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EVALUATION OF A TEFLON BLOCK EXTRACTION PROCEDURE FOR DETERMINATION OF ORGANIC MATERIAL IN AIR PARTICULATE MATTER

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SUMMARY

A Teflon block extraction apparatus for the determination of trace organic material from airborne particulate matter collected on Teflon dichotomous filters has been constructed and evaluated. The total solvent volume of 5-6 ml minimizes artifact introduction from solvents and component loss during condensation. Viton O-rings were found to be a source of artifacts and the total artifact level is reduced significantly upon replacement of the Viton O-ring with Teflon. With the use of the all-Teflon apparatus the expected minimum detectable amount is 10 pg/m³ of air sampled.

INTRODUCTION

The Environmental Protection Agency has been monitoring the size distribution, mass and chemical composition of airborne particulate matter (APM) since 1970 using Hi-Vol samplers¹⁻³. Unfortunately, the large range of sample particulate sizes collected by Hi-Vol filtration causes difficulties in the determination of toxic or hazardous compounds associated with respirable particles. Further, the human respiratory tract is extremely sensitive to particle size^{4,5}, with particles smaller than *ca.* 3 μm capable of penetrating into the lungs and remaining trapped in the body. The dichotomous sampler was developed to overcome these problems, as it separates the APM into respirable and non-respirable size fractions and collects each on separate filter elements for chemical and gravimetric analysis^{6,7}.

Because the total sample collected on dichotomous filters is approximately two orders of magnitude less than for Hi-Vol filters, reduction of the number of sample handling and solvent concentration steps is necessary to minimize contaminant introduction. We have developed a rapid procedure for the analysis of organic material on Teflon dichotomous filters^{8,9} using Soxhlet extraction techniques with solvent volumes of 20 ml. The use of smaller solvent volumes minimizes extensive concen-

tration and transfer steps, which may be sources of contaminant introduction. The procedure we are evaluating involves the ultrasonic extraction of organic compounds with a suitable solvent from a dichotomous filter element placed in a Teflon extraction block. Concentration of large solvent volumes has been eliminated through the use of ultrasonic extraction solvent volumes of 5-6 ml. Ultrasonic extraction has been shown to be effective in the extraction of trace organic species from airborne particulates¹⁰ and fly ash¹¹, with recoveries comparable to conventional Soxhlet techniques¹²⁻¹⁴. Following ultrasonic extraction, the solvent is condensed by a factor of 50-60 and analyzed by gas chromatography (GC) at the highest sensitivity.

EXPERIMENTAL

Standard solution

A standard solution containing *n*-hydrocarbons, *n*-alcohols, phthalates and aromatic hydrocarbons (PAHs) in cyclohexane (GCCAL-II) was prepared and used to evaluate the extraction and recovery efficiency of the ultrasonic extraction procedure. Hydrocarbons and alcohols were obtained as analytical standard kits (Poly-Science, Niles, IL, U.S.A.). Phthalate esters (J. T. Baker, Phillipsburg, NJ, U.S.A.) and PAHs (Sigma, St. Louis, MO, U.S.A.) were obtained as analytical grade. The compounds and their respective concentrations are given in Table I. A standard solution containing *ca.* 100 ng/ μ l of each component in cyclohexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) was prepared and diluted 1:10 and 1:100 for use in evaluating the extraction procedure at 10 and 1 ng/ μ l levels.

Ultrasonic extraction

An extraction apparatus consisting of a threaded plug and a two piece filter support was designed and constructed out of Teflon (Fig. 1). Teflon was chosen for its inertness and low likelihood of artifact introduction. The Teflon dichotomous

TABLE I
COMPOSITION OF STANDARD MIXTURE, GCCAL-II

<i>Compound</i>	<i>Molecular formula</i>	<i>Molecular weight</i>	<i>Concentration (ng/μl)</i>
Octadecane	C ₁₈ H ₃₈	254.5	101
Eicosane	C ₂₀ H ₄₂	282.6	101
Tetracosane	C ₂₄ H ₅₀	338.7	102
Hexacosane	C ₂₆ H ₅₄	366.7	101
Triacontane	C ₃₀ H ₆₂	422.8	102
1-Tetradecanol	C ₁₄ H ₃₀ O	214.4	[33]*
1-Hexadecanol	C ₁₆ H ₃₄ O	224.4	[31]*
Dimethyl phthalate	C ₁₀ H ₁₀ O ₄	194.2	104
Diethyl phthalate	C ₁₂ H ₁₄ O ₄	222.2	102
Biphenyl	C ₁₂ H ₁₀	154.2	102
Fluorene	C ₁₃ H ₁₀	166.2	102
Fluoranthene	C ₁₆ H ₁₀	202.3	101
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252.3	100

* Made from 10% solution and not suitable for quantitation.

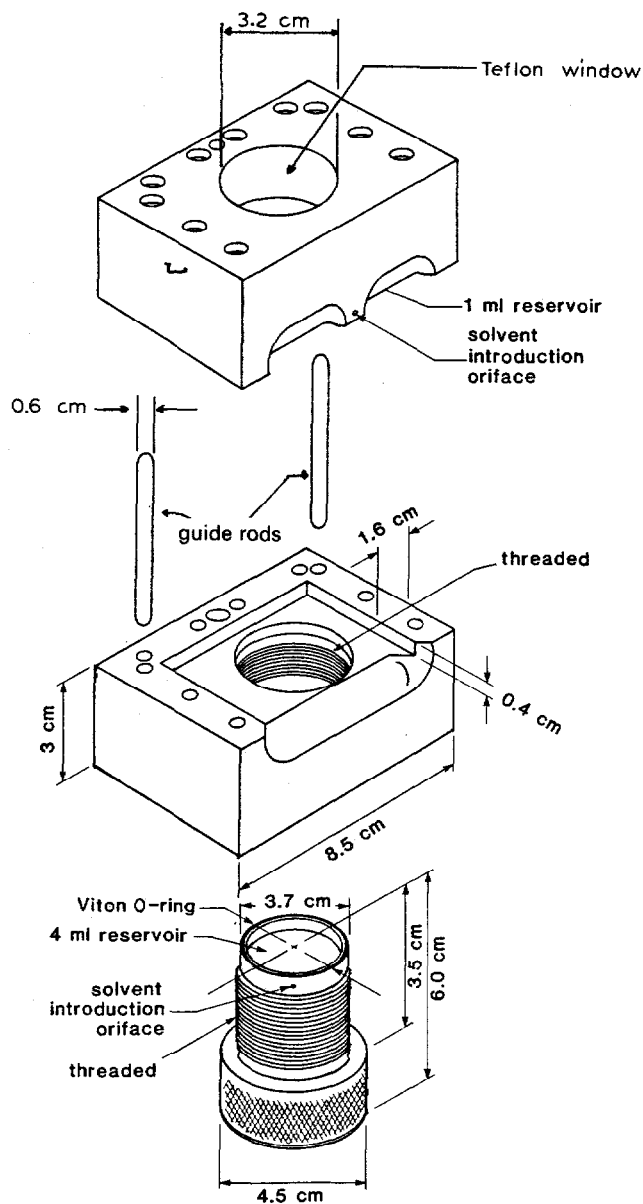


Fig. 1. Expanded view of Teflon extraction apparatus.

filter is positioned in the support block and the Teflon plug threaded until a snug fit is obtained. Solvent is introduced via the solvent introduction orifice by means of an all-glass 10-ml syringe. The apparatus is placed in a 12.5 cm diameter \times 6.5 cm glass dish and placed in an ultrasonic bath (Branson Cleaning Equipment, Shelton, CT, U.S.A.) approximately one-third full of water. The Teflon extraction apparatus has a thin Teflon window machined on one end of the extraction block. This thin window

permits the ultrasonic vibrations to be transmitted to the extracting solvent contained in the apparatus. Methylene chloride (pesticide grade, Fisher Scientific, Fair Lawn, NJ, U.S.A.) is added to the lower three-quarters of the dish to assure that the ultrasonic vibrations are transmitted to the extraction apparatus. The extraction temperature is maintained at 20°C through the use of an ice-water bath. The filter is extracted for the desired period of time, the solvent is removed from the extraction block by syringe and dispensed into a 5-ml reacti-vial or a 10-ml screw-top flask (Wheaton Scientific, Millville, NJ, U.S.A.).

For all analyses an initial extraction period of 30 min using a blank filter was used to determine components introduced by the apparatus and filters. The pretreated filter was then removed from the extraction block, spiked with 100 μl of the desired GCCAL-II solution, replaced in the block and the extraction procedure repeated as necessary. Spiked filters were extracted for 15 min using multiple extractions to assure removal of all components. Filters spiked with 100 ng/ μl GCCAL-II were extracted for 3×15 min; 10 and 1 ng/ μl GCCAL-II spiked filters were extracted for 2×15 min. The extracts were condensed to *ca.* 300 μl using a semi-micro rotary evaporator (Wheaton Scientific) under aspirator vacuum at room temperature. Condensates were quantitatively transferred to 1 ml sample vials (Alltech, Los Altos, CA, U.S.A.) with Teflon-lined screw caps and further reduced to 100 μl by evaporation under a stream of nitrogen.

GC-flame ionization detection (FID) analyses

A Hewlett-Packard 5830A gas chromatograph equipped with a flame ioniza-

TABLE II

COMPONENT RECOVERY FOLLOWING 15-MIN ULTRASONIC EXTRACTION

5 ml with Viton O-ring.

Compound	Percentage recovery*		
	100 ng/ μl	10 ng/ μl	1 ng/ μl **
Biphenyl	58 \pm 21	6 \pm 6	—
Fluorene	78 \pm 20	30 \pm 29	—
Dimethyl phthalate	82 \pm 25	23 \pm 21	—
Octadecane	101 \pm 12	97 \pm 14	—
Diethyl phthalate	93 \pm 17	58 \pm 30	—
1-Tetradecanol	105 \pm 13	84 \pm 16	—
Eicosane	103 \pm 14	92 \pm 9	—
1-Hexadecanol	—**	—**	—
Fluoranthene	77 \pm 9	—**	—
Tetracosane	101 \pm 12	95 \pm 10	—
Hexacosane	108 \pm 9***	97 \pm 12	—
Triacotane	104 \pm 11	99 \pm 12	—
Benzo[a]pyrene	97 \pm 12	86 \pm 7	—
Average recovery	92 \pm 4	70 \pm 5	—

* Normalized for losses due to concentration; except where noted average of three \pm S.D.

** Interference due to artifact.

*** Two samples \pm $\frac{1}{2}$ the range.

tion detector and 1.9 m × 2 mm I.D. glass columns packed with Aue packing were used for all analyses. Aue packing consists of an ultra-thin film of Carbowax 20M which has been physically bonded to exhaustively acid-washed Chromosorb W and has been described in detail¹⁵⁻¹⁷. Analysis conditions were as follows: initial temperature, 90°C; program rate 4°C/min; final temperature, 250°C held for 15-30 min; injection port temperature, 250°C; detector temperature, 275°C; helium carrier flow-rate 35 ml/min.

RESULTS AND DISCUSSION

The Teflon block extraction apparatus was evaluated at solvent volumes of 5

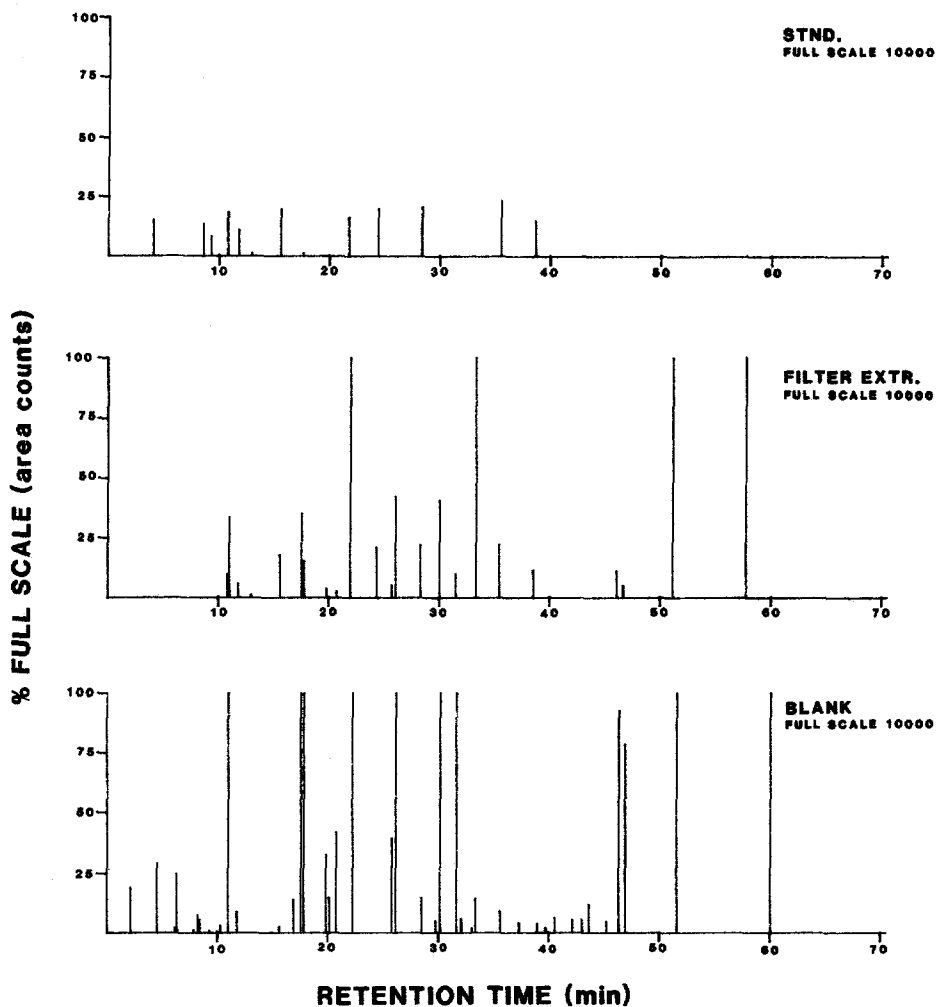


Fig. 2. Comparison of direct injection of 1 ng/ μ l GCCAL-II (top); first 15-min extraction of 1 ng/ μ l spiked filter (middle); filter blank (bottom) for 5-ml extraction apparatus with Viton O-ring. (All injection volumes 5 μ l. Reconstructed chromatograms generated using a program PLOTGC and a Digital Equipment MINC 23 minicomputer.)

and 6 ml. A change in solvent volume is effected by use of a Teflon threaded plug with a reservoir 1 ml less than the desired total volume machined out of the end. The 5-ml total volume Teflon block extraction apparatus utilized a Viton O-ring (State Seal, Phoenix, AZ, U.S.A.) to form a leak-free seal between the threaded plug and the Teflon filter and/or frame.

The 5-ml solvent volume extraction apparatus containing the Viton O-ring was evaluated at spike levels of 100, 10 and 1 ng/ μ l. A 30-min extraction blank was performed prior to spiking all filters. The filter blanks were found to contain several major components and 8-10 other components which interfered significantly with analysis at the 1 ng/ μ l level.

The percentage recoveries for the 5-ml extraction apparatus are given in Table II. Quantitation of components at the 1 ng/ μ l spike level was not possible due to the high levels of artifacts derived from the Viton O-ring, polyester filter frame and the filter itself. These artifacts are better illustrated in Fig. 2, which compares a direct injection of 1 ng/ μ l GCCAL-II, the first 15-min extraction of a spiked filter, and the filter blank.

As a further check of the effectiveness of the ultrasonic extraction procedure, component recoveries from the ultrasonic extraction were compared with component recoveries obtained using the normal Soxhlet extraction. For the Soxhlet technique, the Teflon filters were spiked with 100 μ l of the desired GCCAL-II solution, removed from their polyester frames and Soxhlet extracted with 20 ml of methylene chloride for 2 h. The extracts were condensed and analyzed by GC-FID as described pre-

TABLE III

COMPARISON OF SOXHLET AND ULTRASONIC* EXTRACTION

Compound	Percentage recovery**			
	100 ng/ μ l		10 ng/ μ l	
	Soxhlet	Ultrasonic	Soxhlet	Ultrasonic
Biphenyl	7***	58 \pm 21	—	6 \pm 6
Fluorene	41 \pm 15	78 \pm 20	7***	30 \pm 29
Dimethyl phthalate	44 \pm 21	82 \pm 25	5 \pm 1	23 \pm 21
Octadecane	97 \pm 14	101 \pm 12	86 \pm 12	97 \pm 14
Diethyl phthalate	78 \pm 17	93 \pm 17	19 \pm 18	58 \pm 30
1-Tetradecanol	91 \pm 14	105 \pm 13	71 \pm 18	84 \pm 16
Eicosane	101 \pm 12	103 \pm 14	96 \pm 10	92 \pm 9
1-Hexadecanol	99 \pm 15	— [§]	95 \pm 7	— [§]
Fluoranthene	100 \pm 13	77 \pm 9 ^{§§}	86 \pm 7	— [§]
Tetracosane	100 \pm 14	101 \pm 12	104 \pm 9	95 \pm 10
Hexacosane	103 \pm 13	108 \pm 9	103 \pm 12	97 \pm 12
Triacotane	105 \pm 15	104 \pm 11	99 \pm 16	99 \pm 12
Benzo[a]pyrene	104 \pm 15	97 \pm 12	94 \pm 8	86 \pm 7
Average recovery	82 \pm 4	92 \pm 4	72 \pm 3	70 \pm 5

* 5-ml Teflon block, Viton O-ring.

** Normalized for losses due to concentration; except where noted average of three \pm S.D.

*** One sample only.

§ Interference due to artifact.

§§ Average of two \pm 1/2 the range.

TABLE IV
COMPONENT RECOVERY FOLLOWING 15-MIN ULTRASONIC EXTRACTION
6-ml all-Teflon extraction apparatus.

Compound	Percentage recovery*		
	100 ng/ μ l	10 ng/ μ l	1 ng/ μ l
Biphenyl	109 \pm 31	58 \pm 20	43 \pm 28
Fluorene	71 \pm 46	57 \pm 18	70**
Dimethyl phthalate	95 \pm 54	57 \pm 18	58 \pm 26***
Octadecane	106 \pm 30	78 \pm 19	73 \pm 23
Diethyl phthalate	112 \pm 34	68 \pm 23	71 \pm 38
1-Tetradecanol	105 \pm 39	54 \pm 16	89 \pm 5***
Eicosane	109 \pm 27	65 \pm 12	68 \pm 16
1-Hexadecanol	115 \pm 39	127 \pm 68	— [§]
Fluoranthene	132 \pm 56	— [§]	— [§]
Tetracosane	107 \pm 24	63 \pm 13	52 \pm 11
Hexacosane	102 \pm 23	64 \pm 13	54 \pm 11
Triacontane	101 \pm 23	64 \pm 13	59 \pm 15
Benzo[a]pyrene	83 \pm 21	53 \pm 15	65**
Average recovery	104 \pm 10	68 \pm 7	64 \pm 6

* Normalized for losses due to concentration; except where noted average of three \pm S.D.

** One sample only.

*** Average of two \pm $\frac{1}{2}$ the range.

[§] Interference due to artifact.

viously. A comparison of the two methods is presented in Table III. As can be seen, component recoveries are comparable in both the 100 ng/ μ l and 10 ng/ μ l solutions, with the ultrasonic technique providing higher recoveries of the more volatile components.

Because of the high levels of artifacts found in the 5-ml extractions, it was decided to investigate the use of an all-Teflon extraction apparatus in an effort to eliminate possible artifact introduction from the Viton O-ring. A Teflon plug having a rounded lip and a total solvent volume of *ca.* 6 ml was machined and the apparatus tested. Initial analysis of the data indicated a dramatic reduction in contaminants with recoveries comparable to the apparatus containing the Viton O-ring. The all-Teflon extraction block was evaluated at 100, 10 and 1 ng/ μ l spike levels, with the results given in Table IV. At the 100 ng/ μ l level, both the viton O-ring and all-Teflon block have comparable recoveries. Recoveries at the 10 ng/ μ l level are better for the more volatile components and roughly equivalent for other components for the all-Teflon system. More importantly, switching to the all-Teflon apparatus does allow quantitation at the 1 ng/ μ l level, with percentage recoveries roughly equal to those at the 10 ng/ μ l level. Reconstructed chromatograms of a direct injection and first 15-min extraction of 1 ng/ μ l GCCAL-II, and a filter blank for the all-Teflon extraction apparatus are shown in Fig. 3. It is expected that with the use of gas chromatography-mass spectrometry or a mass-selective type detector, detection limits in the range of 10 pg/m³ air sampled would be achievable¹⁸⁻²⁰. This increased sensitivity is of vital importance for the analysis of the low levels of organic compounds expected on dichotomous filters^{9,21}.

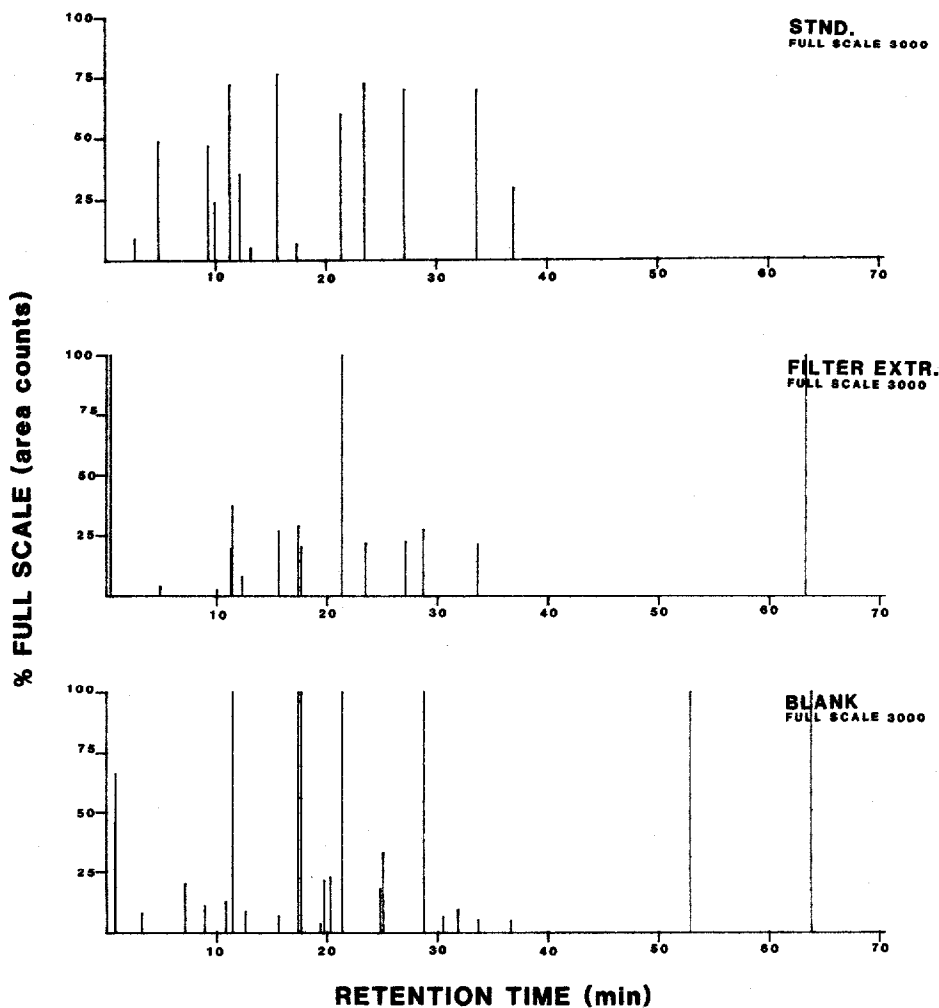


Fig. 3. Comparison of direct injection of 1 ng/ μ l GCCAL-II (top); first 15-min extraction of 1 ng/ μ l spiked filter (middle); filter blank (bottom) for 6-ml all-Teflon extraction apparatus. (All injection volumes 5 μ l.)

Further proof of the reduction in artifacts derived from the omission of the O-ring may be seen in Fig. 4. The upper chromatogram is a filter blank obtained from the Teflon apparatus containing the Viton O-ring; the lower chromatogram is of a filter blank on the all-Teflon system. Note that the full-scale area values for the two plots are the same. The total amount of organics in the Viton O-ring filter blank is *ca.* 196 μ g as compared with 28 μ g in the all-Teflon blank.

Although a significant reduction in the amount of contamination is accomplished when the O-ring is eliminated, two major contaminants at retention times of *ca.* 21 and 60 min are still observed in the all-Teflon apparatus. Current work suggests that the origin of these contaminants is the polyester filter frame, although the filter itself and the plastic box in which the filters are packaged must be considered as potential sources of artifact introduction.

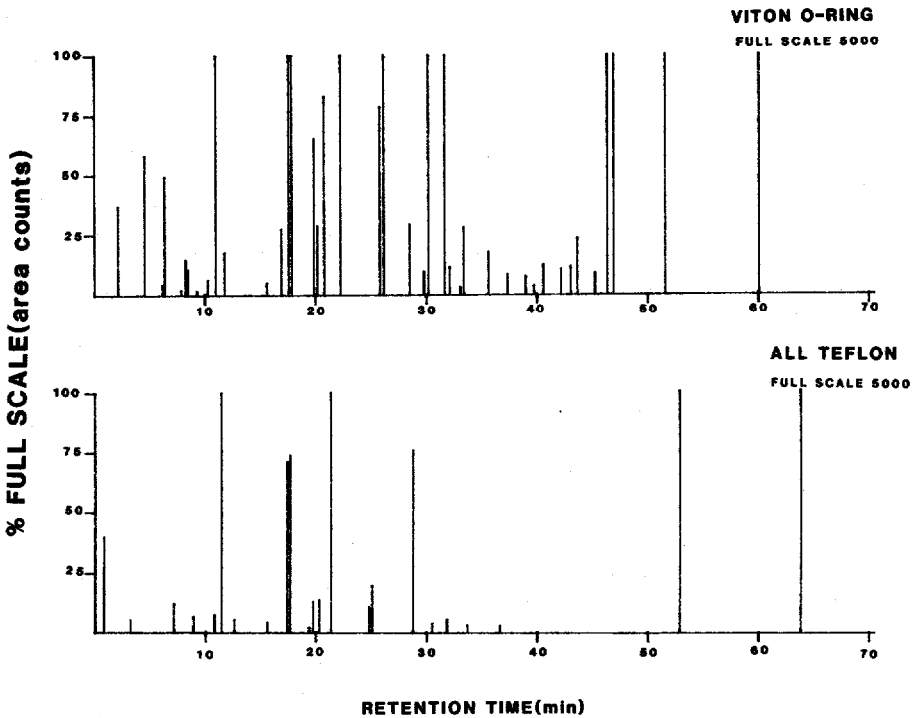


Fig. 4. Comparison of filter blank with Viton O-ring (top) and all-Teflon apparatus filter blank (bottom). (Injection volumes 5 μ l.)

CONCLUSIONS

The Teflon block extraction apparatus has been demonstrated to be better than the Soxhlet procedure for the extraction of organic material absorbed on Teflon dichotomous filters. The Teflon block has the advantage of faster sample throughput with minimal losses due to adsorption, sample transfer and concentration. In the all-Teflon system, artifact introduction is reduced by a factor of 10, with better recoveries for the more volatile components and lower detection limits (*ca.* 1 ng) than the O-ring containing apparatus. With the further improvement of a mass-selective detector such as a mass spectrometer, detection limits could be lowered by a factor of 10–100, allowing quantitation of the extremely low levels of material expected from dichotomous samplers. The expected detection limits using a mass selective detector are in the range of 10 pg/m^3 of air sampled.

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