Direct Mass-spectrometric Analysis of Volatile Chlorinated Hydrocarbons in Water

J. Rivera, M. R. Cuberes and J. Albaigés
Instituto de Química Orgánica de Barcelona (C.S.I.C.) Jorge Girona Salgado, s/n — Barcelona-17 Spain

INTRODUCTION

Major emphasis has been placed in recent years on the detection and estimation, from the health standpoint, of halogenated hydrocarbons in water. Volatile halogenated hydrocarbons are ubiquitous in the environment, especially in water, because of their great industrial production (solvents, polymer monomers, etc.) and their resistance to biodegradation. Water chlorination processes provide an additional input of organic chlorinated compounds to drinking water, where chlorinated solvents have been found to be present in relatively important amounts (GROB and GROB,1974; NOVAK et al.,1973; DOWTY et al.,1975).

Many studies have been conducted on the toxicity of halogenated hydrocarbons, accumulation in living organisms being their principal fate in nature. Vinyl chloride (ANON.,1974) and chloromethyl ether (VAN DURREN,1969) are well known as carcinogenic compounds while carbon tetrachloride, chloroform (I.A.R.C. Report,1972) vinylidene chloride (ANON.,1975) and tetrachloroethylene (ANON.(a), 1975) are suspected carcinogens.

However, little is known about the health implications of the ingestion by man of very low amounts of such compounds for a long period of time, and about the existence of possible synergistic effects in the presence of other compounds.

In any case, specific and quantitative analytical methods are needed for an effective control of such pollutants. Furthermore, highly sensitive methods are necessary for kinetic environmental studies.

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Gas chromatography is, by far, the most widely use method for these purposes. However, its universal applicability is limited by several disadvantages, such as equivocal identification of separated compounds and, in the particular case of organic chlorinated compounds, a rather low sensitivity when using an FI detector (SALOMON and RATCLIFFE,1973). The use of selective detectors (WILLIAMS and UMSTEAD,1968; ERUST and LIEROP, 1975) allows only slight improvements on these aspects.

Another problem is the introduction of the sample into the chromatograph. Direct injection (HARRIS et al., 1974) is not possible, due to the high sensitivity required. Sample concentration by solvent extraction, both directly and by means of a previous adsorbent (GROB, 1973) shows, among others, the disadvantages inherent to solvent interference and partial recovery. Direct thermal desorption from the adsorbent in the injector block of the chromatograph (PURCELL,1975) seems to be the best available method. However, gas chromatography still shows sensitivity and selectivity limitations.

Mass spectrometry, owing to its high sensitivity and analytical diagnostic capability, has been suggested for the direct characterization of the higher organochlorinated contaminants (pesticides) from crude extracts (HUTZINGER et al.,1970; HUTZINGER and JAMIESON, 1971). No extension has been made of this method to the more volatile compounds, although it has been used as a specific chromatographic detector for these pollutants by some authors (GROB and GROB,1974; NOVAK et al., 1973; EVANS et al.,1975; ROSEN et al.,1975).

In the present paper we describe a new, highly sensitive and selective method for the analysis of aliphatic chlorinated hydrocarbons in water, based on their adsorption by stripping on a charcoal filter and quantitation by a mass-spectrometric integrated ion current procedure, with desorption from the charcoal inside a temperature-programmed inlet probe. The method is exemplified in the case of the determination of vinyl chloride in PVC bottled mineral water.

EXPERIMENTAL

Concentration of organic volatiles

The apparatus used for the concentration step, an all-glass system, is shown in Fig.1.

Glassware was cleaned before use with sulfuric acid-dichromate mixture, then throroughly rinsed with distilled water and methanol,and dried.

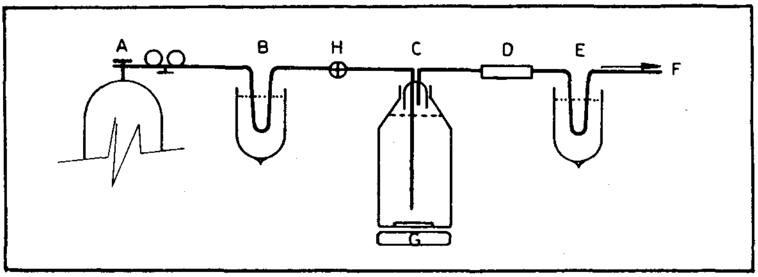

Fig.1.- Stripping system

Helium from a gas-pressure cylinder (A) was purified on a liquid nitrogen cooled trap fitted with activated charcoal (B) and was then bubbled through the water contained in a 1 l. Pyrex glass jar (C). Bubbling was maintained for one hour at a gas flow rate of 150 ml/min., monitored by means of a flow meter at the end of the system (F). Stirring of the water was accomplished by a magnetic stirrer (G).

The gas from the stripper, after drying over 300 mg of magnesium perchlorate (D), was conducted into a dry ice cooled adsorption tube (2 mm ID)(E), containing 5-10 mg of commercial activated charcoal (80-100 mesh), kept in position by a small plug of stainless-steel grid.

The system was provided with a three-way valve (H) to run several samples simultaneously, or standard solutions for quantitative analyses. Similar gas flows were ensured through all traps by restricting the diameter of the tubing at the end of each system. When the bubbling was finished the adsorption tubes were disassembled, sealed with glass stoppers and stored in a refrigerator until the analysis was to be performed.

Mass-spectrometric analysis

The charcoal filter was quantitatively transferred to the previously cooled direct inlet probe of an MS-902S AEI high resolution mass spectrometer, that could be temperature programmed from -150 to +350ºC.

Vinyl chloride desorption took place in the range of -30 to +100ºC. In this temperature interval, and with the use of the peak matching technique (resolution 1000), the signals at m/e 62 and 64, corresponding to the molecular ions $C_2H_3{}^{35}Cl$ and $C_2H_3{}^{37}Cl$, were recorded.

Fig. 2 shows the recording obtained from a problem sample of water (0.2 ppb of vinyl chloride), together with the signal displayed in a memory oscilloscope during desorption. Quantitative measurements of VC in PVC-bottled water were made by interpolating measured curve areas on a linear plot obtained by running standard water samples in the 0.05-10.0 ppb range. Standard deviation was 9%. A series of problem samples is shown in Fig.3. Quantitation became difficult below 0.05 ppt since the method could not be easily standarized at such a low level.

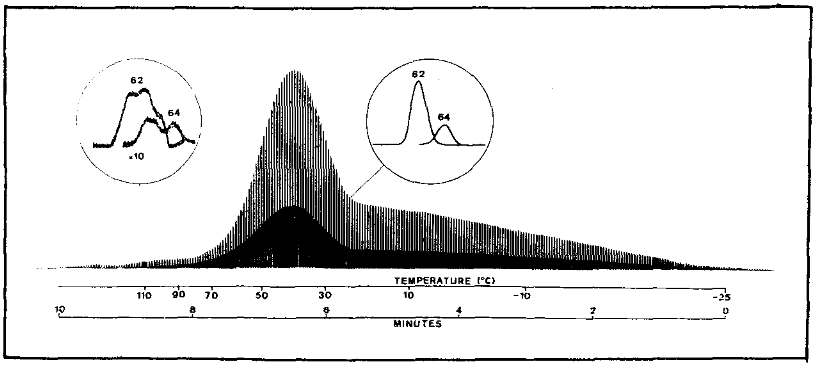

Fig.2.- Desorption profile of the VC in the MS inlet probe

Discussion

The detection of organochlorinated compounds by MS is made easy by the characteristic patterns due to the isotopes ^{35}Cl and ^{37}Cl, the problem in our case being the concentration of these compounds and their suitable introduction into the mass spectrometer.

The method used for the concentration has all the advantages of other methods, previously described, based on stripping and adsorption on activated charcoal (GROB and GROB,1974; NOVAK et al.,1973). Stripping is by far the more efficient method for volatile compounds.

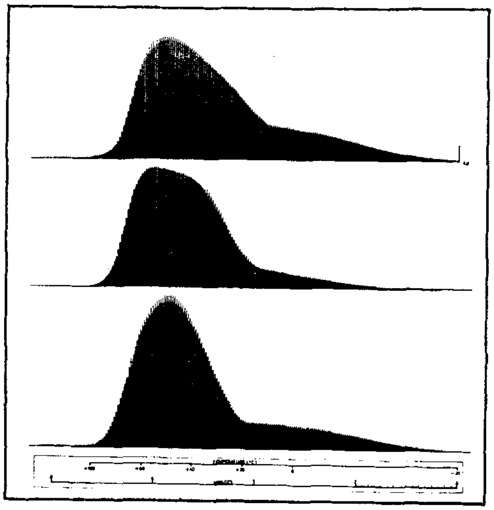

Fig.3.- A series of problem samples

On the other hand, the advantages of charcoal over other adsorbents, such as its higher adsorption capacity even in wet effluents, have been extensively described (GROB,1973; HILL et al., 1976) in the specific case of VC.

Water condensation in the cooled adsorption trap was prevented by a magnesium perchlorate drying filter. Besides water, this dessicating agent will retain only some oxygenated compounds (ketones, esters...)(NARAIN et al.,1972) and accordingly it would not interfere with the present analysis.

The dependence between trapping efficiency and trap temperature arises as a consequence of the volatility of the compounds, and in the case of vinyl chloride cooling of the traps is necessary. Trapping efficiency was monitored by using two consecutive traps; we could not find the studied compounds when the second trap was analyzed, in agreement with the capacity described by CUDDEBACK et al.(1975).

Direct thermal desorption of the adsorbed compounds in the ionisation chamber of a mass spectrometer has been proposed by several authors. However, the adsorbents used [Porapak Q (COLLIER,1972), Amberlite XAD-4 (WITIAK et al.,1973), Chromosorb 101 (EVANS et al., 1975)(ROSEN et al.,1975)] , besides their lower adsorption capacity, may show background problems at the low working concentration level. Consequently their use has been discarded.

The selectivity of the method can be observed in Fig.2. Complex signal, due to desorption of hydrocarbons (high resolution measurements showed the fragments to be C_5H_4 and C_5H_2) from the water or from the adsorbent, arose only at high temperatures, and did not interfere the analyses.

In the experimental part, working conditions for the determination of vinyl chloride in water are described. The method, however, has been used for other volatile chlorinated hydrocarbons. Thus, vinylidene chloride was detected in a mineral water bottled in Saranex [a film of Saran (a vinyl chloride-vinylidene chloride copolymer) recovered by two films of polythene] . In each case the desorption thermal profile, as well as the intensity ratio of the two selected molecular peaks, will be different. A more complete view of these chlorinated compounds in water can be obtained by means of dynamic wide and repeated sweep of spectra during desorption and computer accumulation, but at cost of a considerable loss in sensitivity.

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