

CHROM. 8040

## PRELIMINARY RESULTS ON THE USE OF TENAX® FOR THE EXTRACTION OF PESTICIDES AND POLYNUCLEAR AROMATIC HYDROCARBONS FROM SURFACE AND DRINKING WATERS FOR ANALYTICAL PURPOSES\*

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(Received November 5th, 1974)

### SUMMARY

The use of Tenax GC® for the extraction of organic micro-pollutants such as pesticides and polynuclear aromatic hydrocarbons from water has been studied. In the absence of other contaminants and under conditions standardized at the time as optimal, the recovery of such substances is, on average, over 90%, both for the organochlorine and organophosphorus pesticides and for polynuclear aromatic hydrocarbons.

Research into the effectiveness of extraction with Tenax from natural waters and water artificially contaminated with surfactants, fats and oils etc., in the laboratory is now being carried out.

### INTRODUCTION

The extraction from considerable volumes of surface and drinking waters of organic pollutants, which are usually present at the parts per billion (micrograms per litre) level, such as pesticides and their derivatives, polychlorinated biphenyls and polynuclear aromatic hydrocarbons, for the purpose of their subsequent determination can be achieved with organic solvents and automated liquid-liquid extractors<sup>1,2</sup>, by means of activated carbon absorption and their subsequent elution with chloroform<sup>3,4</sup>, by absorption on sheets of polyethylene immersed in water and their subsequent washing with organic solvents<sup>5</sup>, by absorption on porous polyurethane coated with selective absorbent<sup>6</sup>, and by using stationary phases of a gas chromatographic type<sup>7,8</sup>, such as silicones of the series OV or DC 200.

For pesticides, we have mainly used extraction with solvents<sup>9,10</sup> and achieved excellent recoveries for both organochlorine and organophosphorus pesticides, as well as for some herbicides and fungicides. The main disadvantages are the time necessary for extraction (15-20 h at a rate of 1 l/h), the co-removal of interfering

\* Work carried out under contract to the Institute of Research on Water of the National Council of Research (Italy).

substances which required subsequent difficult clean-up of the extracts, and the practical impossibility of developing "field" apparatus for use in relatively important surveillance programmes. Also, the technique of activated carbon absorption and subsequent elution of the pesticides with chloroform gives excellent recoveries of organochlorine pesticides, but the recoveries of organophosphorus pesticides are inconsistent<sup>4</sup>.

The other techniques mentioned have been investigated on only a limited number of organochlorine pesticides. The method of absorption on sheets of polyethylene is considered to be impracticable<sup>11</sup> because of the variable influence of other contaminants that can be present in river waters, while the other methods require extensive pre-treatment of the supports and the stationary phases.

In the extraction of polynuclear aromatic hydrocarbons from water by automated liquid-liquid methods<sup>12</sup>, considerable difficulties are encountered, particularly on account of the large volumes of water that must be treated with toxic solvents in the laboratory in order to achieve sufficient analytical sensitivity, and also because of the considerable length of time necessary for these operations.

For pesticides, we began with tests for the removal of some of the principal organochlorine products that had been added in known amounts to water, using a mixture of Carbowax 4000 monostearate and *n*-undecane on Chromosorb W, 80-100 mesh; unsatisfactory results were obtained. In the subsequent removal of the pesticides from the stationary phases, the recoveries, at room temperature, were only 60-70% of the amounts originally added.

Subsequently, in the search for a material suitable for our purposes, we used Tenax<sup>®</sup>, which is a new porous polymer based on 2,6-diphenyl-*p*-phenylene oxide made by ENKA (Amsterdam, The Netherlands) and distributed in Italy by BDH.

This polymer, which is stable at temperatures above 350°, was used initially for packing gas chromatographic columns for the separation of polar substances, and the most promising applications appear to be those for the separation of phenols.

Recently, Zlatkis *et al.*<sup>13,14</sup> have used Tenax successfully for trapping the volatile organic constituents of urine.

In this work, we used Tenax for the extraction of pesticides and polynuclear aromatic hydrocarbons from water.

## EXPERIMENTAL AND RESULTS

### *Pesticides*

The most significant preliminary tests that were carried out are summarized in Table I. In these tests, standard solutions of the principal organochlorine and organophosphorus pesticides, prepared in acetone, were added to 3-20 l of water in amounts of 100  $\mu$ l of standard solution per litre of water, so that the concentration of the various pesticides was 1 ppb (1  $\mu$ g/l). For the tests were used (A) a mineral water that contained no carbon dioxide, of pH 6.8, with a fixed residue of about 0.4 g/l consisting chiefly of calcium salts, and which preliminary analyses had shown to be completely free from pesticide residues; (B) a water normally distributed for drinking purposes in the City of Rome, of pH 6.9-7.2, with a fixed residue of about 0.4 g/l and 0.05-0.1 mg/l of free available chlorine.

The water was treated with pesticides in a glass tank that was connected laterally near the base by means of glass joints with a chromatographic glass

TABLE I  
SUMMARY OF PRELIMINARY TRIALS ON THE EXTRACTION OF PESTICIDES

Trial No.	Water quality*	pH	Tenax in column (g)	Volume of filtered water (l)		Flow-rate (l/h)	Pesticides examined	
				Pesticide added	Pesticide free		Organo-chlorine	Organo-phosphorus
1	M	6.8	3.0	2	—	2	+	—
2	M	6.8	1.5	2	—	2	+	—
3	M	6.8	1.5	2	—	4	+	+
4	M	6.8	1.5	2	—	3	+	+
5	P	7.2	1.5	4	—	3	+	—
6	P	7.2	1.5	4	2	3	+	+
7	P	7.2	1.5	4	50	3	+	—
8	P	7.2	1.5	20	—	3	+	+
9	P	1.0	1.5	20	—	3	+	+
10	P	6.9	1.5	20	—	3	—	+
11	M	6.8	1.5	20	—	3	—	+

\* M = mineral water; P = potable water (residual-free chlorine containing).

column 40 cm high and 1 cm I.D. with a porous screen and containing Tenax GC which was covered with a plug of silanized glass-wool. Then the water was percolated through the tube, while the flow was suitably regulated by means of air pressure and a system of valves.

After the percolation, the column was detached from the tank and air was introduced into the tube for a few seconds in order to eliminate as much water as possible from the adsorbent; the absorbed pesticides were extracted from the Tenax with several portions of diethyl ether. The diethyl ether was dehydrated by filtration over anhydrous sodium sulphate (2 g).

In other trials, not all of which are shown in Table I, after the adsorption of the pesticides on Tenax, volumes of pesticide-free water were percolated through the column in order to study the de-adsorption.

The recovery of the pesticides was studied by gas chromatographic analyses with an electron capture or phosphorus detector<sup>10,15</sup>. The following were examined:

(1) the water to which the pesticides were initially added, in order to observe possible degradation of the pesticides before extraction;

(2) the water after filtration over Tenax, by extraction with benzene in a separating funnel;

(3) the fractions of diethyl ether used for elution of the pesticides from the Tenax;

(4) Tenax and untreated water alone, for research into possible interferences.

All of the solvents and reagents used were of the type "for pesticides" (made for "pesticide analysis" by Carlo Erba, Milan, Italy) and all the necessary precautions were taken.

In studying the optimal conditions for the removal of pesticides, we varied the following parameters: amount of Tenax in the column; volume of water filtered; flow-rate of water through the column; pH of the water; and volume of diethyl ether used for the recovery of the pesticides from the Tenax. The concentration of pesticides

in the water was maintained constant and all of the tests were carried out at room temperature. The results of these preliminary tests are shown in Table II.

From the results, we decided to use the following conditions: amount of Tenax GC, 60–80 mesh, in the column, 1.5 g, which fills it to a height of *ca.* 7.5 cm; volume of water used for extraction, up to 20 l; flow-rate of water during extraction, 3 l/h; pH of the water, 6.8–7.2; diethyl ether for extraction of the pesticides from the Tenax, two 10-ml volumes.

#### Observations on the tests with pesticides

With the organophosphorus pesticides, as shown in tests 8 and 10, the recoveries were nil or low when the standard solution was added to drinking water containing 0.05–0.1 ppm of free chlorine; however the recoveries were satisfactory when the standard solution was added to mineral water (tests 3, 4, 11).

We found that this result did not depend on the unfavourable action of the free chlorine on the adsorbent capacity of the Tenax, but rather on the fact that the

TABLE II

## EFFECTIVENESS OF EXTRACTION OF PESTICIDES FROM WATER WITH TENAX

Pesticides present at the 1 ppb\* level. Results are given as percentage recoveries.

Pesticide	Trial No.												
	1	2	3	4	5	6	7	8	9	10	11		
Hexachlorobenzene (HCB)	—	—	71.0	69.6	78.5	86.6	79.4	—	70.6	90.6	91.1	—	—
Aldrin	91.6	74.7	—	60.1	62.1	70.6	63.7	91.5	41.8	88.3	81.1	—	—
Dieldrin	96.9	95.6	—	—	—	—	—	—	—	93.8	87.1	—	—
Heptachlor	102.9	87.7	—	—	—	—	—	—	—	90.5	89.0	—	—
Heptachlorepoxyde	—	—	—	—	—	—	—	—	—	96.5	—	—	—
$\alpha$ -Chlordane	—	—	—	—	—	—	—	98.6	—	—	—	—	—
<i>o,p</i> -DDE	86.4	75.0	—	—	—	—	—	—	—	96.0	—	—	—
<i>p,p</i> -DDE	—	—	—	—	60.4	—	67.1	—	77.9	92.8	—	—	—
<i>o,p</i> -DDT	96.0	108.9	—	—	—	—	—	—	—	92.4	74.0	—	—
<i>p,p</i> -DDT	92.8	90.9	—	—	—	—	—	—	—	91.6	76.4	—	—
<i>o,p</i> -TDE	—	—	—	—	—	—	—	93.2	—	—	—	—	—
<i>p,p</i> -TDE	—	—	—	—	—	—	—	95.6	—	—	—	—	—
<i>p,p</i> -DCBP	—	—	—	—	—	—	80.3	—	83.8	—	—	—	—
$\alpha$ -BHC	—	—	—	81.2	—	—	—	—	—	91.6	—	—	—
$\beta$ -BHC	—	—	61.6	83.8	—	105.6	—	—	—	70.1	—	—	—
$\gamma$ -BHC	—	—	—	93.2	—	—	89.7	—	69.4	92.5	68.3	—	—
$\delta$ -BHC	—	—	76.8	—	—	—	—	—	—	88.4	—	—	—
Methoxichlor	—	—	—	—	—	—	—	—	—	75.0	—	—	—
Ronnel	—	—	—	88.1	—	—	—	—	—	57.1	—	86.1	104.8
Dursban	—	—	—	89.4	—	—	—	—	—	18.8	—	—	—
Diazinon	—	—	—	80.7	—	—	—	—	—	0. —	—	—	—
Malathion	—	—	—	71.3	—	103.8	—	—	—	0. —	—	53.0	85.9
Disyston	—	—	—	—	—	—	—	—	—	0. —	—	—	—
Parathion	—	—	90.2	—	—	—	—	—	—	0. —	78.3	65.3	95.9
Parathion methyl	—	—	83.4	—	—	—	—	—	—	0. —	—	68.0	112.1
Summition	—	—	—	—	—	—	—	108.8	—	0. —	—	—	—

\* Throughout this article the American billion ( $10^9$ ) is meant.

free chlorine oxidized the pesticides\*, and probably partly also favoured a type of isomerization of the pesticides during extraction (this aspect is being studied further).

Therefore, when it is necessary to examine drinking waters for organophosphorus pesticides if free chlorine is present it must be neutralized as soon as the sample has been taken.

Test 9 showed that acidic conditions, such as we used previously<sup>10</sup> in the liquid-liquid method in order to favour the extraction of the pesticides and to prevent microbial degradation during the conservation of the samples, gave unfavourable results in the present Tenax adsorption method.

#### *Polynuclear aromatic hydrocarbons*

For the tests with polynuclear aromatic hydrocarbons, the apparatus was the same as that used with the pesticides.

Drinking water (pH 7.2; fixed residue 0.4 g/l; free chlorine 0.05 ppm) was used, to which were added the principal hydrocarbons at levels of 0.08–0.13 ppb as standard solutions in acetone (0.5–1.0 ml per 20–30 l of water).

TABLE III

#### EFFECTIVENESS OF THE EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS FROM WATER WITH TENAX

Results are given as percentage recoveries.

<i>Hydrocarbon</i>	<i>Trial No.</i>		
	<i>1*</i>	<i>2**</i>	<i>3***</i>
Anthracene	100.0	96.6	—
Perylene	85.5	92.0	—
Indeno[1,2,3- <i>c,d</i> ]pyrene	95.5	86.0	—
Pyrene	—	—	98.5
Fluoranthene	—	—	96.5
3,4-Benzopyrene	—	—	96.6

\* Extraction of hydrocarbons (2 µg) from Tenax after evaporation of the solvent and subsequent percolation of 20 l of hydrocarbon-free water.

\*\* Extraction from 30 l of water containing 0.13 ppb of hydrocarbons.

\*\*\* Extraction from 25 l of water containing 0.08 ppb of hydrocarbons.

In the first test, the hydrocarbons were introduced directly into the column of Tenax in a small volume of acetone, the solvent immediately evaporating, and 20 l of hydrocarbon-free water was passed through the Tenax.

In all of these tests, the subsequent removal of the hydrocarbons from the Tenax was effected with 30 ml of acetone. After filtration of the acetone solution on anhydrous sodium sulphate and subsequent concentration, the hydrocarbons were separated by TLC and the amounts were determined by spectrophotofluorimetry.

The results of these preliminary tests are shown in Table III.

\* Oxidation, when it causes the formation of oxo-derivatives (direct inhibitors of the cholinesterase), does not improve the hygienic characteristics of the water and complicates the analyses.

## DISCUSSION

The analysis of water from which extraction had been effected with Tenax showed no traces of either added pesticides (apart from small amounts of hexachlorobenzene) or polynuclear aromatic hydrocarbons.

The results appear excellent for analyses of this type, particularly the extraction of organophosphorus pesticides, which had never been obtained at such levels with techniques other than direct extraction from water with organic solvents. On the other hand, the extraction of organic micro-pollutants from surface water by means of polymers can be adversely affected by the presence in the water of other contaminants (surfactants, fatty substances, etc.).

The tests we are carrying out concern water artificially contaminated in the laboratory and natural waters, in the latter case extraction being effected by both conventional liquid-liquid techniques and by means of absorption on Tenax with a Celite 545 pre-filter, in which the preliminary results appear favourable.

Based on the preliminary results described here, it seems that the use of Tenax is promising both for the purposes of our research, which are to develop apparatus for the automatic field extraction of organic micro-pollutants such as pesticides, polychlorobiphenyls and polynuclear aromatic hydrocarbons, and for application on a large scale in order to inspect fresh surface water, drinking water and coastal sea water.

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