ANALYSIS OF PESTICIDES AND OTHER ORGANIC POLLUTANTS BY PRECONCENTRATION AND CHROMATOGRAPHIC TECHNIQUES

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(Received January 2, 1981; Revised June 24, 1982)

Abstract. The adsorption properties of Tenax have been studied in order to test the possibility of concentration and recovery of pollutant substances. Pesticides of various classes (chlorinated, phosphorated, carbamates, carbonates) and other organic toxicants having different volatility were employed as substances to be concentrated. They were present in water at 0.1 ppb level of concentration. Recovery was made by solvent extraction or by thermoelution. Revelation and quantitative analysis were performed by gas chromatography and by HPTLC. The effect of the flux was investigated. Tenax is the most suitable material in comparison with other tested adsorbents. Recovery is generally good except for aldrin. An apparatus for stripping and thermoelution is described that allows one to analyze water and air pollutants. Procedures have been tested for single classes of substances or a mixture of them.

1. Introduction

In recent years industrial growth and the need of increasing agricultural productivity have brought about problems due to the presence in water and air of pollutants dangerous at levels lower than ppb. Among these substances pesticides must be watched with particular attention because of their very low limits of tolerability (recently the limit for some chlorinated and phosphorated pesticides was fixed at 0.1 ppb). The large variability of molecular species used as insecticides, herbicides etc. and the very low concentration in water or in aereosols makes a direct determination practically impossible without previous concentration and separation. To this end several methods have been proposed such as liquid-liquid extraction (Mieure and Dietrich, 1973; Parkes et al., 1976) or adsorption on activated charcoal (Versino et al., 1974). These methods are not completely satisfactory as concerns the capacity of trapping pollutants present in very small amounts and their recovery by solvent extraction (Butler and Burke, 1976). Recently (Leinster et al., 1977; Walker, 1978) some chromatographic materials such as Tenax, Chromosorb 101, and Porapak were tested as trapping agents and studied with relation to their collection power, the possibility of depolymerization during the enrichment step, their water affinity and the recovery percentage of trapped substances. According to Butler and Burke (Butler and Burke, 1976) Tenax G.C. is the most suitable trapping agent for high boiling substances owing to its relatively low retention volume which provides an easier desorption. Furthermore its high thermal stability makes it particularly useful when recovery is obtained by thermal flash.

The purpose of this study was to measure the adsorption properties of Tenax, compare it to other adsorbent materials, and to test enrichment, extraction and recovery
procedures for different classes of pesticides (chlorinated, phosphorated, carbamates and carbonates) and other pollutant substances present in water at 0.1 and 0.01 ppb levels. Procedures have been tested for single classes of substances and for complex mixtures of them. Elution was made by solvent extraction or by heating.

Furthermore, a versatile device is described that can be utilized both for water and air pollutants. It allows coupling of thermal flash and solvent extraction in order to separate different classes of substances.

The revelation and quantification techniques were gas chromatography for chlorinated and phosphorated pesticides and other organic substances; quantitative HPTLC was used for carbamates and carbonates.

2. Experimental

2.1. Chemicals

Tenax G.C. (60 to 80 mesh) was obtained from Perkin-Elmer. Other tested adsorbents were Carbopack B/1.5% XE 60/1% H_3PO_4 by Supelco and Amberlite XAD 2 by BDH.

Standard solutions of pesticides by C. Erba and pure pesticides 'Pestanal' by Reidel De Haen AG were employed. All solvents were 'for pesticide residue analysis' grade.

2.2. Apparatus and Procedure

The Sigma 3 Gas Chromatograph by Perkin-Elmer with Ni 63 ECD and two FID's was employed for chlorinated and phosphorated pesticides and other organic substances. It was equipped with a subambient temperature accessory in order to condense the thermoeluted substances at the head of the column. A glass column (3.8 m x 1/4 in I.D.) was packed with OV 17 phenylmethylsilicone supported on chromosorb W. Chromatographic conditions were T 200 °C, flux 40 ml min⁻¹ and N_2 as the carrier gas. Calibration plots were obtained by internal standard method (see Figure 1). Detection limits (dl) for chlorinated and phosphorated pesticides were 8 x 10⁻¹³ and 7 x 10⁻¹² g, respectively. So, for water polluted at 0.01 ppb level, a concentration factor of 1000 or 10000 is needed if volumes of 0.1 l are injected.

Quantification of carbamate and carbonate pesticides was made by a TLC/HPTLC desitometer by Camag in fluorescence quenching mode.

HPTLC plates of 10 x 10 cm with a F_{254} fluorescence marker were obtained from Merck and developed in a HPTLC horizontal developing S chamber by Camag. The choice of the most suitable developing mixture was made utilizing a Vario KS multiple developing chamber (Camag). Several mixtures of ethyl acetate/ethanol/chloroform were tested: the best separation was obtained with a mixture of CHCl_3/CH_3OH 99/1 v/v.

Depositions were made by a TLC/HPTLC deppositor built by us (Caselli, 1981). A micrometric head mounted over the cap of interchangeable Hamilton microsyringes, and a system of two rack screws and a mechanical comparator allow exact deposition