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Losses of explosives residues on disposable membrane filters

T.F. Jenkins, L.K. Knapp and M.E. Walsh

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A number of 0.45 μ m disposable filters were tested for sorption of HMX, RDX, TNB, DNB, tetryl, TNT and 2,4-DNT. Both aqueous and mixed aqueous-organic solvent matrices were tested. For aqueous matrices, the Nalgene (green) cellulose acetate filter sorbed significant amounts of HMX, RDX, TNT and 2,4-DNT. The Gelman Acro LC25 filter, described as a naturally hydrophilic fluoropolymer, also sorbed significant levels of HMX, TNT and tetryl. Where sorption was found, losses were greatest for the first portion of filtrate passed through the filter and for filtration conducted slowly. Addition of 50% organic solvent prior to filtration eliminated sorption problems for all filters tested. When aqueous matrices are filtered, the recommended procedure is to discard the first 10-mL portion of filtrate and retain the second 10-mL portion for analysis. Keywords: TNB(1,3,5-trinitobenzene); DNB(1,3-dinitrobenzene); Explosives; Organic compounds; Water pollution; Laboratory analyses.					
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PREFACE

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ABBREVIATIONS

HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	2,4,6-trinitrotoluene
2,4-DNT	2,4-dinitrotoluene
TNB	1,3,5-trinitrobenzene
DNB	1,3-dinitrobenzene
Tetryl	methyl-2,4,6-trinitrophenylnitramine
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency

LOSSES OF EXPLOSIVES RESIDUES ON DISPOSABLE MEMBRANE FILTERS

by

T.F. Jenkins, L.K. Knap and M.E. Walsh

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organic compounds has also been previously reported. Chiou and Smith (1974) studied the adsorption of 18 acidic and neutral organic compounds on cellulosic filter membranes and found that adsorption 1) was highest for the smallest pore-size filters examined, 2) was highest for compounds of low water solubility, 3) was less for ionic forms of compounds, 4) decreased as the volume of solution filtered increased, 5) was increased by a slow filtration rate, and 6) was reversible. Liu et al. (1977) confirmed Chiou and Smith's findings that ionized forms of compounds are less strongly adsorbed to cellulose acetate membranes than undissociated forms, and noted that polynuclear aromatic compounds were strongly adsorbed.

USATHAMA (1985) defines filter-analyte compatibility in the following way:

1. The filter material must not be changed by the material being filtered.
2. The filter material must not adsorb or leach the chemical species being determined and tests must be conducted to ensure that there was no sorption of specific organic analytes on specific membranes.

This study was conducted to determine if there is any sorption of trace levels of explosives when aqueous matrices are filtered through a wide variety of commercial membrane filters. In addition, if sorption was found, we wanted to determine whether this problem could be mitigated by addition of a miscible organic solvent prior to filtration, as reported elsewhere (Jenkins et al. 1984).

EXPERIMENTAL

Filter units

Table 1 presents the 11 filters tested in this study. The filter membranes' composition and housing are presented along with the pore sizes and filter diameters. Ten of these filters were self-contained, disposable units. The Nuclepore filter unit had a polycarbonate housing in which replaceable polycarbonate membranes were installed for each sample. The Nuclepore unit had been tested previously (Jenkins et al. 1984) and was included in this study for comparison. In the past, carryover from sample to sample was found with the Nuclepore device when soil extracts containing high concentrations of explosive residues were filtered prior to lower level concentration samples.

Table 1. Types of filters tested.

Manufacturer	Type of membrane	Pore size (μ m)	Diameter (μ m)	Housing composition
Millex-HV	Durapore*	0.45	25	Polyethylene
Nalgene (green)	Cellulose acetate	0.45	25	Modified acrylic
Millex-SR†	PTFE	0.5	25	Polyethylene
Spartan T†	Teflon	0.45	30	Polypropylene
Bio-Rad Prep Disc	PTFE	0.45	32	Polypropylene
Spartan 3	Nylon 66	0.45	3	Nylon 66
Spartan 25	Nylon 66	0.45	25	Polypropylene
Nalgene (yellow)	Nylon	0.45	25	Polypropylene**
Spectra/Por	Nylon (+ charged)	0.45	25	Polypropylene**
Gelman Acro LC25	Fluoropolymer††	0.45	25	Polypropylene
Nuclepore	Polycarbonate	0.4	25	Polycarbonate

* Polyvinylidene difluoride.

† Could not be tested with aqueous solution since the surfaces were not wet by water.

** Glass reinforced.

†† Naturally hydrophilic.

Initial study

For the initial testing, we prepared two test solutions, A and B, of HMX, RDX, TNT and 2,4-DNT by diluting small volumes of the stock solutions of these analytes with Milli-Q reagent grade water. These stock solutions were prepared by weighing out SARM* for each analyte and diluting to volume with methanol or methanol-acetonitrile. Analyte concentrations in these solutions are presented in Table 2.

For the first test, both test solutions A and B were analyzed. A series of 48 individual 10-mL replicates of each solution was pipetted into 20-mL glass scintillation vials. To each of these vials, 10 mL of a solution containing 76% methanol and 24% acetonitrile (V/V) was added. Then the solutions were shaken and allowed to stand at least 15 minutes.

For each of the two solutions, the vials were randomly assigned to 12 groups, four to a group; one group for each type of filter (Table 1) and an

*Standard Analytical Reference Materials were obtained from USATHAMA, Aberdeen Proving Ground, Maryland 21010.

Table 2. Analyte concentrations ($\mu\text{g/L}$) in aqueous* solutions used for initial filtration study.

Analyte	Solution A	Solution B
HMX	474	237
RDX	410	205
TNT	208	104
2,4-DNT	156	78

* Residual organic solvent concentration was about 0.35% V/V for solution A and 0.18% V/V for solution B.

unfiltered control group. The solutions were filtered through each type of filter membrane as follows:

1. The plunger was removed from a 10-mL B-D disposable syringe and the syringe was attached by luer-lock to a filter unit.
2. A 10-mL portion of the solution was added and the plunger replaced.
3. The solution was forced through the filter and the first 10-mL portion of filtrate was wasted.
4. The filter unit was removed, the plunger removed, and the remaining 10-mL of solution was poured in and the plunger replaced.
5. This remaining 10-mL portion was filtered into a glass scintillation vial and retained for analysis.

For the second test, both A and B test solutions were analyzed. Forty 20-mL replicates of each solution were pipetted into vials. For each solution the vials were randomly assigned to ten groups, also four to a group, with each of nine groups assigned to a different type of filter* and the 10th group left unfiltered as a control. These aqueous solutions were filtered as described earlier. Once they were filtered, a 10-mL portion of each aqueous filtrate was mixed with 10 mL of methanol-acetonitrile solution (76/24, V/V) and the solutions were retained for analysis.

Both sets of samples were analyzed by RP-HPLC. A 100- μL sample loop was overfilled with the sample and the sample was injected onto an LC-8 column (Supelco) that was eluted with 50/38/12 (V/V/V) water-methanol-acetonitrile at 1.5 mL/min (Jenkins et al. 1984). The retention times for HMX, RDX, TNT and 2,4-DNT were 3.2, 4.3, 8.1 and 9.2 minutes respectively.

* The Millex-SR and Spartan T filters were not used to filter aqueous samples since water does not wet their fluorocarbon membranes.

Quantitative results were generated from peak areas obtained on an HP 3390 digital integrator or peak heights obtained on an HP 7100B strip chart recorder.

After completion of this initial testing phase, test solution C was prepared by dilution of test solution B 1/1 with Milli-Q water. Six replicates were filtered through individual Nalgene (green) filters as described above and compared with six unfiltered replicates.

Throughput study using Nalgene (green) filter

After the initial filtration study using the aqueous matrix, we examined the concentration of the four analytes in successive amounts of filtered solution. We chose the Nalgene (green) type filter for this study, using an aqueous matrix, since results of the initial tests showed significant losses for this filter with the aqueous matrices. Solution B was used for the test. Two replicate Nalgene (green) filters were tested. In each case, 15 mL of aqueous solution was filtered and each successive millilitre of filtrate was collected separately in a glass scintillation vial and analyzed as described previously.

Filtration rate studies

An experiment was conducted to determine whether the rate at which samples were filtered affected the degree of loss of analyte by sorption. The Nalgene (green) filter was studied using test solution B. Duplicates were obtained at each of the following five filtration rates: 10 mL in 3 seconds, 10 mL in 10 seconds, 10 mL in 20 seconds, 10 mL in 60 seconds and 10 mL in 18.5 minutes. The first 10 mL passing through the filter was mixed with 10 mL of methanol-acetonitrile solution and analyzed as described above.

A second filtration rate study was conducted using the Millex-HV, Bio-Rad Prep Disc and Nalgene (yellow) filters. Test solution B was used and we examined three filtration rates for each filter. Samples were processed and analyzed as described previously. For Millex-HV, the rates studied were 10 mL in 3 seconds, 10 mL in 15 seconds and 10 mL in 30 seconds. The three rates studied for the Bio-Rad Prep Disc were 10 mL in 12, 35 and 60 seconds and for the Nalgene (yellow), 10 mL in 4, 10 and 25 seconds.

Table 3. Concentrations of analytes in solution prepared by dissolving solid explosives in Milli-Q water.

Analyte	Concentration ($\mu\text{g/L}$)
HMX	163
RDX	493
TNB	55.3
DNB	50.7
TNT	135
Tetryl	45.7

Fully aqueous study

Because sorption test results in the initial studies may have been affected by small amounts of organic solvent present in the test solutions, a fully aqueous test solution was needed for analysis. Thus, we prepared another test solution by placing solid explosives (HMX, RDX, TNB, DNB, TNT and tetryl) in Milli-Q water and stirring for several weeks. The resulting solution was vacuum filtered through a 0.45- μm Supelco Nylon 66 filter to remove small particles of undissolved material. The concentrations of HMX, RDX, TNB, DNB, tetryl and TNT were determined by RP-HPLC on an LC-18 column eluted with 1.5 mL/min of 50/50 water-methanol. Retention times were 2.6, 3.9, 5.3, 6.4, 7.1 and 8.6 minutes for HMX, RDX, TNB, DNB, tetryl and TNT respectively. Quantitative results were obtained by comparison of peak areas to response factors from analysis of a calibration standard. Use of a single-point calibration procedure for this method has been justified previously (Jenkins et al. 1984).

We further diluted the filtered sample with Milli-Q water by a factor of 75/1925 V/V to obtain concentrations of the above six analytes in a suitable range to enable reproducible quantitation, but keeping the levels as low as possible to enable detection of relatively small losses of analyte. The resulting solution concentrations are given in Table 3.

Aliquots of this solution were filtered through the seven different types of filters that would pass aqueous matrices and the filtrates analyzed as described above. Three replicates for each filter type were compared with a control group of three unfiltered replicates. Filtration was conducted as described in the initial study for the aqueous matrix.

Comparison of first 10 mL of filtrate versus second 10 mL using fully aqueous matrix

An additional study was conducted using the aqueous solution described above to compare the first and second 10-mL portions of filtrate from these seven different filter types. The same six analytes were studied and two replicates were tested for each filter type. Analyses were performed as described earlier.

RESULTS AND DISCUSSION

Initial filtration study

The results of the initial filtration study are presented in Tables A1-A8. A summary of the mean values and standard deviations is presented for the aqueous matrix in Table 4.* These results were subjected to analysis of variance (ANOVA). For solution A, the high-concentration aqueous matrix, a significant difference existed among the filter types for all four analytes. Using Duncan's Multiple Range Test, the concentrations for all four analytes in the filtrate from the Nalgene (green) filters were found to be significantly lower than those for the unfiltered solution and most of the other filters tested. None of the filtrates from the other filters were significantly different from the unfiltered solution for any of the four analytes.

For the lower-concentration aqueous matrix, solution B, the filtrate from the Nalgene (green) filter was found to be significantly lower than the unfiltered solution for TNT and 2,4-DNT but not for HMX or RDX. Filtrates from the Gelman Acro LC25 and Spectra/Por filters were also significantly different from the unfiltered solution for TNT, but not for the other three analytes.

The Nalgene (green) filter was also tested with solution C, which had analyte concentrations one-half of the values given for test solution B in Table 4. The results of this test are shown in Table A9. Using the Student's t test, we found the concentration of 2,4-DNT in the filtrate to be significantly lower than the unfiltered solution at the 95% confidence

*The aqueous solutions used for the initial study contained small amounts of methanol-acetonitrile: 0.35 and 0.18% V/V for the high and low concentration solutions, respectively.

Table 4. Mean values and standard deviations for initial filtration study for analytes in aqueous* matrices (µg/L).

Filter type	HMX		RDX		TNT		2,4-DNT	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
<u>Solution A</u>								
Unfiltered	474 (a)**	17.0	410 (c)	7.2	208 (f)	10.9	156 (g,i)	9.
Millex-HV	462 (a,b)	11.5	410 (c)	7.7	202 (f)	11.8	163 (g)	10.
Nalgene (green)	441 (b)	11.3	385 (d)	10.6	167 (e)	8.1	132 (h)	6.
Millex-SR	†		†		†		†	
Spartan T	†		†		†		†	
Bio-Rad Prep Disc	484 (a)	22.3	405 (c)	9.6	208 (f)	5.9	165 (g)	6.
Spartan 3	480 (a)	10.6	403 (c)	13.8	208 (f)	7.8	156 (g,i)	4.
Spartan 25	465 (a)	8.1	416 (c)	15.6	208 (f)	7.4	161 (g)	7.
Nalgene (yellow)	483 (a)	17.6	422 (c)	9.4	203 (f)	7.9	158 (g)	3.
Spectra/Por	472 (a)	16.1	411 (c)	16.7	207 (f)	11.1	161 (g)	4.
Gelman Acro LC25	460 (a,b)	12.7	414 (c)	11.2	196 (f)	8.6	146 (h,i)	1.
Nuclepore	473 (a)	14.9	417 (c)	6.5	205 (f)	4.3	161 (g)	5.
<u>Solution B</u>								
Unfiltered	237 (k)	7.8	205 (l)	2.6	104 (m)	10.8	78 (r)	7.
Millex-HV	244 (k)	21.3	202 (l)	7.7	104 (m)	9.3	76 (r)	2.
Nalgene (green)	225 (k)	15.9	197 (l)	12.7	82 (q)	6.5	62 (s)	8.
Millex-SR	†		†		†		†	
Spartan T	†		†		†		†	
Bio-Rad Prep Disc	239 (k)	4.7	201 (l)	3.7	102 (m,n,o)	4.4	82 (r)	2.
Spartan 3	239 (k)	11.6	204 (l)	1.8	108 (m)	5.9	77 (r)	4.
Spartan 25	249 (k)	9.7	202 (l)	6.1	99 (m,n,o)	4.8	82 (r)	3.
Nalgene (yellow)	246 (k)	6.9	203 (l)	10.7	103 (m)	2.8	81 (r)	4.
Spectra/Por	231 (k)	13.8	204 (l)	9.5	97 (n,o)	2.8	81 (r)	4.
Gelman Acro LC25	230 (k)	6.9	206 (l)	9.9	92 (o,p)	6.8	74 (r)	3.
Nuclepore	239 (k)	14.7	200 (l)	8.1	98 (m,n,o)	4.5	76 (r)	7.

* High-concentration solution had 0.35% (V/V) organic solvent; low concentration solution had 0.18 % (V/V) organic solvent.

** Numbers designated with the same letter were not significantly different from each other at the 95% confidence level as determined by Duncan's Multiple Range Test.

† Filter did not pass aqueous solutions.

level. Concentrations of the other three analytes were not significantly different from the unfiltered solution at the 95% confidence level but it is worth noting that the mean value for the filtered portions was lower than for the unfiltered ones in each case. With more replication, a significant difference would likely be detected.

The percent losses for the Nalgene (green) filter at the three concentration levels are presented in Table 5. Losses were much higher on a percent basis for TNT and 2,4-DNT than for HMX or RDX. For 2,4-DNT, losses at all three tested concentrations were statistically significant compared to

Table 5. Percent losses of analyte on Nalgene (green) filters from aqueous matrices (concentrations of organic solvent in solutions A, B and C were 0.35%, 0.18% and 0.09% [V/V]).

Analyte	Solution A	Solution B	Solution C
HMX	7.0	NS*	NS
RDX	6.1	NS	NS
TNT	19.7	21.1	NS
2,4-DNT	15.4	20.5	19.7

* NS - Losses were not statistically significant at the 95% confidence level.

the unfiltered solutions and the percent losses remained quite constant with concentration. For TNT, losses were only statistically significant at the higher two concentrations. At these two concentrations, the percent loss was quite similar.

The similarity of percent losses at different concentrations indicates that analyte losses were caused by a partitioning mechanism rather than loss on active sites on the filter, since the latter mechanism would produce a greater percent loss at low concentration. The higher losses for TNT and 2,4-DNT compared with RDX and HMX are also consistent with a partitioning mechanism. Octanol-water partition coefficients for these substances have been estimated at 95 and 68 for 2,4-DNT and TNT but only 7.5 and 1.3 for RDX and HMX (Jenkins, unpublished results). Liu et al (1977) reported a similar finding where the percentage of acetylpromazine adsorbed onto cellulose acetate membranes was independent of concentration over a range of 4 to 80 μm . Chiou and Smith (1974) soaked millipore filter disks (cellulose esters) in various concentrations of griseofulvin and warfarin until adsorption equilibrium was reached and measured the amounts of each lost. Again, the percent adsorbed was independent of initial concentration.

Table 6 presents the mean values and standard deviations for the initial filter test in the mixed aqueous-organic matrix. ANOVA for all four analytes at both concentrations indicated that there were no significant differences at the 95% confidence level in the concentrations of the four analytes in the filtrates from any of the filters compared with those in the unfiltered solution. According to Bartlett's Test, the variances for filtration results from the mixed aqueous-organic solvent and the aqueous matrices were homogeneous, indicating that analytical precision was the

Table 6. Mean values* and standard deviations ($\mu\text{g/L}$) for initial filtration study for analytes in 50/38/12 water-methanol-acetonitrile matrix.

Filter type	HMX		RDX		TNT		2,4-DNT	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
<u>Solution A</u>								
Unfiltered	474	6.3	410	11.3	208	9.0	159	8.8
Millex-HV	503	22.8	408	4.8	201	2.6	157	3.5
Nalgene (green)	475	14.5	406	7.9	209	2.2	159	5.6
Millex-SR	487	13.0	400	14.2	211	11.7	157	7.0
Spartan T	469	30.2	392	8.8	196	3.6	158	8.7
Bio-Rad Prep Disc	475	7.9	394	4.0	208	7.6	158	3.9
Spartan 3	477	7.5	403	12.6	204	6.1	158	2.9
Spartan 25	492	32.8	398	8.7	206	4.4	156	5.9
Nalgene (yellow)	474	5.8	397	10.6	199	5.4	160	6.2
Spectra/Por	492	19.6	408	13.3	204	9.0	161	3.9
Gelman Acro LC25	482	17.6	396	13.2	205	5.4	162	6.7
Nuclepore	505	25.0	392	6.2	208	5.9	154	5.0
<u>Solution B</u>								
Unfiltered	237	11.2	205	4.6	107	6.3	78.0	3.5
Millex-HV	227	13.6	207	6.3	107	3.7	78.7	4.6
Nalgene (green)	240	12.2	212	3.3	107	11.1	79.5	4.8
Millex-SR	240	11.2	204	2.2	105	5.0	79.3	0.7
Spartan T	234	7.7	203	4.0	113	6.1	81.9	7.3
Bio-Rad Prep Disc	230	10.0	210	4.4	115	2.3	79.4	3.2
Spartan 3	245	9.8	202	6.6	109	4.2	81.3	5.6
Spartan 25	236	12.9	203	4.0	103	6.0	74.9	5.4
Nalgene (yellow)	239	8.8	206	10.2	107	6.6	74.6	3.7
Spectra/Por	249	18.2	207	8.1	107	4.9	76.8	1.2
Gelman Acro LC25	239	9.1	209	7.2	106	5.2	76.1	3.2
Nuclepore	232	5.0	205	3.9	106	4.6	81.4	4.3

*No statistically significant difference was found between filter types for any of the analytes.

same in both cases. Thus the addition of 50% miscible organic solvent, prior to filtration, eliminated the sorptive losses observed in filtration of the aqueous solutions. Solvent addition is particularly useful when the filtered solution is to be analyzed by RP-HPLC (Jenkins et al. 1984).

Throughput study

The results of the initial filtration study with aqueous matrices indicated that there were significant sorptive losses with the Nalgene (green) filter. Since the first 10-mL portion of filtrate was discarded and only the second 10 mL analyzed, a throughput study was done to determine whether analyte concentrations in the filtrate changed with respect to the amount of liquid filtered. This was done by individually collecting and analyzing each millilitre of the first 15 mL of filtrate passing through a Nalgene (green) filter.

Table 7. Results of throughput study using Nalgene (green) filter and low-concentration aqueous* solution.

Volume filtered (mL)	Concentration ($\mu\text{g/L}$)							
	HMX		RDX		TNT		2,4-DNT	
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2
1	60.7	89.7	57.6	83.7	<3	<3	<2	<2
2	--	84.1	66.0	76.0	<3	5.9	3.6	3.8
3	112	121	104	112	7.3	8.6	<2	--
4	143	160	124	146	8.9	14.2	6.4	9.6
5	162	164	152	143	15.4	24.9	13.6	16.0
6	188	156	164	152	24.3	25.4	25.9	24.7
7	187	184	169	165	32.7	32.3	31.6	33.6
8	186	181	172	168	39.2	39.9	39.5	41.4
9	212	190	180	172	43.7	44.0	48.6	50.4
10	191	192	172	184	47.9	46.2	51.1	49.5
11	166	177	157	168	50.8	48.8	65.6	61.6
12	176	164	158	165	42.4	42.8	55.6	55.3
13	175	182	164	171	42.2	48.3	58.0	61.0
14	186	191	188	177	46.4	52.5	65.4	65.2
15	191	185	188	170	53.6	44.3	62.0	62.2
Unfiltered	237		205		104		78	

* Solution contained 0.18% (V/V) organic solvent.

The results of this study are presented in Table 7, along with the concentrations present before filtration. For all four analytes, the concentrations present in the filtrate increase with throughput. For TNT and 2,4-DNT, this is particularly striking where concentrations in the first millilitre were below 2 or 3 $\mu\text{g/L}$ and increased to an average of 49 and 62 $\mu\text{g/L}$, respectively, by the 15th millilitre filtered. In neither case, however, did the concentrations in the filtrate reach the values initially present prior to filtration. Concentrations for HMX and RDX were also below the unfiltered values, but not to as great a degree. These results clearly indicate that where sorption occurred, the degree of loss was a function of the amount filtered, the largest losses being associated with the first few millilitres filtered. Liu et al. (1977) sought to minimize errors in the determination of drug solubilities by filtering successive 5-mL portions of saturated suspensions until a constant filtrate concentration was reached. Filtrate concentration reached 95% or more of the maximum value after 10 mL of solution was filtered.

Filtration rate study

Another experiment was conducted to determine if the rate at which a solution was filtered had a significant effect on the concentrations of

Table 8. Results of filtration rate study using Nalgene (green) filter and aqueous* matrix.

Filtration rate	Concentration ($\mu\text{g/L}$)							
	HMX		RDX		TNT		2,4-DNT	
10 mL in 3 sec.	202	218	178	191	74.2	80.2	49.7	51.5
10 mL in 10 sec.	221	215	192	183	69.8	71.5	47.5	49.7
10 mL in 20 sec.	199	202	166	175	54.6	60.4	38.7	42.7
10 mL in 60 sec.	174	176	155	158	39.5	42.2	31.5	27.9
10 mL in 18.5 min	95.9	103	121	111	4.2	8.6	33.7	20.0
Unfiltered	237		205		104		78	

* Solution contained 0.18% (V/V) of organic solvent.

analytes in the filtrate. Again, the Nalgene (green) filter was initially chosen for this study with an aqueous matrix. The results of tests at five different filtration rates ranging from 10 mL in 3 seconds to 10 mL in 18.5 minutes are presented in Table 8. For all four analytes, the rate of filtration had a dramatic effect on the concentrations in the filtrate. The largest difference was found for TNT, where the concentration in the filtrate at the slowest rate of filtration averaged about 6.4 $\mu\text{g/L}$ whereas the concentration at the highest rate averaged 77.2 $\mu\text{g/L}$. Where sorption occurred, the rate of filtration also made an enormous difference in the concentrations present in the filtrate. These results confirm the findings of Chiou and Smith (1974) that slow filtration results in increased analyte loss. Slow filtration has also been associated with increased levels of sample contamination from membranes (Cooney 1980).

A second set of filtration rate experiments was conducted using the Millex-HV, Bio-Rad Prep Disc and Nalgene (yellow) filters. Three different filtration rates were tested in each case, and the results are presented in Table 9. For these filters, no significant differences attributable to filtration rate were found

Fully aqueous filtration study

All of the filtration results discussed thus far for aqueous matrices involve test solutions containing small amounts of organic solvent from the stock solutions prepared in methanol or methanol-acetonitrile. The amount of solvent on a percentage basis was low: ranging from 0.07 to 0.35%. However, when compared to the analyte concentrations, this amount of sol-

Table 9. Results of filtration rate study using Millex-HV, Bio-Rad Prep Disc and Nalgene (yellow) filter and aqueous* matrix.

Filtration rate	Concentration (µg/L)							
	HMX		RDX		TNT		2,4-DNT	
	<u>Millex HV</u>							
10 mL in 3 sec.	239	244	204	202	98	99	76	73
10 mL in 15 sec.	230	234	196	199	97	97	64	67
10 mL in 30 sec.	242	240	215	197	98	102	73	72
	<u>Bio-Rad Prep Disc</u>							
10 mL in 12 sec.	239	244	204	202	110	109	82	79
10 mL in 35 sec.	230	244	195	215	106	102	74	77
10 mL in 60 sec.	237	235	208	200	110	122	80	74
	<u>Nalgene (yellow)</u>							
10 mL in 4 sec.	234	220	211	187	105	101	81	72
10 mL in 10 sec.	235	229	203	198	113	104	78	75
10 mL in 25 sec.	228	233	196	209	105	113	74	78
Unfiltered	237		205		104		78	

* Solution contained 0.18% (V/V) organic solvent.

vent was quite large (hundreds to thousands of parts per million compared to hundreds of parts per billion). The next several experiments were conducted to determine if these small residual levels of solvent affected the results of filtration experiments.

The fully aqueous test solution contained measurable levels of HMX, RDX, TNB, DNB, tetryl and TNT. Filtration tests were conducted on seven different types of filters in triplicate and the results of filtrate analysis are presented in Tables A10-A12. The mean values presented in Table 10 were compared by ANOVA and Duncan's Multiple Range Test.

Of the filters tested, only Nalgene (green) and Gelman Acro LC25 were found to sorb the explosives significantly. The percent losses for these filters are presented in Table 11. For the Nalgene (green) filter, percent losses for RDX and TNT were similar to those discussed earlier for filtration of aqueous matrices (Table 5). Unlike the earlier work, however, we found the Gelman filter to sorb significant levels of HMX and TNT. Apparently, the low level of organic solvent present in the previous tests was sufficient to eliminate this problem for the Gelman filter, but not for the Nalgene (green) filter. Losses of tetryl on both filters was apparently

Table 10. Mean values ($\mu\text{g/L}$) from test of various filters with fully aqueous matrix.

Filter type	HMX	RDX	TNB	DNB	Tetryl†	TNT
Unfiltered	163 (a)*	493 (c)	55.3 (e)	50.7 (f)	45.7	135 (i)
Millex-HV	154 (a,b)	480 (c)	57.4 (e)	51.9 (f)	16.2	125 (i,j)
Nalgene (green)	147 (a,b)	449 (d)	51.0 (e)	46.8 (f)	6.8	108 (j,k)
Spartan 25	159 (a,b)	483 (c)	52.7 (e)	50.9 (f)	30.4	136 (i)
Bio-Rad Prep Disc	165 (a)	489 (c)	51.4 (e)	55.2 (f)	19.3	132 (i)
Nalgene (yellow)	163 (a)	486 (c)	47.2 (e)	51.1 (f)	27.5	128 (i)
Gelman Acro LC25	144 (b)	474 (c)	51.5 (e)	47.2 (f)	3.8	95 (k)
Nuclepore	154 (a,b)	494 (c)	50.0 (e)	55.6 (f)	6.4	124 (i,j)

* Numbers with the same letter in parentheses are not significantly different at the 95% confidence level.

† Variances for the tetryl data were not homogeneous, thus these results could not be compared using Duncan's Multiple Range Test.

Table 11. Percent losses of analyte on Nalgene (green) and Gelman Acro LC25 filters for fully aqueous matrix.

Analyte	Nalgene (green)	Gelman Acro LC25
HMX	NS*	11.7
RDX	8.9	NS
TNB	NS	NS
DNB	NS	NS
tetryl	86.0†	91.7†
TNT	20.0	29.6

* NS is given where concentrations in the filtrate were not significantly different from the unfiltered solution at the 95% confidence level.

† Percent loss reported but statistical significance of losses could not be evaluated since variances among treatments were not homogeneous.

much larger than those for the other analytes tested; however, the statistical significance of these results could not be tested directly since variances among treatments were not homogeneous.

Results for the experiment comparing the first and second 10-mL portions of filtrate are presented in Tables A13-A15. Mean values are presented in Table 12.

Significant sorption losses were consistently found for both the Nalgene (green) and Gelman filters. These losses were as high as 72% for

Table 12. Mean values ($\mu\text{g/L}$) from test of first versus second 10-mL portion of filtrate using aqueous matrix.

Filter type	HMX	RDX	TNB	DNB	Tetryl	TNT
Unfiltered	154.5	473	54.5	49.0	39.8	124.3
Millex-HV						
First 10 mL	155.0	468	48.6	49.1	36.7	116.9*
Second 10 mL	155.5	471	55.6	50.3	32.9	118.8*
Nalgene (green)						
First 10 mL	147.0	443 (+)	53.6*	38.0 (+)	80.8	102.3 (+)
Second 10 mL	144.5(+) [†]	445 (+)	52.2*	46.3	47.0	104.6 (+)
Spartan 25						
First 10 mL	150.0	471	52.1	49.3	42.7	119.4*
Second 10 mL	156.0	474	53.0	47.8	43.5	118.3*
Bio-Rad Prep Disc						
First 10 mL	157.0	477	53.3	50.2	40.7	128.9
Second 10 mL	156.0	475	56.0	47.7	28.5	128.0
Nalgene (yellow)						
First 10 mL	145.5(+)	463	53.7	49.5	38.3	109.0*(+)
Second 10 mL	156.0	468	52.2	49.7	40.3	117.8*
Gelman Acro LC25						
First 10 mL	101.0(+)	359 (+)	32.9 (+)	29.9 (+)	7.9	34.7 (+)
Second 10 mL	142.5(+)	460	53.0	43.6	29.1	101.7 (+)
Nucleopore						
First 10 mL	154.0	472	50.8	49.8	38.9	120.2
Second 10 mL	154.0	478	53.9	48.2	44.6	125.8

* Signifies values determined using peak height measurements.

[†](+) Values significantly different from the unfiltered solution at the 95% confidence level, based on Duncan's Multiple Range Test.

TNT in the first 10-mL portion of filtrate from the Gelman Acro LC25 filter (Table 13). Losses for the Nalgene (green) filter were nearly identical to those found earlier where the small residual level of solvent was present (Table 5). Losses for the Gelman filter, however, were much larger than those in the earlier study in which sorption did not significantly reduce analyte concentrations.

To confirm that sorption was the mechanism of loss, 5 mL of the fully aqueous test solution was filtered through Nalgene (green) and Gelman LC25 filter units and collected in two vials for analysis. Then 5 mL of reagent grade methanol was passed through the same two membranes to recover test analytes sorbed on the filter unit housings or membranes. Finally, the methanol filtrates were mixed 1/1 with reagent grade water and analyzed in random order along with the aqueous filtrates and an unfiltered control.

Table 13. Percent losses of analyte in first 10 mL of filtrate versus second 10 mL.

Analyte	Nalgene (green)		Gelman Acro LC25	
	1st 10 mL	2nd 10 mL	1st 10 mL	2nd 10 mL
HMX	NS*	6	35	8
RDX	6	6	24	3
TNB	NS	NS	40	NS
DNB	22	NS	39	NS
Tetryl	†	NS	80	NS
TNT	18	16	72	18

* NS is given when concentrations in filtrate were not significantly different from the unfiltered solution at the 95% confidence level.

† The concentration of tetryl measured was double the unfiltered value.

Results indicated that analyte lost during aqueous filtration was quantitatively recovered by passing methanol through the filter. This clearly showed that sorption was the mechanism of loss, and that an organic solvent was effective in recovering sorbed analyte.

Where statistically significant differences were found, analyte concentrations in the second 10-mL portion of filtrate were usually much closer to those in the unfiltered solution than those in the first 10-mL portion. This is particularly evident for the Gelman filter. This was also true for the measured value of tetryl in the filtrate from the Nalgene (green) filter, where we found a higher concentration than there was in the unfiltered solution, presumably because of elution of a contaminant that co-eluted with the analyte chromatographically.

CONCLUSIONS

Clearly, the results of this study indicate that there is sorption of various nitroaromatics and nitramines on some 0.45- μ m disposable filters. Of those studied, the Nalgene (green) cellulose acetate filter and the naturally hydrophilic fluoropolymer, Gelman Acro LC25, suffered the worst sorption losses. These losses only occurred when aqueous matrices were filtered. Addition of 50% of a miscible organic modifier such as methanol-acetonitrile prior to filtration eliminated the sorption problem. Thus for analysis conducted by RP-HPLC, solvent addition is a desirable precaution.

A small residual level of organic solvent seemed to reduce sorption losses for the Gelman Acro LC25 filter. For the Nalgene (green) filter, however, sorption losses were unaffected by solvent concentrations below 1%.

Where we observed significant sorption losses, discarding the first 10 mL and using the second 10-mL portion of filtrate for analysis reduced sorption losses. A throughput study with the Nalgene (green) filter demonstrated that large sorption losses occur for the first few millilitres filtered. The rate of filtration was also found to have a large effect on sorption losses, with slower rates resulting in larger losses.

Several other types of filters were tested and did not sorb these analytes significantly. These included Nalgene (yellow), Millex HV, Bio-Rad Prep Disc, Spartan 25, Spartan 3, Spectra Por and Nuclepore polycarbonate.

These filtration tests involved only nitroaromatics and nitramines, which are relatively hydrophilic compared to most of the organic analytes causing environmental concern. Sorption losses for more hydrophobic substances are expected to be even greater if a partitioning mechanism is involved and could occur on filter types where losses were not observed with these relatively hydrophilic analytes.

Based on this study we recommend that specific filters should be tested with the analyte of interest to ensure that sorption does not affect analytical results when new methods are developed.

To eliminate potential sorption problems for the analytes studied here, we suggest dilution with 50% of a miscible organic solvent such as methanol or acetonitrile prior to filtration. The specific solvent should be selected to match the eluent used for RP-HPLC separation. By matrix matching the sample and eluent, the baseline disturbance just ahead of the HMX peak can be minimized, resulting in more reproducible integration of peak areas.

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APPENDIX A: DATA

Table A1. Results of filtration experiment for HMX in aqueous solution ($\mu\text{g/L}$).*

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	499	465	468	463
Millex-HV	470	456	448	472
Nalgene (green)	435	430	441	456
Bio-Rad Prep Disc	475	499	456	504
Spartan 3	481	483	465	490
Spartan 25	470	453	467	470
Nalgene (yellow)	494	469	466	501
Spectra/Por	462	458	472	494
Gelman Acro LC25	444	469	471	455
Nuclepore	490	478	468	455
<u>Solution B</u>				
Unfiltered	247	237	236	228
Millex-HV	219	251	269	236
Nalgene (green)	211	248	222	220
Bio-Rad Prep Disc	242	242	238	232
Spartan 3	253	225	237	242
Spartan 25	263	241	244	249
Nalgene (yellow)	254	241	248	239
Spectra/Por	250	219	223	231
Gelman Acro LC25	221	236	235	229
Nuclepore	257	221	238	240

* Low-concentration solution contained 0.18% (V/V) organic solvent, high-concentration solution 0.35% (V/V).

Table A2. Results of filtration experiment for RDX in aqueous solution ($\mu\text{g/L}$).*

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	417	411	400	412
Millex-HV	415	405	401	417
Nalgene (green)	392	370	393	384
Bio-Rad Prep Disc	415	392	404	408
Spartan 3	410	414	383	405
Spartan 25	435	415	397	418
Nalgene (yellow)	410	433	421	423
Spectra/Por	422	391	427	403
Gelman Acro LC25	428	414	411	401
Nuclepore	421	410	412	423
<u>Solution B</u>				
Unfiltered	205	209	203	204
Millex-HV	195	212	197	204
Nalgene (green)	197	214	190	185
Bio-Rad Prep Disc	203	205	197	199
Spartan 3	202	206	203	205
Spartan 25	199	195	208	206
Nalgene (yellow)	218	196	201	195
Spectra/Por	210	190	208	209
Gelman Acro LC25	220	201	203	200
Nuclepore	208	206	191	196

* Low-concentration solution contained 0.18% (V/V) organic solvent, high-concentration solution 0.35% (V/V).

Table A3. Results of filtration experiment for TNT in aqueous solution ($\mu\text{g/L}$).*

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	219	204	195	215
Millex-HV	196	191	204	218
Nalgene (green)	164	152	176	170
Bio-Rad Prep Disc	207	200	214	210
Spartan 3	200	210	204	218
Spartan 25	214	206	198	213
Nalgene (yellow)	213	195	198	204
Spectra/Por	208	193	220	208
Gelman Acro LC25	189	199	188	206
Nuclepore	211	203	206	201
<u>Solution B</u>				
Unfiltered	96.2	95.1	118.3	106.4
Millex-HV	93.8	105.0	115.7	99.8
Nalgene (green)	77.2	91.1	82.8	77.3
Bio-Rad Prep Disc	98.0	107.3	103.3	98.5
Spartan 3	109.1	107.9	115.1	100.8
Spartan 25	105.8	94.5	99.2	97.4
Nalgene (yellow)	100.8	100.7	106.6	102.9
Spectra/Por	97.4	101.0	95.6	94.7
Gelman Acro LC25	86.3	89.4	90.1	101.8
Nuclepore	98.3	104.2	95.3	94.0

* Low-concentration solution contained 0.18% (V/V) organic solvent, high-concentration solution 0.35% (V/V).

Table A4. Results of filtration experiment for 2,4-DNT in aqueous solution ($\mu\text{g/L}$).*

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	74.6	90.3	85.6	77.8
Millex-HV	73.4	72.7	78.4	77.3
Nalgene (green)	73.9	52.8	61.6	59.3
Bio-Rad Prep Disc	80.0	80.5	82.9	85.2
Spartan 3	80.3	74.0	80.4	73.0
Spartan 25	84.3	83.2	82.7	76.5
Nalgene (yellow)	74.4	82.0	82.4	85.4
Spectra/Por	86.6	76.4	78.6	81.0
Gelman Acro LC25	73.7	70.9	78.3	71.4
Nuclepore	82.7	75.8	66.0	78.5
<u>Solution B</u>				
Unfiltered	160	145	151	167
Millex-HV	153	157	176	164
Nalgene (green)	127	130	142	130
Bio-Rad Prep Disc	164	167	177	157
Spartan 3	155	162	151	155
Spartan 25	169	152	157	165
Nalgene (yellow)	154	162	156	158
Spectra/Por	167	158	162	156
Gelman Acro LC25	144	145	146	148
Nuclepore	152	163	165	163

* Low-concentration solution contained 0.18% (V/V) organic solvent, high-concentration solution 0.35% (V/V).

Table A5. Results of filtration experiment for HMX in 50/38/12 water-methanol-acetonitrile ($\mu\text{g/L}$).

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	476	466	473	481
Millex-HV	492	509	478	531
Nalgene (green)	460	478	494	469
Millex-SR	485	481	505	475
Spartan-T	489	500	436	452
Bio-Rad Prep Disc	470	467	479	484
Spartan 3	467	476	479	485
Spartan 25	529	461	510	468
Nalgene (yellow)	482	468	474	473
Spectra/Por	474	480	518	494
Gelman Acro LC25	500	459	478	490
Nuclepore	498	526	473	523
<u>Solution B</u>				
Unfiltered	253	227	233	235
Millex-HV	223	232	243	211
Nalgene (green)	252	230	249	229
Millex-SR	237	241	227	254
Spartan-T	232	230	228	245
Bio-Rad Prep Disc	241	235	219	224
Spartan 3	242	243	232	256
Spartan 25	249	231	220	243
Nalgene (yellow)	228	243	235	248
Spectra/Por	232	236	271	256
Gelman Acro LC25	252	234	237	232
Nuclepore	227	236	237	229

Table A6. Results of filtration experiment for RDX in 50/38/12 water-methanol-acetonitrile ($\mu\text{g/L}$).

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	407	395	420	417
Millex-HV	401	410	408	412
Nalgene (green)	403	416	406	397
Millex-SR	392	393	421	393
Spartan-T	393	404	384	387
Bio-Rad Prep Disc	394	397	396	388
Spartan 3	394	393	401	421
Spartan 25	394	392	396	411
Nalgene (yellow)	393	412	393	388
Spectra/Por	404	396	405	427
Gelman Acro LC25	413	385	386	400
Nuclepore	385	390	391	400
<u>Solution B</u>				
Unfiltered	206	204	199	210
Millex-HV	198	216	206	213
Nalgene (green)	212	208	213	216
Millex-SR	207	202	203	204
Spartan-T	198	207	205	201
Bio-Rad Prep Disc	208	215	205	212
Spartan 3	209	205	194	199
Spartan 25	209	201	201	201
Nalgene (yellow)	200	199	221	204
Spectra/Por	201	218	201	209
Gelman Acro LC25	199	211	211	216
Nuclepore	203	209	206	200

Table A7. Results of initial filtration experiment for TNT in 50/38/12 water-methanol-acetonitrile (ug/L).

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	219	197	208	209
Millex-HV	199	205	201	200
Nalgene (green)	207	209	212	208
Millex-SR	228	206	205	203
Spartan-T	201	197	194	193
Bio-Rad Prep Disc	202	201	216	213
Spartan 3	201	198	212	206
Spartan 25	202	204	212	204
Nalgene (yellow)	204	191	199	200
Spectra/Por	191	212	204	207
Gelman Acro LC25	213	201	203	203
Nuclepore	206	207	202	216
<u>Solution B</u>				
Unfiltered	106.7	100.5	104.1	115.2
Millex-HV	110.0	108.7	101.8	108.6
Nalgene (green)	110.6	120.2	100.0	95.5
Millex-SR	101.2	102.8	103.8	112.3
Spartan-T	113.3	106.3	110.4	120.7
Bio-Rad Prep Disc	114.7	111.1	116.0	116.1
Spartan 3	110.9	114.2	104.4	107.9
Spartan 25	100.9	106.3	108.0	94.8
Nalgene (yellow)	109.3	97.7	107.9	113.2
Spectra/Por	104.1	112.7	101.7	108.8
Gelman Acro LC25	101.7	108.0	102.2	112.7
Nuclepore	101.0	112.1	106.0	105.8

Table A8. Results of initial filtration experiment for 2,4-DNT in 50/38/12 water-methanol-acetonitrile (ug/L).

Filter type	Replicate			
	1	2	3	4
<u>Solution A</u>				
Unfiltered	169	148	162	158
Millex-HV	159	153	156	161
Nalgene (green)	152	161	157	165
Millex-SR	166	151	152	159
Spartan-T	170	156	150	154
Bio-Rad Prep Disc	163	154	158	156
Spartan 3	155	160	156	161
Spartan 25	151	157	164	152
Nalgene (yellow)	166	153	164	156
Spectra/Por	157	164	165	159
Gelman Acro LC25	171	158	162	156
Nuclepore	147	155	153	159
<u>Solution B</u>				
Unfiltered	80.2	73.2	81.0	77.7
Millex-HV	77.6	83.1	72.8	81.3
Nalgene (green)	73.6	82.4	84.3	77.8
Millex-SR	79.7	78.3	80.0	79.2
Spartan-T	91.2	81.5	73.5	81.2
Bio-Rad Prep Disc	81.1	77.6	75.9	82.8
Spartan 3	84.7	79.6	74.2	86.7
Spartan 25	73.6	80.8	68.0	77.0
Nalgene (yellow)	70.0	73.2	78.0	77.3
Spectra/Por	75.1	77.2	78.0	76.9
Gelman Acro LC25	77.0	76.4	71.7	79.4
Nuclepore	80.0	77.1	87.2	81.4

Table A9. Results of filtration study using aqueous* matrix C and Nalgene (green) filter.

Replicate	Concentration (µg/L)							
	HMX		RDX		TNT		2,4-DNT	
	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered
1	100	130	96	105	45.0	57.9	27.7	39.0
2	112	115	90	95	43.6	58.0	34.9	42.3
3	120	97	106	109	51.1	51.1	30.2	36.0
4	122	127	100	111	47.5	40.3	25.4	39.3
5	101	128	73	104	45.5	53.9	33.4	41.5
6	125	113	101	91	38.9	50.8	36.2	35.9
$\bar{X}$	113	118	94	103	45.3	52.0	31.3	39.0
S	10.8	12.5	11.8	7.9	4.1	6.5	4.3	2.7
	$t = 0.756^\dagger$		$t = 1.432^\dagger$		$t = 2.136^\dagger$		$t = 3.715^\dagger$	

* Solution contained 0.09% (V/V) organic solvent.

† Table value for 95% confidence and 10 degrees of freedom is $t = 2.228$.

Table A10. Results of filtration experiment for HMX and RDX using an aqueous matrix without added organic solvent (concentration in µg/L).

Filter type	HMX			RDX		
	1	2	3	1	2	3
Unfiltered	172	160	157	491	501	488
Millex-HV	148	152	163	475	480	486
Nalgene (green)	158	142	141	449	445	454
Bio-Rad Prep Disc	175	164	155	508	484	475
Spartan 25	153	159	166	489	478	481
Nalgene (yellow)	177	162	150	475	491	492
Gelman Acro LC25	137	151	143	465	472	485
Nuclepore	159	149	154	508	497	477

Table A11. Results of filtration experiment for TNB and DNB using an aqueous matrix without added organic solvent (concentration in µg/L).

Filter type	TNB			DNB		
	1	2	3	1	2	3
Unfiltered	61.2	53.4	51.4	47.1	55.4	49.5
Millex-HV	48.6	55.5	68.1	52.2	53.2	50.4
Nalgene (green)	49.3	53.0	50.8	34.5	50.3	55.5
Bio-Rad Prep Disc	47.7	55.0	51.5	49.7	59.6	56.3
Spartan 25	47.9	52.7	57.6	55.9	48.6	48.3
Nalgene (yellow)	53.6	43.6	44.5	54.8	51.2	47.3
Gelman Acro LC25	48.3	58.7	47.5	46.7	45.0	49.8
Nuclepore	53.9	49.6	46.5	54.7	53.1	59.1

Table A12. Results of filtration experiment for TNT and tetryl using an aqueous matrix without added organic solvent (concentration in $\mu\text{g/L}$).

Filter type	TNT			Tetryl		
	1	2	3	1	2	3
Unfiltered	131	147	126	39.8	48.9	48.3
Millex-HV	120	137	119	31.7	<d*	16.8
Nalgene (green)	113	110	101	20.5	<d	<d
Bio-Rad Prep Disc	130	119	148	37.8	13.4	6.7
Spartan 25	137	125	146	55.2	25.9	10.2
Nalgene (yellow)	130	122	132	36.6	16.5	29.5
Gelman Acro LC	102	84.5	97.9	11.3	<d	<d
Nuclepore	127	131	114	11.1	<d	8.0

* <d signifies value less than detection limit.

Table A13. Results of filtration experiment for HMX and RDX comparing the first 10 mL and the second 10 mL of filtrate using a fully aqueous matrix (concentration in $\mu\text{g/L}$).

Filter type	HMX*				RDX			
	First 10 mL		Second 10 mL		First 10 mL		Second 10 mL	
Unfiltered	157	152	157	152	472	474	472	474
Millex-HV	152	158	158	153	471	464	464	473
Nalgene (green)	148	146	144	145	447	439	448	441
Bio-Rad Prep Disc	150	150	158	154	483	471	476	474
Spartan 25	159	155	159	153	472	469	475	474
Nalgene (yellow)	145	146	158	154	459	468	465	471
Gelman Acro LC25	108	93.9	145	140	372	346	459	461
Nuclepore	153	155	153	155	464	481	475	481

* Signifies values determined using peak height measurements.

Table A14. Results of filtration experiment for TNB and DNB comparing the first 10 mL and the second 10 mL of filtrate using a fully aqueous matrix (concentration in $\mu\text{g/L}$).

Filter type	TNB				DNB			
	First 10 mL		Second 10 mL		First 10 mL		Second 10 mL	
Unfiltered	55.6	55.3	55.6	55.3	50.1	47.9	50.1	47.9
Millex-HV	52.5	44.6	56.6	54.6	44.6	53.6	51.1	49.4
Nalgene (green)	53.6*	53.6*	53.6*	50.7*	35.2	40.7	48.3	44.2
Bio-Rad Prep Disc	54.1	52.4	59.2	52.8	51.5	48.9	44.8	50.6
Spartan 25	52.0	52.2	48.3	57.7	51.0	47.5	46.9	48.6
Nalgene (yellow)	52.7	54.7	53.4	50.9	48.7	50.3	53.0	46.3
Gelman Acro LC25	39.2	26.5	53.4	52.5	31.0	28.7	44.4	42.8
Nuclepore	55.4	46.2	54.5	53.2	49.9	49.6	49.0	47.3

* Signifies values determined using peak height measurements.

Table A15. Results of filtration experiment for TNT and tetryl comparing the first 10 mL and the second 10 mL of filtrate using a fully aqueous matrix (concentration in $\mu\text{g/L}$).

Filter type	TNT				Tetryl			
	First 10 mL		Second 10 mL		First 10 mL		Second 10 mL	
Unfiltered	126.9	121.7	126.9	121.7	43.6	36.0	43.1	36.0
Millex-HV	116.2*	117.5*	120.1*	117.5*	32.0	41.4	40.5	25.2
Nalgene (green)	105.8	98.7	103.7	105.4	82.6	78.9	43.7	50.3
Bio-Rad Prep Disc	128.4	129.3	125.1	130.9	37.6	43.8	31.2	25.7
Spartan 25	121.2*	117.6*	116.6*	122.0*	47.3	38.0	39.0	48.0
Nalgene (yellow)	106.8*	111.2*	115.6*	119.9*	28.6	48.0	42.1	38.4
Gelman Acro LC25	47.1	22.3	107.0	96.3	6.9	8.9	22.0	36.2
Nuclepore	119.7	120.6	122.0	129.6	40.2	37.6	50.0	39.1

* Signifies values determined using peak height measurements.