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Application of activated carbon membranes for on-line cleanup of vegetable and fruit extracts in the determination of pesticide multiresidues by gas chromatography with mass selective detection

Luis E. Sojo[a,*], Andrea Brocke[a], Julie Fillion[b], Susan M. Price[c]

[a]*ASL Analytical Services Laboratories, Ltd. 1988 Triumph St, Vancouver, B.C., Canada V5L-1K5*

[b]*Agriculture and Agri-Food Canada, Laboratory Service Division, Bldg #22, Carling Av., Ottawa, Ontario, Canada K1A-0C6*

[c]*3M New Products Department, Industrial and Consumer Sector, Research and Development, 3M Centre Bldg 220-9E-10, St. Paul, MN 55144-1000, USA*

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Abstract

The feasibility of using activated carbon membranes for the on-line cleanup of vegetables and fruits samples in the determination of pesticide multi-residues was investigated. The interactions of over one hundred pesticides, including organochlorine, organophosphorus and organonitrogen compounds, in various solvents and vegetable and fruit extracts with the activated carbon membranes were studied. It was found that in general pesticides containing benzene rings with small substituents interacted strongly with the carbon membranes when the pesticides were dissolved in acetone, acetonitrile or ethyl acetate. On the other hand, pesticides without benzene rings or with benzene rings containing bulky substituents showed little or no interaction with the carbon membranes when dissolved in the above mentioned solvents. Addition of toluene to solutions of pesticides in either acetone or acetonitrile was necessary to minimize these interactions. A simple cleanup procedure for fruits and vegetables, involving the filtering of a sample slurry in 25% toluene in acetonitrile through an activated carbon membrane, followed by concentration and injection into a gas chromatograph equipped with a mass selective detector was developed. Recovery data from spiked lettuce, green pepper, pear and lemon are presented as well as data from real samples. With a few exceptions, over one hundred pesticides were quantitatively (>80%) recovered using the novel procedure. © 1997 Elsevier Science B.V.

Keywords: Vegetables; Fruit; Carbon membranes, activated; Pesticides

1. Introduction

Screening methods for pesticide multi-residues in vegetables and fruits are necessary for the surveillance and identification of samples containing residue levels higher than maximum allowed values. The analysis of such samples must be rapid and accurate. Due to the complexity of the matrices involved, extraction is usually followed by cleanup before gas chromatographic analysis. While the separation and identification of over 200 pesticides and metabolites in fruits and vegetables can be effectively accomplished by GC–MS [1], the sample preparation and cleanup required for such analysis are still labour intensive and time consuming and

*Corresponding author.

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traditionally employ relatively large quantities of organic solvents [1–3].

Present day cleanup methods involve the use of off-line open column liquid chromatography with solid phases in the cartridge format for the removal of matrix co-extractives and interferences [1–4]. Although these techniques represent an improvement over traditional liquid–liquid partition procedures used in the past [5,6], they still employ relatively large quantities of solvent. With the exception of supercritical fluid extraction methods [7,8], the extraction and cleanup steps are usually separate, requiring concentration and or solvent exchange of the sample extract before cleanup [1–4].

It is desirable to simplify sample extraction and cleanup in order to speed the process, reduce the amount of solvent waste produced and reduce the cost of analysis. An alternative to liquid–liquid partition and open column liquid chromatography is the use of on-line extraction coupled with on-line solid phase cleanup. Such an approach has been successfully applied to water samples using solid phases in the cartridge format [9–11], but to our knowledge has not been applied to solid samples such as fruits and vegetables. Although solid phases in the cartridge format have been extensively used [9–11], there are still a few inherent problems in their application; such as, low solvent flow rates and channelling [12]. Recent advances in membrane technology, in particular the development of techniques to immobilize solid phases in Teflon membranes [13], have provided an alternative to the traditional cartridge format. With the exception of two studies [10,14], these have not yet been utilized in the on-line cleanup mode.

The on-line extraction and cleanup of solid samples for multi-residue analysis can be accomplished by forcing a sample slurry extract through an on-line solid phase in the membrane format as shown in Fig. 1. We considered three modes for performing on-line extraction and cleanup namely: Mode 1 – in which retention of matrix interferences on the solid phase while the analytes go through for further on-line concentration or separation; Mode 2 – in which retention of analytes occurs on the solid phase with the removal of interfering components to waste, followed by subsequent desorption of analytes with appropriate solvent for further separation and; Mode 3 – in which retention of both matrix components and analytes takes place on the solid phase with subsequent desorption of analytes with an appropriate solvent for further separation and detection. These modes represent limiting cases and it is likely that the resolution of some analytes–matrix combinations can be achieved by using more than one of the above modes, depending on the nature of the matrix interferences and the target analytes and their interaction with the solid phase material.

This paper then reports on the feasibility of using activated carbon membranes and the above mentioned Mode 1, for the on-line extraction and cleanup of vegetable and fruit samples for the determination of over 100 pesticide residues by gas chromatography using mass selective detection.

2. Materials

All pesticides standards were purchased from Chem Service (West Chester, Pa, USA) as neat

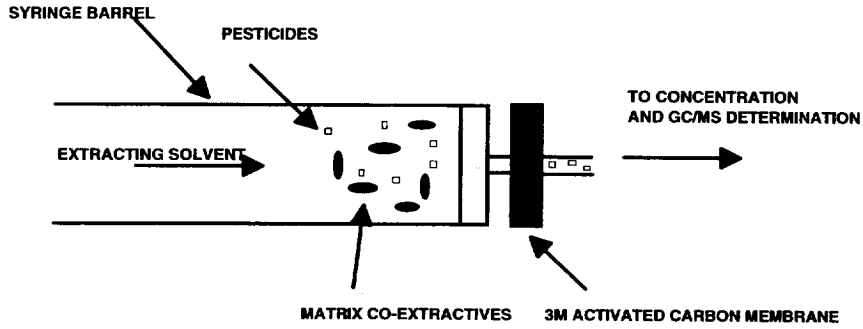

Fig. 1. On-line extraction–cleanup of vegetable slurries.

compounds. Table 1 lists the pesticides used in this study. All solvents, including acetonitrile, acetone, ethyl acetate, methanol and toluene were pesticides grade and purchased from BDH (Vancouver, Canada).

Activated carbon membranes (400–450 mg and 22 mm wide), made of acid-washed coconut charcoal immobilized on a Teflon mesh with approximately 90% (w/w) of carbon per membrane, a surface area greater than 1000 m^2/g and a nominal particle size of 15–20 μm were a gift from the 3M Company, New Products Department (St Paul, MN, USA). The membranes were cleaned and conditioned by flushing them with toluene before use.

Vegetables samples, including romaine lettuce, green peppers, carrots, pears and lemons, were purchased from a local market and were analyzed for incurred residues according to the method described in Ref. [1]. No incurred residues were detected in these matrices.

3. Experimental

Two types of experiments were performed. The first consisted of passing pesticides solutions through the activated carbon membranes as follows: a 50 ml glass syringe containing 25 ml of the pesticide solution was fitted to a filter holder containing the conditioned activated carbon membrane as shown in Fig. 1. The pesticide solution was filtered through the membrane and the eluent was collected. Air was then passed through to the membrane to ensure quantitative recovery of the pesticide solution. All eluents were combined, dried with sodium sulphate, concentrated under vacuum, spiked with internal standards and analyzed by GC–MS. Various solvents were tested in the above scheme including acetonitrile, acetone, ethyl acetate and 25% toluene in acetonitrile.

The second type of experiments involved the use of vegetable and fruit slurries that had been previous-

Table 1
List of pesticides determined in the present study

Organochlorine compounds				*Organonitrogen compounds*		
Alachlor	Dichlofenthion	Methoxychlor	trans-Permethrin	Aspon	Hexazinone	Triadimefon
Aldrin	Dichlofluanid	Mirex	Vinclozolin	Atrazine	Malaoxon	Triallate
alpha-BHC	Dichlorobenil	Nitrofen		Benfluralin	Metolachlor	Trifluralin
beta-BHC	Dicofol	*o,p*-DDT		Cyanazine	Metribuzin	
Captan	Dieldrin	*p,p*-DDE		De-ethyl atrazine	Prometryn	
Chlorfenson	Endosulfan	*p,p*-DDT		Desmetryn	Propazine	
Chlorobenside	Endosulfan-I	Procymidone		Diphenylamine	Quinalophos	
Chloropropham	Endosulfan-II	Pronamide		Eptam	Simazine	
cis-Chlordane	Endrin	Quintozene		Ethalfluralin	Terbutryn	
cis-Permethrin	Folpet	Tecnazene				
Dachtal	HCB	Tetradifon				
Diallate-e	Heptachlor	Tolyfluanid				
Diallate-z	Lindane	*cis*-Permetrin				

Organophoshorus compounds			
Acephate	Diclorvos/Naled	Malathion	Sulfotep
Azinphos-ethyl	Dicrotophos	Methidathion	Terbufos
Bromophos	Dimethoate	Mevinphos	Tetrachlorovinfos
Bromophos-ethyl	Dioxathion	Omethoate	Triadimefon
Carbofenthion	Disulfoton	Parathion	
Chlorfenvinphos	EPN	Parathion-methyl	
Chloropyriphos	Ethion	Phorate	
Chlorothiophos	Fenchlorophos	Phosalone	
Chlropyrifos-methyl	Fenitrothion	Phosmet	
Diazinon	Fenthion	Pirimiphos-ethyl	
Dichlofenthion	Fonophos	Pirimiphos-methyl	
Dichlofluanid	Isofenphos	Profenophos	
Dichlorobenil	Malaoxon	Quinalophos	

ly spiked in house. The spiked samples were prepared by adding appropriate amounts of a multi-pesticide spiking solution in acetone to a 2 g sample of vegetable or fruit homogenate to give a nominal concentration of 0.2 ppm for each analyte. The samples were then mixed with 1 g of sodium chloride and with 15 ml of extracting solvent. The resulting slurry was then filtered through the activated carbon membrane as described above. An extra 5 ml of solvent was then used to rinse the syringe and the membrane. The combined eluents were dried with sodium sulphate, concentrated under reduced pressure, spiked with internal standards, and then analyzed by GC–MS. Various matrices were tested, including romaine lettuce, green peppers, pears and lemons. In addition, in order to check the efficiency of the activated carbon membranes to retain unwanted matrix components, unfortified matrix slurries were prepared in the various solvents and passed through the membranes.

Fruit and vegetable samples were also analyzed following the method described in Ref. [1]. Briefly, spiked samples (20 g) were blended with acetonitrile (100 ml) after addition of salt and centrifuged. An aliquot of the supernatant (10 ml) was concentrated to approximately 1 ml and cleaned up on a 2 g carbon/celite (4:1) cleanup column. Elution of pesticides off the cleanup column was carried out with 50 ml of 25% toluene in acetonitrile. The cleaned extract was then concentrated to near dryness, solvent exchanged to acetone and after the addition of internal standards was analyzed by GC–MS.

The on-line extraction and cleanup procedure was also used to analyze four green pepper samples which had been previously spiked at the Laboratory Service Division (LSD) of Agri-Food and Agriculture Canada. These samples were also analyzed by LSD using the EnviCarb-C_{18} column combination for cleanup step and by our laboratory using the traditional carbon/celite cleanup step [2]. In addition samples containing incurred residues were also analyzed by the three procedures.

4. Gas chromatographic and mass spectrometric conditions

Gas chromatographic analysis was carried out on HP 5890 series II gas chromatograph, HP 5970 or 5971 mass spectrometer and HP 7673 liquid autosampler combination equipped with a DB-1701 capillary gas chromatographic column (30 m×0.25 mm I.D. and 2.5 μm film thickness) from Supelco (Oakville, Ontario, Canada). The oven was temperature programmed as follows: initial temperature 70°C, held for 1.8 min, heated to 150°C at 25°C/min, heated to 250°C at 2°C/min, heated to 280°C at 10°C/min, and held at 280°C for 5 min. Selected masses for target and qualifier ions for each compound were as per Ref. [1]. A HP-UX chemsystem/target software datasystem was used for data acquisition and management.

5. Results and discussion

5.1. Selection of solvent system for on-line extraction and cleanup

Table 2 shows the results of passing the pesticides solutions prepared in the various solvents through the activated carbon membranes. The recovery data were expressed as the percent recovered in the eluents. In general pure acetonitrile gave the lowest recoveries, followed by ethyl acetate and acetone, while 25% toluene in acetonitrile gave the highest recoveries. This dependency of the recovery values on solvent composition reflects the fact that pesticide–membrane interactions are sensitive to solvent–pesticide and solvent–carbon interactions. Because of the large number of pesticides with different polarities and functionalities it is difficult to characterize each of these interactions. But some generalizations are possible.

Some pesticides which were not recovered at all when dissolved in acetonitrile showed significant improvement when dissolved in acetone. For example, tecnazene and diphenylamine were recovered at 2 and 3%, respectively using acetonitrile, while their recoveries using acetone were both 36%. Similarly, quintozene which was not recovered using acetonitrile, gave 19% recovery using acetone. Although acetone gave the best overall recoveries of the neat solvent systems, a number of pesticides still exhibited unacceptable recoveries (<80%). For these compounds further elution and or membrane backflushing with a stronger solvent may be required.

Table 2
Recoveries of pesticides from neat solvents mixtures after filtering through an activated carbon membrane

Pesticide	Acetone		Acetonitrile		Ethyl acetate		25% Toluene[a]	
	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.
Organochlorines								
Dichlobenil	49	10	13	2	35	20	102	8
Tecnazene	36	6	2	1	40	18	71	3
Hexachlorobenzene	1	5	0	20	1	12	16	5
Diallate e	101	6	77	12	88	8	98	8
Diallate z	105	7	77	2	89	15	98	5
Chlrorpropham	85	5	35	22	74	10	95	5
α-BHC	92	8	61	6	92	12	98	4
Quintozene	20	5	0	9	162	19	50	5
Lindane	90	9	57	10	86	15	96	10
Heptachlor	96	4	72	19	89	25	94	4
Dichlofenthion	73	2	16	4	72	19	90	5
Pronamide	90	10	54	18	79	35	99	10
Aldrin	98	3	80	2	93	12	100	8
Alachlor	95	3	78	7	89	17	96	2
Vinclozolin	93	8	70	0	89	30	98	1
β-BHC	95	4	58	7	85	13	98	2
Dicofol	90	5	49	1	72	19	91	2
Dacthal	88	13	53	13	88	44	100	1
Dichlofluanid	94	3	81	0	90	13	98	1
Chlorbenside	6	4	2	1	1	28	35	6
Endosulfan-I	91	6	71	25	86	15	98	1
cis-Chlordane	98	5	78	1	90	5	98	2
Tolyfluanid	91	7	72	2	88	14	95	30
p,p-DDE	77	5	9	10	84	50	87	1
Captan	81	19	59	8	95	29	103	2
Folpet	nd	5	2	1	nd		36	2
Dieledrin	97	6	81	1	94	37	102	1
Procymidone	82	7	52	1	80	28	101	7
Endrin	91	6	70	2	93	40	101	0
Chlrofenson	39	3	1	1	42	9	91	1
Nitrofen	8	9	nd		8	5	49	2
o,p-DDT	89	4	41	20	73	26	90	12
Endosulfan-II	97	2	73	5	83	26	93	2
p,p-DDT	84	2	25	9	87	29	90	3
Mirex	113	8	71	2	90	0	98	1
Endosulfan sulfate	92	7	78	0	92	19	101	3
Methoxychlor	72	7	16	2	66	16	88	1
Tetradifon	60	4	9	3	67	8	91	3
cis-Permethrin	52	5	1	8	56	13	79	1
trans-Permethrin	52	3	1	7	55	74	79	1
Organonitrogen								
Eptam	105	5	87	2	106	15	107	8
Diphenylamine	36	8	3	2	4	25	93	1
Ethalfluralin	100	4	85	1	85	42	88	5
Trifluralin	101	9	89	2	83	29	91	2
Benfluralin	101	8	87	13	85	15	92	10
Des-ethyl Atrazine	97	4	78	5	nd		nd	
Triallate	92	6	57	7	87	12	96	2
Propazine	98	7	83	4	92	10	98	10
Atrazine	96	6	74	5	90	11	98	15
Simazine	96	4	74	3	82	10	97	1
Desmetryn	87	5	53	1	70	11	89	2
Prometryn	95	10	73	2	82	19	94	8
Metribuzin	98	10	83	12	88	14	92	2
Terbutryn	96	7	81	4	82	45	96	2

Table 2. Continued

Pesticide	Acetone		Acetonitrile		Ethyl acetate		25% Toluene[a]	
	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.
Metalaxyl	79	9	69	13	92	4	98	1
Aspon	99	6	85	2	91	26	99	2
Metolachlor	95	5	76	2	90	5	98	5
Triadamefon	94	4	68	1	89	23	92	2
Quinalophos	41	8	2	2	32	14	82	2
Cyanazine	90	6	75	5	88	33	101	1
Hexazinone	93	6	80	1	85	13	99	2
Organophosphorus								
Dichlorvus/Naled	96	7	99	9	102	5	100	3
Mevinphos	95	6	92	0	nd	21	99	3
Acephate	93	32	94	14	79	24	90	3
Demeton	94	6	82	2	nd		nd	
Phorate	100	6	76	1	100	26	95	28
Sulfotep	101	10	91	6	91	31	98	1
Sulfotep	101	10	91	6	91	31	98	1
Omethoate	2	7	87	4	68	25	84	10
Terbufos	9	8	70	6	2	5	95	10
Diazinon	97	6	72	2	89	21	98	4
Fonophos	79	7	59	7	64	30	93	9
Dicrotophos	93	8	91	3	85	30	95	3
Dioxathion	85	8	28	6	77	40	93	2
Disulfoton	9	10	68	15	47	28	97	10
Dichlofenthion	73	10	16	14	72	25	90	3
Dimethoate	94	10	84	2	77	35	97	2
Chlorpyriphos-methyl	54	9	7	1	56	4	87	3
Fenchlorophos	49	14	4	14	54	12	82	5
Pirimiphos-methyl	88	13	41	9	84	66	93	6
Chlorpyriphos	67	10	9	8	67	34	84	30
Parathion-methyl	56	8	1	7	49	49	81	19
Malaoxon	73	8	79	5	87	21	96	11
Fenthion	nd		nd	1	15	5	92	3
Bromophos	42	8	2	2	28	43	77	1
Pirimiphos-ethyl	91	9	44	0	86	33	94	5
Malathion	92	7	74	4	87	17	96	6
Fenitrophion	72	9	21	3	48	3	77	8
Parathion	70	10	15	2	46	12	74	2
Tetrachlorovinphos	95	9	77	1	52	28	72	7
Bromophos-ethyl	50	11	2	4	54	18	73	8
Quinalophos	41	12	2	4	32	29	92	8
Isofenphos	95	9	66	3	74	3	95	4
Chlorfenvinphos	87	9	60	1	79	9	101	7
Methidathion	69	11	24	2	70	32	95	14
Profenophos	53	11	4	4	59	27	80	3
Chlorthiophos	50	11	2	5	47	40	80	5
Ethion	85	12	37	5	77	16	90	15
Carbofenthion	37	9	3	8	28	16	73	15
EPN	15	7	nd		21	10	71	1
Phosmet	7	9	nd		5	10	68	2
Phosalone	19	11	nd		15	37	64	8
Azinphos-methyl	8	11	nd		4	13	66	9

[a] 25% toluene in acetonitrile.

% Rec. is the average of the triplicate results. Pesticides are listed in chromatographic elution order within each class. Naled was determined as dichlorvos due to thermal degradation in the injection port, nd=not detected.

The results using ethyl acetate were in-between those obtained using acetonitrile and acetone. Ethyl acetate was tested to see the effect of a solvent with a lower polarity than acetone and acetonitrile on the recoveries. Ethyl acetate has a polarity index of 4.4 in comparison to 5.8 for acetonitrile and 5.1 for acetone [19]. Because of the wide range of polarity and solubility exhibited by the compounds investigated, it is not surprising that a single neat solvent system cannot provide acceptable recoveries.

Invariably, all of the compounds which were significantly retained on the membranes (lower recoveries from neat solvents) contained at least one benzene ring in their molecular structures. For example, captan and folpet have very similar structures; they both have the same level of chlorination and the same type of functional groups, but captan contains a cyclohexene ring in contrast to folpet which contains a benzene ring. Captan is recovered using acetone at 87% while folpet is only recovered at 38%. The same observation is valid for both pesticides in acetonitrile; captan is recovered at 59% while folpet is recovered at 2%. Another example of this effect is the retention of alpha-BHC, beta-BHC and lindane and HCB. The first group of compounds has a hexachlorinated cyclohexane ring while HCB is a hexachlorinated benzene ring. In acetone, alpha-BHC, beta-BHC and lindane were recovered at 92, 95 and 90%, respectively, while HCB was recovered at 1%. Similar results were found when using acetonitrile (see Table 2).

Increasing levels of chlorination also decreases recoveries from neat solvents. This is an obvious consequence of the increase of the compound's solvophobicity with increasing chlorination level. A typical example is tecnazene and quintozene. The first compound has four chlorine atoms surrounding the nitrobenzene ring, while the second one has five. Tecnazene is recovered at 37% while quintozene is recovered at 19% in neat acetone. This effect is even more evident in acetonitrile. In this case tecnazene is recovered at 2%, while quintozene is not recovered at all.

The presence of a benzene ring is not necessarily indicative that the compound will show low recoveries. Bulky substituents near to or located on the benzene ring tend to increase recoveries (reduced retention on the carbon membranes), as in the example of trifluralin, benfluralin and ethalfluralin, all compounds with benzene rings substituted in various ring positions along with bulky functional groups. Their recoveries in neat acetone and neat acetonitrile are both above 80% (see Table 2). Another striking example is HCB and dacthal. The structure of dacthal is similar to HCB with the exception that two methyl-acetate groups replace chlorine atoms at the 1 and 4 positions of the benzene ring of the HCB molecule. The recoveries of dacthal in acetone, acetonitrile and ethyl acetate are 88, 53 and 72%, respectively, while HCB cannot be recovered at all.

Compounds with two benzene rings joined by a simple linkage such as oxygen or sulphur atoms are also poorly recovered. Nitrofen, a compound containing two benzene rings joined by an oxygen atom exhibited a recovery of 8 and 0% in acetone and acetonitrile, respectively. On the other hand, dicofol which also has two benzene rings joined in this case by a carbon atom containing bulky $-CCl_3$ and $-OH$ groups was recovered at 49 and 90% in acetonitrile and acetone, respectively. Another example of this effect can be seen in the results obtained for the *p,p*-DDT and *o,p*-DDT which also have a bulky $-CCl_3$ group attached to the carbon atom linking the two benzene rings. The recoveries for *p,p*-DDT and *o,p*-DDT in acetone were 84 and 89%, respectively.

These observations point to the widely reported fact that some activated carbon materials are quite selective towards compounds containing electron donating groups [15]. They also indicate the importance of stearic factors. Although not graphitic, the carbon in the membranes seems to behave as a graphitized carbon with selectivity towards compounds rich in electrons and those possessing stearically flat benzene structures. The interactions of the pesticides molecules with this type of carbon seem to be controlled, to a certain extent, by the presence of bulky substituents at or near the benzene rings, which may hinder access to sorption sites deep in the carbon particles within the membrane teflon mesh. This selectivity towards compounds containing benzene rings suggest that solvent mixtures involving aromatic solvents may provide better recoveries than neat solvents.

Table 2 also lists the recoveries of all pesticides from mixtures of 25% toluene in acetonitrile. With a few exceptions, such as folpet and demeton for which quantitation was not reliable, the recoveries of most pesticides were quantitative (>80%). Nitrofen and chlorbenside still gave low recoveries in this solvent system (see Table 2), but their values were significantly improved in comparison to the results obtained with the neat solvents. Results using 25% toluene in acetone (not shown) were quite similar to those using 25% toluene in acetonitrile.

We selected 25% toluene in acetonitrile to test the

cleanup method for the simple reason that this solvent system is also employed in one of the standard methods for pesticide extracts cleanup using carbon/celite columns [1], and it provided a point of comparison between both procedures. Toluene is likely to interact with the active sites on the carbon membranes, allowing the pesticides to go through the membrane unretained as is expected when the membranes are used in Mode 1. The size and electronic distribution of toluene makes it ideal for blocking sorption sites on the carbon, which otherwise would interact with the target pesticides.

6. Effects of matrix type on the recovery of pesticides by on-line extraction–cleanup

Before carrying out the extraction and cleanup of any of the fruits and vegetable samples, the efficiency of the carbon membranes in retaining unwanted matrix components was tested in the same solvent systems used in the previous tests. It was found that for all solvents tested including 25% toluene in acetonitrile, up to 15 ml of a 0.2 g/ml vegetable or fruit slurry could be filtered through a 22 mm carbon membrane before breakthrough of coloured material was detected. The presence of colour was used as an indicator of matrix components breakthrough.

The recovery of pesticides from the various matrices using 25% toluene in acetonitrile as optimum solvent system are listed in Table 3. Recoveries using the carbon/celite column methods are also included for comparative purposes. Each matrix was extracted and analyzed in triplicate. The membrane procedure gave similar recoveries for all pesticides in comparison to the carbon/celite column cleanup method for the matrices studied. The recoveries from spiked lettuce samples were lower than those for the other matrices, regardless of the cleanup method.

The low recoveries from spiked lettuce may be due to formation of complexes with some components in the lettuce matrix which may be retained on the carbon membrane surface, but also due to interferences still present in the extracts after cleanup, making it difficult to quantify some analytes. Figs. 2 and 3 show chromatograms for two of the spiked matrices and real samples analyzed in the present study. It can be seen that the green pepper extract shows a cleaner chromatogram in comparison to that of the lettuce extract. Lettuce extracts may require further cleanup with a second membrane. Matrix effects on the gas chromatographic response of some analytes were compensated for by calibrating the mass spectrometric detector responses with a standard solution prepared by spiking known concentrations of the analytes into the appropriate clean matrix extract [16]. This extract was prepared following the same procedure as for the samples.

It is important to note that the sample size for the membrane method was 2 g as opposed to the carbon/celite cleanup method which uses a 50 g sample. There is an approximately ten-fold reduction in solvent use in the membrane method in comparison to the carbon/celite column method.

7. Recovery from spiked green peppers

Further tests of the procedure were carried out by analyzing four spiked green peppers samples. These samples were prepared by the Laboratory Services Division (LSD) of the Department of Agriculture in Ottawa and were analyzed in our laboratories using the carbon membrane and the carbon/celite cleanup procedures. The samples were also analyzed by LSD using the C_{18}/EnviCarb cleanup method. These last two procedures use an off-line extraction employing 100 ml of acetonitrile per 50 g of sample and a column cleanup step using carbon/celite and C_{18}/EnviCarb columns combinations, respectively.

The percentage recoveries of each pesticide found and determined by the three methods are shown in Fig. 4. In general, with the exception of vinclozolin, bromophos ethyl and tecnazene, recoveries of target compounds using the membrane cleanup method were comparable to those obtained by LSD using the EnviCarb/C_{18} cleanup method and by the carbon/celite cleanup method. The pesticide quintozene was found by all methods in sample No. 3, but quantification of extracts using both carbon/celite and the carbon membrane cleanup methods ware not reliable for comparison. This was not due to the cleanup methods themselves, but to calibration problems. Having said that, the differences among the values obtained using the C_{18}/Envicarb cleanup and both

Table 3
Comparison of carbon/celite (CC) and activated carbon membrane (CM) cleanup methods for pesticide residues in fruits and vegetables

Pesticide	Green peppers				Pears				Lettuce				Lemon			
	CC		CM		CC		CM		CC		CM		CC		CM	
	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.
Organochlorines																
Dichlorbenil	63	10	61	2	72	5	79	20	45	20	12	10	79	26	60	8
Tecnazene	65	6	72	1	75	15	79	12	52	18	27	43	86	14	72	4
HCB	nd	5	nd		nd		nd	2	nd	12	18	43	nd	3	48	5
Diallate-e	87	6	57	12	93	27	82	22	71	8	57	12	93	5	100	8
Diallate-z	73	7	47	2	85	10	75	6	70	15	56	10	77	12	86	5
Chloropropham	98	5	96	22	114	5	85	9	89	10	33	15	96	16	90	5
α-BHC	87	8	98	6	98	9	84	10	82	12	53	14	90	12	97	4
Quintozene	76	5	84	9	87	21	75	19	65	19	20	12	93	2	73	5
Lindane	79	9	87	10	90	21	32	4	80	15	27	13	93	12	124	10
Heptachlor	82	4	70	19	98	11	92	18	70	25	65	3	101	5	104	4
Dichlofenthion	98	2	85	4	109	38	88	2	88	19	52	25	97	5	96	5
Pronamide	92	10	83	18	105	22	86	10	77	35	55	10	107	12	114	10
Aldrin	92	3	82	2	105	15	88	3	86	12	81	14	86	10	99	8
Alachlor	106	3	90	7	112	14	90	3	87	17	73	12	94	6	112	9
Vinclozolin	107	8	75	10	115	2	74	8	95	30	54	11	98	7	81	7
β-BHC	90	4	110	7	91	12	80	4	92	13	44	43	97	5	94	8
Dicofol	150	5	96	1	98	12	63	5	209	19	63	11	88	15	85	9
Dacthal	111	13	38	13	120	12	84	13	101	44	62	11	98	17	96	8
Dichlofluanid	102	3	93	0	68	14	98	15	62	13	46	14	106	14	103	11
Chlorobenside	65	4	87	1	69	15	89	10	56	28	24	16	92	14	43	6
Endosulfan-I	106	6	73	25	124	14	95	12	96	21	79	15	98	45	107	11
cis-Chlordane	108'	5	85	1	118	11	93	19	97	5	80	66	93	13	103	2
Tolyfluanid	106	7	83	2	89	5	98	15	38	14	46	10	106	12	104	30
p,p-DDE	119	5	81	10	124	6	84	25	104	50	59	14	95	14	92	7
Captan	111	19	78	8	117	25	123	19	98	29	87	16	66	25	84	2
Folpet	nd	5	nd		nd		nd		nd		nd		116	5	115	2
Dieldrin	113	6	86	10	122	35	92	10	98	37	87	19	96	2	100	8
Procymidone	100	7	90	10	105	10	76	12	87	28	55	37	85	4	81	7
Endrin	102	6	78	2	110	2	94	19	87	40	86	23	95	8	129	10
Chlorfenson	108	3	81	10	115	21	87	15	98	9	35	14	97	14	74	1
Nitrofen	69	9	77	25	82	14	85	25	48	5	11	4	118	12	60	2
o,p-DDT	101	4	70	20	96	2	92	19	78	26	54	8	89	26	56	12
Endosulfan-II	104	2	156	15	106	2	93	35	85	26	55	3	93	2	67	2
p,p-DDT	99	2	87	9	105	15	85	12	73	29	32	0	112	43	11	3
Mirex	112	8	84	2	117	15	90	17	97	0	100	20	97	9	98	10
Endosulfan sulphate	92	7	84	10	101	13	94	27	77	19	71	20	92	6	92	3
Methoxychlor	107	7	70	2	112	11	75	10	90	16	50	14	93	17	78	13
Tetradifon	106	4	69	3	113	12	83	5	92	8	52	12	91	5	75	3
cis-Permethrin	95	5	68	8	103	6	85	9	82	13	53	16	103	12	87	12
trans-Permethrin	91	3	75	7	98	5	85	21	79	14	54	14	100	5	84	11
Organonitrogen																
Eptam	58	12	65	11	68	25	74	20	40	16	65	11	75	11	38	8
Diphenylamine	nd		54	15	2	15	84	12	3	15	17	27	64	12	79	10
Ethalfluralin	74	12	82	10	85	4	90	15	62	12	79	5	104	5	109	15
Trifluralin	81	5	15	15	94	6	94	14	68	14	89	15	100	8	108	2
Benfluralin	85	5	75	11	100	1	93	11	74	16	86	11	101	9	106	10
De-ethyl atrazine	104	12	82	11	115	18	85	7	86	15	54	15	nd	7	nd	
Triallate	95	10	70	15	105	16	83	8	86	18	60	8	93	1	98	2
Propazine	112	6	32	8	121	17	89	9	93	4	79	19	64	16	178	10
Atrazine	81	7	87	7	118	12	86	16	93	4	65	18	49	11	130	15
Simazine	104	5	81	9	114	11	78	5	88	4	47	19	nd		nd	
Desmetryn	101	15	128	5	112	11	77	14	84	7	49	13	nd		99	2
Prometryn	107	17	80	8	114	8	87	12	82	8	73	11	126	8	110	8
Metribuzin	106	14	71	6	114	47	110	13	96	9	84	8	100	5	121	2
Terbutryn	109	14	77	5	118	23	83	18	91	12	67	9	120	5	108	2

(*continued on page 150*)

Table 3. Continued

Pesticide	Green peppers				Pears				Lettuce				Lemon			
	CC		CM		CC		CM		CC		CM		CC		CM	
	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.	% Rec.	C.V.
Aspon	92	45	82	7	114	21	100	17	73	13	90	6	105	11	108	10
Malaxon	98	13	99	5	101	29	100	1	67	25	53	20	92	8	106	2
Metolachlor	111	12	105	4	118	11	91	8	91	14	78	17	97	2	101	5
Triadimefon	95	27	83	4	103	11	95	6	73	16	72	17	107	5	93	7
Quinalophos	100	10	89	15	106	18	91	7	80	6	47	14	86	4	95	7
Cyanazine	102	5	88	16	116	13	84	5	80	14	104	14	nd		nd	
Hexazinone	107	9	73	3	117	9	83	10	78	10	92	12	99	15	82	5
Organophosphorus																
Diclorvos/Naled	64	7	99	4	68	4	90	5	51	7	72	10	81	4	95	4
Dichlorobenil	63	13	61	5	72	3	79	4	45	5	12	7	79	3	60	3
Mevinphos	87	13	95	9	101	7	96	9	69	13	56	19	96	7	110	8
Acephate	43	14	83	6	57	15	84	21	31	29	31	41	0	15	0	18
Phorate	77	8	99	9	89	10	90	14	57	20	57	27	106	10	117	12
Sulfotep	77	8	82	6	107	20	94	28	63	39	90	55	99	20	115	24
Omethoate	69	12	74	11	83	15	78	21	52	29	29	41	0	15	0	18
Terbufos	81	17	132	17	100	20	93	28	65	39	63	55	110	20	113	24
Diazinon	100	8	81	8	116	31	90	43	88	61	70	85	101	31	109	37
Fonophos	87	12	89	7	103	6	112	9	74	12	49	17	103	6	99	8
Dicrotophos	97	8	80	5	116	4	96	6	76	8	51	11	96	4	0	5
Dioxathion	155	9	37	5	106	4	77	5	63	7	53	10	121	4	93	4
Disulfoton	72	9	77	39	101	10	88	14	67	20	37	28	112	39	99	47
Dichlofenthion	98	10	85	20	109	3	88	4	88	6	52	8	97	12	96	14
Dimethoate	94	9	89	11	105	10	103	14	67	20	52	27	168	38	119	46
Chlropyrifos-methyl	63	12	95	6	71	3	84	4	52	6	41	8	99	12	9	14
Fenchlorophos	82	8	77	10	81	11	138	15	62	22	67	30	160	42	143	51
Pirimiphos-methyl	102	43	80	39	113	15	85	21	85	29	56	41	131	33	126	40
Chloropyriphos	165	56	92	60	105	10	86	14	81	20	80	27	100	22	93	26
Parathion-methyl	139	9	176	2	74	15	90	21	48	30	37	41	127	33	115	40
Malaoxon	98	9	99	8	101	4	100	5	67	7	53	10	92	8	106	9
Fenthion	102	12	91	4	95	4	70	6	77	8	44	12	101	9	89	11
Bromophos	45	6	86	12	41	11	85	15	32	22	39	30	96	24	89	29
Pirimiphos-ethyl	106	10	76	2	113	18	88	25	88	35	59	30	138	24	111	29
Malathion	99	7	82	4	117	18	95	25	75	35	69	31	111	25	103	30
Dichlofluanid	102	4	93	5	68	5	98	7	62	9	46	13	106	11	103	13
Fenitrothion	61	12	92	13	77	6	91	8	47	11	33	15	114	12	98	15
Triadimefon	95	10	83	11	103	7	95	10	73	14	72	20	107	16	93	19
Parathion	79	8	86	11	89	5	96	8	52	11	66	15	116	12	101	14
Tetrachlorovinfos	107	10	70	10	105	5	88	7	87	9	46	13	100	10	113	12
Bromophos-ethyl	94	56	82	45	98	10	86	14	78	20	43	27	91	22	82	26
Quinalophos	100	8	89	7	106	7	91	9	80	13	47	18	86	15	95	18
Isofenphos	106	2	80	5	113	5	96	7	87	10	67	13	105	11	103	13
Chlorfenvinphos	110	12	86	16	103	11	86	15	70	22	57	30	97	24	94	29
Methidathion	82	6	71	8	98	12	94	17	65	24	39	33	160	26	109	32
Profenophos	91	8	87	10	95	11	92	15	65	22	36	30	99	24	92	29
Chlorothiophos	109	28	146	30	104	6	87	8	79	12	47	16	103	13	93	16
Ethion	90	9	80	11	94	12	99	17	61	24	55	33	146	26	126	32
Carbofenthion	92	3	49	12	97	4	95	6	61	8	45	11	163	9	119	11
EPN	57	10	89	8	82	5	91	7	36	10	31	14	194	11	92	13
Phosmet	58	9	81	19	63	17	86	24	39	33	21	47	179	37	92	45
Phosalone	68	9	69	25	74	11	89	15	47	22	28	30	208	30	112	36
Azinphos-ethyl	nd		73	20	nd		85	50	nd		38	35	nd		nd	

% Rec. is the average of the triplicate results. Spike level was at 0.25 ppm. Pesticides listed in chromatographic elution order within each class. Naled determined as dichlorvos due to thermal degradation in the injection port, nd=not detected.

the membrane and the carbon/celite cleanup procedures are likely to be due to interlaboratory variability.

Finally, we analyzed a series of samples provided by LSD which contained unknown incurred residues. The results are listed in Table 4. Again, the results using the membrane method were very close to those obtained at LSD using the EnviCarb/C_{18} method.

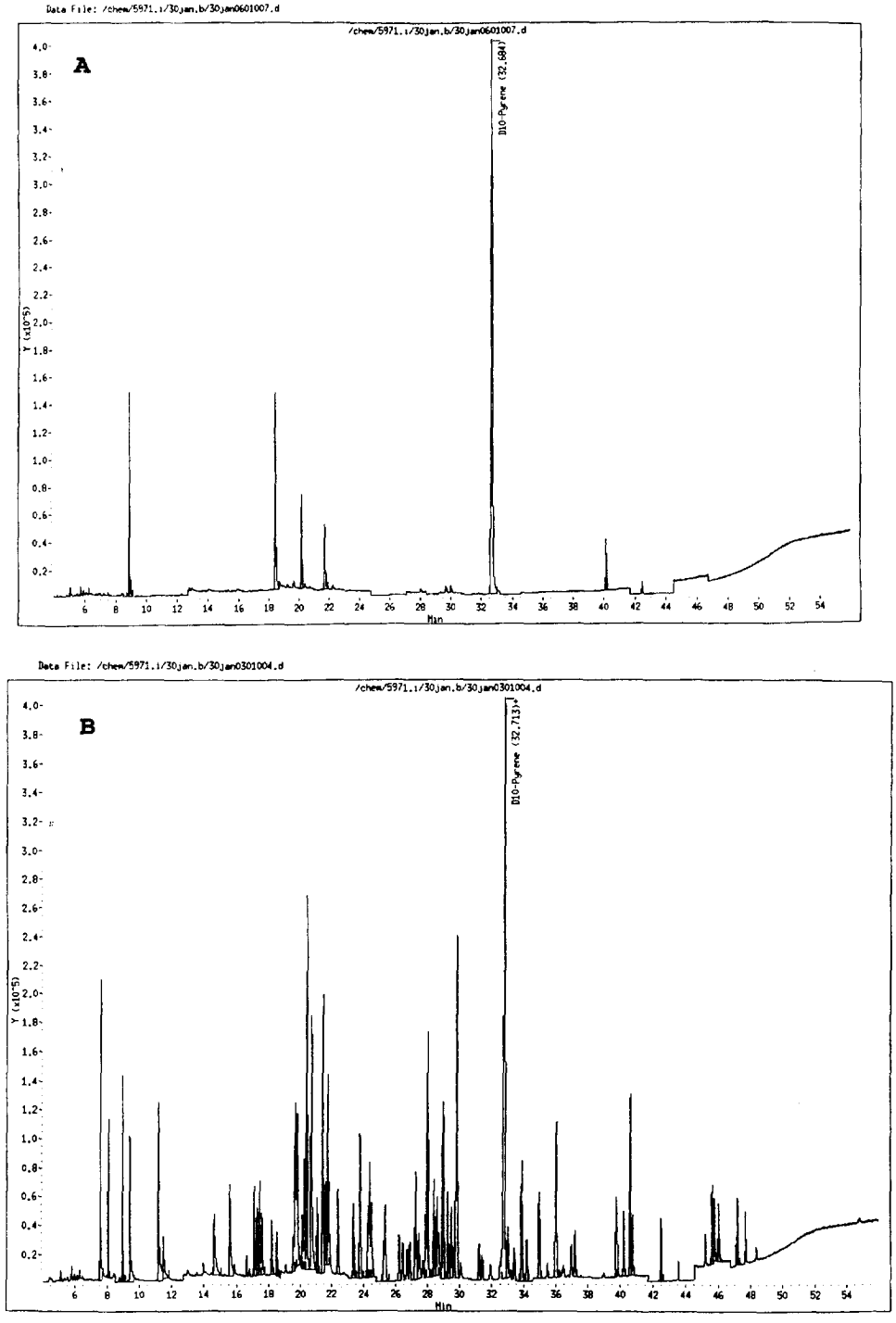

Fig. 2. Reconstructed ion chromatograms for (A) green pepper sample and (B) a spiked green pepper matrix after activated carbon mebrane clenaup. D10-Pyrene used as internal standard.

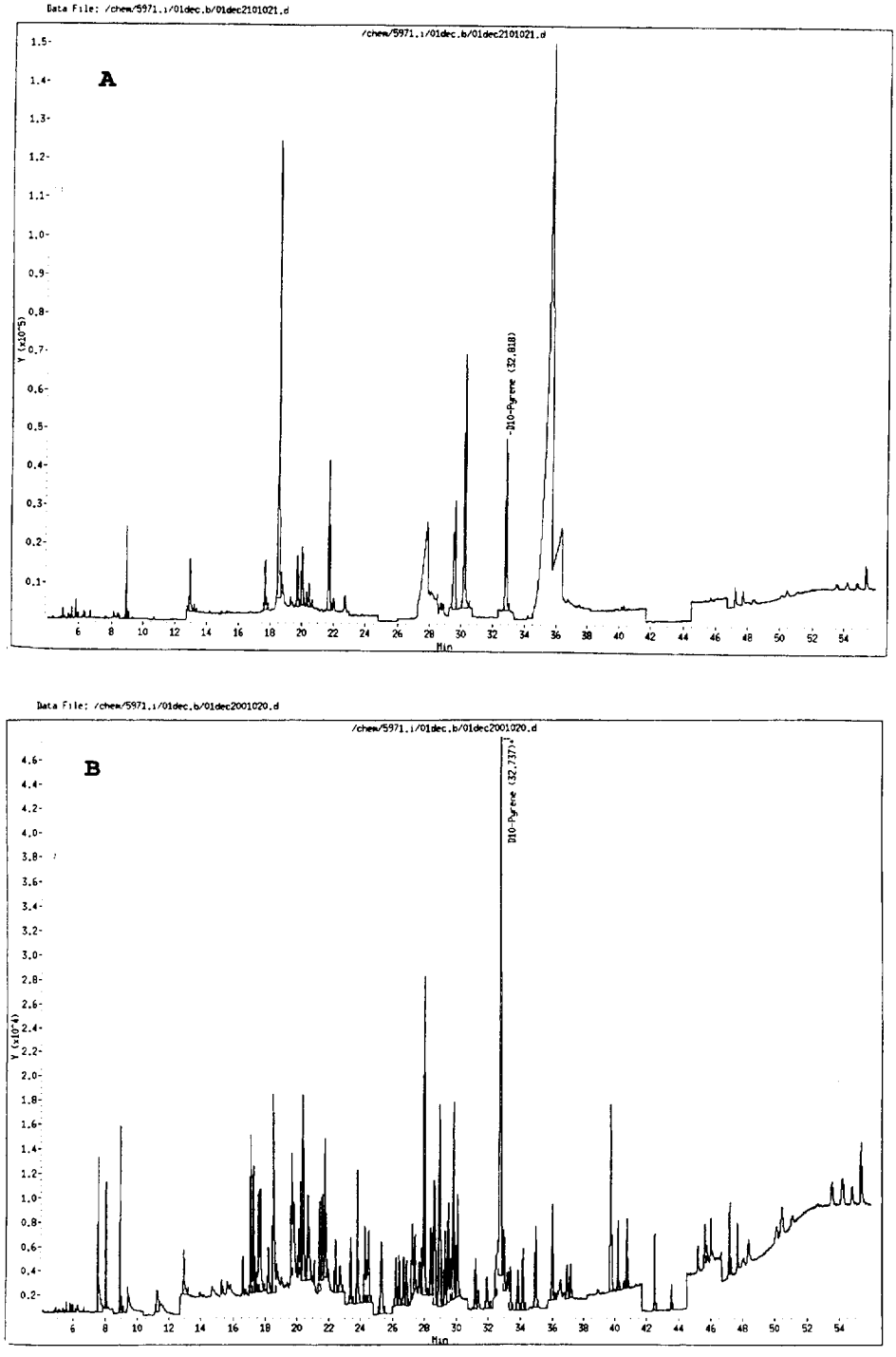

Fig. 3. Reconstructed ion chromatograms for (A) lettuce sample and (B) a spiked lettuce matrix after activated carbon cleanup. D10-Pyrene used as itnernal standard.

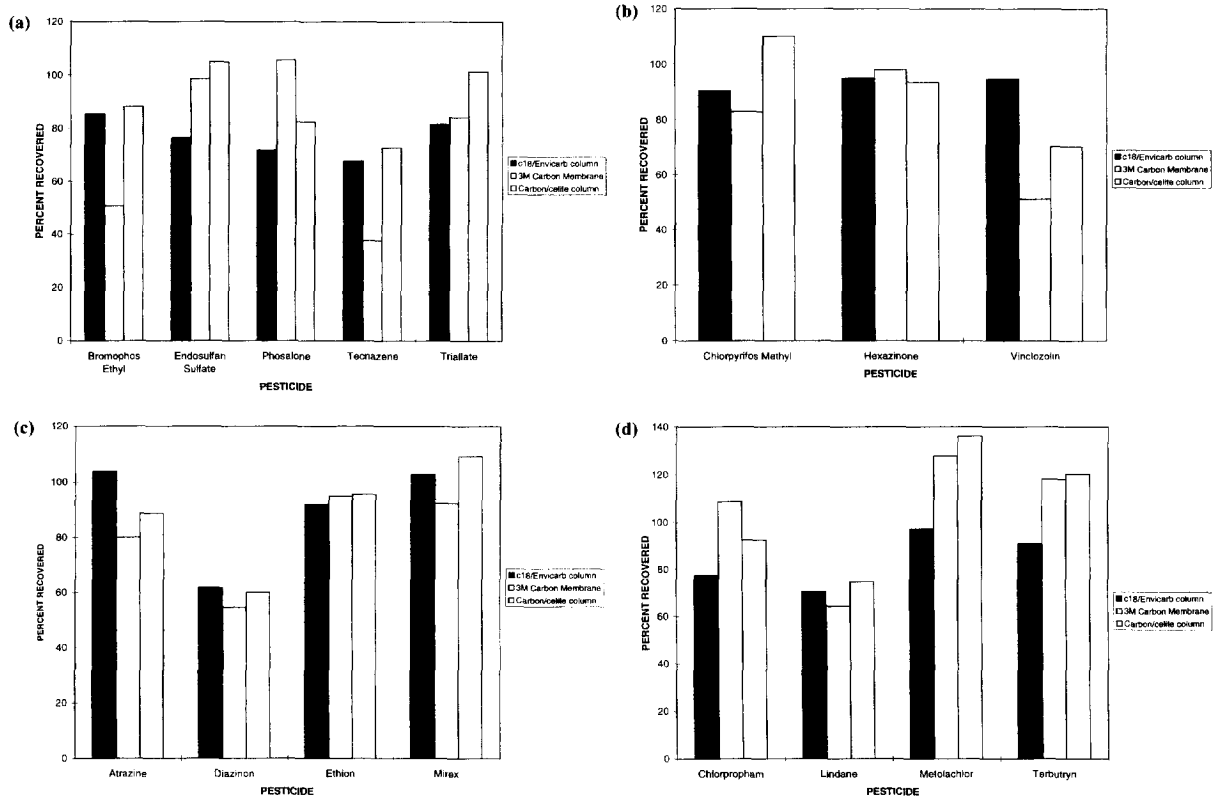

Fig. 4. Comparison of extraction–cleanup procedure on spiked green peppers. (a) Sample No. 1, (b) sample No. 2, (c) sample No. 3, (d) sample No. 4.

Table 4
Incurred pesticides residues determined by both column and membrane cleanup methods

Commodity	Pesticide	EnviCarb/C_{18} cleanup[a] (ppm)	Carbon membrane cleanup (ppm)
Romaine lettuce-A	*cis*-Permethrin	0.16	0.16
	trans-Permethrin	0.16	0.18
Romaine lettuce-B	*cis*-Permethrin	0.14	0.26
	trans-Permethrin	0.17	0.37
Romaine lettuce-C	*cis*-Permethrin	0.66	0.66
	trans-Permethrin	0.77	0.88
Romaine lettuce-D	*cis*-Permethrin	0.085	0.09
	trans-Permethrin	0.067	0.08
Green peppers-A	Acephate	0.68	1.08

[a] Analysis carried out at LSD Agri-Food and Agriculture Canada.

8. Conclusions

The feasibility of using activated carbon membranes as the solid phase for an on-line single step extraction–cleanup of fruits and vegetables for multiresidue screening was studied. A screening method based on this procedure was developed. This represents the first application of these membranes to the cleanup of vegetable and fruits extracts. The type of carbon present in these membranes seems to be able to discriminate between compounds containing benzene rings with small substituents from those with bulky substituents. The origin of this selectivity may be due to the presence of active sites on the carbon surface. It is speculated that these sites are electron deficient sites, which could be deactivated by exposure to reducing agents, such as ascorbic acid. This is a property that could be exploited in the cleanup of samples for the isolation of compounds such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from complex matrices such as soils and sediments.

Research is currently being carried out to understand solute(pesticides)–carbon membrane interactions, the effect of sample size including the determination of the membranes capacity for sample matrix interferences, the minimum sample size for reproducible quantitative results and the use of other available solid phases in the membrane format.

The procedure described here can be automated and placed on-line with GC–MS instrumentation if large volume loop-interfaces are employed, similar to what other investigators [17,18] have reported for interfacing on-line solid phase water extraction systems with gas chromatographs.

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