

Performance of an extraction disk in synthetic organic chemical analysis using gas chromatography–mass spectrometry

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ABSTRACT

Forty-three semi-volatile organic compounds listed in Method 525 of the U.S. Environmental Protection Agency were investigated by gas chromatography–mass spectroscopy in order to test the applicability of the Empore™ extraction disk in water analysis. Accuracy and precision data was determined at two concentrations and compounds were identified by retention time and by comparison with the National Institute of Standards and Testing (National Bureau of Standards) computerized mass spectral library. The results indicate, that the speed of routine analysis can be increased considerably by using the extraction disk instead of extraction cartridges, with practically the same reliability. Data acquired after the completion of the initial work demonstrates that the performance for pentachlorophenol can be markedly enhanced by the use of an unpacked insert in the gas chromatography injector.

INTRODUCTION

As the concern over the quality of our water resources continues to intensify, the demand is increasing for faster and more reliable methods of detecting potentially harmful organic compounds in surface and ground waters. Using automated gas chromatography–mass spectroscopy (GC–MS) techniques a large number of samples can be analyzed per day with a high degree of reliability [1]. However, in semi-volatile analysis, the preparation and pre-concentration of the sample extracts is the time-consuming step. To avoid manipulations with large volumes of solvents, solid-phase extraction was introduced [2,3], and later proposed by the U.S. Environmental Protection Agency (EPA) in a draft method [4]. The cartridge procedure, as presented in EPA Method 525 requires multiple transfers of 10 to 75 ml sample aliquots to the cartridge or cartridge reservoir. At the recommended flow rate, the total extraction time is 2–3 h. The speed of liquid–solid extraction of the semi-volatile organic compounds from the water samples can be dramatically increased by substituting extraction disks in place of extraction cartridges [5].

In the present study we report the performance of the Empore™ extraction disk for 43 semi-volatile organic chemicals and compare the results with those published in the EPA Method 525 [4], where an extraction cartridge was applied.

EXPERIMENTAL

Chemicals

Standards for individual compounds were prepared using analytical-grade materials (Supelco, Bellefonte, PA, U.S.A.). Standard mixtures were provided by Finnigan MAT (San Jose, CA, U.S.A.). [$^2\text{H}_{10}$]Acenaphthene, [$^2\text{H}_{10}$]phenanthrene and [$^2\text{H}_{12}$]chrysene were applied as internal standards (IS) and [$^2\text{H}_{12}$]perylene as surrogate standard (SS). The solvents (dichloromethane, ethylacetate and methanol) were high purity pesticide quality (Burdick & Jackson Labs., Muskegon, MI, U.S.A.).

Instrumentation and capillary column

A Varian (Sunnyvale, CA, U.S.A.) 3500 capillary gas chromatograph was fitted with a J&W Scientific (Folsom, CA, U.S.A.) 30 m \times 0.25 mm I.D. fused-silica capillary column (DB-5.625, 0.25 μm film thickness) directly coupled to the ion trap detector. A Varian Model 8035 autosampler and a 1093 SPI injector was used during the study.

Analytical operating parameters. The final selected GC system conditions were as follows. Carrier gas: ultrapure helium (Air Products). Carrier gas flow-rate: 2.8 ml min^{-1} . Initial oven temperature: 45°C, initial hold time: 2 min; ramp rate 1: 50°C/min, oven temperature 2: 160°C; ramp rate 2: 6°C/min, oven temperature 3: 210°C; ramp rate 3: 20°C/in, oven temperature 4: 250°C; ramp rate 4: 5°C/min, oven temperature 5: 300°C, final hold time 4 min.

Mass spectrometer. A Finnigan MAT ITD 700 ion trap detector was used. Transfer line and exit nozzle were maintained at 250°C and the manifold at 220°C.

Other special equipments and materials

For the extraction EmporeTM extraction disk (C_8 bonded, 47 mm diameter) was used (Analytichem International, Harbor City, CA, U.S.A.), in a 47 mm microanalysis holder (Fisher Scientific, Pittsburg, PA, U.S.A.), in a fashion similar to membrane filters.

For the concentration of the extracts a Turbo-vap evaporation apparatus (Zymark, Hopkinton, MA, U.S.A.) was used.

The chromatograms were interpreted by reference to retention indices and retention times derived from comparison with pure standard mixtures. Mass spectra were interpreted by comparison with pure standard mixtures. Mass spectra were interpreted by comparison with a NIST (NBS) computerized mass spectral library (provided by Finnigan MAT). Concentration range of calibration: 0.1–10.0 $\mu\text{g/l}$ in the original 1 l water sample.

Standard procedure

Summary of the method. Organic compound analytes, internal and surrogate standards were extracted from a water sample by pulling one liter of sample through the Empore disk placed in a 300 ml glass funnel with a fritted glass base. The organic compounds were eluted with 10 ml ethylacetate followed by 10 ml methylene chloride and concentrated to 1 ml final volume. The sample components were separated, identified and measured by injecting 1–3 μl of extract into a high resolution fused silica capillary column of the GC–MS system.

Extraction. 1000 ml water sample was acidified with 2 ml 6 M HCl to pH < 2. A 10- μ l volume of a 500 μ g/ml IS-SS solution was added to the water sample. A 47 mm Empore extraction disk was placed into a fritted glass funnel and washed with 10 ml ethylacetate:dichloromethane 1:1 mixture with vacuum on. The disk was then dried with air suction for 1 min.

The vacuum system used had sufficient capacity to maintain a slight vacuum of about 13 cm (5 in.) of mercury in the vacuum flask.

First 10 ml methanol, then 10 ml organic-free water were pulled through the disk. The vacuum was released immediately after all the water has passed through the disk to prevent the disk from drying.

Immediately after this step a 1000-ml water sample was extracted, with the vacuum adjusted to yield a 20 min extraction time. Finally the disk was dried by air suction for 1 min^a.

Elution. A 50-ml test tube was placed into the suction flask. The sample bottle was rinsed with 10 ml ethyl acetate, then the solvent transferred into the funnel. Gentle vacuum was applied until the first drops of solvent passed the disk. The vacuum was then stopped to allow the elution solvent to penetrate into the disk and elute the chemicals of interest. Approximately 1 min later the vacuum was switched on again and the ethyl acetate was collected in the test tube. This step was repeated with 10 ml dichloromethane. The combined extract was dried over anhydrous sodium sulfate for a few minutes.

Evaporation. The dry extract was transferred into an evaporation flask and the volume was reduced to 0.5 ml using nitrogen flow. Then the extract was transferred into the GC autosampler vial, the evaporation flask was rinsed with a small amount of dichloromethane and this solution was added into the autosampler vial. The final volume in the vial was adjusted to 1 ml.

A 1-3- μ l sample was injected into the capillary column.

RESULTS AND DISCUSSION

In Table I the 43 synthetic compounds included in this study are compiled. These compounds represent a variety in chemical structure and applications in agriculture and industry. Included are pesticides, plasticizers, additives etc. A typical standard chromatogram is shown on Fig. 1. Mean accuracy data and relative standard deviations for all 43 compounds are shown in Table II for 2.0 and 0.2 μ g/l target concentrations. The results represent an average of seven replicate determinations, where the experimental conditions were kept as close to those of the Method 525 [4] as possible, except for the extraction method.

The analysis time is drastically reduced using the extraction disk as the extraction is complete within 20 min compared with the 2-3 h required for the cartridge. Despite the short contact time, the general performance of the disk competes well with that of the extraction cartridge. The mean average method accuracy^b

^a Prolonged air suction may result in losses.

^b For the sake of comparison with the results published in Method 525, compounds 39 and 43 have been excluded from the means.

TABLE I
 COMPILATION OF THE SYNTHETIC ORGANIC COMPOUNDS INVESTIGATED

Compound	Mol.wt. ^a	Chem. Abstracts Service registry number
1 Acenaphthylene	152	208-96-8
2 Alachlor	269	15972-60-8
3 Aldrin	362	309-00-2
4 Anthracene	178	120-12-7
5 Atrazine	215	1912-24-9
6 Benz[<i>a</i>]anthracene	228	56-55-3
7 Benzo[<i>b</i>]fluoranthene	252	205-82-3
8 Benzo[<i>k</i>]fluoranthene	252	207-08-9
9 Benzo[<i>a</i>]pyrene	252	50-32-8
10 Benzo[<i>g,h,i</i>]perylene	276	191-24-2
11 Butylbenzyl phthalate	312	85-68-7
12 α -Chlordane	406	5103-71-9
13 γ -Chlordane	406	5103-72-2
14 <i>trans</i> -Nonachlor	440	39765-80-5
15 Chrysene	228	218-01-9
16 Dibenz[<i>a,h</i>]anthracene	278	53-70-3
17 Di- <i>n</i> -butyl phthalate	278	84-72-2
18 Diethyl phthalate	222	84-66-2
19 Di(2-ethylhexyl) phthalate	390	177-81-7
20 Di(2-ethylhexyl) adipate	370	103-23-1
21 Dimethyl phthalate	194	131-11-3
22 Endrin	378	72-20-8
23 Fluorene	166	86-73-7
24 Heptachlor	370	76-44-8
25 Heptachlor epoxide	386	1024-57-3
26 Hexachlorobenzene	282	118-74-1
27 Hexachlorocyclopentadiene	270	77-47-7
28 Indeno[1,2,3, <i>c,d</i>]pyrene	276	193-39-5
29 Lindane	288	58-89-9
30 Methoxychlor	344	72-43-5
31 2-Chlorobiphenyl	188	2051-607
32 2,3-Dichlorobiphenyl	222	16605-91-7
33 2,4,5-Trichlorobiphenyl	256	15862-07-4
34 2,2',4,4'-Tetrachlorobiphenyl	290	2437-79-8
35 2,2',3',4,6-Pentachlorobiphenyl	324	60233-25-2
36 2,2',4,4',5,6'-Hexachlorobiphenyl	358	60145-22-4
37 2,2',3,3',4,4',6-Heptachlorobiphenyl	392	52663-71-8
38 2,2',3,3',4,5',6,6'-Octachlorobiphenyl	426	40186-71-8
39 Pentachlorophenol	264	87-865
40 Phenanthrene	178	85-01-8
41 Pyrene	202	129-00-0
42 Simazine	201	122-34-9
43 Toxaphene mixture		8001-35-2

^a Monoisotopic molecular weight (mol.wt.) calculated from the atomic masses of the isotopes with the smallest masses.

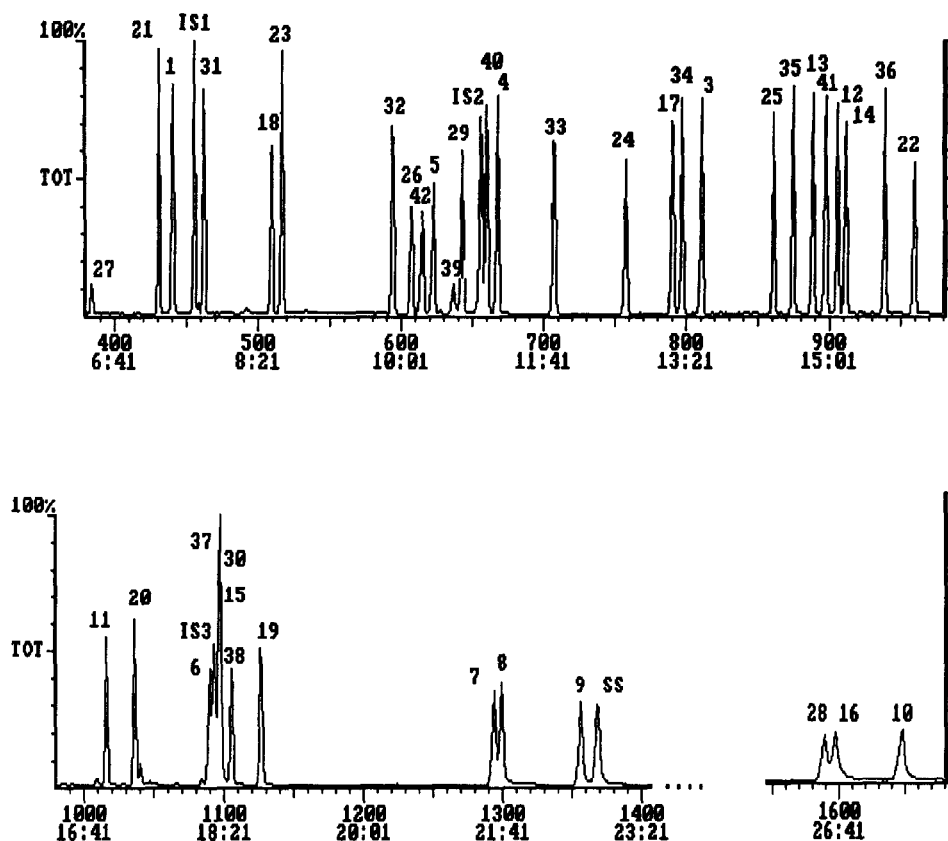


Fig. 1. A typical total ion chromatogram of the compounds investigated (except compound 2). Direct injection of 3 μ l of a 5 ng/ μ l solution (20 ng/ μ l for pentachlorophenol). For other experimental conditions see text. Horizontal scales: scan No. (top) and time in min:s (bottom).

(concentration determined as a % of the true concentration) for the 43 compounds at 2.0 and 0.2 μ g/l target concentration is 108 and 103% respectively, compared with the 91 and 95% of the cartridge method [4]. The average relative standard deviation in our measurements is 15 and 33% for the high and low concentration range respectively. The experiments with cartridge extraction [4] gave 15 and 25%. These figures indicate that the disk is more sensitive for the concentration of the compounds investigated. As we go from 2 μ g/l target concentration to 0.2 μ g/l, the number of compounds with relative standard deviations higher than 10% increases from 14 to 37. In the case of the extraction cartridge these figures are 25 and 33, respectively. The number of cases, where the systematic error is higher than 50% increases from 3 to 16; for the cartridge these values are 4 and 9. Our results with packed extraction columns [6] support the observation, that the cartridge generally performs better in the low concentration range than the disk.

The results presented here apply for the C_8 bonded disk. Results for a C_{18} disk under the same experimental conditions were very close to those with the C_8 bonded

TABLE II

ACCURACY AND PRECISION DATA (%) FROM SEVEN DETERMINATIONS FOR THE 43 COMPOUNDS INVESTIGATED

R.S.D. = Relative standard deviation.

Compound number	True concentration ($\mu\text{g/l}$)			
	2.0 ^a		0.2 ^b	
	R.S.D.	Mean accuracy	R.S.D.	Mean accuracy
1	4.8	116	19.5	58
2	6.8	103	9.0	103
3	5.7	114	13.5	99
4	3.4	118	13.1	46
5	11.9	139	8.2	129
6	2.6	103	30.0	39
7	8.5	93	18.6	81
8	10.4	97	39.8	61
9	4.4	111	18.8	51
10	2.9	111	20.3	68
11	6.1	109	52.4	242
12	49.5	82	55.8	68
13	31.4	82	27.3	85
14	23.8	18	139.8	37
15	6.2	96	27.5	40
16	3.5	114	24.8	62
17	7.3	149	37.2	519
18	5.8	134	46.7	167
19	14.1	133	22.8	372
20	4.7	108	17.0	161
21	7.1	117	11.9	123
22	10.0	126	34.5	128
23	8.1	114	15.8	51
24	3.2	116	8.4	131
25	11.4	122	11.4	141
26	52.5	60	120.1	27
27	18.9	131	23.0	98
28	6.8	93	67.6	19
29	12.4	113	11.7	122
30	6.1	95	24.6	48
31	8.3	112	10.9	78
32	10.5	125	8.2	101
33	7.0	108	12.7	90
34	8.1	144	11.6	97
35	9.6	118	16.3	106
36	9.5	131	27.9	95
37	134.5	15	134.7	30
38	52.5	102	90.9	45
39	15.1	132	68.0	773
40	6.2	113	14.3	51
41	4.9	119	31.6	41
42	6.5	112	9.8	110
43	6.6	304	—	—

^a For compounds 39 and 43 the real concentrations were 12 and 37.5 $\mu\text{g/l}$, respectively.^b For compound 39 the real concentration was 0.8 $\mu\text{g/l}$.

disk. The average mean accuracy with C_{18} disk is slightly worse but the mean standard deviation is smaller in the low concentration range than the values presented above for the C_8 bonded disk. It should be noted, however, that in the case of the C_{18} bonded disk the extraction time was only 10 min, and 2×5 ml eluent was used.

Besides the differences mentioned above, the "problem compounds" are slightly different for the two kinds of liquid-solid extraction. In the case of the extraction

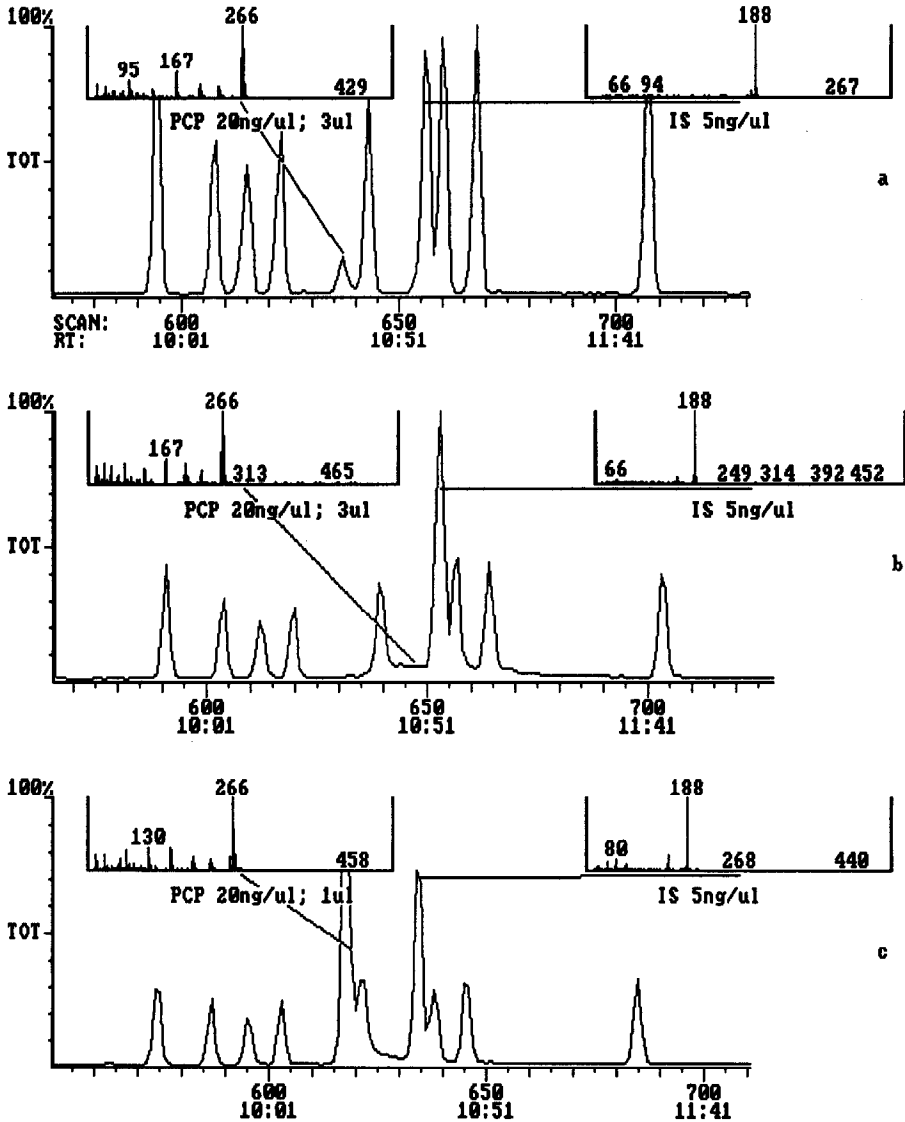


Fig. 2. Effect of the insert packing on the separation and detection limit for pentachlorophenol (PCP), direct injection. (a) Lightly packed insert, new DB-5.625 column, 60 ng PCP. (b) Tightly packed insert, six months old column, 60 ng PCP. (c) Unpacked high-performance insert, six months old column, 20 ng PCP.

cartridge some polycyclic aromatic compound have relatively low recovery, while the disk gave better results both in accuracy and precision (*e.g.* compounds 6, 10, 16, 28). The systematic error for phthalate esters and similar plasticizers is high due to the high and mostly uncontrollable background concentration.

Pentachlorophenol is problematic in both cases, the disk performance is especially poor in the low concentration range.

Despite the general recommendations, our results indicate, that for this compound an unpacked insert in the GC injector is more satisfactory, as shown in Fig. 2. Compared with an average glass wool packing (Fig. 2a), a tightly packed insert results in a broad, nearly undetectable pentachlorophenol peak (Fig. 2b). In the latter case the quantitation ion can be found everywhere in the 630–675 scan number range (10:30–11:20 retention time). This makes the quantitative analysis unreliable. The adsorption on the glass wool packing can be avoided by using a high performance unpacked insert (Varian), Fig. 2c, in this case 1 μ l injection is enough. (Due to the ageing of the column and the corresponding changes in the column length, the retention times are slightly different on the chromatograms. There are differences in the concentration of the other compounds as well, but these parameters hardly affect the separation). It is also worth noting, that in some cases solid particles in the water sample can plug the pores of the disk. To avoid this a pre-filtration step may be necessary. However, potential losses of extraction efficiency must be investigated.

CONCLUSION

The results presented here demonstrate that the speed of routine analysis and consequently the productivity of a testing laboratory can be increased considerably by using extraction disks in place of packed columns with practically the same reliability under normal conditions. The applicability of the extraction disk for extremely low target concentrations is subject to further investigation.

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