environ. Contam. Toxicol.*, 14 (1975) 453.
26 A. A. Nicholson, O. Meresz and B. Lemyk, *Anal. Chem.*, 49 (1977) 814.
27 K. Hammarstrand, *Varian Instr. Appl.*, 10 (1976) 2–4.
28 L. E. Harris, W. L. Budde and J. W. Eichelberger, *Anal. Chem.*, 46 (1974) 1912.
29 T. Fujii, *J. Chromatogr.*, 139 (1977) 297.
30 W. R. Supina, *The Packed Column in Gas Chromatography*, Supelco, Bellefonte, Pa., 1974, p. 49.
31 J. Kertzman, ISA AID 73425 (1973) 121.
32 C. McAuliffe, *Chem. Tech.*, Jan. (1971) 46.
33 R. Theiler, J. C. Cook, L. P. Hager and J. F. Siuda, *Science*, 202 (1978) 1094.
34 O. C. Zafiriou, *J. Mar. Res.*, 33 (1975) 75.
35 B. Foulger and P. G. Simmonds, *Anal. Chem.*, (1979) in press.
36 B. B. Baker, Jr., *Amer. Ind. Hyg. Assoc. J.*, Nov. (1974) 735.