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A Simple Spectrophotometric Technique for the Determination of Pentachlorophenol in Water

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Pentacnlorophenol (PCP) and its sodium salt are the second most widely used biocides in the United States (CIRRELLI 1978) with the annual world production exceeding 20,000 tons (RAPPE & NILSSON 1972). The inevitable contamination of aquatic and marine environments resulting from agricultural and industrial usage of PCP has prompted a number of investigations concerning the fate and effects of this chlorophenol in animals and the environment (RAO 1978).

Several techniques have been developed to quantify PCP in aqueous solutions. The most sensitive and selective methods utilize gas chromatography with electron capture detection and mass spectrometry for verification of the derivatives (RUDLING 1970; BUHLER et al. 1973). However, these sophisticated techniques are often either unavailable, prohibitively expensive, or too time-consuming for routine monitoring. Therefore a simple, relatively sensitive, reliable, spectrophotometric method for quantifying PCP in water was developed.

MATERIALS AND METHODS

This technique was developed for use with seawater samples but may also be used for fresh or brackish water samples. The samples can be stored at 4°C in the dark for several weeks or extracted immediately. The water samples were transferred to glass reagent bottles with ground glass stoppers and acidified with concentrated HCl (1 mL HCl/100 mL sample) to liberate pentachlorophenol from salts which may be present. Ten mL of chloroform were added to the acidified sample (100-1000 mL) and the mixture was shaken vigorously for at least 60 sec. The sample was then transferred to a separatory funnel, and the organic fraction was collected once the phases had completely separated. Five mL of the chloroform were then transferred to a glass test tube with a ground stopper. Two mL of 200 mM NaOH were then added to the chloroform extract and the mixture was vortexed for 30 sec. (If an emulsion forms in the aqueous fraction, the sample should be centrifuged for 5 min at 5000 g in order to obtain a clear aqueous phase.). The aqueous fraction was transferred to a cuvette and the absorbance at 320 nm measured with a Pye Unicam SP 1800 double beam UV spectrophotometer with 200 mM NaOH as the blank. The concentration of PCP in the

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samples was calculated from the regression equation of a standard curve produced by taking a series of samples of known PCP concentration through the same extraction procedure. Spectrophotometric grade reagents are recommended but reagent grade reagents are acceptable in most instances. Depending on the sample size, the detection limit varies from 50 ppb (100 mL water sample) to 5 ppb (1000 mL sample). A linear relationship exists between the absorbance at 320 nm and the PCP concentration from the detection limit up to 5 ppm, which is near the saturation limit of PCP in seawater. In order to determine the extraction efficiency of this method, a series of extractions with ^{14}C-PCP in seawater was conducted. A 100 µg/L ^{14}C-PCP standard in 35 ppt Instant Ocean seawater (Aquarium Systems, Inc., Eastlake, OH) was prepared and various volumes of the stock standard were carried through the extraction procedure. The radioactivity in aliquots of the 200 mM NaOH fraction was measured with a Tri-Carb liquid scintillation spectrophotometer and the extraction efficiency determined after quench correction.

RESULTS AND DISCUSSION

The results of the extraction efficiency study with ^{14}C-PCP are shown in Table 1. More than 90% of the PCP in the water samples was extracted using 200 mM NaOH for the final extraction. It has previously been shown that a high pH is necessary for the efficient extraction of PCP into an aqueous medium (ERNE 1958).

Table 1. Extraction efficiency and coefficient of variation for two different samples sizes.

Sample Volume (mL)	N	Extraction Efficiency	Coefficient of Variation (%)
100	10	92%	3.4
250	10	102%	4.4

The increased extraction efficiency for the larger sample size was probably due to the increased interface area between the sample and chloroform phases, as the 250 mL samples were prepared in 500-mL bottles, whereas the 100 mL samples were prepared in 125-mL bottles.

Although this technique is not as sensitive or specific as the gas chromatographic analyses, the number of potentially interfering compounds is limited. Most organochlorine pesticides and polychlorinated biphenyls remain in the organic phase after the last extraction (RUDLING 1970). Most phenolic compounds which would be extracted into the alkaline aqueous fraction have UV absorbance maxima much lower than PCP (FOUNTAINE et al. 1975).

Numerous attempts were made to adapt this technique for analysis of PCP in tissues. Due to the presence of interfering substances which could not be removed by florisil treatments or

by using different extraction media, the technique was found to be unsatisfactory for the analysis of PCP in complex invertebrate tissues, although the characteristic absorption spectra of PCP in an aqueous solution between 310 and 330 nm were very distinct in PCP contaminated tissues. Discrete organ tissues such as brain or liver which characteristically produce a homogenate supernatant that is low in UV absorbing substances could conceivably be analyzed for PCP by an adaptation of this technique.

The primary advantages of the spectrophotometric technique over more sophisticated methods are that it is rapid, simple and inexpensive. This method has been used routinely to monitor the exposure concentration of PCP during chronic toxicity studies with marine animals (THOMAS et al. 1980; CARR & NEFF 1981) and probably will be most useful for monitoring the aqueous concentration of PCP in laboratory studies.

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