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THE USE OF TENAX FOR THE EXTRACTION OF PESTICIDES AND POLYCHLORINATED BIPHENYLS FROM WATER

II. TESTS WITH ARTIFICIALLY POLLUTED AND NATURAL WATERS

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SUMMARY

The application of Tenax® to the extraction of organic micro-pollutants such as pesticides and polychlorobiphenyls from waters has been studied, and it has been observed that also in the presence of other pollutants (oil, surface-active substances, etc.) the results obtained with an absorption column of Tenax–Celite are equivalent to those obtained with the continous liquid–liquid extraction technique. For natural waters that contain solids in suspension that adsorb pesticides, it may be necessary to filter the water before extraction with Tenax and then to extract the suspended solids separately. Analyses of river and estuarine sea waters, filtered before extraction, showed the effectiveness of Tenax, and the extracts obtained for the pesticides analysis prove to be much less contaminated by interfering substances than the corresponding extracts obtained by the liquid–liquid technique.

INTRODUCTION

Surface waters can be polluted by many organic substances, most of which are present in small or trace amounts. Among such substances, pesticides are of particular importance owing to their high toxicity towards aquatic animals and the possibility that they may not be completely eliminated by water-treatment processes and may therefore reach man. Recently, tolerance limits for some organochlorine pesticides in drinking water have been proposed[1] at the 0.1 ppb (μg/l) level; therefore, in order to effect analytical controls it is necessary to develop suitable techniques for the concentration of the pollutants. Favourable results have been obtained for the concentration of many organic substances[2] and recently also for some pesticides[3–5] using macromolecular resins of the Amberlite XAD-2 type; progress has also been made in liquid–liquid extraction techniques[6].

In a previous investigation, we showed the possibility of using Tenax (a porous polymer; trade mark registered by Enka N.V.; developed by AKZO Research Labs.,

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Arnhem, The Netherlands) for the extraction of organic micro-pollutants such as pesticides and aromatic polycyclic hydrocarbons[7] from waters. The recoveries of these substances from unpolluted waters (mineral and drinking waters) when added at the level of 1 ppb averaged 90%. The use of Tenax, compared with the other techniques mentioned, has the advantages of requiring no preliminary treatment (activation or purification) and of permitting the utilization of automated equipment for field extraction of the pollutants.

The physical characteristics of Tenax were examined by Sakodynskii *et al.*[8] and recent applications have included the analysis of atmospheric pollutants[9,10] and the volatile components of wines[11]. On the other hand, as noted by Beyermann and Eckrich[12], the capacity of polymers to extract organic micro-pollutants from waters can be adversely affected by the presence in the waters of larger amounts of other pollutants. For instance, in the particular case of a hydrophobic polymer such as Tenax, mineral oils could "deactivate" the adsorbents and result in low recoveries of the micro-pollutants.

This paper describes tests carried out in order to study these phenomena and to ascertain the possibilities of the use of Tenax. Initially, mineral and drinking waters were enriched with pesticides and then artificially polluted with various products (surfactants, mineral oils, emulsifying agents) and, on the basis of the results obtained for the recoveries of some pesticides, the absorption column was partially modified. Using the modified absorption column and the liquid–liquid extraction technique[13–15], extraction tests were carried out with natural waters (sweet surface and coastal sea waters). The results of these tests showed the fields in which extraction with Tenax can be applied.

EXPERIMENTAL

The equipment used for the extraction experiments is illustrated in Fig. 1 and consists of the following components. A glass container (1) of 20 l capacity was used. The silicone rubber hose (3) (type MCO/3, Cellai, Milan, Italy), in order to eliminate eventual interfering substances, was extracted before use by immersion in light petroleum for 48 h, changing the solvent after the first 24 h. Watson-Marlow Type MHRE/88 peristaltic pumps (4) with the canals and variable speed (Watson-Marlow Ltd., Marlow, Buckinghamshire, Great Britain) were used. The flow-rate of water through successive absorption columns (5) was regulated at about 3 l/h using two canals of the pump (the first incoming and the second, inverted outgoing). Therefore, with one of these pumps it is possible to carry out five extractions simultaneously. The glass absorption column (5), dimensions 48 cm × 1 cm I.D., was fitted with a porous septum. During preliminary tests, the column was filled exclusively with 1.5 g of Tenax, while during standard tests it was filled from the bottom with 1.5 g of Tenax (60–80 mesh), a layer (about 2 cm high) of glass pellets of diameter about 3 mm; a layer (about 10 cm high) of a mixture of 1–1.5 g of Celite 545 (Johns-Manville, Denver, Colo., U.S.A.) and plugs of silanized glass-wool (Applied Science Labs., State College, Pa., U.S.A.); and a layer of glass pellets (2 cm high).

The extraction and recovery tests were carried out with waters to which pesticides and other pollutants had been added, and with natural waters. In the recovery

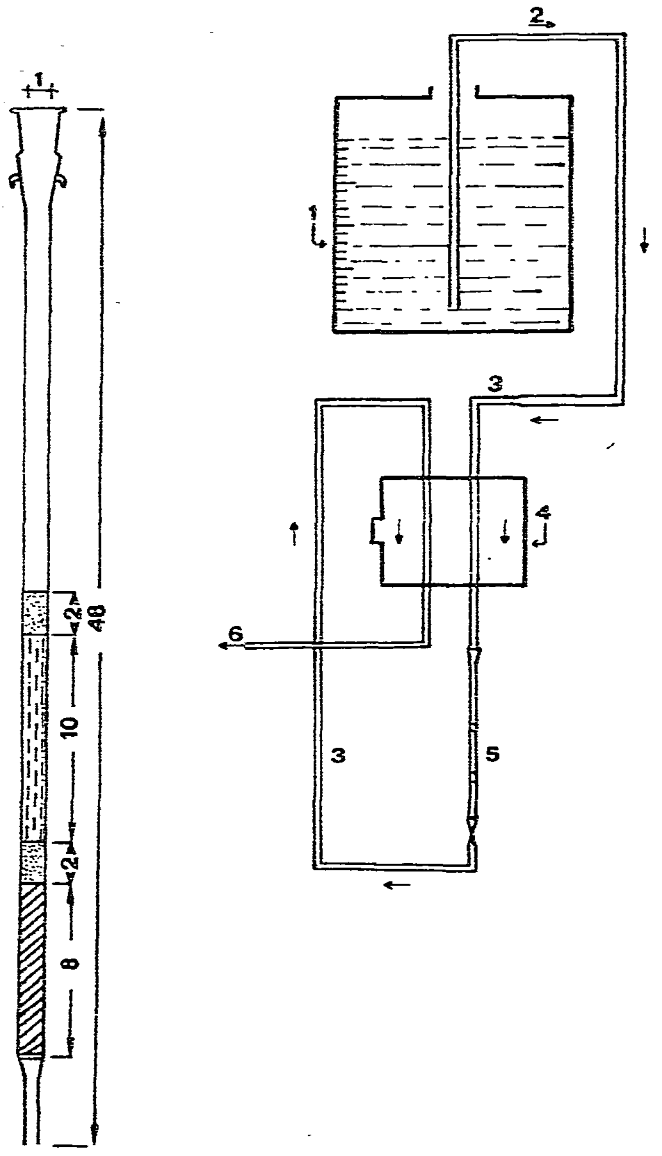

Fig. 1. Right: Equipment used for the extraction of micro-pollutants. 1, Glass container; 2, glass tubes; 3, silicone rubber hose; 4, peristaltic pump; 5, glass absorption column; 6, extracted water discharge. Left: adsorption column (dimensions in cm). From bottom to top: Tenax, glass pellets, mixture of Celite and plugs of silanized glass-wool, glass pellets.

tests, standard mixtures of pesticides prepared in acetone were added to 8–15 l of water at a level of 100 µl of standard solution per liter of water, so that the concentration of the various pesticides was 1 ppb (1 µg/l).

The various water samples were then passed through the peristaltic pump into the absorption column at a flow-rate of about 3 l/h. When the absorption was completed, the pesticides were eluted with three 10-ml volumes of diethyl ether, in such a way that the solvent also passed through the section of hose through which the water reached the column. Finally, the diethyl ether was dried over anhydrous sodium sulphate. The water container was washed with light petroleum in order to remove the pesticides adsorbed by the glass walls, and the washing solution, after concentration, was added to the eluate obtained from the absorption column.

For recovery tests carried out with mineral waters enriched with pesticides and other known pollutants, the mixed diethyl ether and light petroleum extract was evaporated just to dryness, the residue dissolved in *n*-hexane and the solution analyzed directly by gas chromatography with an electron-capture or phosphorus detector. However, for the analysis of naturally polluted waters, the mixed diethyl ether and light petroleum extract was evaporated, the residue dissolved in light petroleum and the solution partially purified by partitioning with acetonitrile saturated with light petroleum[15,16]. The acetonitrile partitioning is not needed for samples that are not highly polluted or for sea waters.

The resulting solution was evaporated just to dryness, the residue dissolved in 1 ml of *n*-hexane and pesticides and polychlorobiphenyls were separated into four fractions by deactivated silica-gel microcolumn chromatography[15] (silica gel Type Grace 950, 60–200 mesh). The deactivation of the absorbent was effected by adding 7–10% of water, instead of the 5% used previously[15], in order to compensate for the increased activity observed in recent years in many batches of the product. For the standardization of the adsorbent, a yellow dye, *p*-methoxyazobenzene, was also used as suggested by Claeys and Inman[17]. The various eluates from the silica gel were then analyzed by gas chromatography[18].

All solvents and reagents used were of "for pesticide residue analysis" grade (Carlo Erba, Milan, Italy), except for the light petroleum (b.p. 40–60°, BDH, Poole, Great Britain) which was distilled before use. All necessary precautions for analyses of this type were taken and a few blank trials were carried out.

It is noteworthy that the recoveries of hexachlorobenzene during the acetonitrile partitioning were not greater than 75%, and therefore for the calculations a correction factor was used. In order to evaluate the effectiveness of extraction from natural waters with the Tenax–Celite column, the samples were also extracted simultaneously by the liquid–liquid technique using the equipment suggested by Kahn and Wayman[13], consisting of three consecutive chambers; light petroleum was used as the solvent in the first and second chambers and benzene in the third. Before the extraction by the liquid–liquid method, the water was acidified to pH 1–3 with hydrochloric acid.

RESULTS

Table I indicates the tests effected, adding pesticides and other pollutants to a mineral water (pH 6.8 with a constant residue of about 0.4 g/l, consisting mainly of calcium salts and containing no carbon dioxide) that had been shown to be pesticide free prior to the analyses. These recovery trials were carried out with the pesticides most frequently found in Italian surface waters, usually also polluted by organophosphorus pesticides[19–21].

TABLE I

SUMMARY OF TRIALS ON THE TENAX EXTRACTION OF PESTICIDES FROM WATERS ARTIFICIALLY POLLUTED WITH PESTICIDES (1 ppb) AND OTHERS SUBSTANCES

Trial No.	*Volume of extracted water (l)*	*Pollutant*	*Adsorption columm*	*Pesticides examined*	
				Organo-chlorine	*Organo-phosphorus*
1	10	0.1 ppm of Arkopal N-100	Tenax	+	+
2	10	0.1 ppm of alkylbenzene-sulphonate (Na salt)		+	+
3	10	3% NaCl (marinesalt)		+	+
4	10	0.1 ppm of alkylbenzene-sulphonate + 1 ppm of mineral oil		+	+
5	10	1 ppm of mineral oil + 2 ppm of Tween 80		—	+
6	8			—	+
7a	14		Tenax—Celite	—	+
7b	10	1 ppm of mineral oil + 4 ppm of Tween 80		+	+
7c	10			+	+
7d	10			+	+
7e	10			—	+

Table II shows the results obtained. In the absorption with Tenax alone, the first three trials gave satisfactory results, while in the presence of mineral oil (trials 4,5 and 6) a considerable proportion of the organophosphorus pesticides (particularly malathion and methylparathion) was not adsorbed and was recovered in the filtered water. Test 7 (7a–7e) showed that this drawback can be overcome by placing, ahead of the layer of Tenax in the absorption column, a layer of Celite 545 which, in order to prevent blocking of the column, is mixed with silanized glass-wool plugs (Fig. 1).

A number of analyses of surface and estuarine sea waters were carried out by this modified Tenax column and simultaneously by the liquid–liquid extraction technique. To some of the samples taken, standard mixtures of pesticides were also added, each at the level of 1 ppb, *i.e.*, in concentration from 13 to 500 times higher than that usually found in the waters analyzed. One recovery trial also specifically concerned polychlorobiphenyls. The scheme of these tests is shown in Table III and the results obtained are given in Tables IV and V.

Table IV (trials 8, 9 and 11) shows that the two extraction methods, when applied to surface waters that were not filtered before extraction, yielded very similar results for many pesticides, with the exception of compounds of the DDT series, for which discordant results were frequently obtained (see the differences between trials 8a and b and 11a and b). Similarly, as shown in Table V (trial 11c), when the standard mixture of pesticides was added to a nonfiltered surface water, *i.e.*, containing suspended solids, the recoveries of active substances such as DDT and malathion were unsatisfactory. It is known that some pesticides that are present in waters are partially adsorbed by suspended or sedimentable solids[22]; therefore, such adsorbed

TABLE II

PERCENTAGE RECOVERY OF PESTICIDES ADDED AT THE 1 ppb LEVEL FROM MINERAL OR DRINKING WATERS ARTIFICIALLY CONTAMINATED IN THE LABORATORY WITH OIL, SURFACTANTS, ETC.

Pesticides and trials	*Adsorption with Tenax alone*							*Adsorption with Tenax–Celite*								
	1	*2*	*3*	*4*	*5*	*6**	*6***	*7a*	*7b**	*7b***	*7c**	*7c***	*7d**	*7d***	*7e**	*7e***
Hexachlorobenzene	93.5	82.5	94.7	102.9	—***	—	—	—	—	—	—	—	88.8–85.9	Abs.§	—	—
Dieldrin	85.9	95.6	98.9	89.4	—	—	—	—	92.0	Abs.	100.6	Abs.	87.2–80.0	Abs.	—	—
Heptachlor	82.2	79.7	85.2	96.0	—	—	—	—	—	—	—	—	—	—	—	—
o,p'-DDE	73.2	83.9	77.7	101.3	—	—	—	—	—	—	—	—	—	—	—	—
o,p'-DDT	75.6	83.2	82.9	111.8	—	—	—	—	77.8	Abs.	87.0	Abs.	86.5	Abs.	—	—
p,p'-DDT	75.9	89.2	83.9	106.9	—	—	—	—	93.4	Abs.	95.4	Abs.	88.1	Abs.	—	—
γ-BHC	—	—	—	87.7	—	—	—	—	—	—	—	—	85.8	Abs.	—	—
β-BHC	—	—	—	—	—	—	—	—	—	—	—	—	86.3–79.3	Abs.	—	—
Ronnel	93.4	85.5	98.9	82.9	—	—	—	—	—	—	—	—	—	—	—	—
Dursban	—	—	—	—	98.1	88.6	Abs.	89.6	—	—	—	—	—	—	88.7	Abs.
Malathion	—	—	—	—	12.0	20.1	64.9	78.0	50.0	33.3	32.8	38.1	32.6	30.7	82.2	20.0
Parathion	96.5	87.2	96.6	51.2	66.3	74.5	13.3	85.0	—	—	—	—	—	—	98.7	Abs.
Methylparathion	76.6	68.4	87.5	—	27.3	39.9	43.0	81.0	—	—	59.1	27.2	71.4	23.2	91.9	Abs.
Trithion	—	—	—	—	—	—	—	—	—	—	—	—	—	—	94.2	Abs.
Ethion	—	—	—	—	—	—	—	—	—	—	—	—	—	—	90.5	Abs.

* Percentage recovery of the column, hose and container.

** Percentage recovery in the filtered water on the Tenax column.

*** Not determined.

§ Abs. = absent.

TABLE III

SUMMARY OF TRIALS OF TENAX AND LIQUID–LIQUID EXTRACTION OF PESTICIDES FROM NATURAL POLLUTED WATER

Trial No.	*Sample*	*Trials effected*
8	Tiber river water (30 l)	8a: 15 l, Tenax–Celite extraction
		8b: 15 l, liquid–liquid extraction
9	Sea-coast water (20 l)	9a: 10 l, Tenax–Celite extraction
		9b: 10 l, liquid–liquid extraction
10	Sea-coast water (30 l)	10a: 10 l, Tenax–Celite extraction
		10b: 10 l, liquid–liquid extraction
		10c: 10 l + 1.6 ppb standard of PCB* and Tenax–Celite extraction
11	Tiber river water (30 l)	11a: 10 l, Tenax–Celite extraction
		11b: 10 l, liquid–liquid extraction
		11c: 10 l + 1 ppb standard of pesticides and Tenax–Celite extraction
12	Tiber river water (30 l) filtered before extraction	12a: 10 l, Tenax–Celite extraction
		12b: 10 l, liquid–liquid extraction
		12c: 10 l + 1 ppb standard of pesticides and Tenax–Celite extraction

* PCB made by Caffaro (Milan), Italy, added as standard mixture of Fenclor 42, 54 and 60 equivalent to 1.6 ppb of decachlorobiphenyl in total.

TABLE IV

DETECTION OF PESTICIDES IN SURFACE WATER SAMPLES EXTRACTED BY ADSORBTION ON TENAX–CELITE (SERIES a) AND BY THE LIQUID–LIQUID TECHNIQUE (SERIES b)

Results expressed in ppt (ng/l).

Pesticide identified	*Trial No.*							
	*8a**	*8b**	*9a**	*9b**	*11a**	*11b**	*12a***	*12b***
Hexachlorobenzene	5.4	5.8	3.3	3.8	2.6	—	8.1	6.6
Dieldrin	5.8	6.4	—	—	15.6	8.2	14.6	14.6
Heptachlor	1.5	1.7	—	—	0.9	0.9	7.1	2.7
p,p'-DDE	2.2	3.5	—	—	2.8	2.5	10.6	5.2
o,p'-DDT	5.0	12.2	—	—	13.0	12.3	24.8	19.8
p,p'-DDT	8.8	18.0	9.0	15.7	32.2	24.7	37.2	35.5
α-BHC	—	—	—	—	5.2	4.0	—	—
β-BHC	37.2	43.9	6.0	5.7	75.8	77.5	58.4	67.5
γ-BHC	9.7	13.6	—	—	19.4	17.3	10.5	15.5
Ronnel	18.9	21.7	—	—	2.1	2.1	—	—
Dursban	27.5	29.4	—	—	41.2	43.3	—	—
Diazinon	37.4	37.4	—	—	—	—	19.7	22.3
Malathion	26.5	31.7	—	—	27.0	31.0	27.3	27.3
Parathion	—	—	—	—	37.5	39.3	—	—
Methylparathion	32.6	38.2	—	—	21.0	26.0	—	—
Total (ppt)	218.6	263.5	18.3	25.2	296.3	289.1	218.3	217.0

* Waters not filtered before extraction.

** Waters filtered through paper before extraction.

TABLE V

RECOVERY TESTS ON EXTRACTION WITH TENAX-CELITE OF PESTICIDES AND POLYCHLOROBIPHENYLS ADDED TO SURFACE WATERS AT LEVELS OF 1.0 AND 1.6 ppb, RESPECTIVELY.

All results for corresponding non-treated samples are corrected. Results given are percentage recoveries.

Pesticides + additives	*Trial*		
	*10c**	*11c**	*12c***
PCB	100.2		
Hexachlorobenzene (HCB)		84.8	83.9
o,p'-DDT		38.0	81.8
p,p'-DDT		47.0	93.1
β-BHC		70.0	73.0
γ-BHC		84.9	92.0
Dieldrin		75.4	92.7
Methylparathion		82.3	101.0
Malathion		25.0	93.3

* Water not filtered before addition of standards and extraction.

** Water filtered through paper before addition of standards and extraction.

amounts cannot be extracted by filtration procedures on polymers while, at least to a great extent, they can be extracted by procedures in which the water is extracted with solvents. Trials 12a and b (Table IV) show that when the two extraction techniques are applied to filtered water, almost identical results were obtained, and trial 12c (Table V) shows that with Tenax extraction the recoveries of pesticides added to a filtered surface water before extraction were satisfactory.

During the tests it was observed that amounts of up to 30% of some pesticides can be adsorbed by the walls of the hose and the container, so that at the end of the extraction it is essential to wash these surfaces with solvents.

We consider that the tests described above have defined the fields in which Tenax extraction can be applied.

CONCLUSIONS

The extraction of pesticides from waters by absorption on Tenax, yields results equivalent to those obtained by the liquid–liquid procedure when applied to mineral, drinking and surface waters that completely or almost completely lack solid matter in suspension. For waters that contain suspended solids that can adsorb some pesticides in considerable amounts, the results of the two methods are equivalent only if the water has previously been filtered. In these instances, therefore, the analysis will involve filtered water as well as the residue of filtration.

Compared with liquid–liquid extraction, the main advantages of Tenax are the considerable amount of time saved, the possible automation of the process and that gas chromatographic analysis shows the "extracts" obtained with Tenax to be less contaminated by interfering substances. Another advantage of Tenax is that the product can be used "as received", without preliminary treatment.

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