BACKUP DATA REPORT

NIOSH Method No. 7908

Title: NON-VOLATILE ACIDS (Sulfuric Acid and Phosphoric Acid)

Analyte: Sulfuric Acid and Phosphoric Acid

Author/developer: Dietmar Breuer, Dr. rer. nat., Institute for Occupational Safety and Health of the German Social Accident Insurances, Sankt Augustin, Germany; and Kevin Ashley, Ph.D., NIOSH (retired)

Issue 2 revised by Ronnee N. Andrews, Ph.D., Jennifer L. Roberts, and Peter Shaw, Ph.D., NIOSH

Date: 11/16/2023

Issue 1

NIOSH 7908 Issue 1 was published May 10, 2014. The method data used to support Issue 1 can be found in [1-3]. The user check data can be found in [4].

Issue 2

Storage Stability

Quartz Fiber Filters

Through the Comprehensive Analytical chemistry Services Contract (CASC), NIOSH conducted a series of storage stability studies using quartz fiber filters. These studies are reported in Sequence 11947-CE report and summarized below.

Materials and Methods

37-mm quartz fiber filters (SKC #225-9033, Lot 12328) were spiked using concentrated sulfuric acid (J.T. Baker, Instra-analyzed Reagent grade for trace metal analysis, ≥95%, catalog #9673-33) and phosphoric acid (Sigma-Aldrich, 85%, 00.00% trace metal basis, catalog #345245) at 2 levels (10 µg and 40 µg). A mixed spiking solution was prepared using 544 µL sulfuric acid and 698 µL phosphoric acid diluted to 1 L using deionized water for a final solution concentration of 1000 ppm. Depending upon the level, either 10 µL or 40 µL of the mixed spiking solution was spiked onto each stored filter. Samples were prepared in triplicate. Filters were stored at ambient temperature, either within a closed-faced cassette (CFC) assembly or in 15-mL polypropylene tubes, and analyzed at Days 0, 7, and 14. For filters stored in polypropylene tubes, the extraction was performed in the same tube as the filter was stored. Limits of detection (LOD) and limits of quantitation (LOQ) were determined using spiked media at 0.5 – 4 µg of each acid.

Results and Discussion

For sulfuric acid, the reported LOD was 1 µg/sample and the LOQ was 3.5 µg/sample. For phosphoric acid, the reported LOD was 0.5 µg/sample and the LOQ was 1.7 µg/sample. Sulfuric acid results can be found in the Appendix - Table A1A (tube storage) and A1B (cassette storage). Media blanks were stored in polypropylene tubes only. No blank correction was applied to any of the sample results because the amount detected on the blank filters was below the LOD. Phosphoric acid results can be found in the Appendix - Table A2A (tube storage) and A2B (cassette storage). N/A indicates not applicable and ND indicates none detected.

Conclusions

For sulfuric acid, both levels generally recovered quantitatively. However, the recoveries are greater for the lower-level spikes of sulfuric acid. For the lower-level spikes, the analyte was quantitatively recovered when stored in the cassette or tube for up to 14 days. At the higher level, the sulfuric acid recovery dropped to 87% when stored in the cassette and 88% when stored in the tube. For this reason, it is suggested that samples containing sulfuric acid be prepared within 7 days of sampling. Phosphoric acid was quantitatively recovered regardless of concentration or storage vessel over the 14 days of the study.

ISO 21438-1 [5] states that quartz fiber samples used to collect sulfuric acid are stable four weeks after sample collection, but also includes immediate desorption of quartz fiber filters in the procedural steps and information that anecdotal evidence suggests that immediate extraction of quartz fiber filter samples is necessary for quantitative recovery of sulfate.

PTFE Filters

Also, through the CASC, NIOSH conducted additional storage studies using PTFE filters. These studies are reported in Sequence 11947-CH (phosphoric acid only), 11947-CI (sulfuric acid only), and 11947-CJ (both phosphoric and sulfuric acids) reports and summarized below.

Materials and Methods

37-mm, 0.45-µm PTFE filters (Zefon FPTP4537, Lot 23603) were placed into individual aluminum weigh pans for spiking and were spiked using concentrated sulfuric acid (J.T. Baker, Instra-analyzed Reagent grade for trace metal analysis, ≥95%, catalog #9673-33) and phosphoric acid (Sigma-Aldrich, 85%, 00.00% trace metal basis, catalog #345245) at 4 levels (n=4): 10, 40, 160, and 1000 µg either alone or in combination. Spiking solutions were prepared at 1000 and 10,000 ppm of sulfuric acid and/or phosphoric acid in deionized water. For the 10, 40, and 160 µg spike levels, filters were spiked with the 1000 ppm single acid solution with spiking volumes of 10, 40, and 160 µL, respectively. For the 1000 µg level, filters were spiked using 100 µL of the 10,000 ppm single acid solution. Four samples were prepared at each target level. After spiking, the filters were allowed to dry 30 minutes (10 µg) or overnight (all other levels) before placement stored within acid-resistant polystyrene cassettes at ambient temperature. Filters were prepared and analyzed at Days 1, 7, 14, 21, and 28. Two media blanks were run with each analysis. Limits of detection (LOD) and limits of quantitation (LOQ) were determined using spiked media at 0.25 – 2 µg of each acid.

Due to the hydrophobic nature of PTFE filters, the liquid spike beaded on top of the filter, rather than absorbing into it. A small bead of acid was visible after overnight drying and on filters stored over the 28 days of the study. The presence of the bead complicated transfer of the filters and extra preventative measures were undertaken to minimize loss of the spike.

Results and Discussion

For sulfuric acid, the reported LOD was 0.3 µg/sample and the LOQ was 0.83 µg/sample. For phosphoric acid, the reported LOD was 0.5 µg/sample and the LOQ was 1.6 µg/sample. Individual samples results are shown in the Appendix Tables A3A-A3C. The generalized extreme statistical deviate (ESD) many-outliers procedure [6] was used to test for outliers. The generalized ESD procedure indicated that the data included outliers, for which the percent recovered was less than or equal 72.2239. Outlier results are noted with * in Appendix Tables A3A-A3C. Summary results are shown in Tables 1A-1D, after the removal of outliers. Most of the media blank results were below the reported LODs. N/A indicates not applicable and ND indicates none detected. Values in brackets are between the LOD and LOQ.

Table 1A. Mean recoveries for phosphoric acid on spiked PTFE filters for the storage stability study[A]

Days stored	Mean (µg/sample)	Standard deviation (SD) (µg/sample)	% Recovery
1	10.5	0.0706	105
7	9.46	0.379	94.6
14	9.25	0.265	92.5
21	9.11	0.0960	91.1
28[B]	9.36	0.263	93.6
1	43.1	0.425	108
7[B]	38.3	0.0879	95.9
14	37.0	1.07	92.6
21	36.6	0.658	91.5
28	36.8	0.144	92.0
1	157	11.2	98.1
7	154	3.59	96.5
14	147	2.30	91.9
21	150	1.49	93.8
28	147	2.29	92.1
1[B]	1087	6.25	109
7	986	20.2	98.6
14	941	9.22	94.1
21	946	17.7	94.6
28	914	5.72	91.4

[A]Cells are highlighted in grey at the maximum stability for each level tested.
[B]Outliers removed.

Table 1B. Mean recoveries for sulfuric acid on spiked PTFE filters for the storage stability study[A]

Days stored	Mean (µg/sample)	Standard deviation (SD) (µg/sample)	% Recovery
1	10.4	0.0812	104
7	9.65	0.154	96.5
14	9.34	0.232	93.4
21	9.45	0.140	94.5
28	9.55	0.0691	95.5
1	42.2	0.446	106
7	37.8	0.898	94.4
14	36.3	0.527	90.8
21[B]	37.6	0.0604	94.0
28	37.4	0.0992	93.5
1	168	6.70	105
7[B]	150	4.82	93.6
14[B]	146	1.42	91.2
21	152	3.00	95.3
28[B]	152	0.181	94.9

Days stored	Mean (µg/sample)	Standard deviation (SD) (µg/sample)	% Recovery
1	1020	131	102
7	964	12.3	96.4
14	925	13.2	92.5
21	973	14.9	97.3
28	943	10.4	94.3

[A]Cells are highlighted in grey at the maximum stability for each level tested.
[B]Outliers removed.

Table 1C. Mean recoveries for phosphoric acid on spiked (with sulfuric acid) PTFE filters for the storage stability study[A]

Days stored	Mean (µg/sample)	Standard deviation (SD) (µg/sample)	% Recovery
1	10.7	0.359	107
7	9.63	0.158	96.3
14	9.34	0.0724	93.4
21	9.56	0.167	95.6
28[B]	9.34	0.170	93.4
1	42.5	1.77	106
7	38.4	1.29	96.0
14	36.7	0.309	91.7
21	36.7	0.130	91.8
28	37.1	0.240	92.8
1	163	10.9	102
7	149	3.33	93.3
14	140	9.47	87.4
21	139	9.69	86.6
28	140	7.90	87.2
1[B]	1100	18.0	110
7[B]	972	94.4	97.3
14	915	6.51	91.5
21	933	5.35	93.3
28	902	18.1	90.2

[A]Cells are highlighted in grey at the maximum stability for each level tested.
[B]Outliers removed.

Table 1D. Mean recoveries for sulfuric acid on spiked (with phosphoric acid) PTFE filters for the storage stability study[A]

Days stored	Mean (µg/sample)	Standard deviation (SD) (µg/sample)	% Recovery
1	10.3	0.218	103
7	9.59	0.183	95.9
14	9.45	0.0887	94.5
21	9.68	0.0766	96.8
28[B]	9.65	0.137	93.9
1	41.7	1.95	104
7	38.0	1.33	95.1
14	36.6	0.392	91.5
21	37.8	0.115	94.5
28	37.6	0.146	94.0
1	160	10.0	99.9
7	150	3.44	93.6
14	141	9.63	87.9
21	145	10.2	90.7
28	144	8.12	90.2
1[B]	1090	9.80	109
7[B]	939	44.8	93.9
14	919	5.70	91.9
21	973	6.23	97.3
28	937	18.7	93.7

[A]Cells are highlighted in grey at the maximum stability for each level tested.
[B]Outliers removed.

Relative uncertainties for filters spiked with a single acid are shown in Table 2A and 2B. Tables 2C and 2D show the relative uncertainties for each acid when spiked along with the other acid.

Table 2A. Relative uncertainty for phosphoric acid on spiked PTFE filters for the storage stability study

Spike level	Day 1	Day 7	Day 14	Day 21	Day 28
10 µg	1%	4%	3%	1%	3%*
40 µg	1%	1%*	3%	2%	<1%
160 µg	7%	2%	2%	1%	2%
1000 µg	1%*	2%	1%	2%	1%

*Several samples did not recover detectable amounts of phosphoric acid or were identified as outliers. Results shown do not include those samples.

Table 2B. Relative uncertainty for sulfuric acid on spiked PTFE filters for the storage stability study

Spike level	Day 1	Day 7	Day 14	Day 21	Day 28
10 µg	1%	2%	2%	1%	1%
40 µg	1%	2%	1%	2%*	<1%
160 µg	4%	3%*	1%*	2%	<1%*
1000 µg	10%	1%	1%	2%	1%

*Several samples did not recover detectable amounts of sulfuric acid or were identified as outliers. Results shown do not include those samples.

Table 2C. Relative uncertainty for phosphoric acid on spiked (with sulfuric acid) PTFE filters for the storage stability study

Spike level	Day 1	Day 7	Day 14	Day 21	Day 28
10 µg	3%	2%	1%	2%	2%*
40 µg	4%	3%	1%	<1%	1%
160 µg	7%	2%	7%	7%	6%
1000 µg	2%*	10%*	1%	1%	2%

* Several samples did not recover detectable amounts of sulfuric acid or were identified as outliers. Results shown do not include those samples.

Table 2D. Relative uncertainty for sulfuric acid on spiked (with phosphoric acid) PTFE filters for the storage stability study

Spike level	Day 1	Day 7	Day 14	Day 21	Day 28
10 µg	2%	2%	1%	1%	1%*
40 µg	5%	3%	1%	<1%	<1%
160 µg	6%	2%	7%	7%	6%
1000 µg	1%*	5%*	1%	1%	2%

* Several samples did not recover detectable amounts of sulfuric acid or were identified as outliers. Results shown do not include those samples.

Initially, a linear model was used to test the impact of all independent variables: chemical identity (phosphoric or sulfuric acid), chemical status (spiked alone or together), period (storage days), mass level (10, 40, 160, and 1000 µg/sample), and the interaction of period and mass level. Results are shown in Table 3 and indicate that the variables of period and mass level are significant, and the other variables are not.

Table 3. Results of linear model to test the impact of all independent variables.

Source	Degrees of Freedom	Type III Sum of Squares	Mean Square	F Value	p-value
Chemical Identity	1	2.4406	2.4406	0.03	0.8676
Chemical Status	1	115.5265	115.5265	1.32	0.2520
Period	4	9516.7939	2379.1985	27.12	<.0001
Mass Level	3	1021.7728	340.5909	3.88	0.0095
Period*Mass Level	12	1397.8324	116.4860	1.33	0.2014

The model was then reduced with just the explanatory variable of period and mass level included. The least square means resulting from this reduced model are shown in Table 4A. Most of the recovery variation in *period (storage time)* is due the differences between day 1 and the other days. Table 4B in fact shows this, in that the only significant differences in recovery are due to difference between day 1 and the other days. The p-values shown in Table 4B are Tukey-adjusted, meaning that they are adjusted to take into account multiple comparisons.

Table 4A. For *period* – Results of the least squares means for the reduced model.

Period (days)	Least Squares Means	Lower 95% Confidence Limit	Upper 95% Confidence Limit
1	104.6958	102.3431	107.0485
7	91.3042	89.0069	93.6014
14	91.2453	88.9480	93.5426
21	92.8227	90.5254	95.1199
28	89.3523	87.0369	91.6678

Table 4B. For *period* – Results of comparing least squares means for the reduced model. Table shows Tukey-adjusted p-values.

Period (days)	1	7	14	21	28
1		<.0001	<.0001	<.0001	<.0001
7	<.0001		1.0000	0.8892	0.7644
14	<.0001	1.0000		0.8747	0.7840
21	<.0001	0.8892	0.8747		0.2254
28	<.0001	0.7644	0.7840	0.2254	

The least square means for different mass levels resulting from this reduced model are shown in Table 5A. As shown in Table 5B the only significant difference is between the least squares mean for masses of 160 and 1000.

Table 5A. For *mass level* – Results of the least squares means for the reduced model.

Mass Level (µg/sample)	Least Squares Means	Lower 95% Confidence Limit	Upper 95% Confidence Limit
10	94.7244	92.6534	96.7954
40	93.7004	91.6298	95.7710
160	91.1111	89.0406	93.1817
1000	96.0003	93.9412	98.0594

Table 5B. For *mass level* – Results of comparing least squares means for the reduced model. Table shows Tukey-adjusted p-values.

Mass Level (µg/sample)	**10**	**40**	**160**	**1000**
10		0.9016	0.0740	0.8257
40	0.9016		0.3049	0.4092
160	0.0740	0.3049		0.0060
1000	0.8257	0.4092	0.0060	

SAS's procedure MIXED (with outliers removed) was used to determine whether the four (or almost always four) repetitions at each of the treatment combinations were independent observations. The mixed model used the same fixed factors as the linear regression that was used above with the addition of a random component for treatment combination (i.e., the 80 different treatment combinations including chemical identity (phosphoric or sulfuric acid), chemical status (alone or mixed), target mass (10, 40, 160, or 1000), and days stored (1, 7, 14, 21, 28)). The purpose was to determine whether the random component was significant or not. Essentially this meant determining whether the intraclass correlation (ICC) was significant. An ICC of 0.0 would indicate that the repetitions could be considered independent. An ICC of 1.0 would indicate that the treatment combination accounted for all of the variance. In other words, having the repetitions would provide no useful information.

Models with and without the random component for treatment combination were used and compared with a maximum likelihood ratio test. The test showed that there was a significant effect due to the inclusion of the random effect for treatment combinations ($p = 0.0143$). The ICC was 0.1238.

Two things follow from the analysis. First, the ICC was not very high, meaning that there was considerable value in running the repetitions. In essence, n=4 was a useful approach. Second, the results were essentially the same as with the linear regression model that was used before. The results which included the treatment combination as a random variable are shown in Table 6.

Table 6. Results of mixed model to test the impact of all independent variables (type 3 tests of fixed effects)

Effect	Numerator DF	Denominator DF	F Value	p-value
chemical identity	1	57.1	1.29	0.2608
chemical status	1	57.1	1.29	0.2611
chemical identity*chemical status	1	57.1	0.01	0.9181
Days stored	4	57.2	102.17	<.0001
Target Mass	3	57.4	10.23	<.0001
Days stored*Target Mass	12	57.1	0.99	0.4696

In these results, as before, the only fixed factors that were significant were days stored and target mass.

Conclusions

According to NIOSH Publication No. 95-117 [7], a sample can be considered stable if the recovery does not drop by more than 10% from the Day 1 recovery over the storage period. For those samples where the Day 1 recoveries were greater than 100%, a recovery of 90% was used as the cut-off for storage stability determination. For filters spiked separately with either phosphoric acid (Table 1A) or sulfuric acid (Table 1B), recoveries were quantitative at each storage time and samples can be considered stable for at least 28 days. For filters spiked with both phosphoric and sulfuric acids at 10, 40, and 1000 µg levels, recoveries were quantitative at each storage time tested. For the 160-µg level, both phosphoric acid and sulfuric acid acceptably recover for a minimum of 7 days when spiked along with the other acid (Tables 1C & 1D). At Day 14, the recovery for the 160-µg level samples drops below 90% (87.4% for phosphoric acid and 87.9% for sulfuric acid). For sulfuric acid, the recoveries when stored for either 21 or 28 days are quantitative and above 90%. It is likely that these results are not indicative of a storage stability issue and all samples can be stored for at least 28 days before analysis. The issues related to sample spiking and preparation complicate determining overall stability difficult.

Filter Variability

Also, through the CASC, NIOSH conducted studies on the background levels of sulfuric and phosphoric acid in quartz fiber and PTFE filters. These studies are reported in Sequence 11947-CF and -CG.

Materials and Methods

Quartz fiber filters were tested from three manufacturers (Whatman, Millipore, and Zefon). PTFE filters were tested from two manufacturers (SKC and Zefon). Multiple lots were tested, when available.

Results and Discussion

Quartz fiber filters

Individual sulfuric acid results for quartz fiber filters can be found in the Appendix - Table A4A and mean, standard deviation and percent relative standard deviation (% RSD) can be found in Table 7. LODs and LOQs

were determined using Millipore-Sigma filters (Lot # R8PA57621). For both analytes, the reported LOD was 0.5 µg/sample and the LOQ was 1.7 µg/sample.

TABLE 7. Mean amount detected, standard deviation (SD), and percent relative standard deviation (% RSD) for blank quartz fiber filters analyzed for sulfuric acid

Manufacturer and Media Lot	**Mean (n=6) (µg/sample)**	**SD (µg/sample)**	**% RSD**
Whatman A16225264	1.91	0.132	6.9%
Whatman A22835264	1.29	0.246	19.2%
Whatman A20300264	2.09	1.45	69.4%
Millipore R8HA81834	1.91	0.513	26.9%
Millipore R8PA57621	1.96	0.357	18.2%
Millipore R9DA23329	1.04	0.0968	9.3%
Zefon 510966	2.10	0.308	14.7%

A sulfuric acid background was found on all filters, with % RSDs ranging from 7% (Whatman A16225264) to 69% (Whatman A20300264). No phosphoric acid background was detected on the quartz fiber filters; all reported results were ND.

PTFE filters

Individual sulfuric acid results for PTFE filters can be found in Table 8. LODs and LOQs were determined using SKC filters (Lot # 27082065). For sulfuric acid, the reported LOD was 0.3 µg/sample and the LOQ was 1.0 µg/sample. For phosphoric acid, the reported LOD was 0.5 µg/sample and the LOQ was 1.8 µg/sample. N/A indicates not applicable and ND indicates none detected.

TABLE 8. PTFE filters analyzed for sulfuric acid

Manufacturer and Media Lot	Sample ID	Analyzed Mass (µg/sample)
SKC T70881	1	ND
SKC T70881	2	0.354*
SKC T70881	3	ND
SKC T70881	4	ND
SKC T70881	5	0.396*
SKC T70881	6	0.378*
SKC T71243	1	ND
SKC T71243	2	ND
SKC T71243	3	ND
SKC T71243	4	ND
SKC T71243	5	ND
SKC T71243	6	ND
SKC 27082065	1	ND
SKC 27082065	2	ND
SKC 27082065	3	ND
SKC 27082065	4	ND
SKC 27082065	5	ND
SKC 27082065	6	ND
Zefon 47046	1	ND
Zefon 47046	2	ND
Zefon 47046	3	ND
Zefon 47046	4	ND
Zefon 47046	5	0.443*
Zefon 47046	6	ND

*Results are between the reported LOD and LOQ.

One lot (of three tested) from SKC had a variable sulfuric acid background (110% RSD) and one filter from Zefon had a sulfuric acid response. In each instance, the responses were near the LOD. No phosphoric acid background was detected on the PTFE filters; all reported results were ND.

Overall conclusions of updated method

The limited storage stability study (both in terms of levels and time periods tested) of quartz fiber filters indicate that immediate field desorption is not necessary. However, timely (within 7 days of sampling for sulfuric acid and within 14 days of sampling for phosphoric acid) preparation and analysis of the filters is prudent. Method users are also cautioned to the anecdotal evidence and procedure methodology stated within ISO 21438-1 that field desorption of quartz fiber filters is necessary.

The storage stability study of PTFE filters is (for the most part) supportive of the stability listed in ISO 21438-1. The issues related to sample spiking and preparation for the study shown here complicate a determination of overall stability of PTFE filter samples.

Background levels of sulfate on quartz fiber filters are variable. There was limited background detected on PTFE filters. Method users are encouraged to adequately assess and understand the background response when analyzing samples for sulfuric acid.

References

[1] Breuer D [1999]. Measurement of vapor-aerosol mixtures. J Environ Monit *1*:299-305.

[2] Breuer D [2002]. Inorganic acid mists (H_2SO_4, H_3PO_4). In: Kettrup A, Greim H, eds. Analyses of hazardous substances in air (Deutsche Forschungsgemeinschaft). Vol. 6. Weinheim, FRG: Wiley-VCH. pp. 67-78.

[3] Breuer D [2013]. Anorganische säuren, partikulär: phosphorsäure, schwefelsäure (Inorganic acid mists: phosphoric acid, sulfuric acid), in IFA Working Folder, Sheet No. 6173. Berlin, FRG: Erich- Schmidt Verlag. ISBN 978-3-503-13084-9.

[4] Breuer D, Howe A [2006]. Performance of methods for measurement of exposure to inorganic acids in workplace air. J Environ Monit *8*:120-126.

[5] ISO [2021]. ISO 21438-1: Workplace atmospheres – Determination of inorganic ions by ion chromatography – Part 1: Non-volatile acids (sulfuric acid and phosphoric acid). Geneva, Switzerland: International Organization for Standardization (ISO).

[6] Rosner B [1983]. Percentage points for a generalized ESD many-outlier procedure. Technometrics *25*:165-172.

[7] NIOSH [1995]. Guidelines for Air Sampling and Analytical Method Development and Evaluation, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH). Publication No. 95-117. [https://www.cdc.gov/niosh/docs/95-117/default.html]

Appendix

Sample Stability using Quartz Fiber Filters

TABLE A1A. Storage study of sulfuric acid quartz fiber filter samples stored in polypropylene tubes

Days stored	Sample ID	Target Mass (µg/sample)	Analyzed Mass (µg/sample)	% Recovery
0	BLNK 1	N/A	0.708*	N/A
0	BLNK 2	N/A	0.173*	N/A
0	T1	10	10.15	101.5%
0	T2	10	10.37	103.7%
0	T3	10	10.05	100.5%
0	T1	40	38.71	96.8%
0	T2	40	39.34	98.4%
0	T3	40	39.27	98.2%
7	BLNK 1	N/A	0.682*	N/A
7	T1	10	9.15	91.5%
7	T2	10	9.70	97.0%
7	T3	10	10.2	102.1%
7	T1	40	37.7	94.2%
7	T2	40	38.3	95.7%
7	T3	40	36.5	91.1%
14	BLNK 1	N/A	0.931*	N/A
14	T1	10	9.19	91.9%
14	T2	10	9.48	94.8%
14	T3	10	9.67	96.7%
14	T1	40	35.8	89.6%
14	T2	40	34.1	85.1%
14	T3	40	35.6	89.1%

*Results shown are below the reported LOD of 1 µg.

TABLE A1B. Storage study of sulfuric acid quartz fiber filter samples stored in CFC assemblies

Days stored	Sample ID	Target Mass (µg/sample)	Analyzed Mass (µg/sample)	% Recovery
0	C1	10	10.44	104.4%
0	C2	10	9.98	99.8%
0	C3	10	9.68	96.8%
0	C1	40	38.8	97.0%
0	C2	40	38.9	97.2%
0	C3	40	38.9	97.1%
7	C1	10	10.1	100.6%
7	C2	10	9.33	93.3%
7	C3	10	9.31	93.1%
7	C1	40	38.5	96.2%
7	C2	40	36.7	91.8%
7	C3	40	37.6	94.0%
14	C1	10	9.20	92.0%
14	C2	10	9.22	92.2%
14	C3	10	9.55	95.5%
14	C1	40	34.4	86.1%
14	C2	40	34.9	87.3%
14	C3	40	34.9	87.3%

TABLE A2A. Storage study of phosphoric acid quartz fiber filters samples stored in polypropylene tubes

Days stored	Sample ID	Target Mass (µg/sample)	Analyzed Mass (µg/sample)	% Recovery
0	BLNK 1	Blank	ND	N/A
0	BLNK 2	Blank	ND	N/A
0	T1	10	10.4	103.7%
0	T2	10	10.4	103.7%
0	T3	10	9.87	98.7%
0	T1	40	40.9	102.2%
0	T2	40	41.8	104.5%
0	T3	40	41.9	104.8%
7	BLNK 1	Blank	ND	N/A
7	T1	10	9.63	96.3%
7	T2	10	10.0	100.1%
7	T3	10	10.2	101.9%
7	T1	40	39.6	98.9%
7	T2	40	40.6	101.4%
7	T3	40	38.7	96.7%
14	BLNK 1	Blank	ND	N/A
14	T1	10	9.46	94.6%
14	T2	10	9.31	93.1%
14	T3	10	9.44	94.4%
14	T1	40	38.5	96.3%
14	T2	40	36.0	89.9%
14	T3	40	38.1	95.3%

TABLE A2B. Storage study of phosphoric acid quartz fiber filter samples stored in CFC assemblies

Days stored	Sample ID	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
0	C1	10	10.6	106.0%
0	C2	10	10.2	102.1%
0	C3	10	9.88	98.8%
0	C1	40	41.1	102.7%
0	C2	40	41.4	103.6%
0	C3	40	41.4	103.5%
7	C1	10	10.0	100.2%
7	C2	10	9.65	96.5%
7	C3	10	9.79	97.9%
7	C1	40	40.8	102.1%
7	C2	40	39.0	97.4%
7	C3	40	39.8	99.5%
14	C1	10	9.51	95.1%
14	C2	10	9.40	94.0%
14	C3	10	9.20	92.0%
14	C1	40	36.0	90.0%
14	C2	40	36.8	92.1%
14	C3	40	37.6	94.0%

Sample Stability using PTFE Filters

Table A3A. Storage study results for phosphoric acid on spiked PTFE filters

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
BLNK 1	1	Blank	ND	N/A
BLNK 2	1	Blank	ND	N/A
A1	1	10	10.5	105%
A2	1	10	10.5	105%
A3	1	10	10.6	106%
A4	1	10	10.6	106%
B1	1	40	42.7	107%
B2	1	40	43.1	108%
B3	1	40	43.0	107%
B4	1	40	43.7	109%
C1	1	160	149	93.0%
C2	1	160	155	97.1%
C3	1	160	150	93.9%
C4	1	160	173	108%
D1	1	1000	ND*	N/A
D2	1	1000	1091	109%
D3	1	1000	ND*	N/A

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
D4	1	1000	1082	108%
BLNK 1	7	Blank	ND	N/A
BLNK 2	7	Blank	ND	N/A
A5	7	10	8.95	89.5%
A6	7	10	9.81	98.1%
A7	7	10	9.40	94.0%
A8	7	10	9.66	96.6%
B5	7	40	12.3*	30.8%
B6	7	40	38.3	95.7%
B7	7	40	18.2*	45.5%
B8	7	40	38.4	96.0%
C5	7	160	152	95.3%
C6	7	160	153	95.6%
C7	7	160	160	99.9%
C8	7	160	152	95.3%
D5	7	1000	981	98.1%
D6	7	1000	971	97.1%
D7	7	1000	1016	102%
D8	7	1000	977	97.7%
BLNK 1	14	Blank	ND	N/A
BLNK 2	14	Blank	ND	N/A
A9	14	10	9.23	92.3%
A10	14	10	9.43	94.3%
A11	14	10	8.88	88.8%
A12	14	10	9.46	94.6%
B9	14	40	35.7	89.3%
B10	14	40	38.1	95.3%
B11	14	40	37.7	94.1%
B12	14	40	36.7	91.7%
C9	14	160	148	92.5%
C10	14	160	144	90.0%
C11	14	160	147	91.7%
C12	14	160	149	93.4%
D9	14	1000	951	95.1%
D10	14	1000	932	93.2%
D11	14	1000	946	94.6%
D12	14	1000	935	93.5%
BLNK 1	21	Blank	ND	N/A
BLNK 2	21	Blank	ND	N/A
A13	21	10	9.00	90.0%
A14	21	10	9.14	91.4%
A15	21	10	9.22	92.2%
A16	21	10	9.07	90.7%

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
B13	21	40	35.7	89.2%
B14	21	40	37.1	92.8%
B15	21	40	36.6	91.6%
B16	21	40	37.0	92.5%
C13	21	160	149	93.0%
C14	21	160	149	93.0%
C15	21	160	151	94.4%
C16	21	160	152	94.8%
D13	21	1000	958	95.8%
D14	21	1000	952	95.2%
D15	21	1000	920	92.0%
D16	21	1000	953	95.3%
BLNK 1	28	Blank	ND	N/A
BLNK 2	28	Blank	ND	N/A
A17	28	10	9.55	95.5%
A18	28	10	3.66*	36.6%
A19	28	10	9.18	91.8%
A20	28	10	ND*	N/A
B17	28	40	36.7	91.8%
B18	28	40	37.0	92.4%
B19	28	40	36.6	91.6%
B20	28	40	36.8	92.0%
C17	28	160	149	92.8%
C18	28	160	148	92.7%
C19	28	160	149	92.9%
C20	28	160	144	90.0%
D17	28	1000	921	92.1%
D18	28	1000	907	90.7%
D19	28	1000	916	91.6%
D20	28	1000	913	91.3%

*Outlier

Table A3B. Storage study results for sulfuric acid on spiked PTFE filters

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
BLNK 1	1	Blank	ND	N/A
BLNK 2	1	Blank	ND	N/A
E1	1	10	10.3	103%
E2	1	10	10.4	104%
E3	1	10	10.5	105%
E4	1	10	10.3	103%
F1	1	40	42.8	107%
F2	1	40	42.4	106%
F3	1	40	41.8	104%
F4	1	40	42.0	105%
G1	1	160	169	105%
G2	1	160	173	108%
G3	1	160	173	108%
G4	1	160	159	99.2%
H1	1	1000	825	82.5%
H2	1	1000	1078	108%
H3	1	1000	1109	111%
H4	1	1000	1066	107%
BLNK 1	7	Blank	ND	N/A
BLNK 2	7	Blank	ND	N/A
E5	7	10	9.78	97.8%
E6	7	10	9.75	97.5%
E7	7	10	9.44	94.4%
E8	7	10	9.65	96.5%
F5	7	40	36.8	92.1%
F6	7	40	38.9	97.2%
F7	7	40	37.3	93.2%
F8	7	40	38.1	95.2%
G5	7	160	62.4*	39.0%
G6	7	160	76.7*	47.9%
G7	7	160	146	91.4%
G8	7	160	153	95.7%
H5	7	1000	971	97.1%
H6	7	1000	949	94.9%
H7	7	1000	959	95.9%
H8	7	1000	977	97.7%
BLNK 1	14	Blank	0.88	N/A
BLNK 2	14	Blank	[0.3]	N/A
E9	14	10	9.20	92.0%
E10	14	10	9.61	96.1%
E11	14	10	9.11	91.1%
E12	14	10	9.47	94.7%

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
F9	14	40	36.6	91.6%
F10	14	40	36.1	90.2%
F11	14	40	36.9	92.3%
F12	14	40	35.8	89.4%
G9	14	160	147	92.1%
G10	14	160	145	90.4%
G11	14	160	146	91.0%
G12	14	160	96.7*	60.4%
H9	14	1000	920	92.0%
H10	14	1000	910	91.0%
H11	14	1000	941	94.1%
H12	14	1000	930	93.0%
BLNK 1	21	Blank	ND	N/A
BLNK 2	21	Blank	ND	N/A
E13	21	10	9.62	96.2%
E14	21	10	9.29	92.9%
E15	21	10	9.40	94.0%
E16	21	10	9.49	94.9%
F13	21	40	38.1	95.2%
F14	21	40	17.0*	42.5%
F15	21	40	37.8	94.4%
F16	21	40	36.9	92.3%
G13	21	160	148	92.6%
G14	21	160	154	96.1%
G15	21	160	153	95.4%
G16	21	160	155	97.0%
H13	21	1000	981	98.1%
H14	21	1000	962	96.2%
H15	21	1000	990	99.0%
H16	21	1000	959	95.9%
BLNK 1	28	Blank	ND	N/A
BLNK 2	28	Blank	ND	N/A
E17	28	10	9.55	95.5%
E18	28	10	9.65	96.5%
E19	28	10	9.48	94.8%
E20	28	10	9.54	95.4%
F17	28	40	37.3	93.3%
F18	28	40	37.4	93.4%
F19	28	40	37.3	93.4%
F20	28	40	37.5	93.9%
G17	28	160	116*	72.2%
G18	28	160	84.3*	52.7%
G19	28	160	152	94.8%

Sample ID	Days Stored	Target (µg/sample)	Amount detected (µg/sample)	% Recovery
G20	28	160	152	95.0%
H17	28	1000	944	94.4%
H18	28	1000	935	93.5%
H19	28	1000	957	95.7%
H20	28	1000	934	93.4%

*Outlier

Table A3C. Storage study results for phosphoric acid and sulfuric acid on spiked PTFE filters

Sample ID	Days Stored	Target (µg/sample)	Phosphoric acid detected (µg/sample)	Phosphoric acid % Recovery	Sulfuric acid detected (µg/sample)	Sulfuric acid % Recovery
BLNK 1	1	Blank	ND	N/A	ND	N/A
BLNK 2	1	Blank	ND	N/A	ND	N/A
I1	1	10	11.1	111%	10.3	103%
I2	1	10	10.4	104%	10.0	100%
I3	1	10	10.4	104%	10.3	103%
I4	1	10	10.9	109%	10.5	105%
J1	1	40	40.6	102%	39.2	98.1%
J2	1	40	42.6	107%	42.0	105%
J3	1	40	44.8	112%	44.0	110%
J4	1	40	41.8	105%	41.4	104%
K1	1	160	163	102%	160	100%
K2	1	160	173	108%	170	106%
K3	1	160	167	104%	164	102%
K4	1	160	148	92.4%	146	91.3%
L1	1	1000	ND*	N/A	ND*	N/A
L2	1	1000	1121	112%	1095	110%
L3	1	1000	1085	108%	1077	108%
L4	1	1000	1102	110%	1092	109%
BLNK 1	7	Blank	ND	N/A	ND	N/A
BLNK 2	7	Blank	ND	N/A	ND	N/A
I5	7	10	9.77	97.7%	9.83	98.3%
I6	7	10	9.46	94.6%	9.39	93.9%
I7	7	10	9.76	97.6%	9.62	96.2%
I8	7	10	9.54	95.4%	9.54	95.4%
J5	7	40	38.4	96.0%	38.6	96.4%
J6	7	40	38.8	96.9%	38.2	95.4%
J7	7	40	39.8	99.5%	39.2	98.0%
J8	7	40	36.7	91.7%	36.1	90.4%
K5	7	160	152	94.7%	152	94.9%
K6	7	160	152	95.1%	153	95.7%
K7	7	160	149	93.0%	149	93.1%
K8	7	160	145	90.5%	145	90.8%

Sample ID	Days Stored	Target (µg/sample)	Phosphoric acid detected (µg/sample)	Phosphoric acid % Recovery	Sulfuric acid detected (µg/sample)	Sulfuric acid % Recovery
L5	7	1000	689*	68.9%	684*	68.4%
L6	7	1000	891	89.1%	888	88.8%
L7	7	1000	1076	108%	961	96.1%
L8	7	1000	951	95.1%	969	96.9%
BLNK 1	14	Blank	ND	N/A	0.88	N/A
BLNK 2	14	Blank	ND	N/A	[0.3]	N/A
I9	14	10	9.35	93.5%	9.55	95.5%
I10	14	10	9.31	93.1%	9.40	94.0%
I11	14	10	9.26	92.6%	9.35	93.5%
I12	14	10	9.44	94.4%	9.49	94.9%
J9	14	40	37.1	92.7%	37.1	92.7%
J10	14	40	36.3	90.9%	36.1	90.3%
J11	14	40	36.6	91.5%	36.5	91.3%
J12	14	40	36.7	91.9%	36.6	91.6%
K9	14	160	131	81.6%	132	82.3%
K10	14	160	148	92.5%	149	92.9%
K11	14	160	148	92.5%	149	93.3%
K12	14	160	133	82.9%	133	83.0%
L9	14	1000	913	91.3%	915	91.5%
L10	14	1000	919	91.9%	922	92.2%
L11	14	1000	920	92.0%	925	92.5%
L12	14	1000	906	90.6%	913	91.3%
BLNK 1	21	Blank	ND	N/A	ND	N/A
BLNK 2	21	Blank	ND	N/A	ND	N/A
I13	21	10	9.60	96.0%	9.57	95.7%
I14	21	10	9.65	96.5%	9.72	97.2%
I15	21	10	9.68	96.8%	9.74	97.4%
I16	21	10	9.32	93.2%	9.69	96.9%
J13	21	40	36.9	92.2%	37.8	94.4%
J14	21	40	36.6	91.4%	37.6	94.1%
J15	21	40	36.7	91.8%	37.9	94.7%
J16	21	40	36.7	91.7%	37.9	94.7%
K13	21	160	139	87.1%	146	91.1%
K14	21	160	125	78.1%	131	81.7%
K15	21	160	148	92.3%	154	96.4%
K16	21	160	142	88.9%	150	93.5%
L13	21	1000	930	93.0%	975	97.5%
L14	21	1000	939	93.9%	977	97.7%
L15	21	1000	937	93.7%	975	97.5%
L16	21	1000	928	92.8%	964	96.4%
BLNK 1	28	Blank	ND	N/A	ND	N/A
BLNK 2	28	Blank	ND	N/A	ND	N/A
I17	28	10	4.58*	45.8%	4.84*	48.4%

Sample ID	Days Stored	Target (µg/sample)	Phosphoric acid detected (µg/sample)	Phosphoric acid % Recovery	Sulfuric acid detected (µg/sample)	Sulfuric acid % Recovery
I18	28	10	9.22	92.2%	9.60	96.0%
I19	28	10	9.26	92.6%	9.55	95.5%
I20	28	10	9.53	95.3%	9.81	98.1%
J17	28	40	37.2	92.9%	37.6	94.1%
J18	28	40	37.2	93.0%	37.6	93.9%
J19	28	40	37.3	93.4%	37.8	94.5%
J20	28	40	36.8	92.0%	37.4	93.6%
K17	28	160	139	86.6%	144	89.7%
K18	28	160	143	89.6%	148	92.7%
K19	28	160	147	92.1%	152	95.2%
K20	28	160	129	80.6%	133	83.4%
L17	28	1000	926	92.6%	954	95.4%
L18	28	1000	904	90.4%	946	94.6%
L19	28	1000	896	89.6%	937	93.7%
L20	28	1000	882	88.2%	911	91.1%

*Outlier

Filter Variability

TABLE A4A. Sulfuric acid content for blank quartz fiber filters from different manufacturers and lots

Manufacturer and Media Lot	**Sample ID**	**Analyzed Mass (µg/sample)**
Whatman A16225264	1	2.16
Whatman A16225264	2	1.84
Whatman A16225264	3	1.79
Whatman A16225264	4	1.93
Whatman A16225264	5	1.88
Whatman A16225264	6	1.89
Whatman A22835264	1	1.10
Whatman A22835264	2	1.13
Whatman A22835264	3	1.26
Whatman A22835264	4	1.17
Whatman A22835264	5	1.76
Whatman A22835264	6	1.30
Whatman A20300264	1	1.53
Whatman A20300264	2	1.44
Whatman A20300264	3	1.46
Whatman A20300264	4	1.66
Whatman A20300264	5	5.05
Whatman A20300264	6	1.41
Millipore R8HA81834	1	1.26

Manufacturer and Media Lot	Sample ID	Analyzed Mass (µg/sample)
Millipore R8HA81834	2	1.62
Millipore R8HA81834	3	2.74
Millipore R8HA81834	4	1.69
Millipore R8HA81834	5	1.97
Millipore R8HA81834	6	2.17
Millipore R8PA57621	1	1.44
Millipore R8PA57621	2	1.87
Millipore R8PA57621	3	1.82
Millipore R8PA57621	4	2.09
Millipore R8PA57621	5	2.53
Millipore R8PA57621	6	2.01
Millipore R9DA23329	1	0.909
Millipore R9DA23329	2	1.19
Millipore R9DA23329	3	1.09
Millipore R9DA23329	4	1.07
Millipore R9DA23329	5	0.984
Millipore R9DA23329	6	1.00
Zefon 510966	1	1.81
Zefon 510966	2	1.72
Zefon 510966	3	2.08
Zefon 510966	4	2.20
Zefon 510966	5	2.57
Zefon 510966	6	2.20