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Determination of Hexachlorocyclopentadiene at the Nanogram per Liter Level in Drinking Water

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Hexachlorocyclopentadiene (HCCP), a precursor for numerous widely used pesticides, is listed as a priority pollutant in the EPA consent decree primarily as the result of one incident (MORSE et al. 1979) where large quantities of HCCP, disposed of illegally via the wastewater system, caused noxious effects on the workers in the water treatment plant. However, HCCP has rarely been reported as a contaminant in drinking water (THRUSTON 1978). In the course of our investigations on the use of XAD-2 macroreticular resin for the extraction of trace neutral organics from drinking water, we have detected HCCP in numerous samples although this compound was not found in the raw waters tested at the same time. In spite of our most careful efforts when using XAD-2 resin to extract HCCP we were unable to obtain precise quantitative estimations of the levels of HCCP in drinking water. We noted however that the concentration of HCCP in our extracts appeared to decrease with time. A solvent extraction method for the determination of HCCP in drinking water has, therefore, been developed.

MATERIALS AND METHODS

Solvents and Chemicals. All solvents were of "distilled in glass" quality. HCCP monomer was obtained from Aldrich Company Inc. and was used as received.

XAD-2 Sampling Cartridges. Sample preparation has been reported in detail by LEBEL et al. (1979) and is briefly summarized here. Sampling cartridges, containing ca. 15 g Amberlite XAD-2 (Rohm and Haas, Philadelphia, PA) macroreticular resin that had been previously cleaned by the method of MCNEIL et al. (1977) were rinsed with 250 mL acetone and washed with at least 1 L of purified water. The cartridges were attached to a potable water tap in our laboratory and the flow of water was controlled at ca. 70 mL/min. When the required volume (ca. 200 L) of water had been passed through the cartridge, the cartridge was disconnected from the tap and as much water as possible was removed from the cartridge by careful draining followed by the application of vacuum from a water aspirator. The XAD-2 resin was eluted with 300 mL of 15:85 (v/v) acetone: hexane solution at a flow rate of ca. 5 mL/min. The organic layer was dried by

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passage through a drying column containing sodium sulfate over a glass wool plug. Both the sodium sulfate and the glass wool plug were cleaned by successive washings with dichloromethane, acetone and hexane prior to use. The dried solution was concentrated to a volume of ca. 3 mL using a rotary evaporator, then quantitatively transferred with acetone to a graduated vial and was further concentrated, using a gentle stream of dry nitrogen gas, to a final volume of 1 mL.

Organic Solvent Extraction. A 2 L sample of water was extracted with 3 x 150 mL organic solvent (dichloromethane or hexane) using a separatory funnel. The organic layers were combined, dried and concentrated as described above to a final volume of 0.3 mL for GC/MS analysis.

Florisil Column. A column containing 15 g Florisil was prepared. The organic extract was concentrated to 0.1 mL and transferred to the head of the column which was subsequently eluted with 15 mL hexane. The eluate was concentrated to 0.3 mL using a gentle stream of dry nitrogen prior to GC/MS analysis.

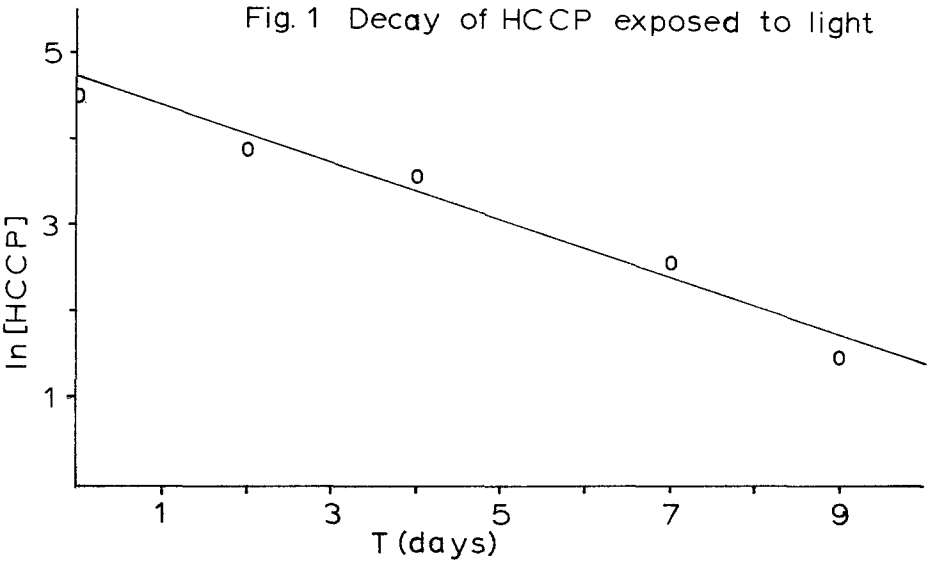
Sample Analysis. A 10-uL aliquot of the concentrated extract was injected into a Finnigan 4000 GC/MS coupled to a 6110 data sytem. A 1.8 m x 2 mm i.d. glass column, packed with 3% OV-17 on 80/100 mesh Chromosorb 750, was operated at an initial temperature of 100°C for 0.1 min and was programmed to a final temperature of 150°C at a rate of 3°/min and held at that temperature. The flow of helium carrier gas was set at 20 mL/min and the injection port temperature set at 200°C. The glass jet separator and the ion source temperatures were set at 260 and 250°C, respectively. Data acquisition was under the control of the Finnigan 6110 data system. The mass range, 35 to 400 amu, was scanned at a rate of 2.1 s/scan and the mass spectra stored on magnetic disk for subsequent analysis. Quantitative estimation of the HCCP levels in the field samples was achieved by comparison of the peak areas of selected characteristic ions (m/z 201, 203, 235, 237, 272, 274) obtained from reconstructed mass chromatograms against a HCCP solution of known concentration.

RESULTS AND DISCUSSION

Decomposition of HCCP. Although HCCP has been reported as stable under environmental conditions (LU et al. 1975) the decrease with time of HCCP levels in our stored solutions and the scatter in our quantitative data indicated that light-induced decomposition of HCCP was occurring in both field and standard samples which were stored in clear glass containers. To verify this conclusion a HCCP solution of known concentration in hexane was divided; one half was stored in the dark and the other half was left exposed in a clear glass container on the laboratory bench for a period of nine days. The concentrations in the two samples were compared every two days by GC/MS analysis. A steady decrease in the concentration of HCCP in the exposed solution

relative to the "stored in the dark" solution was observed. When the natural logarithm of the HCCP concentration was plotted against time (fig. 1) a straight line (1) of negative slope was

$$\ln (HCCP) = -0.32\ T + 4.6 \qquad (1)$$



obtained indicating a unimolecular decay in HCCP for which a half-life of ca. 2.2 days was calculated. The decomposition of HCCP in hexane solution was even more rapid under conditions of more intense light radiation, e.g. upon exposure to outdoor light (cloudy conditions) the HCCP was 99% destroyed within 8 h, upon exposure to a u.v. lamp the HCCP was destroyed completely within 4 h. Similar results were obtained with aqueous HCCP solutions.

We conclude that HCCP is light sensitive in both organic and aqueous solutions and that the rate of decay is dependent on the intensity of the incident radiation. If accurate results are to be obtained for the determination of HCCP levels in water, the water samples, the extracts and the standard HCCP solutions must be protected from light sources at all times. We have found that adequate protection can be obtained by storing HCCP containing solutions in amber or in red (low actinic) coloured glassware. In all subsequent experiments sample manipulations were conducted under conditions of subdued light whenever exposure of the sample to light was inevitable (e.g. extraction, drying, concentration) and all samples were stored in either amber or red (low actinic) coloured glassware.

No extensive effort was made to determine the products of the decomposition but tetra- and penta-chlorocyclopentadienes were detected in the course of the GC/MS analyses for HCCP. The presence of these products indicated that a solvent interaction (hydrogen displacement) was operative. However, the quantities of tetra- and penta-chlorocyclopentadienes were not comparable to the original quantities of HCCP, hence these compounds were not likely the major products of the HCCP decomposition. One possible pathway for the loss of HCCP in solution is the dimerization of HCCP to form mirex, but when the samples were analysed for mirex none was detected; nor was photomirex, an important product of the decomposition of mirex under radiation in the environment, detected.

XAD-2 Resin. The efficiency of XAD-2 resin to extract HCCP from water was estimated by passing tap water through two cartridges containing XAD-2 resin connected in series such that the effluent from the first (A) was passed through the second (B). In these experiments fresh resin as well as used resin was utilized. One of the advantages of using macroreticular resins for the analysis of water for organic contaminants is the possibility of using the same resin a number of times providing that a suitable solvent cleanup to remove adsorbed materials is carried out following each use. The results in Table 1 show that fresh resin does not retain all of the HCCP at levels that are present in tap water but that ca. 9% of the HCCP is transmitted through the first cartridge.

Table 1. Extraction Efficiency of HCCP From Water By XAD-2 Resin

Times Resin Used Previously	Amount HCCP (ng/L) Retained Cart. A.	Cart. B	Ratio B/A
0	67.5	6.1	0.09
1	50.1	9.4	0.19
7	44.4	11.9	0.27

Resins that had been used previously were less efficient (Table 1), with the greater loss of efficiency occurring following only one use (from 9 to 19% transmission). This decrease in efficiency was not found with other neutral organics in our previous studies (LEBEL et al. 1979, BENOIT et al. 1979a,b). In a second experiment, the second cartridge of the pair was artificially loaded with a known quantity of HCCP to estimate the recovery efficiency of the XAD resin. The best recovery was only 58% of the loaded HCCP and occurred when fresh XAD-2 resin was used.

We conclude that the extraction of HCCP from water with XAD-2 macroreticular resin cannot be used to quantify accurately

the level of HCCP in drinking water but may be used to screen water samples qualitatively.

Solvent Extraction. BURGASSER et al. (1979) used organic solvents (15% benzene in hexane) to extract standard HCCP solutions at the 100 ng/L level but did not apply their method to field samples. The authors did not report any instability of HCCP to light. One advantage of using XAD-2 resin over solvent extraction is the ability to analyse large volumes of water (ca. 200 L) when determining trace contaminants. In the present case, the anticipated levels of HCCP in drinking water are sufficiently high that analysis of low water volumes (ca. 2 L) by solvent extraction is possible. However, the lower limit of detection is higher by a factor of 100 (0.5 ng/L for XAD-2 method vs. 50 ng/L for solvent extraction method) because of the smaller sample size that can be manipulated in the solvent extraction method.

The efficiency of recovery of artificially loaded HCCP from water was estimated as follows. A tap water sample was irradiated for ca. 4 h to destroy any HCCP that was present while preserving the remaining organics in the water matrix as confirmed by GC/MS analysis. The water was then loaded at the ca. 100 ng/L HCCP level and analysed by solvent extraction. With care (subdued laboratory lighting, minimal exposure to light) it was possible to recover from 79 to 88% of the loaded HCCP (Table 2). In one recovery experiment a Florisil column was used to re-

Table 2. Recovery of HCCP From Drinking Water by Organic Solvent Extraction

Solvent	Amount Loaded ng/L	Fraction Recovered
hexane	123	0.88
hexane	92	0.79
dichloromethane	99	0.84
dichloromethane[a]	118	0.82

[a] - Florisil cleanup.

move extraneous organic materials from the extract prior to GC/MS analysis. This extra step does not reduce the recovery efficiency and is not necessary for the detection of HCCP by GC/MS since the characteristic ion peaks for HCCP are located in an area of the chromatogram that does not contain interferences; however, a Florisil cleanup does reduce the quantity of extraneous material deposited on the head of the GC column.

Samples of Ottawa raw and drinking waters were collected directly at the water treatment plant and stored in amber bottles prior to analysis by solvent extraction. No HCCP was detectable

(<50 ng/L) in the raw waters analysed whereas HCCP levels ranging from 57 to 110 ng/L (Table 3) were observed in the treated

Table 3. Levels of (ng/L) HCCP in Ottawa Waters

Date	Raw Water	Treated Water
April 23, 79	n.d.	57
September 4, 79	n.d.	100
April 28, 80	-	86
April 29, 80	-	110

n.d. - not detectable, (<50 ng/L).

waters. In our earlier experiments with XAD-2 resin where the lower limit of detection was ca. 0.5 ng/L no HCCP was detected in the raw waters also. Although the XAD-2 method is inaccurate it certainly indicates that the level of HCCP in the raw water is much lower (≤0.5 ng/L) than the limit of detection of the organic solvent method (ca. 50 ng/L). These results suggest that HCCP is introduced during the treatment process. Current work is aimed at the identification of the source of HCCP in drinking water.

We would caution analysts to consider the possibility that certain environmental contaminants are light sensitive.

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REFERENCES

BENOIT, F.M., G.L. LEBEL, D.T. WILLIAMS: Intern. J. Environ. Anal. Chem. 6, 277 (1979a).
BENOIT, F.M., G.L. LEBEL, D.T. WILLIAMS: Bull. Environ. Contam. Toxicol. 23, 774 (1979b).
BURGASSER, A.J., and J.F. COLARUOTOLO: Anal. Chem. 51, 1588 (1979).
LEBEL, G.L., D.T. WILLIAMS, G. GRIFFITH, F.M. BENOIT: J. Assoc. Off. Anal. Chem. 62, 241 (1979).
LU, P.Y, R.L. METCALF, A.S. HIRWE, J.W. WILLIAMS: J. Agric. Food Chem. 23, 967 (1975).
MCNEIL, E.E., R. OTSON, W.F. MILES, R.J.M. RAJABALEE: J. Chromatogr. 132, 277 (1977).
MORSE, D.L., J.R. KOMINSKY, C.L. WISSEMAN, P.J. LANDRIGAN: J. Am. Med. Assoc. 241, 2177 (1979).
THRUSTON, A.D.: J. Chromatog. Sci. 16, 254 (1978).

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