

Review of Sodium Ion Contamination Issue for the Speciation Trends Network (Revised)

**Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711**

EPA Contract No. 68-D-03-038

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January 19, 2005

Ms. Joann Rice
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
MDC339-02
Research Triangle Park, NC 27711

Dear Ms. Rice:

Attached in PDF format is RTI's REVISED report titled "Review of Sodium Ion Contamination Issue for the Speciation Trends Network."

Also, enclosed is separate sheet addressing the questions you had regarding this report.

If you have any questions or comments, please feel free to call me at 541-6483, or e-mail at rkmj@rti.org.

Sincerely,

R. K. M. Jayanty, Ph.D.
Program Manager

/dmh

Enclosures

cc: V. Presnell
91U-08858

Q: Page 1: "As a result of this original problem, all sodium ion data reported to AQS for the period September 2001 through January 2002 were invalidated." Does this mean that sodium ion data has been removed from AQS for this period? Or is the data there with a flag?

A: The data are flagged as suspicious in AQS ('4' - possible lab contamination).

Q: Page 2, Section 7.0: "Background sodium levels on Teflon filters, which are used for ion analysis with some STN sampler types,..."
Can we say what sampler types? You mention URG, but what are the others?

A: Two sampler types sample ions on Teflon: URG MASS and the R&P FRMs operated by Texas. Only data for the URG samplers were included in Figure 2, which shows sodium ion on Teflon.

Q: Page 3, Figure 1: What is the difference between dots and lines? The dots are difficult to see on a printout of the report. Also, according to the data in the graph, it looks like the data were bad into March of 2002 (based on the x-axis), but data were invalidated only up to January 2002.

A: Dots represent individual filters; the lines are moving averages. Definitions have been added to each figure caption and the dots have been made darker so that they will reproduce better.

Q: Page 5: Figure numbers and captions are missing for these 2 graphs.

A: Captions for Figures 3 and 4 have been added.

Q: All Figures: How do the background levels (for sulfate, sodium, potassium) relate to typical ambient air measurements? How big of a background do we have from trip/field blanks?

A: The new Figure 5 shows graphically the comparison for Sodium ion. It appears that the Routine running average (blue line) is still elevated during February 2002. The running average for sodium ion seems to be back to normal by March 2002. Some contaminated filters may have been used during February 2002. Since it is impossible to know which individual values are elevated due to remaining supplies of contaminated filters, we recommend that the data for sodium ion during February 2002 be used with caution.

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- A The Question of High Sodium Values in the Fall of 2001 RTI PM2.5 Speciation Program
- B Standard Operating Procedure for Cleaning Nylon Filters Used for Collection of PM2.5 Material

1.0 Introduction

RTI previously reported an analysis problem with sodium ion during the period of approximately September 2001 - January 2002. The original report of the problem is presented in Appendix A. As a result of this original problem, all routine sodium ion data above 1 microgram per filter for the period September 1, 2001 through January 31, 2002 were marked as suspicious (flag of '4' - possible laboratory contamination). Additional review of the sodium data acquired during early 2002 indicate that some contaminated filters remained in the system into February; however, it would be very difficult to identify which specific filters were contaminated, so that the routine sodium ion data for February 2002 should be used with caution.

The filter contamination problem was discovered in late 2001 and procedures were developed to reduce the background levels of sodium in the nylon filters purchased for the program from Whatman. The revised filter washing procedures are found in RTI's Standard Operating Procedure (SOP) "Standard Operating Procedures for Cleaning Nylon Filters used for Collection of PM_{2.5} Material" attached as Appendix B.

2.0 Current Cleaning Procedure

In brief, the current washing procedure involves tumbling the nylon filters in "polished" deionized water using a TCLP apparatus (Toxicity Characteristic Leaching Procedure, EPA SW-846 Method 1311). Fifty filters are placed in a 2 liter polypropylene jar with about 1000 mL of "polished" deionized water (18 Megaohm; water that has been passed through a secondary deionization system). The filters are shaken in the water for two minutes and the water is decanted off and discarded. This process is repeated once more. The jar is then completely filled with polished deionized water and placed on the TCLP apparatus. The jar is rotated for 7 to 8 hours and the water is replaced with fresh polished deionized water. The jar is then rotated overnight for 14 to 16 hours before the water is replaced again. After another 24 hours of washing, the filters are collected in a plastic colander. The order of extended washing may vary; that is, the sequence may be 24 hours, 7 to 8 hours, and then 12 to 14 hours rather than 7 to 8 hours, 12 to 14 hours, 24 hours. Finally, the filters are dried in a convection oven set at 45°C, checked for residual contamination, and packaged for later use.

3.0 Acceptance Criteria

One filter from each cleaned batch is selected at random for analysis. For lot acceptance, the ion concentrations of interest (sodium, potassium, ammonium, nitrate, and sulfate) must each be less than 1.0 ug/filter. If any ion exceeds the limit, the entire lot must be rejected. Rejected lots may be re-cleaned using the same procedure. Each accepted batch of filters is assigned a unique number. Each filter's batch number is recorded in the STN database when it is loaded into a sample module in the SHAL. The lot number can be used to trace the acceptance test results in case there is a question about any filter.

It should be noted that there are acceptance limits for the deionized water used in the laboratory which are equivalent to 0.25 ug/filter (nitrate, sulfate, ammonium, and sodium) or 0.50 ug/filter (potassium).

4.0 History of Nylon Filter Washing Procedure and Related Issues

The washing procedure went through some changes until it was deemed effective. The current version of the filter washing SOP is found in Appendix B. Nylon filters used from the beginning of the program through January 2002 were washed less rigorously.

5.0 Extraction Tube Pre-cleaning

Another issue that impacted sodium ion levels was the pre-cleaning of extraction tubes. RTI had been rinsing the new tubes used for extracting filters. However, there were concerns that the rinsing process was introducing contamination from cleaning solutions used for other procedures carried out in the washing laboratory, so in August 2003, RTI stopped rinsing the new tubes, and now the new extraction tubes are checked for contamination as received and are subjected to the same acceptance criteria as the rinsed tubes. To date, no extraction tubes have been rejected. Coincidentally, the levels in sodium and other ions in trip and field blanks seem to go down at approximately the same time, as shown in the figures below.

6.0 Sodium Ion Background on Nylon Filters

Figure 1 shows the history of trip and field blanks for the STN program from the beginning (February 2000), through August 2004. As shown in the figure, the background sodium levels in the trip and field blanks increased dramatically in September 2001 due to contamination in filters as received from the manufacturer. All figures show the individual blank results as points; the moving averages of these data are shown as solid lines. The number of points used in the moving averages varies from 40 to 200 to get adequate smoothing of the data.

Trip and field blank data from February 2001 through approximately August 2003 showed reduced levels of sodium ion as RTI fine-tuned the filter cleaning process. By October 2003, the average sodium level in trip and field blanks had gone down to approximately 0.2 micrograms per filter, and has remained at this low level.

As a result of our original investigation (Appendix A), all routine sodium ion data above 1 microgram per filter for the period September 1, 2001 through January 31, 2002 were marked as suspicious (flag of '4' - possible laboratory contamination). Additional review of the sodium data shown in Figure 1 indicate that some contaminated filters remained in the system into February; however, it would be very difficult to identify which specific filters were contaminated, so that the routine sodium ion data for February 2002 should be used with caution.

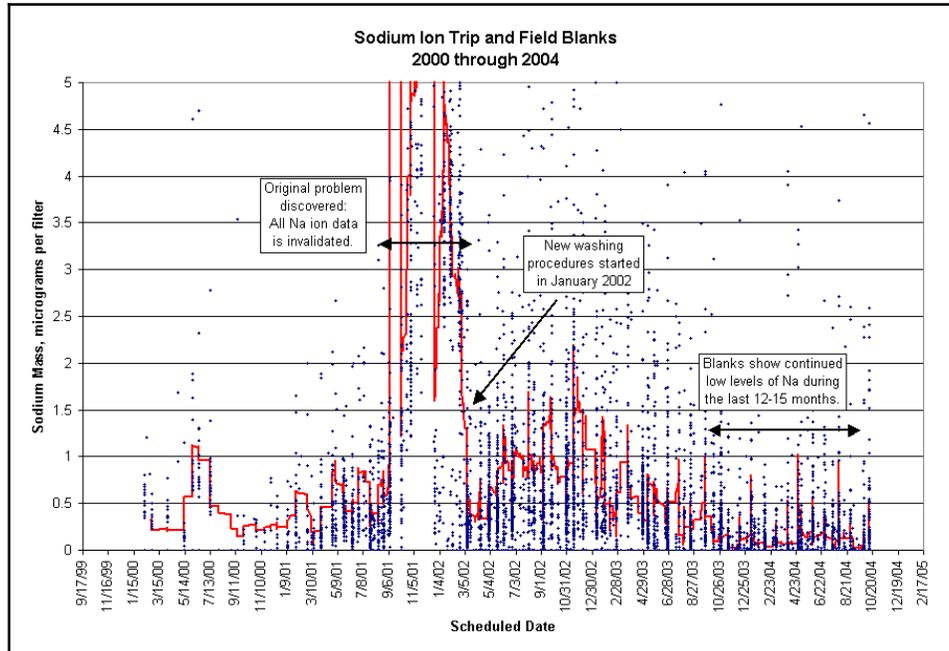


Figure 1. Sodium Ion on Nylon Filters: Trip and Field Blanks 2000-2004. Dots indicate individual observations, lines are moving averages.

7.0 Sodium Ion Background on Teflon Filters

Background sodium levels on Teflon filters, which are used for ion analysis with two STN sampler types (the URG MASS samplers and the R&P FRM-type samplers used by Texas), did not show any of the outliers seen for the Nylon filters during the period from late 2001 and early 2002, which helps confirm that the problem was with filter manufacturing, not the laboratory. Figure 2 shows trip and field blank data for Teflon filters from the URG MASS samplers. Teflon filters are not pre-washed, and there have never been any issues regarding manufacturing contamination. This figure shows that average sodium levels are uniformly below 0.5 micrograms per filter.

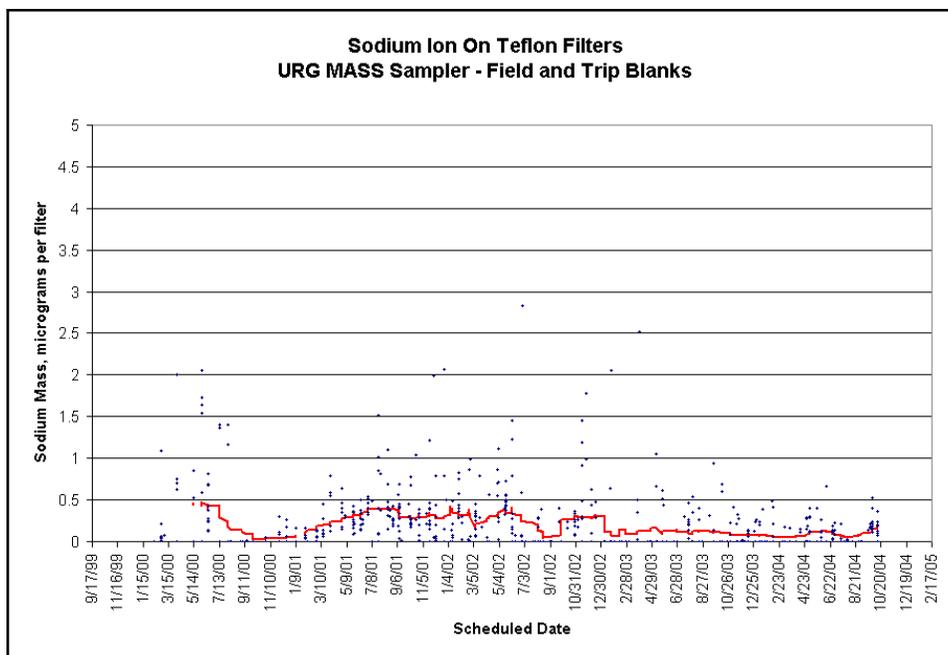


Figure 2. Sodium Ion on Teflon Filters, URG MASS Sampler: Trip and Field Blanks 2000-2004. Dots indicate individual observations, lines are moving averages.

8.0 Background of Other Ions on Nylon

Trip and field blank data were also examined to verify that there had been no contamination problems with other ions (nitrate, sulfate, potassium, and ammonium). Plots for potassium and sulfate are shown below in Figures 3 and 4. There are a number of outliers in the potassium data, but these do not affect the overall averages very much because of the large number of points with zero concentrations. Sulfate blank levels are typically higher than other ions, as reflected in Figure 4. Like the other ions, there may be some improvement after August 2003 when rinsing of the extraction tubes was discontinued.

9.0 Comparison between Blank Levels and Routine Samples

Figure 5 shows a comparison of Routine (sampled) results vs. Trip/Field Blank results for sodium on nylon filters. The dark blue curve is the moving average for Routine data, and the red curve is the moving average for Trip and Field Blanks. The Routine data for September 2001 through January 2002 is omitted because much of this data was marked with the '4' flag. The Routine Sodium average appears elevated during February 2002, but has returned to more normal levels by March 1. There is a broad increase in blank levels during mid-2002, but by approximately September 2003, blank levels have gone down to an average of approximately 0.2-0.5 micrograms per filter, where they have remained except for intermittent outliers.

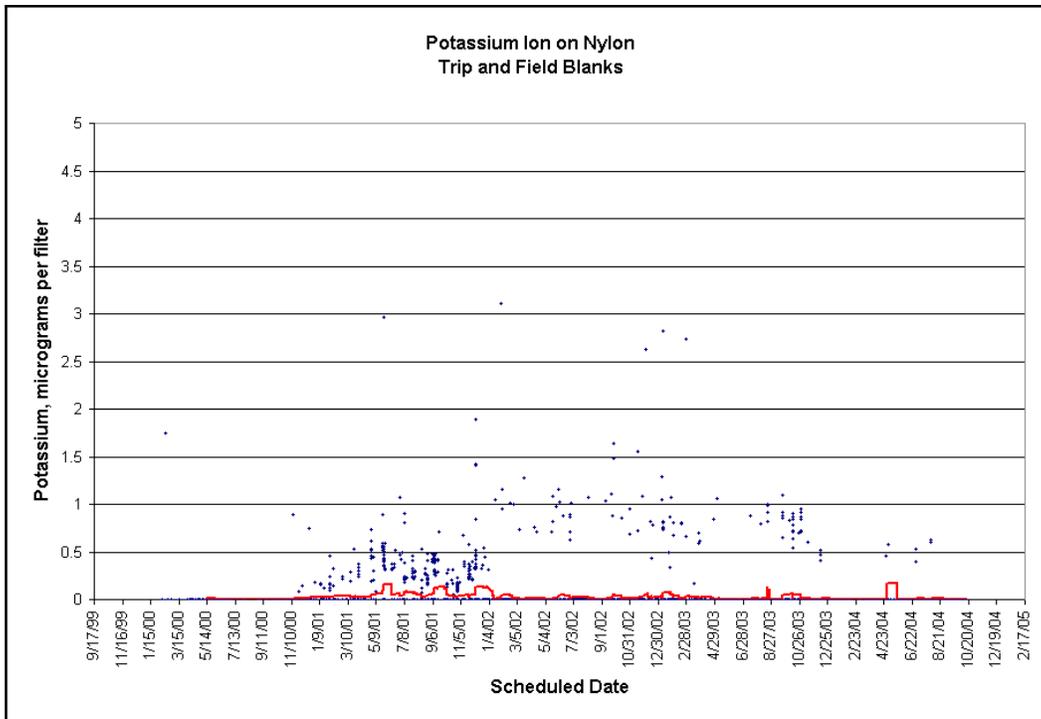


Figure 3. Potassium Ion on Nylon Filters, URG MASS Sampler: Trip and Field Blanks 2000-2004. Dots indicate individual observations, lines are moving averages. Many observations are zero and coincide with the x-axis.

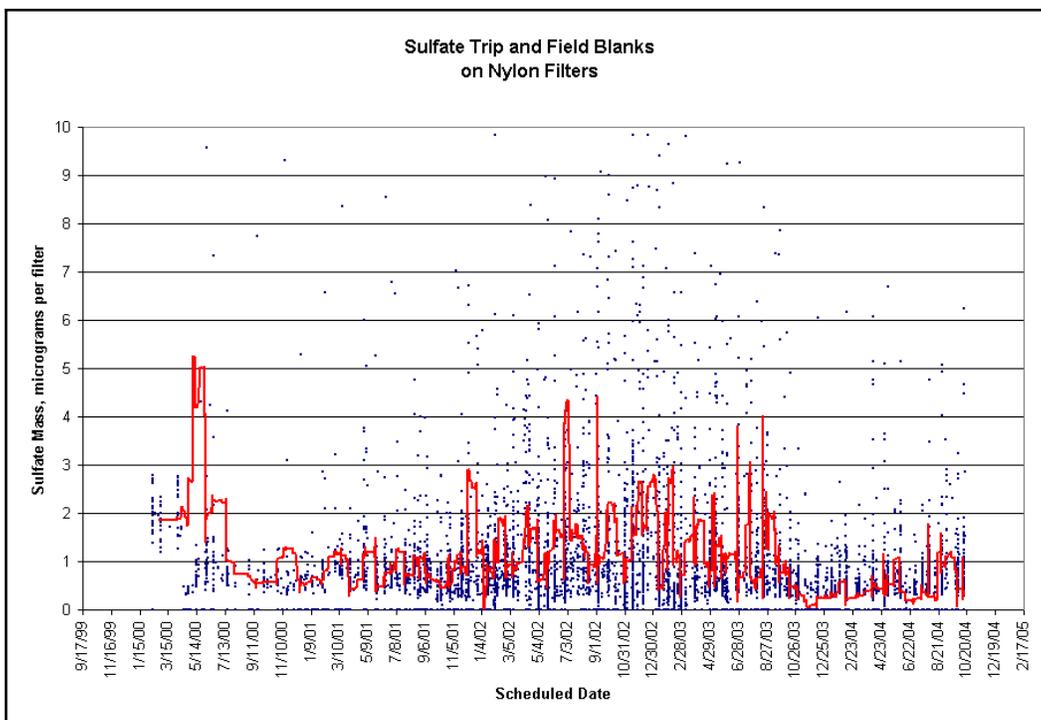


Figure 4. Sulfate Ion on Nylon Filters, URG MASS Sampler: Trip and Field Blanks 2000-2004. Dots indicate individual observations, lines are moving averages.

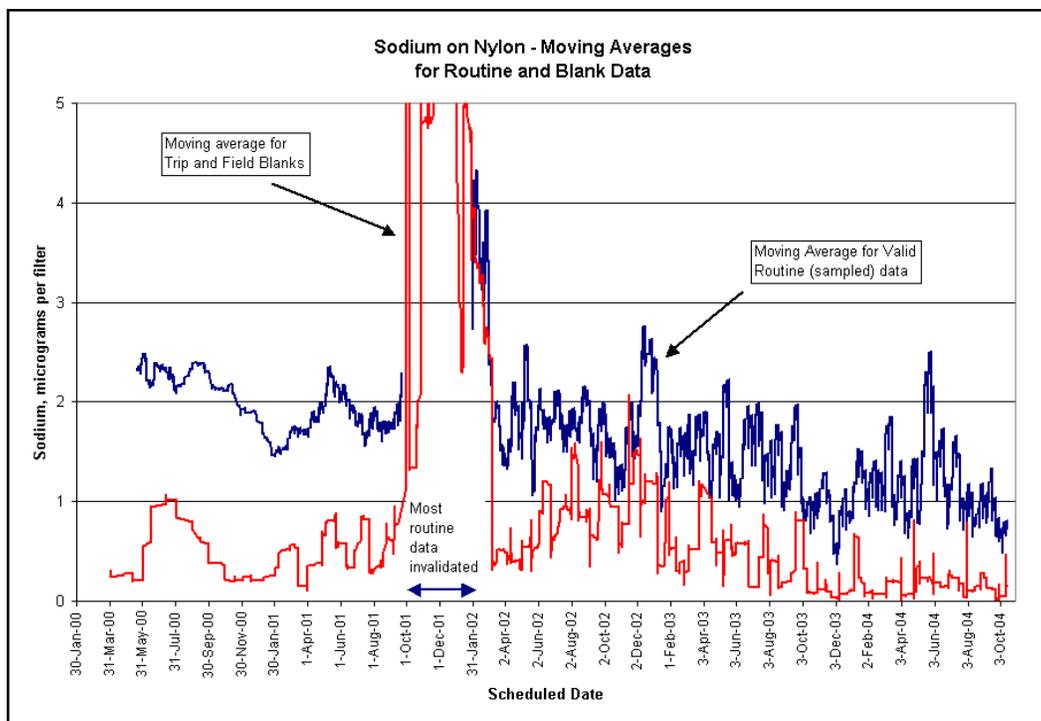


Figure 5. Comparison of Routine and Trip/Field Blank results (moving averages). Blue curve is the moving average for Routine data; red curve is the moving average for Trip/Field Blank data. For clarity, individual data points are not shown.

10.0 Comparison between STN and IMPROVE Ion Backgrounds

In addition to analyzing filters for the STN program, RTI also analyzes filters for the IMPROVE program. There are two significant differences between the treatment of blank data by the two programs:

- IMPROVE nylon filters for ion analysis are not pre-rinsed like the STN filters
- IMPROVE routine (sampled) filter data are corrected for background levels, whereas the STN data are not blank-corrected. IMPROVE calculates a batch-average background level and applies subtracts the appropriate background number depending on filter batch. Since the STN background levels are lower because of pre-rinsing, it is hoped that background subtraction is less important for the STN data; however, blank data for the STN program are soon to be available on AQS, which will allow data users to apply their own corrections if they deem it necessary for their application.

11.0 Conclusions

- The enhanced filter washing procedures implemented by RTI in 2002 have eliminated the extreme levels of contamination seen during the period of September 2001 through January 2002. The corresponding sodium ion data were invalidated in the AQS database.
- Use of new extraction tubes as received (rather than rinsing the tubes prior to use) may have resulted in further improvements for sodium and other ions beginning around August 2003.
- There appears to be no problem with sodium ion contamination on Teflon filters, or with other ions on nylon filters.

Appendix A

The Question of High Sodium Values in the Fall of 2001 RTI PM2.5 Speciation Program

The Question of High Sodium Values in the Fall of 2001

RTI PM2.5 Speciation Program

Introduction

RTI was recently notified by a data user from New York State that an excessive number of relatively high sodium values was observed in their STN data reported for late 2001. The user from New York indicated that they were considering invalidating all data taken on nylon filters during this time period as "laboratory error."

RTI has subsequently investigated the problem. First, it should be noted that approved data validation procedures were in place and applied to these data; however, it is also clear that these procedures did not lead to flagging of all suspect data. Following our investigation, we conclude that all of the sodium data for samples taken using nylon filters during this time period should, in fact, be considered suspect; however, we believe that other data acquired on the nylon filters (potassium, ammonium, sulfate, and nitrate) are acceptable, and should not be flagged or invalidated.

The paragraphs below describe the apparent origin and cause of the problem and corrective actions that have been taken in the laboratory. Specific actions that might be taken with the data are proposed at the end of this document. On the basis of a better understanding of this issue, data validation procedures have been reviewed and tightened so that unanticipated problems leading to suspect data can be detected sooner and flagged more effectively.

Background

In early September, 2001, RTI noted that the PM2.5 ion chromatographic (IC) data had become somewhat erratic. The sodium and sulfate levels were high for some of the blanks, and duplicates were somewhat variable. At the same time, we noted a very fine black material was building up on the filter frits that are part of the IC autosampler injection vials and also on the filter frits at the heads of the Dionex IC guard columns. The problem occurred with each of the IC's. We were not sure of the sources of this material, but thought that the ions from one sample might be "hanging up" on this material and then coming out in a subsequent run. The black material was also found in the tubing and injection valves in the ICs. One possibility considered was that the problem was with the in-house, deionized water supply. We thought the ion exchange resin might be breaking down, yielding the fine black material. We tried water from another source, but the results were inconclusive. Therefore we purchased all new cylinders for the house deionized water supply. Also, the Dionex technician was brought in several times to try and solve the problem. First he ran a dilute bleach solution through each system to destroy any mildew. When this did not solve the problem, he replaced all the tubing and thoroughly cleaned all the injection valves in the ICs; that is, he essentially replumbed the ICs. These two efforts (new deionizing tanks and IC replumbing) seemed to reduce the problem, and with more reliable QC measurements, we found that the nylon filters were not always meeting specifications for sodium background; it should be noted, however, that some large proportion of the filters were found to be acceptable, meaning the contamination was variable. Up to this time,

the nylon filters had been acceptable after washing following the in-place, RTI procedure, but apparently some change occurred in the filter manufacturing.

(Special note: We are once again [10/02] seeing the black material on the IC systems, though it does not seem to be as pervasive now as it was in 2001. The IC systems are working well enough to determine that the nylon filter blanks are acceptable. We are now performing a series of tests to isolate the source of the black material. Electron microscopy has been performed on the black material showing up on the frits, and it is an amorphous, sooty looking material. X-ray fluorescence shows the material to be principally carbon, with small amounts of oxygen and iron. As this same problem occurred last fall at about the same time, we wonder if there is a seasonal relationship with the “outbreak” of this material.)

About the same time we were dealing with the IC problems and high sodium and sulfate problems, another problem observed with the nylon filters was that they seemed to be disintegrating during the cleaning process. After shaking the filters in deionized water overnight, the wash water was milky white and a fine white material was seen at the bottom of the bottles. It appeared that particles of nylon were eroding from a web-like substrate. The supplier was contacted and nylon filters from a new lot were ordered. In light of the unacceptable sodium values and the disintegrating filter media, the filter washing procedure was modified to include a longer wash time on a rotating TCLP apparatus rather than a shaking table, and also a reduction in the number of filters per bottle from 100 to 50; reducing the number of filters per bottle meant more direct contact with the wash water for each filter surface. These changes brought the blank levels for the nylon filters back into compliance.

In the midst of these problems that started in September, 2001, which included the unavailability of clean filters from the manufacturer, we gave consideration to suspending the use of nylon filters until all the problems could be solved. This would have meant no ion data for as much as two months. We decided, instead, to move ahead and use the nylon filters which did not always meet specs and try to solve the various problems “on the fly.” The ion data generated during this time was subjected to EPA-approved quality assurance tests before submission to the States, and as noted in “Validation Issues” below, unacceptable data values were flagged.

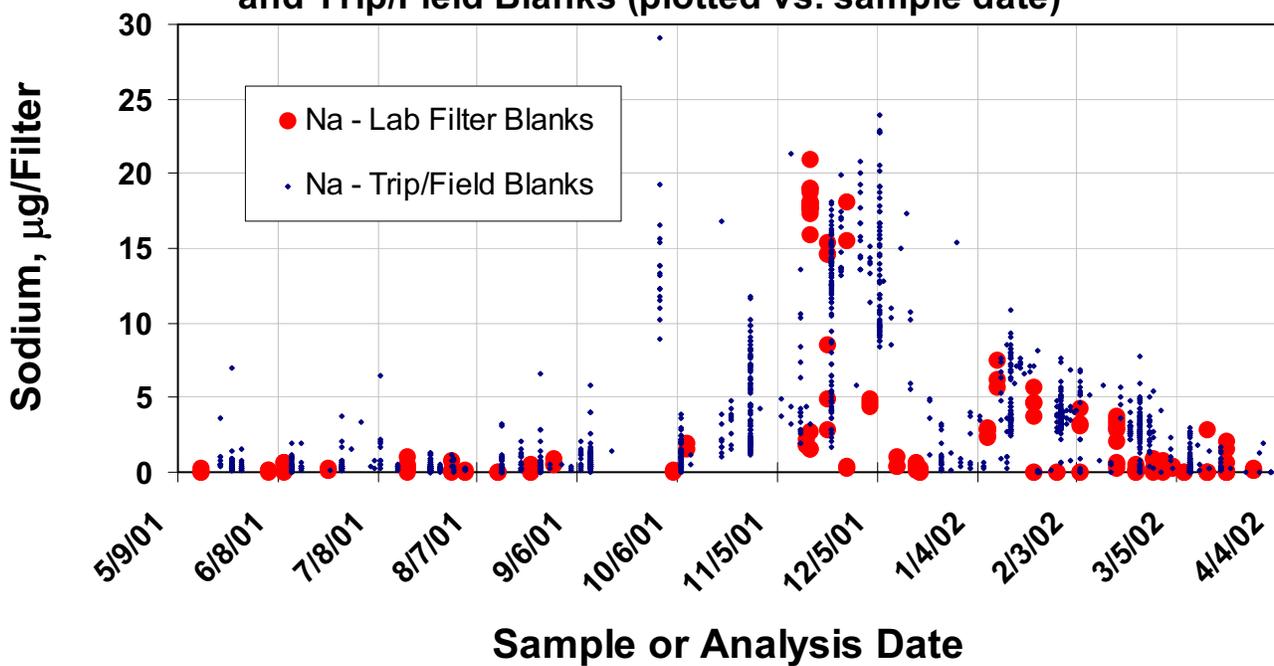
Figure 1 shows the history of Laboratory Blanks and Trip/Field Blanks during this time period. The large gap in analyses during September 2001 reflects the IC downtime. Filters with high sodium levels remained in the system and were used through early December, 2001. A new lot of nylon filters was received from the manufacturer and were used during most of December, but contaminated filters were again received in January, 2002; however, by this time the contamination problem had been recognized as a separate problem, and steps were taken to clean the filters more aggressively. Washing procedures were upgraded. Blank levels improved during that period, as shown in Figure 1. The more aggressive washing procedure used starting in late January/early February, 2002, is as follows:

- Manually rinse the filters in a bottle (50 filters in a ½ gallon poly bottle) with 100 to 200 mL of deionized water for about 1 minute and discard the wash water. Repeat this process with 6 bottles for a total of 300 filters..

- Repeat the manual wash process.
- Fill the bottles to the very top and put on the lids so as to exclude any air bubbles. Place the bottles in the TCLP apparatus. Wash the bottles for 14 to 20 hours.
- Discard the water from each bottle and refill the bottles, and repeat the washing on the TCLP apparatus as described above.
- Pour the contents of each bottle through a large plastic sieve to collect the filters.
- Dry the filters in a cleanroom in a convection oven at 40 °C

This procedure resulted in nylon filters meeting the specifications of less than 1 μg of analyte per filter.

Figure 1. Nylon Filter Lab Blanks (plotted vs. analysis date) and Trip/Field Blanks (plotted vs. sample date)



Note: From these data, we see that the sodium values from about 9/1/01 through 12/1/01 may have a bias as high as 1 $\mu\text{g}/\text{m}^3$ and that the sodium values from about 12/1/01 to 3/1/02 may have a bias of 0.2 to 0.3 $\mu\text{g}/\text{m}^3$.

Validation Issues

RTI's routine data validation procedures detected an excessive number of outliers in the Anion/Cation ratios approximately two months after the initial batch of contaminated nylon filters had been received. By this time, the lab had identified the problem. Four delivery batches (24-27) were affected by the nylon filter contamination problem. Table 1 shows the proportion of samples that had been flagged with the QAC data flag, which denotes that the calculated ratio of anion charge to cation charge was outside limits established during MiniTrends. Normally, only about 2-5% of filters receive this flag. The table shows that only data from analyzers that use nylon filters for sampling of ionic species were affected. Ion data from Teflon filters were unaffected.

Table 1. Percentage of Samples with Calculated Ratio of Anion Charge to Cation Charge Outside Established Limits

Batch	MetOne	R&P 2300	Andersen	R&P 2025*	URG*
23	1.7%	1.4%	0.0%	5.7%	0.8%
24	18.0%	14.1%	16.8%	0.8%	4.4%
25	34.5%	24.4%	35.4%	7.1%	4.2%
26	39.0%	29.1%	33.3%	2.8%	5.5%
27	16.8%	16.9%	15.6%	8.2%	5.7%
28	3.6%	9.3%	5.4%	1.5%	2.2%

* R&P 2025 and URG MASS samplers - Ions are sampled on Teflon filters, which were unaffected by the sodium contamination problem.

RTI has investigated other ways of validating and screening data using an additional between-analyte checks of sodium by XRF vs. sodium by IC; however, the IC and XRF are so poorly correlated for sodium that implementing a validation screen based on the difference between IC and XRF results would lead to far too many false positive outlier detections to be worthwhile. Instead, RTI is monitoring the percentages of data flagged using the existing validation flags. Significant month-to-month changes in the number of outliers detected will be investigated with regard to systematic problems.

With regard to data validation in the laboratory, the IC laboratory's SOP will be reviewed to ensure that all questionable QC results are acted on immediately, even though this could potentially affect laboratory throughput. Protocols for communicating significant laboratory problems to management and ultimately to EPA will be reviewed and enhanced as necessary.

Corrective Actions

As noted, a new washing procedure was implemented in early 2002. This procedure, as presented above, was further modified in late summer, 2002, when an occasional unacceptable sulfate blank was observed. A third 24-hour washing step was added at that time. We found, however, that this additional effort did not allow us to deliver the requisite number of cleaned filters to the SHAL, about 500 per week. A further modification is now being used; the filters are manually rinsed as described above, then washed in the TCLP for 7 hours (to the end of the first washing day) and then washed twice more, once for about 16 hours and then again for about 24 hours. Six filters from each washing batch (one from each bottle) are analyzed before the filters are released to the SHAL for sampling. As noted earlier, further corrective action included working with the supplier in late 2001 to obtain a lot of filters that were physically stable during the washing process.

The new washing method is successfully reducing contamination of the nylon filters for sodium and sulfate, as well as for other ions. Filter wash batches are now labeled by date; and the washing date is entered by SHAL when assembling modules.

Communication Issues

While the IC and filter problems were communicated to EPA/OAQPS as RTI identified them, it is apparent that RTI did not effectively pass the information to the data users in a timely way, nor were the implications for the data clearly explained. At the very least, a warning about the possible effects of the problems described above should have been provided to the data users. This will certainly be done with any future events that may result in suspect analytical data.

Proposed Action Regarding Sodium Data Acquired during Late 2001

It is proposed that the extent of the problem with the sodium data collected during the period, September, 2001, through December, 2001, be brought to the attention of the users in more detail through distribution of this document. Furthermore, RTI will introduce a #4 flag into AQS to indicate the sodium data to be suspect. Our data show that only sodium was affected by the filter contamination problems described above, so we recommend that data for the other analytes (potassium, ammonium, sulfate, and nitrate) not be flagged or invalidated.

Appendix B

**Standard Operating Procedure for
Cleaning Nylon Filters
Used for Collection of PM2.5 Material**

**STANDARD OPERATING PROCEDURE FOR
CLEANING NYLON FILTERS
USED FOR COLLECTION OF PM2.5 MATERIAL**

Environmental and Industrial Sciences Division
Research Triangle Institute, Research Triangle Park, North Carolina

Prepared by: _____ Date: _____

Reviewed by: _____ Date: _____

Approved by: _____ Date: _____



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**STANDARD OPERATING PROCEDURE FOR
CLEANING NYLON FILTERS
USED FOR COLLECTION OF PM2.5 MATERIAL**

1.0 Procedural Section

1.1 Purpose and Applicability

Nylon filters are used for the collection of PM2.5 material in the chemical speciation particulate samplers. These filters are analyzed for the following ions: nitrate, sulfate, ammonium, sodium, and potassium. The filters, as purchased and received from different manufacturers, show unacceptable levels of these ions, often exceeding the maximum level of 1 µg per filter for a particular ion. This has prompted development of a procedure, described in this Standard Operating Procedure (SOP), for cleaning the nylon filters prior to their use for field sampling.

1.2 Summary of Method

Fifty filters are placed in a 2 liter polypropylene jar with about 100 mL of “polished” deionized water (18 Megaohm; water that has been passed through a secondary deionization system). The filters are shaken in the water for about 1 minute and the water is decanted off and discarded. This process is repeated once more. The jar is then filled with polished deionized water and placed on a TCLP apparatus (Toxicity Characteristic Leaching Procedure, EPA SW-846 Method 1311). The jar is rotated for 7 to 8 hours and the water is replaced with fresh polished deionized water. The jar is then rotated overnight for 14 to 16 hours before the water is replaced again. After another 24 hours of washing, the filters are collected in a plastic colander. The order of extended washing may vary; that is, the sequence may be 24 hours, 7 to 8 hours, and then 12 to 14 hours rather than 7 to 8 hours, 12 to 14 hours, 24 hours. Finally, the filters are dried in a convection oven set at 45°C, checked for residual contamination, and packaged for later use.

1.3 Health and Safety Warnings

The PM2.5 filter preparation operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of gloves rinsed with deionized water is required for all steps of the filter cleaning process and will minimize the potential for laboratory contamination.

2.0 Apparatus and Reagents

Several pieces of apparatus are used for cleaning the nylon filters. Included are:

1. Two-liter polypropylene wide-mouth Mason jars (VWR Catalog no. 16128-660 or equivalent)
2. TCLP apparatus (Toxicity Characteristic Leaching Procedure, EPA SW-846 Method 1311) that hold six (6) 2-liter jars.
3. Programmable timer (VWR Lab Controller or equivalent)
4. Convection drying oven (VWR Model 1320 or equivalent)
5. 11-in. by 11-in. glass drying rack (custom made from 1/4-in. glass rods in parallel rows attached to 3/8-in. glass rods serving as a frame; center to center distance for the 1/4-in. parallel glass rods is 1/2 in.)
6. Plastic colander about 8 inches in diameter from kitchen appliance store.

Reagents needed are as follows:

1. Polished deionized water (18 Megaohm; water that has been passed through a secondary deionization system)
-

3.0 Filter Cleaning

3.1 Cleaning Procedure

The nylon filters are cleaned using the following procedure, which should be started at the beginning of a work day. The date that the cleaning is started is entered into the log book and the batch is identified by this date.

1. Fifty 47-mm nylon filters are carefully removed from the manufacturer's filter container using either gloves or forceps and are placed in a 2-liter polypropylene jar that contains about 100 mL of polished deionized water. The lid is attached and the jar is shaken gently for about 1 minute. The water is then carefully poured out of the jar without losing any filters. This rinse procedure is repeated once more. This duplicate rinse procedure is then performed with five other 2-liter jars each loaded with 50 filters. Each jar is labeled with a letter, i.e., A, B, C, etc., using a marker.
2. Each jar is carefully filled with polished deionized water until it is overflowing; it is then capped tightly and placed on the TCLP apparatus. The apparatus is then run to the end of the day, that is, 7 to 8 hours. The water is carefully poured out of each jar and the jars are again carefully filled to overflowing. The jars are placed on the apparatus, which is then run overnight, or for 14 to 16 hours. The beginning of the next work day, the water is poured out once again, the jars are filled to overflowing, capped, and placed on the apparatus for about 24 hours, or to the beginning of the next work day. Depending on one's work schedule, the order of the extended washing may be varied; that is, the sequence may be 24 hours, 7 to 8 hours, and then 12 to 14 hours rather than 7 to 8 hours, 12 to 14 hours, 24 hours.

<p>NOTE: The filters tend to stick to the sides of the jars. Therefore, the TCLP apparatus is connected to the power source through a timer. This timer is programmed to rotate the jars for 15 minutes and then allow them to be still for 2 minutes. During this rest period, the filters stuck to the sides of the jar slip away and fall to the lower part of the jar of water. The procedure for programming the time is given in Attachment A.</p>

3. The jars are removed from the TCLP apparatus after the final wash and taken to a Class 100 clean room for drying of the filters. The lid of a jar is removed and the water along with filters are gently poured into a pre-cleaned plastic colander placed in a sink in the clean room. It may be necessary to add polished deionized water to the jar several times in order to remove all the filters. The excess water is allowed to drain from the filters and colander for several minutes. Any filters that fall into the sink during this process are to be discarded.
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4. With gloves and a clean forceps, the filters are removed from the colander one by one and laid separately on the drying rack (which has been thoroughly pre-rinsed with polished deionized water shortly before use). The loaded rack is carefully placed in the oven which is set at 45°C. The filters are allowed to dry for one-half hour. The filters may curl slightly during the drying process. A large amount of curling indicates that the oven temperature is too high.

NOTE: The drying oven must be kept free of any dust or particulate material and should only be operated in a clean environment. The oven should be visually inspected for any contamination prior to each use. A new oven used only for drying filters is recommended.

5. The dried filters are removed from the drying rack using a clean forceps and placed in the same manufacturer's plastic containers that they were taken from for the purpose of cleaning. These containers are washed with deionized water and dried before use. Filters shall be inspected for pin holes and/or tears; any damaged filter shall be discarded. Twenty-five (25) filters are placed in each container. Each container is labeled with the batch number (i.e., start date for cleaning) and the jar identifier (i.e., A, B, C, etc.).

3.2 Filter Acceptance Testing

One filter from each jar of cleaned filters is selected at random for analysis. Blank filters are analyzed according to the analytical procedure described elsewhere in the SOPs for Anion¹ and Cation² analysis contained in the laboratory Quality Assurance Project Plan (QAPP). For lot acceptance, the ion concentrations of interest (sodium, potassium, ammonium, nitrate, and sulfate) must each be less than 1.0 µg/filter. If any ion exceeds the limit, the entire lot must be rejected. Rejected lots may be re-cleaned using the same procedure.

Each accepted batch of filters is assigned a unique number. Each filter's batch number is recorded in the database when it is loaded into a sample module in the SHAL. The lot number can be used to trace the acceptance test results in case there is a question about any filter.

NOTE: Several different cleaning procedures were used during the course of the STN contract, which began in early 2000. This note summarizes the procedures used for cleaning nylon filters prior to finalization of the method described in this SOP.

Prior to 3/28/2000, filters were soaked three times for 30 minutes in deionized water without shaking or ultrasonication. Drying and acceptance procedures were identical to those described above.

Prior to 12/1/2001, filters were cleaned using a shaker for the final 24 hour wash in deionized water. In fall 2001, some batches of filters received from the supplier were noted to be partially disintegrating in the shaker. It was concluded that the filter durability was somewhat variable and that shaking for 24 hours was too “forceful” for the less durable filters. Therefore, the more gently rolling method was adopted.

Prior to 2/1/02, filters were placed in a polypropylene jar of sodium carbonate/sodium bicarbonate solution (the eluent used for anion analysis). The jar containing the filters was placed in an ultrasonic bath for 1 hour. The filters were then rinsed three times with deionized water, rinsed gently using a jar roller mill in deionized water for about 1 hour, again rinsed manually three or four times and then rinsed gently in fresh deionized water for 24 hours using the jar roller mill. This procedure was abandoned for the following reasons: the ultrasonic bath sometimes caused partial disintegration of the filters; sodium from the eluent solution was sometimes still present on the filters ; and the TCLP apparatus was better than a roller because it provides end-over-end mixing. The method described in this SOP was subsequently adopted.

4.0 Quality Control

The quality control activities include the following:

1. Perform ion analyses of the polished deionized water whenever the deionizer beds are changed in order to determine that the ions of interest are below their maximum allowable concentration, as presented in Table 1 below.

**Table 1. Maximum Allowable Concentration (MAC)
for Ions of Interest**

Ion of Interest	MAC, µg/mL
Nitrate	0.01
Sulfate	0.01
Ammonium	0.01
Sodium	0.01
Potassium	0.02

Replace the ion exchange beds in the water deionization system if these limits are exceeded.

2. Keep all jars closed and stored in a clean environment when not in use.
3. Periodically wipe down the inside of the drying oven with wet, lint-free tissues.

5.0 References

1. Hardison, Eva. Standard Operating Procedure for PM2.5 Anion Analysis. Quality Assurance Project Plan Chemical Speciation of Particulate Matter, Volume II, Appendix A-5.1, revision 2, September 8, 1999.
 2. Hardison, Eva. Standard Operating Procedure for PM2.5 Cation Analysis. Quality Assurance Project Plan Chemical Speciation of Particulate Matter, Volume II, Appendix A-5.2, revision 2, September 8, 1999.
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Attachment A

Method for Programming the VWR Lab Controller

The device is programmed for the repeat mode, which permits repeatedly turning equipment on or off at one or two unique time intervals.

1. Press the CHANNEL SELECT key until the OUTLET channel is selected.
 2. Delete all time-of-day program times by pressing the C key and then the REPEAT key.
 3. Press the OUTLET ON/OFF key to ON.
 4. Press the 1, 5, 0, and 0 keys to program 15 minutes (15.00) power on.
 5. Press the REPEAT key.
 6. Press the 2, 0, and 0 keys to program 2 minutes power off.
 7. Turn on the toggle switch on the TCLP apparatus (if not already on) and press the START/STOP key to begin counting down.
 8. At zero, the outlet switches to OFF, the alarm sounds for two seconds, the display automatically returns to the programmed 2 minutes, and the timer begins counting down. At the next zero it switches, alarms, displays 15.00 and begins counting down. This process will repeat until the C key is pressed.
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