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Determination of pesticides in drinking water by on-line solid-phase disk extraction followed by various liquid chromatographic systems

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ABSTRACT

C-18 Empore extraction disks were coupled on-line with liquid chromatography–rapid scanning UV–VIS detection and post-column fluorescence detection for the isolation and trace enrichment of various pesticides [carbamates, (aldicarb, carbofuran, carbaryl), carbamate transformation products (TPs) (aldicarb sulfoxide, aldicarb sulfone, 3-hydroxycarbofuran, 3-hydroxy-7-phenol carbofuran, 3-keto-carbofuranphenol and 3-ketocarbofuran) and herbicides (chlortoluron, isoproturon and metolachlor)] spiked at concentration levels of 0.2 and 5 μg/l in drinking water samples. Recoveries were dependent on the pesticide level and preconcentrated water volume (50 ml to 1000 ml) using LC with rapid scanning UV–VIS detection. The same on-line system coupled with LC–post-column derivatization fluorescence detection has needed only 10 ml of water to achieve similar levels of determination for the carbamate insecticides.

INTRODUCTION

Drinking and ground waters within the European Community were recently reported to be polluted with various pesticides with levels varying from 0.01 μg/l to over 0.1 μg/l, the latter of which is the maximum allowable concentration established by the Commission of the European Communities Drinking Water Directive (CEC-DWD) [1]. These pesticides have been also detected at similar concentration levels in various ground waters in the US [2]. The carbamate insecticides aldicarb and carbofuran are rather toxic, and their TPs are even more toxic [1,3]. They are formed both by hydrolysis or photolysis in water under laboratory conditions [3] as well by microbial degradation in soils and hydrolysis in waters [4,5]. It is thus hardly surprising that the National Pesticide Survey (NPS), in a joint project between EPA's Office of Drinking Water and the Office of Pesticide Programs has included many of these pesticides and TPs in their monitoring programmes [6,7].

A variety of adsorbents (*e.g.*, C-8 or C-18 bonded silica, Carbopack B) are currently used in SPE cartridges for concentrating polar pesticides and various TPs [8–15]. On-line systems [SPE coupled on-line with liquid chromatography] have been developed from SPE methods using a precolumn consisting of C-8 or C-18 bonded silica phase or a styrene–divinylbenzene polymer phase (PRP-1 or PLPR-S) [16–20]. One other alternative to trace enrichment uses membrane extraction disks (that contain C-8, C-18 or styrene–divinylbenzene polymer phase) and were used in the off-line [21–26] and on-line [27–28] modes in LC. The 4.6 mm O.D. disks used in the on-line mode are obtained from the conventional 47 mm O.D. disks (500 mg of C-18) by using a cutting device [28].

The aim of this work was to develop an on-line

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SPE method using membrane extraction disks to determine various pesticides and their polar TPs at levels below the values fixed by the CEC-DWD of 0.1 μg/l in drinking water. Development of methods for carbamate TPs was encouraged in a recent report from the CEC [1]. The different compounds were detected by rapid scanning UV–VIS, so confirmation was always possible. However, many of the compounds studied (*e.g.*, aldicarb and carbofuran and their corresponding TPs and metolachlor [3,19]) have their UV maxima below 220 nm, with molar extinction coefficients lower than 10.000, so problems in confirmation from LC–diode array spectra were encountered [3,19,20]. Complementary confirmation could also be achieved for some carbamate pesticides by using post-column derivatization with fluorescence detection. The method is valid for the analysis of water samples containing N-methylcarbamates and O-(methylcarbomyl)oxime pesticides [29,30]; and it is currently recommended by the US EPA [31] and applied through the NPS [6,7].

EXPERIMENTAL

Chemicals

HPLC-grade water, acetonitrile gradient grade LiChrosolv and methanol from Merck (Darmstadt, Germany) were passed through a 0.45 μm filter before use. Analytical reagent grade standards aldicarb, carbofuran, carbaryl, aldicarb sulfoxide, aldicarb sulfone, 3-hydroxycarbofuran, 3-hydroxy-7-phenol carbofuran, 3-ketocarbofuranphenol, 3-ketocarbofuran, chlortoluron, isoproturon and metolachlor were purchased from Promochem (Wesel, Germany). The names and structures of the pesticides are given in Fig. 1.

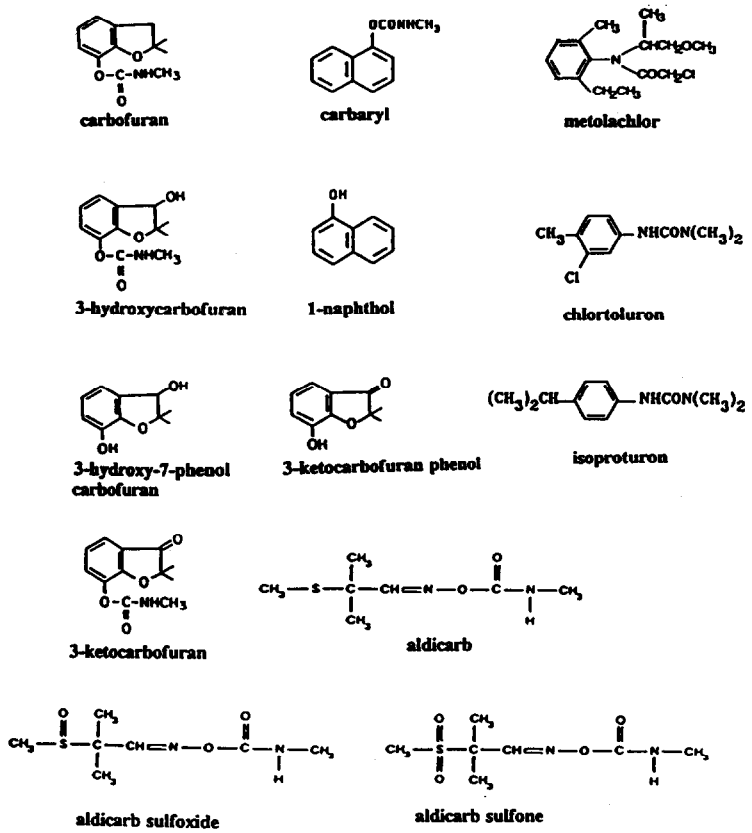

Fig. 1. Chemical structures of the model compounds used.

Rapid scanning UV–VIS detection

The LC eluent was provided by two Knauer 64 high-pressure pumps (Bad Homburg, Germany) coupled to a Chrom-A-Scope rapid scanning UV–VIS detector from Barspec (Rehovot, Israel). Quantitation by LC–UV was performed using UV absorption at 220 nm with external standard calibration methods. The calibration graphs were constructed for eight of the studied analytes (3-hydroxycarbofuran, aldicarb, 3-ketocarbofuran, carbofuran, carbaryl, chlortoluron, isoproturon and metolachlor) over a concentration range of 0.1–0.7 μg/l using preconcentration volumes of 250–400 ml. The other analytes were either not recovered (aldicarb sulfoxide, aldicarb sulfone, 3-hydroxy-7-phenol carbofuran) or exhibited recoveries below 70% (3-ketocarbofuranphenol and 1-naphthol).

The system used was similar to one described elsewhere [27,28]. After the membrane disks were placed in the disk holder, this holder was fitted in a MUST column switching device from Spark Holland (AS Emmen, Netherlands) and connected to an SSI Model 300 LC pump from Scientific Systems (State College, PA, USA) which delivered the water samples containing the pesticides. The disks were first conditioned by flushing 10 ml of methanol and then 10 ml of HPLC water at 1 ml/min. Water volumes from 50 to 1000 ml spiked with pesticides and TPs at concentrations of 0.2 and 5 μg/l were preconcentrated on 10 membrane extraction disks of 4.6 mm diameter at flow-rates varying from 2.5 to 5 ml/min. Following the preconcentration step, the MUST valve was switched and the components were desorbed and separated in a LiChrocart cartridge column (25 cm x 4.6 mm I.D.) packed with 4-μm Supersphere 60 RP-8 from Merck (Darmstadt, Germany) by using the following gradient elution program: from 5% of A [acetonitrile–methanol–water (40:40:20)] and 95% of B [acetonitrile–water (10:90)] to [20% A/80% B] in 15 min; from [20% A/80% B] to [30% A/70% B] in 20 min; from [30% A/70% B] to [65% A/35% B] in 20 min; and finally from [65% A/35% B] to 100% A in 7 min at a flow-rate of 0.8 ml/min. The column was returned to initial conditions in 5 min and held for post-run, 10 min. By flushing 5 ml of acetonitrile followed by 5 ml of water through the disks after each analysis, the memory effects in the disks were found to be less than 1%. Desorption of the pesticides from the membrane disk holder was done in the back-flush mode thus preventing chromatographic tailing and thereby enhancing carbamate resolution [16] and preventing extra band-broadening [28]. Since for river water samples the determination of pesticides is in the range of few μg/l [18], the preconcentrated volumes can also be reduced by a factor of 10 as compared to this work.

Post-column fluorescence derivatization

The above described on-line preconcentration system was coupled to an LC-post-column fluorescence system. The LC column eluent was delivered by a Model 250 Binary LC pump from Perkin Elmer (Norwalk, Connecticut, USA) coupled to a PCX 5000 carbamate post-column analysis module from Pickering Laboratories (Mountain View, CA, USA). Post-column reaction was carried out as described elsewhere [33]. A difference was the use of thiofluor instead of 2-mercaptoethanol. A Model LC 240 fluorescence detector from Perkin Elmer (Beaconsfield, UK) was used at excitation and emission wavelengths of 330 nm and 465 nm, respectively. A PE Nelson Model 1020 data system was used for data collection. 10-ml drinking water samples were needed for preconcentration.

RESULTS AND DISCUSSION

Breakthrough volumes

In order to determine the breakthrough volumes of all the test compounds, up to 100–150 ml (depending on the compound) of a solution containing the individual substances at a concentration of 1 mg/l was used. Breakthrough experiments were performed at a flow-rate of 2 ml/min, similar to that described elsewhere [18,19]. The breakthrough volumes were read off the recorded breakthrough curves at 1% of the sample absorbance observed at complete breakthrough; the values thus obtained are given in Table I. As compared to few recent literature data, breakthrough volumes of 1, 30 and >100

TABLE I

ABSORBANCE DATA AND BREAKTHROUGH VOLUMES DURING ON-LINE PRECONCENTRATION

HPLC water containing the individual substances at a concentration of 1 mg/l. Flow-rate: 2 ml/min.

Compound	Peak no.	λ_{max} (nm)	Breakthrough volume (ml)
Aldicarb sulfoxide	1	235	3
Aldicarb sulfone	2	220	4
3-Hydroxy-7-phenolcarbofuran	3	220	5
3-Hydroxycarbofuran	4	220	80
3-Ketocarbofuran phenol	5	258	40
Aldicarb	6	220	112
3-Keto-carbofuran	7	258	108
Carbofuran	8	220	150
Carbaryl	9	220	123
Chortoluron	10	245	102
1-Naphthol	11	234	80
Isoproturon	12	245	105
Metolachlor	13	200	150

ml were obtained for aldicarb sulfone, aldicarb and metolachlor when using a 10 mm × 2 mm I.D. precolumn of PLRP-S [19]. From these results one can conclude that using 10 membrane extraction disks of C-18 bonded silica material increases the breakthrough volume of many of the compounds of interest as compared to other conventional packing materials. This can be

TABLE II

AVERAGE % RECOVERY OF PESTICIDES IN WATER USING ON-LINE SPE

SPE with 10 C-18 Empore disks of 4.6 mm O.D. preconcentrating several water volumes at 2 ml/min. Spiking level: 5 μg/l. Detection: rapid scanning UV–VIS. R.S.D. (%) varied from 3–6% [calculated for sample volumes of 50 and 80 ml ($n = 5$)].

Compound	Water volume (ml)				
	20	50	50 [a]	80	180
Aldicarb sulfoxide	nd [b]	23	23	18	9
Aldicarb sulfone	nd	27	21	19	10
3-Hydroxy-7-phenolcarbofuran	nd	27	25	20	10
3-Hydroxycarbofuran	78	84	90	70	29
3-Ketocarbofuran phenol	72	71	68	50	19
Aldicarb	85	83	79	72	37
3-Ketocarbofuran	85	75	67	50	25
Carbofuran	95	93	94	70	66
Carbaryl	94	91	89	82	66
Chortoluron	92	91	90	80	69
1-Naphthol	78	74	75	67	37
Isoproturon	94	92	95	80	56
Metolachlor [c]	95	93	95	80	56

[a] Drinking water samples spiked with pesticides (see Fig. 2B).
[b] Not detected, below detection limits.
[c] Calculated after subtraction of spectrum at 220 nm.

ascribed to the higher trapping capacity of C-18 membrane disks of 8 μm particle size in an on-line combination.

Recovery values with rapid scanning UV–VIS detection

Tables II and III show the average recoveries of the studied pesticides at the spiking levels of 5 and 0.2 μg/l as preconcentrated from different volumes (20–1000 ml) of water samples. Table II gives the recoveries obtained with water volumes from 20 to 180 ml. We should note that the highest recoveries for all the compounds were obtained by preconcentrating 50 ml of water spiked with 5 μg/l of each pesticide. Preconcentrating 180 ml of the different pesticides spiked at 5 μg/l will be equivalent to load a maximum of 0.6 μg of each pesticide (at recoveries of 66–69%) onto the disks, so an overall amount of *ca.* 7 μg was loaded. From previous studies it was suggested to use a maximum loading of 15 μg for the sum of all adsorbed species in C-18 or PRP1 precolumns [35]. The difference in the maximum loading of the disks can be attributed to the water matrix constituents, *e.g.*, detergents in the case of drinking water samples. The recoveries obtained at 180 ml for aldicarb sulfoxide and sulfone were extremely low. In this case the effect of overloading the disks was obviously more important owing to the nature of the solutes.

A volume of <50 ml would be ideal for compounds with low breakthrough volumes, *e.g.*, aldicarb sulfoxide, sulfone and 3-hydroxy-7-phenol carbofuran. The problem is that these three TPs are not detected by the UV (see Table II). The percent recoveries for the rest of the compounds were all consistent with those obtained by breakthrough measurements. We should also note the absence of remarkable differences in using HPLC and drinking water samples, as can be seen in the chromatograms in Fig. 2, which correspond to 50 ml of HPLC water (A) and 50 ml of drinking water both spiked with all the studied pesticides at 5 μg/l (B) and a blank of 50 ml of drinking water (C).

TABLE III

AVERAGE % RECOVERY OF PESTICIDES IN WATER USING ON-LINE SPE

SPE with 10 C-18 Empore disks of 4.6 mm O.D. preconcentrating several water volumes at flow-rates varying from 2.5 to 5 ml/min. Spiking level: 0.2 μg/l. Detection: rapid scanning UV–VIS. R.S.D. (%) varied from 3 to 6% (calculated for sample volumes of 350 and 500 ml ($n = 5$) except for aldicarb sulfoxide, aldicarb sulfone and 3-hydroxy-7-phenolcarbofuran.

Compound Recovery (%)	Water volume (ml)/flow-rate (ml/min)					
	250/2.5	350/3.5	350/5 [a]	400/5	500/5	1000/5
Aldicarb sulfoxide	– [b]	–	–	–	–	–
Aldicarb sulfone	–	–	–	–	–	–
3-Hydroxy-7-phenolcarbofuran	–	–	–	–	–	–
3-Hydroxycarbofuran	94	89	78	92	63	57
3-Ketocarbofuranphenol	–	40	35	46	31	20
Aldicarb	79	92	74	78	62	43
3-Ketocarbofuran	80	85	75	88	68	69
Carbofuran	80	82	71	82	68	74
Carbaryl	74	76	73	79	64	55
Chortoluron	75	73	73	77	66	64
1-Naphthol	62	71	66	66	50	[c]
Isoproturon	80	83	76	84	67	70
Metolachlor [d]	95	94	92	95	91	95

[a] Drinking water was used.
[b] Not detected, below detection limits.
[c] Coelution problems (see Fig. 3).
[d] Calculated after subtraction of spectrum at 220 nm.

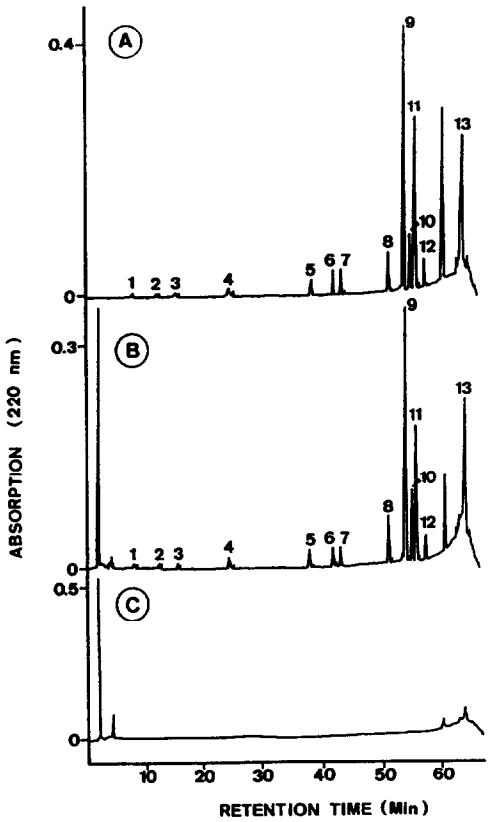

Fig. 2. LC–UV chromatograms obtained after preconcentration on C-18 Empore extraction disks of 50 ml of (A) HPLC water and (B) drinking water both spiked at 5 μg/l with the pesticide mixture indicated below, and (C) a drinking water blank. Peaks: 1 = aldicarb sulfoxide; 2 = aldicarb sulfone; 3 = 3-hydroxy-7-phenolcarbofuran; 4 = 3-hydroxycarbofuran; 5 = 3-ketocarbofuranphenol; 6 = aldicarb; 7 = 3-ketocarbofuran; 8 = carbofuran; 9 = carbaryl; 10 = chlortoluron; 11 = 1-naphthol; 12 = isoproturon; 13 = metolachlor. LC gradient elution programme: from 5% of A [acetonitrile–methanol–water (40:40:20)] and 95% of B [acetonitrile–water (10:90)] to [20% A/80% B] in 15 min; from [20% A/80% B] to [30% A/70% B] in 20 min; from [30% A/70% B] to [65% A/35% B] in 20 min; and from [65% A/35% B] to 100% A in 7 min. Back to initial conditions: 5 min; post-run, 10 min; flow-rate: 0.8 ml/min; stationary phase: 4 μm Supersphere 60 RP-8.

The blank shows that interferences can only occur in the last part of the gradient elution. The profile of the drinking water blanks analysed in our experiments is more consistent with the on-line preconcentration of other types of drinking waters [17,32,34,35].

Water solutions containing 0.2 μg/l of each pesticide were preconcentrated by using water volumes from 250 up to 1000 ml (Table III). As can be seen from the table, the recoveries obtained for all the compounds were quite similar for 350–400 ml of preconcentrated water. Such recoveries did not change on varying the flow-rate through the precolumn from 3.5 to 5 ml/min. This was also observed previously for several carbamates, the retention of which was not significantly affected by the flow-rate (flow-rates below 6 ml/min were recommended to avoid column back-pressure for precolumns containing 5-μm packing material [32]). As can also be seen from the tables, aldicarb sulfoxide, aldicarb sulfone and 3-hydroxy-phenol carbofuran were not detected at all owing to their low breakthrough volumes (their preconcentration on the disks at this low spiking level of 0.2 μg/l was not sufficient to be measured by LC–rapid scanning UV detection).

On comparing Table II and III, it is seen, as already observed in the preconcentration study, that breakthrough volumes increase with decreasing concentration, thus affecting analyte recoveries, similarly as reported previously [34,36]. Thus, in previous studies [36] it was shown that a concentration factor increase of 10 results in a breakthrough volume factor decrease of 5–7. Similarly, in our experiments, for compounds with relatively good recovery values, in preconcentrating water volumes of 50 and 350 ml containing 5 μg/l and 0.2 μg/l, respectively, it is seen that a concentration factor of 25 results in a breakthrough volume factor increase of 7 but a loading decrease of more than a factor of 3 is noticed (obtained from the recovery values). Inasmuch as preconcentration of 350 ml (see Table III) provided reasonable good recoveries for most of the compounds, we can state that the proposed preconcentration system provides good recoveries for loading capacities not exceeding *ca.* 0.064 μg (*e.g.*, for aldicarb, 92% recovery) for each compound and for the water type studied in this paper.

One other inference from both Tables II and III involves the recoveries obtained by loading similar amounts of pesticides. If we compare the recoveries obtained by preconcentrating 20 ml of water containing 5 μg/l with those achieved by preconcentrating 500 ml of water spiked with 0.2 μg/l, 0.1 μg of each pesticide was loaded in both

cases. The recoveries obtained were better using 20 ml of water for almost all the compounds, except metolachlor, which, owing to its high breakthrough volume (>150 ml), featured identical recoveries with both water volumes and concentrations. Other compounds had recoveries of 85% *vs.* 68 (3-ketocarbofuran) and 92 *vs.* 66% (chlortoluron) for 20 ml against 500 ml of water at the same pesticide concentration. These observations are consistent with the results obtained by loading 1 μg of chlortoluron onto a C-18 precolumn, with reported recoveries varying from 100 to 15% for water volumes of 10 to 500 ml, respectively [34]. From Tables II and III we can conclude that the recommended volumes for preconcentration of the different analytes will be 50 ml and 350 ml, for 5 and 0.2 μg/l spiked pesticides, respectively, since they are the minimum volumes required to achieve acceptable recoveries (>70%) for 10 and 8, respectively, of the studied analytes. Recently [37], 150 ml of enriched Rhine river drinking water was preconcentrated on-line on PLPR-S cartridges with various spiking levels of pesticides; it was impossible to determine 0.1 μg/l concentrations for the early eluting compounds (10–35 min), even at such high preconcentrated water volume. As noted earlier, this can be ascribed to the higher trapping capacity of the membrane C-18 disks relative to polymeric material.

Our on-line system containing 10 membrane extraction disks of 4.6 mm diameter performed well in the analysis of at least ten (six) 350-ml HPLC (drinking) water samples. Since each 47-mm diameter disk provides *ca.* 40 disks of 4.6 mm diameter the cost per analysis is relatively low.

LC–post-column fluorescence detection

By using the on-line system described in the Experimental section, 10 ml of HPLC and drinking water spiked with the carbamate pesticides and their TPs at a concentration of 0.2 μg/l were preconcentrated. Fig. 3 shows the different chromatograms obtained following LC–post-column fluorescence detection of spiked HPLC water (A), drinking water (B) and a drinking water blank (C). Two major conclusions can be drawn: (i) only N-methylcarbamates and O-(methylcarbomyl) oxime pesticides can be detected by this

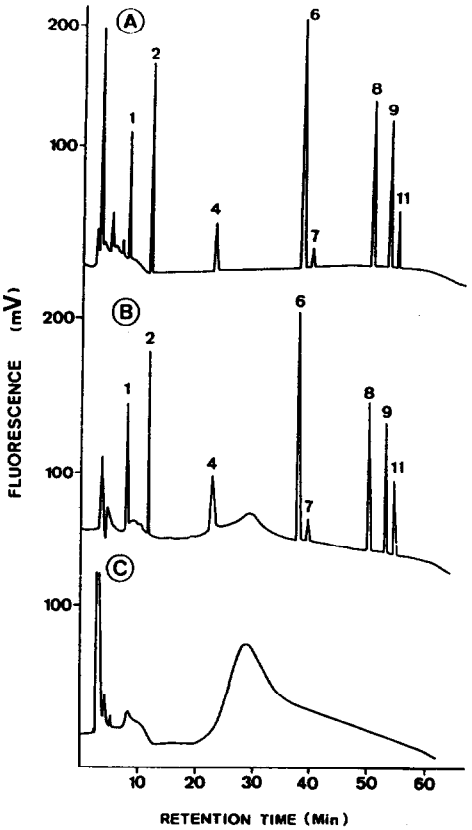

Fig. 3. LC-post column fluorescence detection chromatograms obtained after on-line preconcentration using C-18 Empore extraction disks of 10 ml of (A) HPLC water and (B) drinking water both spiked at 0.2 μg/l with the pesticide mixture indicated in Fig. 2, and (C) a drinking water blank. Other experimental conditions as in Fig. 2.

technique, which allows 8 of the 13 compounds studied to be determined; and (ii) despite the low breakthrough volumes of aldicarb sulfoxide and aldicarb sulfone (see Table I), the system permits an excellent determination of these compounds at such low concentration level, with recoveries higher than 70% (see Table IV). Fig. 3B and C also shows the interferences from the drinking water matrix, which were not observed with the LC–rapid scanning UV detection. Since the level of interference corresponds to an amount lower than 0.02 μg/l level, they do not represent a problem in the analysis of the carbamates or their TPs being attributed to either water and/or the disk matrices. Surprisingly, they were never reported in connection with water analyses, *e.g.*, well water [29,30]. Since the

TABLE IV

AVERAGE % RECOVERY AND RELATIVE STANDARD DEVIATION (R.S.D.) OF PESTICIDES IN DRINKING WATER

On-line SPE with 10 C-18 Empore extraction disks of 4.6 mm O.D. diameter at a flow-rate of 2 ml/min. Spiking level: 0.2 μg/l. $N = 7$ for each pesticide. Determination by LC post-column fluorescence detection. Water volume: 10 ml.

Compound	Av. (%)	R.S.D. (%)
Aldicarb sulfoxide	73	6
Aldicarb sulfone	71	3
3-Hydroxycarbofuran	73	5
Aldicarb	94	5
3-Ketocarbofuran	74	8
Carbofuran	95	6
Carbaryl	78	3
1-Naphthol	73	5

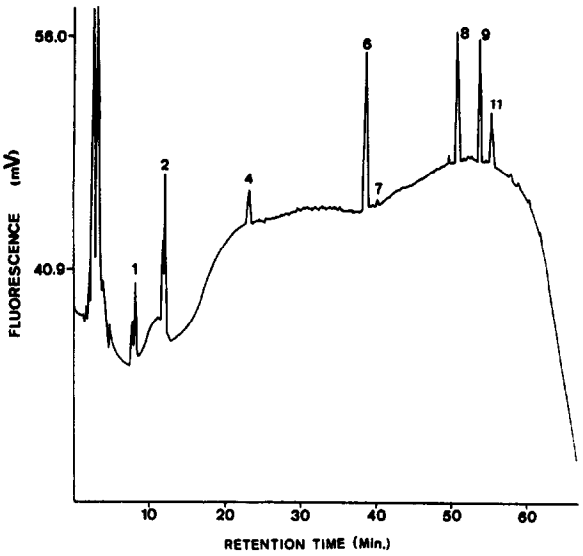

Fig. 4. LC–post-column fluorescence detection chromatogram obtained after preconcentration on C-18 Empore extraction disks of 10 ml of drinking water spiked at 0.01 μg/l with the pesticide mixture indicated in Fig. 2. Other experimental conditions as in Fig. 2.

proposed system also detects compounds with native fluorescence, (*e.g.*, naphthol), matrix interference may arise from such compounds (*e.g.*, humic substances) which were detected by LC–diode array in analyzing surface Rhine river waters [20,37]. The interferences noticed in the fluorescence signal have also been detected in previous studies of preconcentration of drinking water samples [38]. In any case, no problems were observed for the determination of the studied carbamate pesticides or their TPs, as can be seen in the traces of Fig. 3B and more clearly in Fig. 4, where 10 ml of drinking water sample spiked at 0.01 μg/l level was analysed.

Limits of detection

Table V shows the different limits of detection (L.O.D.s) obtained by using the on-line systems described in this paper either followed by rapid scanning UV–VIS detection or by post-column fluorescence. The L.O.D.s were calculated by using a signal-to-noise (S/N) ratio of 3 and assuming that 1 cm was the minimum peak height that could be measured with reasonable confidence. We shall note that, in general, for achieving L.O.D.s of *ca.* 0.01 μg/l we need to preconcentrate either 350 or 10 ml of water, for rapid scanning UV–VIS or post-column fluorescence detection, respectively. This indicates the higher selectivity and sensitivity of the well established method based on post-column reaction with fluorescence detection for N-methylcarbamates and O-(methylcarbomyl)oxime pesticides. In Table V the L.O.D.s obtained with the on-line system proposed in this paper are compared with those afforded by the US EPA method [30,31]. We should note that the L.O.D.s of the EPA methods are higher than those achieved in this work since NPS requirements lie in the low μg/l level, so there is no need to lower them further. An additional advantage of our method is that it is performed on-line whereas in the EPA method a direct injection of 500 ml is performed. Such large injection volumes can cause broad peaks and reduce resolution in early eluting compounds, which may interfere with some of the carbamate TPs. Also the L.O.D.s are somewhat better in ref. 30 than in ref. 31, which may have resulted from using a different fluorescence detector (in ref. 30 they used the same type as in this work, whereas in ref. 31 it was an older type of instrument, a Schoffel Model 970). From the results listed in Table V it is apparent that the LC–post-column fluorescence approach provides

TABLE V

LIMITS OF DETECTION (μg/l) AFTER ON-LINE PRECONCENTRATION

(A) 350 ml of drinking water followed by LC with rapid scanning UV–VIS at 220 nm and (B) 10 ml of drinking water followed by LC post-column reaction and fluorescence detection (C) according to US EPA method 531.1 using direct aqueous injection of 500 μl (ref. 31) or (D) 400 μl (ref. 30) at $S/N = 5$.

Compound	A	B	C	D
Aldicarb sulfoxide	5	0.008	2.0	0.4
Aldicarb sulfone	5	0.008	2.0	0.4
3-hydroxy-7-phenolcarbofuran	5	nd [a]	nd	nd
3-Hydroxycarbofuran	0.2	0.010	2.0	0.6
3-Ketocarbofuran phenol	0.2	nd	nd	nd
Aldicarb	0.03	0.005	1.0	0.2
3-Ketocarbofuran	0.03	0.040	ni [b]	ni
Carbofuran	0.02	0.005	1.5	1.5
Carbaryl	0.01	0.005	1.5	0.2
Chortoluron	0.01	nd	nd	nd
1-Naphthol [c]	0.01	0.010	ni	0.6
Isoproturon	0.02	nd	nd	nd
Metolachlor	0.01	nd	nd	nd

[a] nd = Not detected.
[b] ni = Not investigated.
[c] 1-Naphthol was measured by its native fluorescence.

much better L.O.D.s for the carbamate pesticides and their TPs that can be determined by this technique over LC–rapid scanning UV. The proposed method is especially recommended for the determination of aldicarb sulfoxide and aldicarb sulfone.

CONCLUSIONS

We assessed the use in the on-line approach of Empore extraction disks at different water volumes (from 10 to 1000 ml) in order to develop a method capable determining pesticides and some toxic TPs in drinking water at or below the concentrations required by the CEC-DWD (0.1 μg/l). From the results it was concluded that 350 ml of drinking water sample are needed to achieve a L.O.D. of 0.01–0.03 μg/l for the complete determination of the 8 compounds with on-line LC–rapid scanning UV detection.

The on-line preconcentration system was also coupled to LC–post-column fluorescence detection, thereby achieving L.O.D.s in the order of *ca.* 0.005–0.040 μg/l when preconcentrating 10 ml of drinking water containing 8 carbamates and their TPs. Empore extraction disks proved to have reasonably long lifetimes and to be fairly inexpensive since each conventional 47 mm disk provides *ca.* 40 4.6-mm disks, and hence various pre-columns can be prepared. The proposed method meets the requirements recently established by the DWD-CEC [1] and in this sense the method developed permits the determination of 10 pesticides and their TPs in drinking water samples at levels below 0.1 μg/l [1].

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