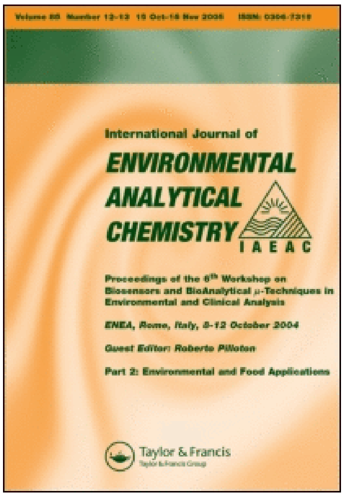

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AQUEOUS EXTRACTION OF AIRBORNE PARTICULATE MATTER COLLECTED ON HI-VOL TEFLON FILTERS

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An extraction method was developed for the quantitative recovery of fine particles collected on Hi-Vol Teflon filters and in a form suitable for assessment of the biological reactivity of atmospheric aerosols. Two major criteria identified for the selection of a procedure were maximum recovery and minimization of the introduction of chemicals into the extract solution. Experiments were conducted with different volumes of a pre-wetting agent (ethanol) and sonication times to select the appropriate conditions for the aqueous extraction of material from the hydrophobic Teflon surface. The developed procedure involved the pre-wetting of a filter (cut into 8 pieces) with 2 mL ethanol and sonication in 400 mL ultra pure water for 30 minutes. Results of gravimetric analyses indicated high mass recoveries (91 ± 7%) of material from the Teflon filters. Analyses for polycyclic aromatic hydrocarbons (PAHs) were performed on organic extracts of portions of Teflon filters with particles and portions of the same filters subjected to aqueous extraction. Comparison of the results revealed high percentages (92 ± 11 %) of PAHs were transferred into the aqueous solution using the extraction method developed. Inorganic analyses performed on Teflon filters (loaded with particles) and freeze-dry residues of aqueous extracts of Teflon filters also suggested high transfer rates (84 ± 33%) of inorganics into the aqueous extracts.

KEY WORDS: Hi-Vol sampler, Teflon filter, airborne particulate matter, aqueous extraction.

INTRODUCTION

The wide range of particulate sizes and the diversity of toxic compounds associated with airborne particles cause difficulties in assessing the human health effects of atmospheric aerosols[1-8]. In the past, studies on the mutagenicity, carcinogenicity and analytical chemistry of organic material in respirable airborne combustion particles have been based largely on organic solvent extracts of particles collected on filters. For example, different types of filters exposed to diesel engine exhaust were extracted with dichloromethane and subsequently acetonitrile[7] or with dichloromethane only[9]. Hawley-Fedder *et al.*[8] developed an extraction procedure for the determination of trace organic compounds from airborne particles collected on Teflon dichotomous filters. Sonication of Teflon filters spiked with n-hydrocarbons, n-alcohols, phthalates and PAHs for 15 minutes at 20°C with dichloromethane using a Teflon block apparatus gave better extraction efficiencies compared to the Soxhlet extraction process. Derrick and Moyers[10] extracted water soluble ions from Teflon filters. The extraction was conducted with direct application of ethanol to the filter, allowing a dilute perchloric acid solution to contact the collection surface and extract the water soluble ions. These authors indicated that the hydrophobic nature of the Teflon filters made the complete dissolution of water soluble ions exceptionally difficult and that the pre-wetting of the Teflon filters with ethanol minimized dissolution and extraction problems.

As part of a study to assess the biological reactivity of atmospheric aerosols, an extraction procedure was developed to recover from Hi-Vol Teflon filters fine particles in a form suitable for the assessment of the cytotoxicity of the complete chemical nature. Two major criteria identified for the selection of a procedure were maximum recovery and minimization of the introduction of chemicals into the extract solution. Heating had to be avoided to reduce losses of volatile components and potential alteration in toxicity of samples, which excluded the use of Soxhlet extraction. Chemical agents which could modify composition and toxicity of particulate extracts also had to be omitted or minimized. We have therefore excluded the use of commonly applied organic solvents and acidic/basic solutions, and selected ultra-pure water as the extraction medium and evaluated its effectiveness for extraction of fine particles from Teflon filters. The effects of ethanol as a wetting agent and time of sonication on the extraction efficiency were examined in order to optimize extraction.

EXPERIMENTAL SECTION

Sample collection and preparation. The 8" x 10" Teflon filters used were Gelman Zeflour supported PTFE of 3 µm pore size (Gelman Sciences Inc., Ann Arbor, MI). Teflon filters were used because they are inert and their membrane design should prevent contamination of extracts with filter material which can confound cytotoxicity. The filters as received were packaged in paper boxes with each filter covered with yellow tissue paper on both sides. After sampling, the exposed filters were kept also with the same yellow tissues on both sides but in 9" x 13" LDPE Zip-loc bags (Baxter Diagnostics Corp., Toronto, ON) and stored at −10°C before processing.

Hi-Vol samplers with cascade impaction plates for 2.5 µm cut size (Model #GL-2000H, General Metal Works Inc., Cleves, OH) were used to sample the ambient air at a flow rate of 40 cubic feet per minute for 12 to 48 hours. The Teflon filters were weighed on a Sartorius 2004 MP analytical balance (Sartorius GmbH, Gottingen, Germany) before and after the sampling to determine the mass of particles collected. Both unexposed and air exposed Teflon filters were preconditioned for 24 hours at 52 ± 2% relative humidity (R.H.) prior to any weighing.

Filters to be extracted were each cut into 8 uniform pieces using a surgical blade on a Teflon cutting board which had been rinsed with iso-propanol and dried at room temperature (23°C–25°C). The filters were handled by wearing clean polythene gloves (Almedic, Montreal, PQ) and using a pair of Teflon tweezers. Clean hygienic conditions were maintained at all times during the work to reduce the possibility of contaminant introduction, minimize losses of material and prevent the Teflon filter surfaces from being damaged.

Filter extraction. The de-ionized water used for extraction was obtained from a Barnstead NANOpure® system (Barnstead/Thermolyne Corp., Dubuque, IA) at a maximum resistivity of 18.4 megohms/cm and stored in a 50 L polypropylene bottle (Nalgene Co./Sybron Corp., Rochester, NY). To examine the effects of ethanol as a wetting agent on the aqueous extraction recovery of particles, denatured ethanol (glass distilled, BDH Inc., Toronto, ON) was applied to some filter pieces before extraction or added directly to the water to be used for extraction. Application of ethanol was via disposable pipette tips coupled to a Centaur Micropipette (supplied by Chromatographic Specialties inc., Brockville, ON). All glasswares used in the work were washed with soap and water, rinsed with iso-propanol and dried in the oven at 100 ± 5°C for four hours. The ultrasonic water bath used was a Model B-2200R-4 from Branson Cleaning Equipment Co., Shelton, CT.

Determination of mass recovery. To determine the mass recovery of particulate matter from the Teflon filter, each piece of cut filter was individually placed into a pre-weighed beaker (100 mL). The Teflon filter pieces were weighed in their respective beakers on the Sartorius 2004 MP analytical balance. These beakers were then placed in the ultrasonic water bath and the filter pieces were extracted, each in 40 mL of deionized water, under sonication with different test variables (e.g. the time of sonication, the amount of the wetting agent, and how the wetting agent was applied). The extracted filters were dried in pre-weighed beakers in an oven (Shel Lab Model #1620, Sheldon Manufacturing Inc., Portland, OR) at 100 ± 5°C for four hours, allowed to cool to room temperature and stabilize in a chamber at R.H. 52 ± 2%, and re-weighed to determine the weight difference before and after extraction. The recovery (R) was determined as the ratio of the weight difference between the exposed filter (W_s) and the aqueous extracted filter (W_e) to that between the exposed filter and the un-exposed filter (W_u):

$$R\,(\%) = \frac{(W_s - W_e)}{(W_s - W_u)} \times 100$$

The aqueous extracts of 36 field samples were frozen and lyophilised to dryness. Each residue was re-suspended in a small volume of ethanol and then water, and transferred to a pre-weighed 40 mL precleaned sampling vial (Fischer Scientific, Montreal, PQ), frozen and lyophilised. The masses recovered from freeze drying the aqueous extracts were determined and compared to filter weight losses in order to verify that the data based on the weight difference before and after the extraction reliably reflected the mass extracted into and recoverable from the aqueous solution.

Determination of inorganic and organic recoveries. To evaluate the effectiveness of the aqueous extraction method for recovery of organics and inorganics from the Teflon filter, six pairs of exposed Teflon filters were used. Each pair (which had been collected simultaneously at the same sampling site) were cut into twelve equal pieces, of which 10 pieces were extracted in 400 mL of water with ethanol (2 mL) pre-wetting. A 30 mL aliquot was freeze dried and the residue was used for inorganic analyses. One of the two remaining Teflon filter pieces was used for inorganic analyses and the other was soxhlet extracted with dichloromethane for PAH analysis.

The freeze-dry residue and the filter piece for inorganic analyses were each leached with 20 mL deionized water. Each leachate was divided into two equal aliquots, one used for ion chromatographic (IC) analysis for major ions and the other combined with the extract of acid digestion (with concentrated nitric acid) of the filter piece (or the freeze-dry residue) for trace metal analyses. Metal analyses were performed on filtrates of the acid digested filter piece and freeze-dry residue with inductively coupled plasma/atomic emission spectroscopy (ICP/AES) based on NIOSH Method No. 7300 for alkaline metals and U.S. EPA Method No. 200.7 for trace metals, and with atomic absorption spectrophotometry (AAS) based on U.S. EPA Methods No. 206.2 for arsenic, No. 213.2 for cadmium, No. 239.2 for lead and No. 270.2 for selenium. IC analyses were performed on the water leachates of the filter piece and the freeze-dry residue with U.S. EPA Method No. 300.0 for chloride, nitrate and sulphate. Comparison of the filter and freeze-dry residue results provided information on the aqueous extraction recovery (R) of inorganics from the Teflon filters, which was calculated according to:

$$R\,(\%) = \frac{M_r}{M_f} \times 100$$

where M_f and M_r are the analyte masses determined, respectively, on the exposed filter and the freeze-dry residue of the aqueous extract of the corresponding filter.

Although there are a variety of organic compounds associated with atmospheric aerosols[2,3], the majority of available data are for PAHs[4,5]. Therefore, high performance liquid chromatography (HPLC) analysis with a variable scan spectrofluorimetric detector was performed (based on modified U.S. EPA Method 610) on organic extracts (in dichloromethane) of portions of Teflon filters with particles and portions of the same Teflon filters, which had been subject to aqueous extraction, to determine the difference in PAH loadings on the filter portions. This difference was used to calculate the recovery (R) of PAHs from the exposed filter, which served as an indicator of the extent of extraction of organic materials. The calculation of recovery was based on:

$$R\,(\%) = \frac{(M_0 - M_a)}{M_0} \times 100$$

where M_0 and M_a are the analyte masses determined, respectively, in the organic extract of a portion of an exposed filter and in the organic extract of the aqueous extracted portion of the corresponding filter.

All analytical blanks were determined. Replicate analyses performed on samples and laboratory spikes indicated analytical precisions of better than 15% relative standard deviation. Analyses performed on laboratory spikes and a standard reference material (SRM 1649, Urban Dust, from National Institute of Standard and Technology, Gaithersburg, MD) indicated analytical accuracies of ±30%.

RESULTS AND DISCUSSION

Evaluation of extraction method—gravimetric analysis. Table 1 is a summary of the extraction results of blank filters using water only, by means of pre-wetting the filter (1/8 of the whole) with 200 µL of ethanol, or by the addition of 200 µL of ethanol to the extraction solutions. The weight changes after extraction were all negligible for these three different means. The mass of particles on one eighth of a particle laden filter was typically between 2 to 8 mg, while the weight changes associated with extraction of blank filters were less than 0.1 mg. The uncertainty in the weight measurements was ±0.01 mg and it was therefore satisfactory to perform gravimetric analysis required in this work.

The effects of extraction parameters on the recovery of particles from exposed filters are summarized in Table 2. It was found that 100 µL of ethanol was not sufficient to wet

Table 1 Weight change (mg) of blank filter after extraction.

Sample #	*No wetting agent*	*Ethanol pre-wetting*	*Ethanol to solution*
1	0.00	0.00	–0.03
2	0.06	0.00	–0.01
3	0.03	0.02	0.01
4	0.01	0.01	–0.01
Average	0.03	0.01	–0.01

Note: Filter pieces weigh approximately 0.9 g each, with a surface area of 10 square inches.

Table 2 Effects of extraction parameters on efficiency.

Volume of ethanol (μL)	*Means of applying ethanol*	*Sonication time (min)*	*Average recovery (%)*	*Standard deviation*	*Number of replicates*
0	Pre-wetting	60	53.0	10.4	6
100	Pre-wetting	60	71.4	6.6	4
200	Pre-wetting	60	90.3	6.5	4
200	Pre-wetting	30	91.3	6.7	3
300	Pre-wetting	60	95.5	0.2	3
500	Pre-wetting	60	93.6	4.7	3
500	To solution	60	84.2	4.7	3

Note: The temperature was kept below 40°C during extraction. The surface area of each filter piece was 10 square inches.

the entire surface area (10 square inches) of the filter piece (one eighth of a whole filter). This was also reflected by the low recovery of 71.4 ± 6.6%. Taking into consideration the need to reduce alteration of composition, pre-wetting the filter piece with 200 to 300 μL of ethanol (corresponding to 0.5 to 0.75% in the extraction solution) appeared to be appropriate, resulting in greater than 90% recovery as determined by filter weight loss. The difference between 60 minutes sonication (90.3 ± 6.5%) and 30 minutes sonication (91.3% ± 6.7%) was not significant and 30 minutes sonication was therefore used for later work. Pretreatment of the extraction solution with ethanol was less effective (84.2 ± 4.7%) compared to pre-wetting of the filter with ethanol. Extraction of exposed filters by sonication for 60 minutes without any wetting agent yielded an average mass recovery of 53.0% ± 10 4%

Based on above results, an extraction protocol was established. Sample filters to be used for biological reactivity studies were each cut into 8 pieces and the cut pieces of each filter were pre-wetted with 2 mL of ethanol, extracted in 400 mL water under sonication for 30 minutes. The temperature of the ultrasonic water bath was kept below 40°C by the addition of ice cubes during the sonication process. After extraction, the aqueous extracts were transferred to 500-mL pre-cleaned short glass jars with Teflon lined caps (Fischer Scientific, Montreal, PQ), frozen, and stored for later tests. The method was applied to the extraction of field samples and was further evaluated.

Application and further evaluation of the extraction method. 36 field samples were processed using the aqueous extraction method developed. Masses ranging from 3 to 210 mg per sample were estimated (based on weight differences) to have been extracted into the aqueous solutions. The ratios of the masses recovered from freeze drying of the extracts to those based on filter weight losses ranged from 0.58 to 1.69 with an average of 0.98. Among them 30 (i.e. 83%) were between 0.75 and 1.25. The correlation of the masses actually recovered from the extracts and those based on filter weight differences is plotted in Figure 1, with a slope of 0.95 and a correlation coefficient (r) of 0.92. This indicates that the data based on the weight difference before and after the extraction reliably reflected the mass extracted into and recovered from the aqueous solution.

Chemical analyses were performed on some samples as an important measure of the effectiveness of the extraction method. Quantifiable amounts of ions (chloride, nitrate and sulphate) and metals (Ca, Cu. Fe, Mg, Mn, Pb, Zn, K, and Na) were measured in 6 composite samples each collected from a different sampling site. Loadings of As, B, Ba, Be, Cd, Co, Cr, Mo, Ni, Sr, Ti, and V were each near or below the detection limit of 0.01 mg/filter and, therefore, the aqueous extraction recoveries of these metals can not be assessed due to the lack of reliable data.

Tabulated in Table 3 are the aqueous extraction recoveries of the quantifiable inorganics, with standard deviations of the average recoveries determined, the ranges of quantifiable masses per filter for individual analytes and their quantifiable frequencies (n). The recoveries of the three ions were good, ranging from 91 ± 23% to 120 ± 15%. The recoveries of the metals ranged from 47 ± 27% (Mg) to 108 ± 18% (Na). The overall

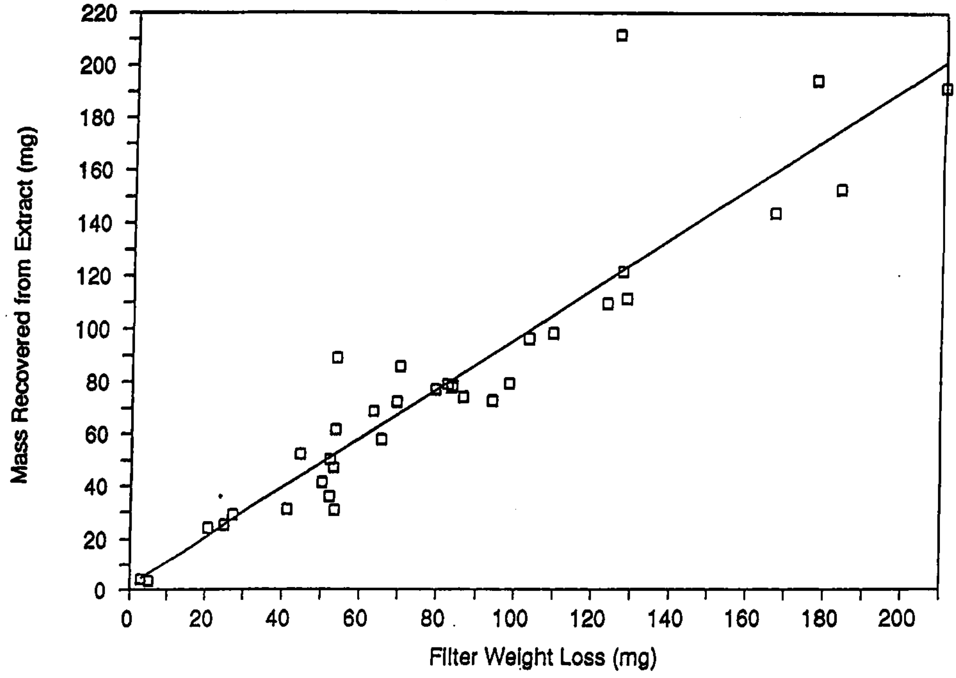

Figure 1 Correlation of data based on mass recovered from freeze-drying and on filter weight loss. $Y = 1.86 + 0.95X$, $r = 0.922$

Table 3 Aqueous extraction recoveries (%) of inorganics.

Analyte	*Range of mass per filter (mg)*	*Average recovery (%)*	*Standard deviation*	*n*
Chloride	0.04–8.72	120	15	6
Nitrate (as N)	0.02–1.93	101	17	6
Sulphate	3.63–15.6	91	23	6
Calcium	0.39–3.33	87	30	6
Copper	0.01–0.23	87	31	6
Iron	0.15–0.95	53	31	6
Lead	0.02–0.07	56	19	6
Magnesium	0.08–0.69	47	27	6
Manganese	0.01–0.36	59	5	5
Potassium	0.17–1.35	107	52	4
Sodium	0.84–5.17	108	18	4
Zinc	0.03–0.10	91	17	5
Overall		84	33	66

average recovery of these 9 elements and the three ions from the 6 samples was 84% ± 33%. The recovery level was comparable to the mass recovery (91 ± 7%) of particles based on gravimetry. The variation in inorganic recovery (33% overall) was understandable, taking into consideration of the analytical accuracy that can normally be achieved for trace metal analysis. As stated in the experimental section, the analytical accuracy was ±30%. Nevertheless, the high overall recovery level (84%) of inorganics was in support of the results summarized in Table 2 which indicates that more than 90% of the particulate matter was recovered with the aqueous extraction method.

The aqueous extraction recoveries of PAHs were determined based on comparison of the amounts of PAHs in dichloromethane extracts of exposed filters and the exposed filters which had previously been subjected to aqueous extraction. Among the 20 target PAHs, acenaphthene, fluorene, and acenaphthylene were not detectable on any of the six samples (< 0.2 ng/filter). The quantifiable mass ranges of the remaining 17 PAHs loaded on each exposed filter, their average recoveries and standard deviations, and the quantifiable frequencies (n) are tabulated in Table 4. If the amount of a PAH was quantifiable on an exposed filter but < 0.2 ng on the corresponding aqueous-extracted filter, 0.2 ng was applied to the aqueous-extracted filter for calculating the recovery. The average recoveries of individual PAHs from the 6 samples spanned from 67.8 ± 24.0% for benzo(ghi)perylene to 99.6 ± 0.2% for indeno(1,2,3-c,d)pyrene (Table 4). The standard deviations of PAH recoveries were less significant than those of metals. The overall average recovery of these 17 PAHs from the 6 samples was 92 ± 11%, similar to the mass recovery (91 ± 7%) of particles based on gravimetry.

In conclusion, an aqueous extraction method has been developed to recover from hydrophobic Teflon filters fine particles in a form suitable for the assessment of the cytotoxicity of the complete chemical nature. The main objective has been achieved with demonstrated high recoveries of 91%, 84%, and 92%, respectively, for particulate mass, inorganic and organic constituents, based on gravimetric, inorganic (metals and major ions) and organic (PAHs) analyses. Results of toxicological assays performed on the particles recovered using this method, and their environmental and health effect implications will be discussed in a separate series of manuscripts.

Table 4 Aqueous extraction recoveriy (%) based on PAH analysis.

Analyte	*Range of mass per filter (ng)*	*Average recovery (%)*	*Standard deviation*	*n*
Phenanthrene	30 - 227	92.7	3.7	6
Anthracene	2 - 20	92.1	7.2	4
Fluoranthene	28 - 467	96.5	1.9	6
Pyrene	18 - 315	96.5	2.3	6
Triphenylene	14 - 107	90.7	10.5	4
Benzo(ghi)fluoranthene	57	99.6	–	1
Benzo(a)anthracene	7 - 129	88.0	9.2	5
Chrysene	23 - 351	94.9	3.0	5
Benzo(e)pyrene	27 - 298	96.5	3.5	5
Benzo(b)fluoranthene	14 - 364	88.5	16.9	5
Dibenz(a,c)anthracene	6 - 60	89.3	6.7	4
Benzo(k)fluoranthene	8 - 267	94.9	3.2	5
Benzo(a)pyrene	10 - 373	94.2	4.2	5
Benzo(ghi)perylene	13 - 380	67.8	24.0	4
Dibenz(a,h)anthracene	6 - 70	90.0	14.3	4
Indeno(1,2,3-c,d)pyrene	37 - 391	99.6	0.2	4
Anthanthrene	4 - 6	95.9	0.1	3
Overall		91.9	11.1	76

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