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Extended Semi-Annual Data Summary Report for the Chemical Speciation of PM2.5 Filter Samples Project

October 1, 2002 through June 30, 2003

Prepared for:
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Office of Air Quality Planning and Standards
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1.0 Introduction

1.1 Program Overview

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter. The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations (µg/cubic meter of air) of particles with aerodynamic diameters less than 10 micrometers (the PM10 standard) and less than 2.5 micrometers (the PM2.5 standard). Currently, a 1500-site mass measurements network and a 230-site chemical speciation monitoring network have been established.

The ambient air data from the first network, which measures solely the mass of particulate matter, will be used principally for NAAQS comparison purposes in identifying areas that meet or do not meet the NAAQS criteria and in supporting designation of an area as attainment or non-attainment.

The smaller chemical Speciation Trends Network (STN) consists of a core set of 54 trends analysis sites and some 176 other sites. Chemically speciated data will be used to serve the needs associated with development of emission mitigation approaches to reduce ambient PM2.5 concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM2.5 and its components, and evaluating potential linkages to health effects.

RTI is assisting in the PM2.5 STN by shipping ready-to-use filter packs and denuders to the field sites and by conducting gravimetric and chemical analyses of the several types of filters used in the samplers. The details of the quality assurance (QA) activities being performed are described in the RTI QA Project Plan (QAPP) for this project. This QAPP focuses on the QA activities associated with RTI's role in performing these analyses, as well as in validating and reporting the data, and should be considered a companion document to this annual QA report.

Prior to operation of the core and additional sites, EPA ran a prototype network informally known as the "mini-trends" network. This network was composed of approximately 13 monitoring stations at sites throughout the U.S. Each site had two or more PM2.5 chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000 to July 31, 2000. Subsequently, the network sites have been increased and as of June 30, 2003, RTI is providing support for 230 sites which include the 54 trends analysis sites under the STN.

1.2 Project/Task Description

The STN laboratory contract involves four broad areas:

1. Supplying each site or state with sample collection media (loaded filter packs, denuders, and absorbent cartridges) and field data documentation forms. RTI ships the collection media to monitoring agencies on a schedule specified by the Delivery Order Project Officer (DOPO).

2. Receiving the samples from the field sites and analyzing the sample media for mass and for an array of chemical constituents including elements (by EDXRF), soluble anions and cations (by ion chromatography), and carbonaceous species (using the Sunset thermal degradation/laser transmittance system). Analysis of semi-volatile organic compounds and examination of particles by electron or optical microscopy have been performed on a very limited basis.

3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data to the Aerometric Information Retrieval System (AIRS) data bank 60 days after initial data reports are first submitted to the DOPO and the states.

4. Establishing and applying a comprehensive quality assurance/quality control (QA/QC) system. RTI's Quality Management Plan, QAPP, and associated Standard Operating Procedures (SOPs) provide the documentation for RTI's quality system.

1.3 Schedule

The initial portion of the STN program was a six-month pilot project at 13 different sites. This "mini-trends" project was conducted from February 2000 to July 2000. This period gave all participants an opportunity to work out technical and logistical problems. Additional sites have been added. As of June 30, 2003, we were providing support to 230 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples from October 1, 2002 through June 30, 2003.

1.4 Major Laboratory Operational Areas

This report addresses the operation of the Sample Handling and Archiving Laboratory (SHAL) and QA/QC for the four major analytical areas active this past year. These analytical areas are the: (1) gravimetric determination of particulate mass on Teflon® filters; (2) determination of 48 elements on Teflon® filters using X-ray fluorescence spectrometry; (3) determination of nitrate, sulfate, sodium, ammonium and potassium on nylon or Teflon filters using ion chromatography; and (4) determination of organic carbon, elemental carbon, carbonate carbon, and total carbon on quartz filters using thermal optical transmittance. Also addressed is denuder refurbishment, data processing, and QA and data validation.

1.5 Significant Corrective Actions Taken

Any significant problems and corrective actions taken during this period under each analytical laboratory are described in this section. A detailed description of the problems encountered and corrective actions taken are given in Section 2.0.

- Gravimetric Mass – Corrective actions in response to facility problems are described in Section 2.1.3.
- Elemental Analysis – No significant corrective actions have been taken. Currently four XRF instruments are used for elemental analysis.
- Ion Analysis – In late November and December 2002, higher than acceptable sodium levels were observed in extracts of cleaned nylon filters. The filters in the affected lots were rejected for use in the network, and experiments were begun to determine the source of the contamination. See Section 2.2.5 for more information.
- OE/EC Analysis – No significant corrective actions have been taken.
- Sample Handling and Archiving Laboratory (SHAL) – No significant corrective actions have been taken except for the severe ice storm in December 2002, which is described in Section 2.5.2.
- Data Processing – No significant correction actions have been taken.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

The laboratory's two weigh chambers were used to tare 17,241 filters between September 2002 and June 30, 2003 (8,277 in Chamber 2, 8,964 in Chamber 1).

2.1.1 Personnel and Facilities

No changes in Gravimetry Laboratory personnel or facilities have occurred since the previous QA report. Corrective actions in response to facilities problems are summarized in **Tables 1 and 2**.

2.1.2 Statistical Summary of QC Results

PM2.5 STN sample throughput data for the Gravimetry Laboratory are summarized in **Table 3**. QC data for the laboratory (types and frequency as recommended in Guidance Document 2.12) are summarized in **Table 4**.

2.1.3 Data Validity Discussion

Issues affecting Gravimetry Laboratory data quality during the period covered by this report were excursions in laboratory environmental criteria (relative humidity), debris on filters (possible contamination), and high blank filter mass values. Each of these issues is discussed below.

<u>Laboratory environmental criteria out of limits</u>: Weigh Chamber 2 experienced a water chiller malfunction early in December 2002, resulting in erratic relative humidity (RH) levels below 30%. Both weigh chambers lost power several days later due to a severe winter storm. Details concerning the malfunction and subsequent ice storm are provided in Table 1. Permanent repair of the chiller was delayed by the ice storm, which significantly impacted all of RTI's main campus. Repairs from the ice storm occupied RTI HVAC for the remainder of the month of December. Gravimetric analysis continued in spite of the low and erratic RH levels in order to avoid expiration of sampled filters and to maintain the SHAL's shipment schedule. As a result, 1,366 filters were flagged due to laboratory environmental criteria being out of limits during pre- and/or post-sampling analyses during December 2002.

Due to an operational oversight, 735 of the filters weighed while the RH was outside of acceptance limits were not flagged appropriately prior to data transfer. The data were subsequently flagged in January 2003. A checklist for the review of gravimetry data for PM2.5 Chemical Speciation batches was developed and implemented in January 2003 to ensure adequate laboratory QA review before data transfer.

Table 1. Gravimetry Laboratory - Corrective Actions in Response to Facility Problems – RTI HVAC Reference Chamber 2

Duration of Problem	Nature of Problem	Corrective Action
11/29/02 - 12/02/02	High temperature Low RH "Connect fail" message when Laboratory Supervisor tried to access DataTalk® to monitor chamber environment	12/02/02 - DataTalk access resolved – RTI HVAC personnel discovered loose network connection, possible result of new data-jack installation late in the previous week. RTI HVAC personnel determined that system alarms were triggered by loss of chilled water flow due to a leak in the Bay 6 air handling unit chilled water coil. HVAC personnel valved off the coil and refilled the system until permanent repairs could be arranged. Follow-up: Laboratory Supervisor contacted HVAC Supervisor on January 27, 2003, to inquire about status of coil. HVAC Supervisor said that he was working with A/C Corporation to determine whether the coil should be repaired or replaced (dependent upon price).
12/06/02 - 12/10/02	Power failure	RTI's main campus lost power due to a severe winter ice storm. All chamber systems lost power; the laboratory was inoperable. All systems were brought back online with no permanent damage after power was restored to the campus. Note: Due to the low ambient winter temperatures, impact on filters in the laboratory was minimal.
01/09/03	Low RH	01/09/03 - RTI HVAC personnel determined low RH caused by a safety switch on the humidifier cover and loose connections on the control board and the power terminal strip. HVAC tightened the connections and installed an adjustment screw to accommodate the offset in the switch bracket.
03/01/03		RTI HVAC personnel replaced the chilled water valve and actuator because the manufacturer had indicated persistent water leak above chamber was from the control valve stem and was most likely caused by the constant position changes. Note: After the last (August 2002) actuator replacement, HVAC personnel placed a two-gallon bucket under the valve body because they could not repair the vapor barrier well enough to stop the condensation leaks from the valve body and piping. On Saturday, 03/01/03, HVAC personnel replaced the bucket and left a quantity of dry rags until the insulation can be properly replaced.
03/25/03	High temperature	RTI laboratory personnel paged HVAC personnel to report temperature alarm in Chamber 1 from 10:26 to 11:02. RTI HVAC personnel determined that alarm was caused by high entering water temperatures due to an internal safety shut down of one of the two chillers that provide cooling water for Building 11. Although chamber 2 temperature was rising slowly it did not go into alarm before HVAC personnel responded.

Table 2. Gravimetry Laboratory - Corrective Actions in Response to Facility Problems – RTI HVAC Reference Chamber 1

NOTE: Began to routinely utilize Chamber 1 for Chemical Speciation project in February 2002

Duration of Problem	Nature of Problem	Corrective Action
11/29/02 - 12/02/02	High temperature Low RH "Connect fail" message when Laboratory Supervisor tried to access DataTalk® to monitor chamber environment	12/02/02 - DataTalk access resolved – RTI HVAC personnel discovered loose network connection, possible result of new data-jack installation late in the previous week. RTI HVAC personnel determined that system alarms were triggered by loss of chilled water flow due to a leak in the Bay 6 air handling unit chilled water coil. HVAC personnel valved off the coil and refilled the system until permanent repairs could be arranged. Follow-up: Laboratory Supervisor contacted HVAC Supervisor on January 27, 2003, to inquire about status of coil. HVAC Supervisor said that he was working with A/C Corporation to determine whether the coil should be repaired or replaced (dependent upon price).
12/06/02 - 12/10/02	Power failure	RTI's main campus lost power due to a severe winter ice storm. All chamber systems lost power; the laboratory was inoperable. All systems were brought back online with no permanent damage after power was restored to the campus. Note: Due to the low ambient winter temperatures, impact on filters in the laboratory was minimal.
03/07/03	Low RH	Alarmed out on low humidity at 01:12 and cleared at 03:30 due to the steam generator cover safety switch.
03/25/03	High temperature	RTI laboratory personnel paged HVAC personnel to report temperature alarm from 10:26 to 11:02. RTI HVAC personnel determined that alarm was caused by high entering water temperatures due to an internal safety shut down of one of the two chillers that provide cooling water for Building 11. Note: Although chamber 2 temperature was rising slowly it did not go into alarm.

Table 3. Sample Throughput for the Gravimetry Laboratory

Number of Filters	Previous QA Report	This QA Report
Tared	11580 (2/17/02-8/23/02)	17241 (8/28/02-5/27/03)
Tared in Weigh Chamber 1	5521	8964
Tared in Weigh Chamber 2	6059	8277
Retained by Grav Lab for use as Lab Blanks	40 (0.35%)	56 (0.32%)
Not Transferred to SHAL; does not include lab blanks	3 filters damaged before transfer to SHAL	0
Initially Transferred to SHAL to be Loaded into Sampler Modules	11537	17185
Used for Background Monitoring of SHAL Facilities after Maintenance Activities	9	0
Total Transferred to and Retained by SHAL for Sampler Modules	11528	17185
Returned to Grav Lab by SHAL for Final Weighing	11025 (95.6% return rate) (3/12/02-10/7/02)	16292 (94.8% return rate) (9/10/02-6/30/03)
Voided by SHAL and Grav Lab (% of samples returned)	4 (0.03%)	1 (0.01%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab (% of samples returned)	90 (0.82%)	0
Flagged by Grav Lab for Laboratory Environmental Criteria Being Out of Limits (% of samples returned)	291 (2.6%)	1366 (8.4%)
Filters reweighed at request of SHAL (% of samples returned)	23 (0.21%)	13 (0.08%)

Table 4. Summary of QC Checks Applied in the Gravimetry Laboratory

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Working standard reference weights (mass reference standards)	Verified value ± 3 µg (Standard reference weights verified by North Carolina Department of Agriculture (NCDA) Standards Laboratory)	100-mg (Chamber 2) Verified Value = 99.957 mg (NCDA 8/01) 200-mg (Chambers 1 and 2) Verified Value = 199.978 mg (NCDA 8/01) 100-mg S/N 41145 (Chamber 1) 10/25/02 Troemner Class 1 Calibration: 100.0008 mg ± 0.0024 200-mg S/N 41147 (Chamber 1) 10/25/02 Troemner Class 1 Calibration: 200.0066 mg ± 0.0024 100-mg S/N 41144 (Chamber 2) 10/25/02 Troemner Class 1 Calibration: 100.0068 mg ± 0.0024 200-mg S/N 41148 (Chamber 2) 10/25/02 Troemner Class 1 Calibration: 200.0076 mg ± 0.0024	99.954 mg ± 0.001 for 673 weighings 199.977 mg ± 0.001 for 410 weighings 99.998 mg ± 0.001 for 1206 weighings 200.008 mg ± 0.001 for 1170 weighings 100.004 mg ± 0.001 for 1196 weighings 200.008 mg ± 0.001 for 1074 weighings	Lab mean falls within range. Lab mean falls within range. Lab mean falls within range. Lab mean falls within range. Lab mean falls within range. Lab mean falls within range.
Laboratory (Filter) Blanks	Initial weight ± 15 µg	554 total replicate weighings of 56 lab blanks	Mean difference between final and initial weight: 3 µg ± 4 µg	None of the 554 replicate weighings exceeded the 15 µg limit.
Replicates	Initial weight ± 15 µg	1717 Pre-sampled (Tared) Replicates (8/28/02-5/27/03) 1762 Post-sampled Replicates (9/10/02-6/30/03)	0 µg 0 µg	Max = 4 µg; within required range Max = 4 µg; within required range

Table 4. (Continued).

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Lot Blanks (Lot Stability Filters)	24-hour weight change < ± 5 µg	Whatman Lot 2207003 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes) Whatman Lot 2214004 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -1 µg 72 hours = 1 µg 96 hours = -2 µg 24 hours = 1 µg 48 hours = 2 µg 72 hours = 1 µg 96 hours = -1 µg	Fall well within required range.
Polonium Strips	Each filter placed near strips for minimum of 60 seconds to minimize electrostatic charge	Replace strips every 6 months	N/A	New polonium strips placed in service 4/25/03.
Calibrations – Balances (Chamber 2 Balance B- S/N 1118311244 and Chamber 1 Balance C - S/N 1118252777)	Auto (internal) calibration daily External calibration annually or as needed	Daily Last inspected and calibrated by Mettler Toledo on July 17, 2002 using NIST-traceable weights	N/A N/A	 Inspection and calibration scheduled for July 2003
Calibrations (continued) – RH/T Data Logger	Annually	Purchased and placed in service Dickson data logger (S/N 00102174) in Weigh Chamber 2 in April 2001 Placed Dickson data logger (S/N 01042219) in Weigh Chamber 1 in February 2002	N/A	

Table 4. (Continued).

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Audits – Balances (Chamber 2 Balance B - S/N 118311244 and Chamber 1 Balance - S/N 118252777) (internal audit)	Annually	Last performed by RTI QA October 8, 2002 using Class S-1 NIST-traceable weights	N/A	Included environmental evaluation, level test, scale-clarity test, zero-adjustment test, off-center (corner load error) test, precision test, and accuracy test; balances performed adequately. Auditor noted that balance in Chamber 1 displayed some drift that was resolved after allowing a 200-mg reference weight to sit on weigh pan for approximately 5 minutes after start-up possibly attributable to "warm-up" of balance's internal microprocessor.

The Gravimetry Laboratory also selected a group of 30 FRM state-client filters weighed using the same procedure on the same day, in the same chamber, and on the same balance as some of the flagged Speciation filters to verify that the data generated during the RH excursion were valid. The 30 filters were pulled from archives, reconditioned, and reweighed when chamber RH was 36%. The data for these filters are summarized in **Table 5**. The average difference between the original and reweighed net mass loadings for the test filters was -1 μg. The range was +6 μg to -9 μg. Since these values are well within the laboratory's acceptance limits for laboratory blanks, the RH excursion is not expected to have had an adverse affect on data quality.

Minimization of filter contamination: The SHAL and the Gravimetry Laboratory have coordinated to minimize filter contamination. The Gravimetry Laboratory updated its PM2.5 gravimetry SOP in December 2002 to include a section on cleaning the laboratory. This section outlines the procedures for thoroughly cleaning the laboratory monthly, after any maintenance or repair activity in the vicinity of the weigh chambers, or as needed to minimize contamination in the weighing environment. The working area around the balances and sample inventory and conditioning areas are cleaned daily by laboratory staff. The SHAL and the Gravimetry Laboratory purchased rubber pipette bulbs in April 2003. The bulbs are used to direct a gentle stream of ambient conditioned air onto the surface of unsampled filters to dislodge small fibers and other debris prior to tare weighing in the Gravimetry Laboratory and loading into sampler modules in the SHAL.

Table 5. Verification of Impact of RH Excursion on Data Quality Using State (FRM) Client Filters

State Client Filter ID Number	Original Postweigh Date	Original RH (%)	Original Temp (°C)	Original Postweight (mg)	Reweigh Date	Reweigh RH (%)	Reweigh Temp (°C)	Reweight (mg)	Difference (µg)
2002405	01/07/03	19	21	141.604	2/21/03	36	21	141.599	-5
2002406	01/07/03	19	21	142.336	2/21/03	36	21	142.332	-4
2002407	01/07/03	19	21	140.143	2/21/03	36	21	140.141	-2
2002408	01/07/03	19	21	141.035	2/21/03	36	21	141.032	-3
2002409	01/07/03	19	21	142.403	2/21/03	36	21	142.402	-1
2002410	01/07/03	19	21	142.943	2/21/03	36	21	142.949	6
2002411	01/07/03	19	21	143.564	2/21/03	36	21	143.568	4
2002434	01/07/03	19	22	146.527	2/21/03	36	21	146.527	0
2002436	01/07/03	19	22	145.615	2/21/03	36	21	145.612	-3
2002437	01/07/03	19	22	144.259	2/21/03	36	21	144.263	4
2002439	01/07/03	19	22	142.755	2/21/03	36	21	142.746	-9
2002440	01/07/03	19	22	146.739	2/21/03	36	21	146.746	7
2002441	01/07/03	19	22	147.083	2/21/03	36	21	147.084	1
2002455	01/07/03	19	22	145.187	2/21/03	36	21	145.186	-1
2002456	01/07/03	19	22	145.265	2/21/03	36	21	145.267	2
2002475	01/07/03	19	22	144.949	2/21/03	36	21	144.948	-1
2002476	01/07/03	19	22	143.202	2/21/03	36	21	143.199	-3
2002525	01/07/03	19	22	144.045	2/21/03	36	21	144.048	3
2002540	01/07/03	19	22	145.471	2/21/03	36	21	145.475	4
2002541	01/07/03	19	22	148.955	2/21/03	36	21	148.958	3
2002542	01/07/03	19	22	149.257	2/21/03	36	21	149.252	-5
2002543	01/07/03	19	22	149.048	2/21/03	36	21	149.046	-2
2002544	01/07/03	19	22	148.889	2/21/03	36	21	148.890	1
2002545	01/07/03	19	22	150.866	2/21/03	36	21	150.872	6
2002546	01/07/03	19	22	142.574	2/21/03	36	21	142.580	6
2002557	01/07/03	19	22	143.160	2/21/03	36	21	143.162	2
2002558	01/07/03	19	22	142.838	2/21/03	36	21	142.831	-7
2002559	01/07/03	19	22	143.615	2/21/03	36	21	143.608	-7
2002560	01/07/03	19	22	143.996	2/21/03	36	21	143.994	-2
2002561	01/07/03	19	22	144.930	2/21/03	36	21	144.926	-4

To evaluate the impact of visible debris ("lint") on filter mass, the Gravimetry Laboratory selected six filters that had been identified and returned by SHAL with visible debris. Each of the filters was weighed. Visible debris was then carefully removed from the filter surface with laboratory forceps and the filters were reweighed. The results of this experiment are summarized in **Table 6**. The average change in recorded mass was -0.5 μg. The range was -1 μg to +1 μg. Based on these limited data, the small amount of nuisance dust noted in the SHAL does not seem to significantly impact recorded filter mass. However, we speculate that the potential cumulative effect of nuisance dust deposited on the filter surface during each stage of filter handling and transport would be significant. RTI will continue to investigate and control possible sources of contamination and to investigate its underlying causes.

High blank filter mass values: A small number of field and trip blank filters with net mass loadings in excess of the acceptance criteria provided in Guidance Document 2.12 are received each month. Starting with reporting Batch 31, the SHAL returned some of these blank outliers to the Gravimetry Laboratory for reweighing in an attempt to identify systematic sources of error such as misidentification of filters or contamination. Blanks with net mass loadings above 50 μg were identified by the data validation staff and these filters were returned to the Gravimetry Laboratory with a request for reweighing. A total of 13 filters were returned for reweighing during the period covered by this report. Reweighing was performed approximately one to two months after initial postweighing and after XRF analysis under vacuum.

Data from the reweighing of blank outliers returned to the Gravimetry Laboratory during the period covered by this report are summarized in **Table 7**. Filters have been returned to the Gravimetry Laboratory for reweighing from Batches 31, 32, 38, 39, 40 and 41. No outliers were returned from Batches 33, 34, 35, 36, or 37. The average change in mass was –104 ug. The range was +11ug to -559ug.

The last column of the table indicates filters for which a significant reduction in filter weight has been identified. A significant reduction is defined as a lower reweigh result that brings the blank back into the "normal"range typically observed by data validation staff for trip and field blanks. Because reweighing occurs after XRF analysis subjects the filters to a high vacuum, masses may reasonably be expected to decrease slightly. However, the decrease in sample mass due to the vacuum is expected to be small and does not seem to be a significant contributor to the data shown in Table 7.

Of the 13 samples returned to the Gravimetry Laboratory, reweighing results for nine samples fell within the "normal" range typically observed by data validation staff for trip and field blanks, while the remaining four filters remained above 50 μg. No definitive cause for the changes in mass for the nine filters has been identified, but we speculate that small pieces of debris ("fluff," dust, fibers, etc.) may have become attached to the filters during the shipping and handling process and were present when the filters were reweighed after sampling. We speculate that the debris was knocked off the ten filters with significant weight reductions during post-weighing transfer to the XRF Laboratory or during XRF analysis and handling. At this time we do not have an explanation for the remaining four outliers, but recognize that it may be related to the issue of debris on filters. SHAL and the Gravimetry Laboratory have investigated

Table 6. Evaluation of Impact of Visible Nuisance Dust on Filter Mass

Filter ID	1st Weight 03/31/03 (mg)	2nd Reweight (After Removal of Fibers) 03/31/03 (mg)	Mass Attributable to "Lint" (µg)
2022651	142.344	142.344	0
2022890	138.428	138.429	1
2023510	142.700	142.699	-1
2031080	142.707	142.706	-1
2036299	139.394	139.393	-1
2036457	138.369	138.368	-1
		Mean	-0.5

Table 7. High Blank Filter Reweighings

Batch Number	Aliquot Barcode	Original Postweigh Date	Original Postweight (mg)	Reweigh Date	Reweight (mg)	Original Blank Net Mass Loading (ug)	Reweight (ug)	Change in Net Mass Loading (ug)	Significant Reduction
39	A222006Y	03/03/03	143.076	04/17/03	142.983	103	10	-93	*
39	A221568N	03/03/03	142.147		142.147	92	92	0	
39	A218945F	03/04/03	141.138		141.149	74	85	11	
39	A222363G	03/12/03	145.672		145.619	58	5	-53	*
40	A238215Y	04/07/03	141.434	05/30/03	141.333	114	13	-101	*
40	A2382465	04/07/03	141.094		141.041	62	9	-53	*
41	A235800X	05/08/03	142.828	06/16/03	142.269	568	9	-559	*
41	A241930V	05/21/03	142.569		142.579	84	94	10	
41	A236118Q	05/13/03	142.636		142.542	125	31	-94	*
							Mean	-104	

* A significant reduction occurs when the reweight is in the normal range for a blank, indicating that the originally reported weight may be suspect.

possible filter switches in the laboratory or in the database, but none of the outliers could be attributed to misidentification. RTI will continue to identify blank outliers and will continue to look for underlying causes.

2.1.3.1 Invalidated Data – One (0.01%) of the filters analyzed was invalidated by SHAL because it had an illegible filter ID number and an anomalous loading.

2.1.4 Audits, Performance Evaluations, Training, and Accreditations

The Gravimetry Laboratory is accredited by the State of Louisiana, Department of Environmental Quality, for the performance of the federal reference method for the determination of PM2.5 in ambient air. In accordance with Louisiana Administrative Code (LAC), the Louisiana Environmental Laboratory Accreditation Program (LELAP) conducted its biannual on-site assessment of the laboratory on April 10, 2003. The LELAP assessor reported two quality systems findings, as noted below. The scope of the assessment was specific to the laboratory's separate and discrete support of the Louisiana state FRM network. Any comments that are pertinent to the Chemical Speciation Program will be incorporated into the next revision of the STN Gravimetric Laboratory SOP.

Finding 1: Review of the Quality Assurance Project Plan and the PM2.5 Gravimetric Analysis SOP confirmed that the following requirements stated under LAC 33:5301.F.1 are not fully met. LAC 33:5301.F.1 requires that method SOPs also include the following items in a SOP format:

- b applicable matrix or matrices - applicable sample matrix is not described.
- c. detection limit - detection limit of the method is not stated.
- i. reagents and standards - readability and repeatability for zero and autocalibrate steps should be defined.
- p. pollution prevention - state steps employed or address as <Reserved>.
- q. data assessment and acceptance criteria for quality control measures - define the acceptance criteria.
- r. corrective actions for out-of-control or unacceptable data - need to state what triggers the "problem" that requires a corrective action under Section 1.12.11 in the SOP. The last two bullets in Section 1.12.1 should require a corrective action when the listed problem occurs.
- s. contingencies for handling out-of-control or unacceptable data - need to address the contingency to be taken for out-of-control or for unacceptable data.
- t. waste management - a statement needs to be made or addressed as <Reserved>.
- v. QAPP tables 6, 7, 9, 10, 11, 12, 13, and 14 specific to the PM2.5 test method should be attached to the SOP for PM2.5 gravimetric analysis.

Finding 2: Failure of the Quality Manual (and in the operating procedures) to state all records must be retained for a minimum of 10 years.

2.2 Ion Analysis Laboratory

2.2.1 Facilities

Ion chromatographic analyses are performed by personnel from RTI's Environmental Industrial Chemistry Department (EICD). Six ion chromatographic systems were used for performance of the measurements. These are described in **Table 8**. The use of these six systems was determined by the workload.

Table 8. Description of Ion Chromatographic Systems used for Analysis of PM2.5 Filter Samples

System No.	Dionex IC Model	Ions Measured
1	Model 500 (S1A)	SO_4, NO_3
2	Model 500 (S2A)	SO_4, NO_3
3	Model 500 (S3A)	SO_4, NO_3
4	DX-600 (D6A)	SO_4, NO_3
5	Model 500 (D5C)	Na, NH_4, K
6	DX-600 (D6C)	Na, NH_4, K

2.2.2 Description of QC Checks Applied

QC checks for ion analyses are summarized in **Table 9**. For ion analyses, a daily multipoint calibration (7 points for cations; 8 points for anions) is performed over the range 0.05 to 25.0 ppm for each ion (Na^+, NH_4^+, and K^+ for cation analyses; NO_3^- and SO_4^{2-} for anion analyses) followed by QA/QC samples including (1) a QC sample containing concentrations of each ion in the mid- to high-range of the calibration standard concentrations, (2) a QC sample containing concentrations of each ion at the lower end of the calibration standard concentrations, and (3) a commercially prepared, NIST-traceable QA sample containing known concentrations of each ion.

The regression parameters (a,b,c and correlation coefficient, r) for the standard curve for each ion are compared with those obtained in the past. Typically, a correlation coefficient of 0.999 or better is obtained for each curve. If the correlation coefficient is <0.999, the analyst carefully examines the individual chromatograms for the calibration standards and reruns any standard that is judged to be out of line with respect to the other standards or to values (peak area and/or height) obtained in the past for the same standard. Possible causes for an invalid standard run include instrumental problems such as incomplete sampling by the autosampler. If necessary, a complete recalibration is performed.

Table 9. Ion Analysis of PM2.5 - Quality Control/ Quality Assurance Checks

QA/QC Check	Frequency	Requirements
Calibration Regression Parameters	Daily	r $\geq$ 0.999
Initial QA/QC Checks:		
- QC sample at mid to high range concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- QC sample at lower end concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- Commercially prepared, NIST traceable QA sample	Daily, immediately after calibration	Measured concentrations within 10% of known values
Periodic QA/QC Checks:		
- Replicate sample	Every 20 samples	RPD = 5% at 100x MDL* RPD = 10% at 10x MDL* RPD = 100% at MDL*
- QA/QC sample	Every 20 samples	Measured concentrations within 10% of known values
- Matrix spiked sample extract	Every 20 samples	Recoveries within 90 to 100% of target values

* MDL = Minimum Detectable Limit RPD = Relative Percent Difference

When all individual calibrations have been judged acceptable, the results for the QA/QC samples are carefully examined. If the observed value for any ion being measured differs by more than 10 percent from the known value, the problem is identified and corrected. Any field samples are then analyzed.

During an analysis run, a duplicate sample, a QA/QC sample, and a spiked sample are analyzed at the rate of at least one every 20 field samples. Precision objectives for duplicate analyses are ±5 percent for concentrations that equal or exceed 100 times the minimum detectable limit (MDL), ±10 percent for concentrations at 10 times the MDL, and ±100 percent for concentrations at the MDL. The observed value for any ion being measured must be within 10 percent of the known value for the QA/QC samples, and ion recoveries for the spiked samples must be within 90 to 110 percent of the target value. If these acceptance criteria are not met for any QA/QC or spiked sample, the problem is identified and corrected. All field samples analyzed since the last acceptable check sample are then reanalyzed.

2.2.3 Summary of QC Results

2.2.3.1 Anions – QC checks performed included:

- Percent recovery for QC samples (standards prepared by RTI)
- Percent recovery for QA samples (commercial standards)
- Relative percent difference (RPD) for replicates
- Spike recovery
- Reagent blank (elution solution and DI water)

Table 10 shows recoveries for NO_3^- with low, medium, and high concentration QC samples (prepared by RTI) and with low and medium-high QA samples (commercially prepared and NIST-traceable) for the instrument used for anion analysis. Average recoveries for the three QC samples ranged from 98.6% to 102.3% over the nine month period; average recoveries for the two QA samples ranged from 99.0% to 101.3%.

Table 11 shows recoveries for SO_4^{2-} with low, medium, and high QC samples and with low and medium-high QA samples for the instrument used for anion analysis. Average recoveries for the three QC samples ranged from 98.6% to 101.9% over the nine month period; average recoveries for the two QA samples ranged from 98.1% to 100.9%.

Figure 1 shows a plot of the original nitrate concentration vs. the duplicate nitrate concentration for replicate measurements of the filter extracts. The plot shows excellent agreement for the duplicate measurements over the entire concentration range.

Figure 2 shows a plot of the original sulfate concentration vs. the duplicate sulfate concentration for replicate measurements of the filter extracts. Again, the plot shows excellent agreement for the duplicate measurements over the entire concentration range.

Table 12 shows percent recovery for nitrate and sulfate spikes for the nine month period. The average recoveries of nitrate for ranged from 99.1% to 102.7%, while the average recoveries for sulfate ranged from 99.1% to 102.9%.

Table 13 presents filter blank (N BLANK) and reagent blank values for nitrate and sulfate over the nine month period. The highest average value for filter blanks was 0.008 ppm (25 mL extract) for nitrate and 0.006 ppm for sulfate; the highest average reagent blank was 0.006 ppm for nitrate and 0.019 ppm for sulfate.

Table 10. Average Percent Recovery for Nitrate QA and QC Samples

Inst	QC Sample	Count	Conc., ug/mL	Av NO_3 Rec	SD NO_3	Min NO_3 Rec	Max NO_3 Rec
D6A	CPI QA-LOW	180	0.6	99.0%	1.3%	91.6%	102.5%
D6A	CPI QA-MED-HI	110	3	100.7%	1.3%	95.0%	102.7%
D6A	RTI QC-HIGH	163	6	101.4%	1.3%	93.7%	102.7%
D6A	RTI QC-LOW	217	0.6	98.8%	1.3%	92.7%	102.3%
D6A	RTI QC-MED	287	1.5	98.6%	1.2%	91.6%	101.3%
S1A	CPI QA-LOW	4	0.6	99.3%	0.5%	98.6%	99.9%
S1A	CPI QA-MED-HI	2	3	100.5%	0.6%	100.0%	100.9%
S1A	RTI QC-HIGH	3	6	101.5%	0.5%	100.9%	101.9%
S1A	RTI QC-LOW	5	0.6	100.1%	1.2%	98.5%	101.1%
S1A	RTI QC-MED	6	1.5	98.8%	0.3%	98.5%	99.2%
S2A	CPI QA-LOW	141	0.6	99.1%	0.8%	96.3%	101.4%
S2A	CPI QA-MED-HI	87	3	100.8%	0.8%	94.9%	102.1%
S2A	RTI QC-HIGH	127	6	101.5%	0.4%	100.1%	103.1%
S2A	RTI QC-LOW	173	0.6	99.1%	0.8%	97.1%	101.2%
S2A	RTI QC-MED	222	1.5	98.8%	0.7%	96.6%	100.6%
S3A	CPI QA-LOW	64	0.6	99.4%	1.6%	96.9%	107.3%
S3A	CPI QA-MED-HI	40	3	101.3%	1.8%	91.6%	103.6%
S3A	RTI QC-HIGH	51	6	101.9%	0.5%	100.4%	102.8%
S3A	RTI QC-LOW	80	0.6	102.3%	20.2%	96.7%	274.8%
S3A	RTI QC-MED	107	1.5	99.3%	1.3%	95.7%	104.4%

Table 11. Average Percent Recovery for Sulfate QA and QC Samples

Inst	QC Sample	Count	Conc.,ug/mL	Av SO_4 Rec	SD SO_4	Min SO_4 Rec	Max SO_4 Rec
D6A	CPI RTI QC-LOW	180	1.2	98.3%	1.6%	89.5%	102.5%
D6A	CPI RTI QC-MED-HI	110	6	100.0%	1.4%	94.1%	101.5%
D6A	RTI QC-HIGH	163	12	101.2%	1.2%	93.7%	102.6%
D6A	RTI QC-LOW	217	1.2	98.9%	1.8%	88.9%	104.8%
D6A	RTI QC-MED	287	3	99.2%	1.2%	92.4%	102.3%
S1A	CPI RTI QC-LOW	4	1.2	98.2%	1.1%	96.8%	99.4%
S1A	CPI RTI QC-MED-HI	2	6	99.7%	0.9%	99.0%	100.3%
S1A	RTI QC-HIGH	3	12	101.0%	0.6%	100.3%	101.4%
S1A	RTI QC-LOW	5	1.2	99.6%	0.8%	98.4%	100.4%
S1A	RTI QC-MED	6	3	99.3%	0.4%	98.9%	100.0%
S2A	CPI RTI QC-LOW	141	1.2	98.1%	2.2%	94.4%	116.6%
S2A	CPI RTI QC-MED-HI	87	6	100.0%	0.9%	94.1%	101.5%
S2A	RTI QC-HIGH	127	12	101.5%	0.6%	98.9%	103.4%
S2A	RTI QC-LOW	173	1.2	98.6%	1.3%	94.6%	102.7%
S2A	RTI QC-MED	222	3	99.0%	0.9%	96.8%	101.0%
S3A	CPI RTI QC-LOW	64	1.2	98.1%	1.2%	94.6%	101.1%
S3A	CPI RTI QC-MED-HI	40	6	100.9%	1.6%	91.7%	101.9%
S3A	RTI QC-HIGH	51	12	101.9%	0.5%	100.4%	102.8%
S3A	RTI QC-LOW	80	1.2	99.1%	1.4%	96.3%	107.1%
S3A	RTI QC-MED	107	3	100.0%	0.8%	96.9%	102.3%

Figure 1. Nitrate Duplicate Analyses

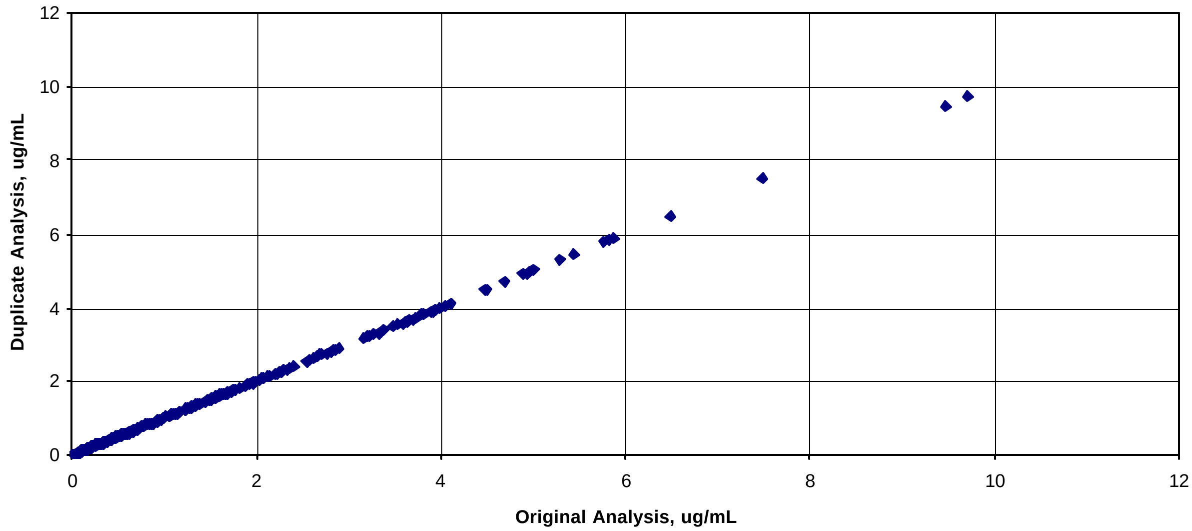


Figure 2. Sulfate Duplicate Analyses

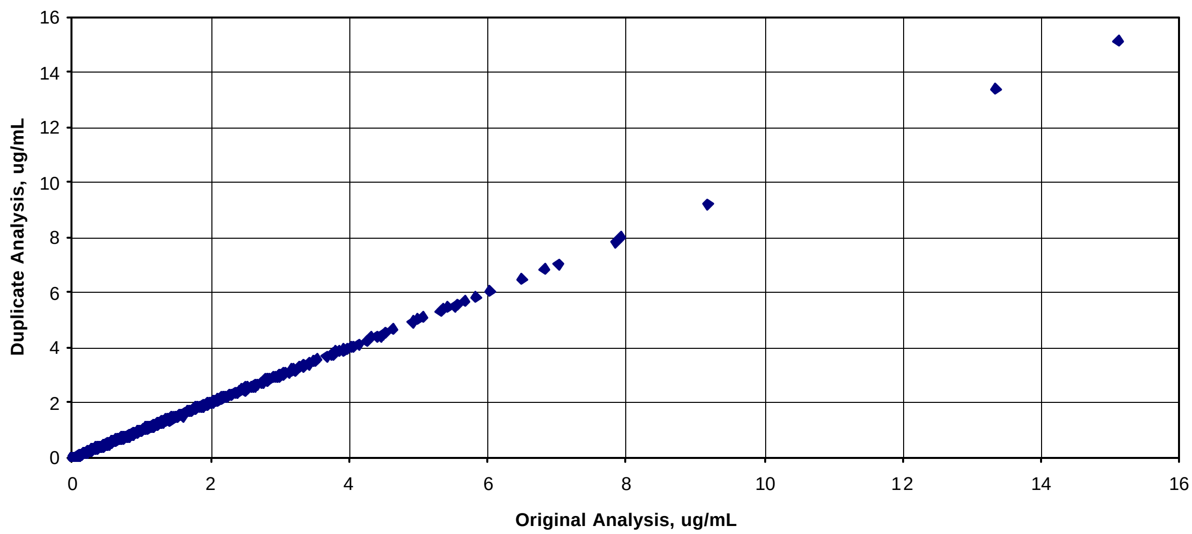


Table 12. Average Percent Recovery for Nitrate and Sulfate Spikes

Inst	D6A								
Analyte	Nitrate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	99.09%	100.89%	102.74%	99.87%	100.46%	101.42%	99.90%	99.31%	98.92%
St Dev:	2.97%	2.66%	5.05%	1.39%	2.01%	2.03%	1.55%	1.85%	1.44%
Count:	40	29	15	29	39	43	46	46	44
Min Recovery:	92.61%	97.64%	97.43%	97.57%	97.34%	98.42%	97.03%	96.55%	96.55%
Max Recovery	105.09%	108.93%	116.26%	102.47%	105.49%	107.30%	102.89%	102.86%	102.49%
Inst	S2A								
Analyte	Nitrate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	99.85%	99.93%	100.24%	100.16%	100.55%	99.82%	99.76%		102.01%
St Dev:	1.76%	1.24%	1.06%	2.11%	1.36%	1.03%	1.24%		0.21%
Count:	34	28	48	42	33	37	23		3
Min Recovery:	96.62%	97.58%	98.30%	97.91%	97.84%	97.82%	97.80%		101.78%
Max Recovery	102.92%	102.00%	104.41%	109.43%	103.53%	102.49%	102.38%		102.15%
Inst	S3A								
Analyte	Nitrate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	99.41%	100.76%		100.38%	99.98%	101.90%	99.12%	100.66%	101.34%
St Dev:	1.14%	1.87%		0.80%	1.72%	0.24%	0.97%	2.32%	2.16%
Count:	15	12		12	8	3	9	32	30
Min Recovery:	96.88%	97.65%		98.86%	97.24%	101.66%	97.68%	97.22%	98.36%
Max Recovery	101.57%	102.87%		101.58%	101.87%	102.14%	100.59%	107.40%	106.58%
Inst	D6A								
Analyte	Sulfate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	99.29%	101.07%	102.94%	100.07%	100.43%	101.30%	99.97%	99.64%	99.15%
St Dev:	2.28%	2.25%	5.18%	1.15%	1.71%	2.08%	1.52%	1.72%	1.44%
Count:	40	29	15	29	39	43	46	46	44
Min Recovery:	92.56%	97.17%	97.83%	97.66%	97.91%	98.29%	96.53%	95.49%	95.94%
Max Recovery	104.26%	107.82%	115.28%	102.39%	105.57%	107.94%	102.99%	102.43%	102.09%
Inst	S2A								
Analyte	Sulfate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	100.06%	99.96%	99.85%	99.92%	100.05%	99.71%	99.81%		101.30%
St Dev:	1.35%	1.22%	1.06%	2.10%	1.46%	1.10%	1.33%		0.33%
Count:	34	28	48	42	33	37	23		3
Min Recovery:	96.51%	97.76%	96.49%	96.36%	96.64%	97.15%	96.86%		100.92%
Max Recovery	102.79%	101.96%	101.82%	108.45%	103.33%	101.97%	102.32%		101.52%
Inst	S3A								
Analyte	Sulfate								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	99.96%	100.93%		100.45%	100.02%	101.13%	100.31%	100.40%	99.07%
St Dev:	1.07%	1.33%		0.97%	1.79%	0.31%	0.67%	1.65%	2.20%
Count:	15	12		12	8	3	9	32	30
Min Recovery:	98.08%	97.92%		98.06%	97.19%	100.93%	99.10%	97.17%	95.49%
Max Recovery	101.88%	102.82%		101.21%	101.71%	101.48%	101.14%	103.75%	102.76%

Table 13. Filter Blank (N) and Reagent Blank Values (ppm) for Nitrate and Sulfate

Inst	Blank Type	Count	Av NO_3	STD NO_3	Min NO_3	Max NO_3
D6A	Nylon	142	0.008	0.012	0.000	0.041
D6A	Reagent	314	0.006	0.022	0.000	0.249
S2A	Nylon	130	0.008	0.012	0.000	0.044
S2A	Reagent	250	0.001	0.005	0.000	0.032
S3A	Nylon	30	0.002	0.007	0.000	0.030
S3A	Reagent	108	0.006	0.018	0.000	0.086

Inst	Blank Type	Count	Avg SO_4	STD SO_4	Min SO_4	Max SO_4
D6A	Nylon	142	0.004	0.008	0.000	0.038
D6A	Reagent	314	0.010	0.025	0.000	0.203
S2A	Nylon	130	0.006	0.010	-0.007	0.055
S2A	Reagent	250	0.019	0.040	-0.007	0.340
S3A	Nylon	30	0.005	0.012	0.000	0.039
S3A	Reagent	108	0.012	0.025	-0.003	0.127

2.2.3.2 Cations – QC checks performed included:

- Percent recovery for QC samples
- Percent recovery for QA samples
- RPD for replicates
- Spike recovery tests
- Reagent and filter blank tests

Table 14 presents the average percent recovery value for sodium for both QA and QC samples for the instruments used for these measurements. The average recovery for the QA samples over the nine month period ranged from 99.5% to 102.6%. The average recovery for the QC samples ranged from 99.9% to 100.6%.

Table 15 presents the average percent recovery value for ammonium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the nine month period ranged from 99.2% to 101.2%. The average recovery for the QC samples ranged from 99.5% to 100.2%.

Table 16 presents the average percent recovery value for potassium for both QA and QC samples for the instrument used for these measurements. The average recovery for the QA samples over the nine month period ranged from 98.8% to 99.9%. The average recovery for the QC samples ranged from 99.3% to 100.5%.

Table 14. Average Percent Recovery for Sodium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av Na rec	SD Na	Min Na Rec	Max Na Rec
D5C	GFS 0.4 PPM QA	214	0.400	102.6%	2.7%	94.2%	112.0%
D5C	GFS 4.0 PPM QA	250	4.000	99.5%	0.9%	96.5%	102.4%
D5C	RTI 2.0 PPM QC	210	2.000	100.4%	1.1%	97.2%	104.2%
D5C	RTI 5.0 PPM QC	185	5.000	99.9%	1.0%	96.7%	102.9%
D6C	GFS 0.4 PPM QA	229	0.400	101.4%	1.5%	98.5%	109.6%
D6C	GFS 4.0 PPM QA	268	4.000	99.9%	0.6%	98.2%	102.0%
D6C	RTI 2.0 PPM QC	212	2.000	100.5%	0.9%	96.0%	102.9%
D6C	RTI 5.0 PPM QC	195	5.000	100.6%	1.8%	93.1%	122.2%

Table 15. Average Percent Recovery for Ammonium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av NH_4 rec	SD NH_4	Min NH_4 Rec	Max NH_4 Rec
D5C	GFS 0.4 PPM QA	214	0.400	99.7%	3.8%	81.3%	109.6%
D5C	GFS 4.0 PPM QA	250	4.000	99.6%	1.4%	93.9%	107.9%
D5C	RTI 2.0 PPM QC	210	2.000	99.5%	2.0%	92.6%	106.7%
D5C	RTI 5.0 PPM QC	185	5.000	100.2%	1.6%	94.7%	108.7%
D6C	GFS 0.4 PPM QA	229	0.400	101.2%	2.4%	96.2%	116.2%
D6C	GFS 4.0 PPM QA	268	4.000	99.2%	1.4%	91.1%	107.1%
D6C	RTI 2.0 PPM QC	212	2.000	100.0%	1.4%	93.8%	105.8%
D6C	RTI 5.0 PPM QC	195	5.000	100.2%	1.5%	90.9%	106.7%

Table 16. Average Percent Recovery for Potassium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av K rec	SD K	Min K Rec	Max K Rec
D5C	GFS 0.4 PPM QA	214	0.400	98.8%	5.7%	85.3%	118.4%
D5C	GFS 4.0 PPM QA	250	4.000	99.2%	1.2%	95.9%	104.4%
D5C	RTI 2.0 PPM QC	210	2.000	99.7%	2.0%	92.8%	104.8%
D5C	RTI 5.0 PPM QC	185	5.000	99.3%	1.4%	95.4%	103.0%
D6C	GFS 0.4 PPM QA	229	0.400	99.9%	2.5%	83.4%	109.9%
D6C	GFS 4.0 PPM QA	268	4.000	99.8%	0.8%	96.2%	103.0%
D6C	RTI 2.0 PPM QC	212	2.000	100.5%	0.9%	97.0%	104.1%
D6C	RTI 5.0 PPM QC	195	5.000	100.4%	0.8%	97.4%	104.7%

Figure 3 shows a plot of the original sodium concentration vs. the duplicate sodium concentration for replicate measurements of the filter extracts. The plot shows good agreement for the duplicate measurements with a small amount of scatter at the lower concentration range. RTI continues to look for sources of contamination and methods to reduce the scatter.

Figure 4 shows a plot of the original ammonium concentration vs. the duplicate ammonium concentration for replicate measurements of the filter extracts. This plot also shows excellent agreement for the duplicate measurements over the entire concentration range.

Figure 3. Sodium Duplicate Analyses

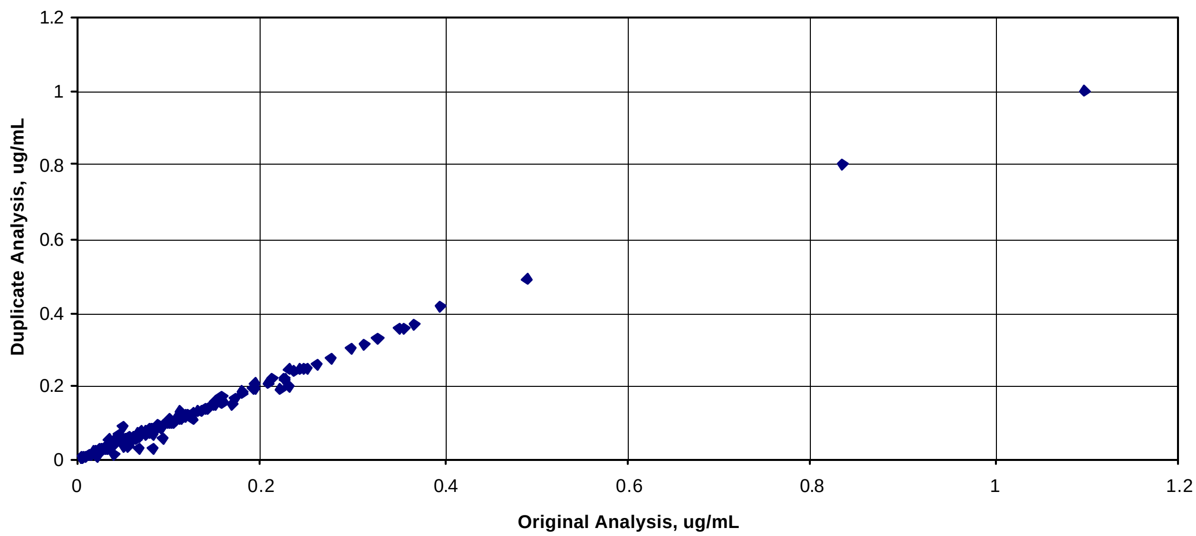


Figure 4. Ammonium Duplicate Analyses

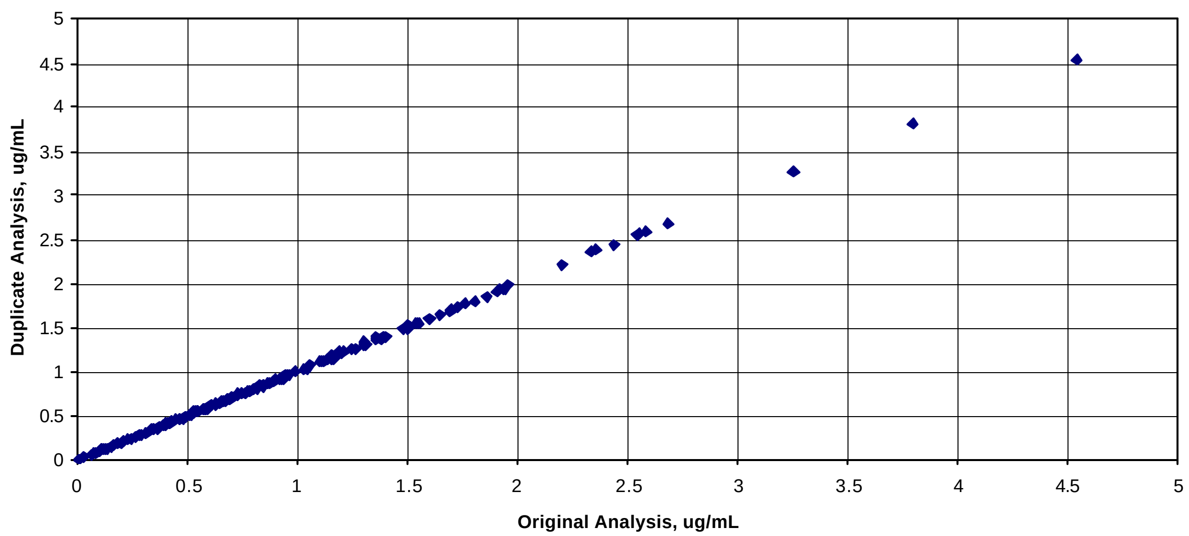


Figure 5 shows a plot of the original potassium concentration vs. the duplicate potassium concentration for replicate measurements of the filter extracts. Again, the plot shows good agreement for the duplicate measurements over the entire concentration range.

Figure 5. Potassium Duplicate Analyses

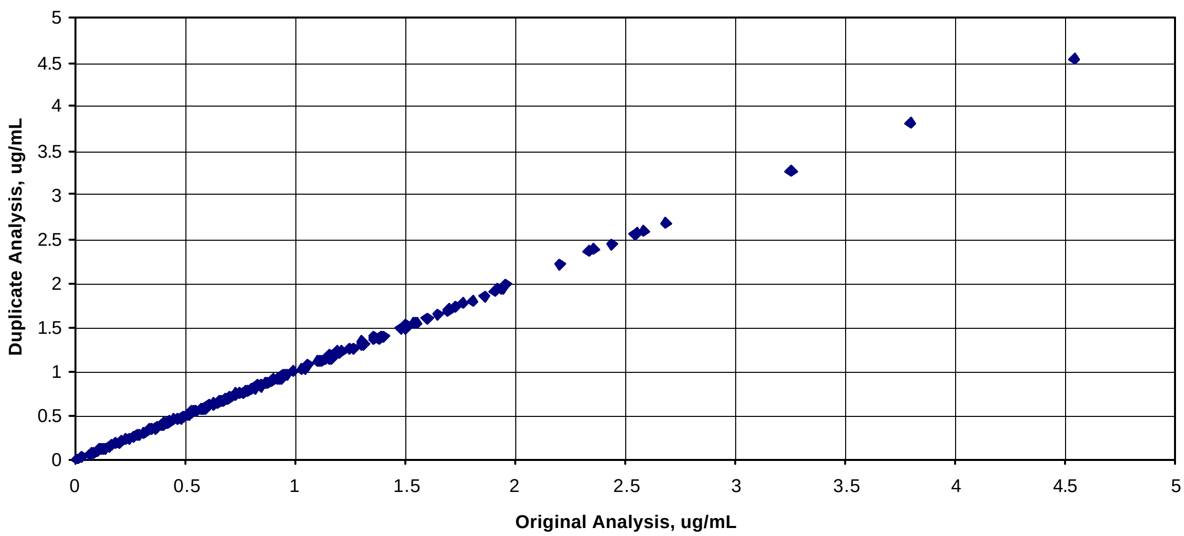


Table 17 shows average percent recovery for spikes of sodium, ammonium, and potassium over the nine month period. The average recovery values for ranged from 97.7% to 100.9% for sodium, 97.6% to 100.3% for ammonium, and 91.8% to 98.8% for potassium.

Table 18 presents filter (N BLANK) and reagent blank values for sodium, ammonium, and potassium for the instruments used for these measurements. The highest average sodium values over the nine month period were 0.007 ppm for the nylon filter blanks (25 mL extract) and 0.010 ppm for the reagent blank. The highest average ammonium values were 0.000 ppm (25 mL extract) for the nylon filter blanks and 0.000 ppm for the reagent blanks. The highest average potassium value was 0.000 ppm for nylon filter blanks (25 mL extract) and the highest average value was 0.000 ppm for the reagent blank.

2.2.4 Data Validity Discussion

During this period, no data were invalidated as a result of errors in the ion chromatography (IC) laboratory. Any inconsistencies that were observed in the filter samples were flagged on the IC data report when it is submitted for entry into the database. For example, on a few occasions, two or more filters were found in one petri dish. The filters were extracted and analyzed as one, and this was noted on the data report for that batch of samples.

Table 17. Average Percent Recovery for Sodium, Ammonium, and Potassium Spikes

Inst	D5C								
Analyte	Sodium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	98.39%	99.04%	99.85%	98.98%	98.69%	98.47%	97.66%	98.35%	98.41%
St Dev:	1.51%	2.65%	1.95%	1.56%	1.40%	2.21%	1.61%	1.72%	1.56%
Count:	42	28	19	40	34	47	27	30	48
Min Recovery:	94.87%	93.16%	96.96%	95.91%	96.59%	94.62%	94.94%	95.19%	94.85%
Max Recovery	100.72%	105.93%	103.83%	102.76%	102.46%	108.99%	100.83%	101.89%	101.61%
Inst	D5C								
Analyte	Ammonium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	97.98%	100.00%	98.99%	97.64%	99.46%	99.40%	99.74%	98.48%	99.34%
St Dev:	3.76%	3.64%	2.54%	3.21%	2.25%	2.49%	3.07%	3.16%	3.01%
Count:	42	28	19	40	34	47	27	30	48
Min Recovery:	89.58%	90.57%	90.84%	91.21%	94.62%	93.54%	94.37%	94.39%	92.95%
Max Recovery	105.66%	107.69%	102.16%	106.08%	105.09%	106.01%	107.38%	107.59%	108.90%
Inst	D5C								
Analyte	Potassium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	93.60%	93.06%	95.72%	94.34%	94.05%	94.20%	93.94%	92.36%	91.84%
St Dev:	2.58%	2.37%	2.69%	3.27%	3.06%	3.10%	2.06%	1.97%	2.84%
Count:	42	28	19	40	34	47	27	30	48
Min Recovery:	88.60%	89.66%	91.04%	87.65%	88.92%	87.48%	91.01%	89.75%	85.63%
Max Recovery	98.51%	100.33%	100.73%	100.38%	98.63%	103.73%	98.51%	97.51%	98.76%
Inst	D6C								
Analyte	Sodium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	100.89%	99.62%	100.39%	99.25%	100.22%	99.25%	99.40%	99.49%	99.45%
St Dev:	2.11%	0.91%	1.09%	0.89%	1.18%	1.28%	1.29%	1.76%	1.19%
Count:	41	40	36	42	41	37	42	41	18
Min Recovery:	97.18%	97.99%	98.37%	97.34%	98.21%	96.18%	96.43%	96.07%	97.41%
Max Recovery	105.26%	101.66%	103.10%	101.31%	104.41%	102.14%	103.22%	104.41%	101.71%
Inst	D6C								
Analyte	Ammonium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	100.28%	98.84%	99.05%	99.36%	100.00%	99.66%	99.30%	99.99%	99.38%
St Dev:	3.57%	2.18%	1.88%	1.25%	1.09%	1.70%	1.66%	1.95%	1.15%
Count:	41	40	36	42	41	37	42	41	18
Min Recovery:	90.05%	93.24%	93.32%	95.88%	96.31%	93.98%	94.40%	94.95%	96.17%
Max Recovery	106.54%	103.46%	103.03%	103.12%	102.53%	102.86%	102.64%	106.02%	100.84%
Inst	D6C								
Analyte	Potassium								
Date:	Oct-02	Nov-02	Dec-02	Jan-03	Feb-03	Mar-03	Apr-03	May-03	Jun-03
Avg Recovery:	97.75%	95.92%	97.11%	96.81%	98.78%	97.68%	97.34%	96.79%	95.88%
St Dev:	2.28%	2.11%	2.88%	2.64%	1.56%	2.17%	1.70%	2.79%	2.17%
Count:	41	40	36	42	41	37	42	41	18
Min Recovery:	94.39%	91.03%	90.62%	87.25%	93.84%	92.53%	94.53%	90.43%	91.09%
Max Recovery	102.21%	99.94%	101.83%	99.95%	101.53%	102.40%	102.74%	101.05%	98.56%

Table 18. Filter Blank and Reagent Blank Values (ppm) for Sodium, Ammonium, and Potassium

Inst	TYPE (Short Name)	Count	Av Na	STD Na	Min Na	Max Na
D5C	Nylon	113	0.000	0.006	-0.029	0.039
D5C	Reagent	214	0.002	0.010	-0.033	0.059
D6C	Nylon	227	0.007	0.012	-0.001	0.045
D6C	Reagent	239	0.010	0.024	-0.002	0.223

Inst	TYPE (Short Name)	Count	Avg NH_4	STD NH_4	Min NH_4	Max NH_4
D5C	Nylon	113	0.000	0.000	0.000	0.000
D5C	Reagent	214	0.000	0.000	0.000	0.001
D6C	Nylon	227	0.000	0.000	-0.002	0.000
D6C	Reagent	239	0.000	0.002	-0.007	0.024

Inst	TYPE (Short Name)	Count	Avg K	STD K	Min K	Max K
D5C	Nylon	113	0.000	0.000	0.000	0.000
D5C	Reagent	214	0.000	0.000	0.000	0.000
D6C	Nylon	227	0.000	0.000	0.000	0.000
D6C	Reagent	239	0.000	0.004	0.000	0.047

2.2.5 Corrective Actions Taken

In late November and December 2002, higher than acceptable sodium levels were observed in extracts of cleaned nylon filters. The filters in the affected lots were rejected for use in the network, and experiments were begun to determine the source of the contamination. During the course of the investigation, it was observed that some of the Nalgene tubes used for extraction of the filters had a small amount of a white residue in the caps. The tubes had been submitted to a labware cleaning group within RTI with instructions to rinse thoroughly with hot water (no soap) followed by a thorough rinse with deionized water. However, it was hypothesized that the residue could have been caused by accidental exposure to soap from other washing procedures within the same cleaning laboratory. Therefore, all subsequent rinsing of extraction tubes was performed in the ion analysis laboratory. Additional experiments were performed to determine the background levels of the PM2.5 ions of interest in extracts of the tubes as received (directly out of the box). It was found that the lot tested was acceptable as received. The Ion Analysis Laboratory now tests each lot of tubes as they are received and prior to use for filter extraction. The tubes are rinsed only if contamination is observed.

2.3 OC/EC Laboratory

The OC/EC Laboratory analyzed and reported results for 15,739 quartz filter samples under the laboratory support contract during the period October 1, 2002, to June 30, 2003.

2.3.1 Description of QC Checks Applied

Quality control (QC) checks, acceptance criteria, and corrective actions for the OC/EC Laboratory are summarized in the table below.

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	annually	MDL $\leq$ 0.5 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples.
Calibration Peak Area	every analysis	Within 95% to 105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter.
Instrument Blank	daily	Blank $\leq$0.3 µg/cm^2	Determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples.
Three-Point Calibration	weekly	Correlation Coefficient (R^2) $\geq$0.99 [with force-fit through 0,0]	Determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed.
Calibration Check	daily	(1) 90% to 110% recovery, and (2) calibration peak area 90% to 110% of average for the weekly three-point calibration.	Initiate corrective action, if necessary, to solve the problem before analyzing samples.
Duplicate Analyses	10% of samples	(1) TC Values greater than 10 µg C/cm^2-- Less than 10% RPD, (2) TC Values 5 - 10 µg C/cm^2-- Less than 15% RPD, (3) TC Values less than 5 µg C/cm^2-- Within ±0.75 µg C/cm^2.	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

2.3.2 Statistical Summary of QC Results

The method detection limit for total carbon (TC) is determined annually or when the oven in an analyzer is replaced, whichever comes sooner. All three OC/EC carbon analyzers met the required limit of ≤0.5 µg C/cm^2 for all MDLs determined during the period. A new MDL was determined each time the oven was changed in an analyzer. The Retrofit analyzer MDL was 0.10 µg C/cm^2 on August 30,2002, (MDL at beginning of reporting period); 0.09 µg C/cm^2 on January 13, 2003; 0.19 µg C/cm^2 on March 6, 2003; and 0.20 µg C/cm^2 on June 18, 2003. The Second analyzer MDL was 0.12 µg C/cm^2 on August 27, 2003, (MDL at beginning of reporting period); 0.15 µg C/cm^2 on January 13, 2003; and 0.13 µg C/cm^2 on June 17, 2003. The Third analyzer MDL was 0.07 µg C/cm^2 on August 3, 2002; 0.18 µg C/cm^2 on February 28, 2003; and 0.09 µg C/cm^2 on March 4, 2003.

Calibration peak area, which is the response of the FID to the internal standard, is plotted for every analysis run on a given day. Any filter analysis for which the calibration peak area is outside the range of 95% to 105% of the average calibration peak area for that day is repeated with a second punch.

Routine QC samples analyzed in the OC/EC Laboratory include (1) daily instrument blanks, (2) weekly three-point calibration standards, (3) daily mid-level calibration check standards, and (4) duplicate analyses on 10% of quartz filter samples analyzed. Each of these is described separately below.

Routine QC samples analyzed in the OC/EC Laboratory include (1) daily instrument blanks, (2) weekly three-point calibration standards, (3) daily mid-level calibration check standards, and (4) duplicate analyses on 10% of quartz filter samples analyzed. Each of these is described separately below.

Figure 6 shows measured TC for daily instrument blanks and instrument blanks run after about 30 samples on the Retrofit, Second, and Third OC/EC analyzers during the reporting period (October 1, 2002, through June 30, 2003). The instrument blank must be ≤0.3 µg C/cm^2 (bold line at the top of Figure OC/EC1). Mean and standard deviation of blank responses by instrument over the reporting period are summarized in the table below.

Blank Statistic	OC/EC Analyzer		
	Retrofit	Second	Third
Number of Instrument Blanks	324	346	349
Mean Response (µg C/cm^2)	0.046	0.038	0.074
Standard Deviation	0.050	0.037	0.070

None of the daily instrument blanks or instrument blanks run after 30 samples on any of the three instruments exceeded the acceptance criterion of ≤0.3 µg C/cm^2.

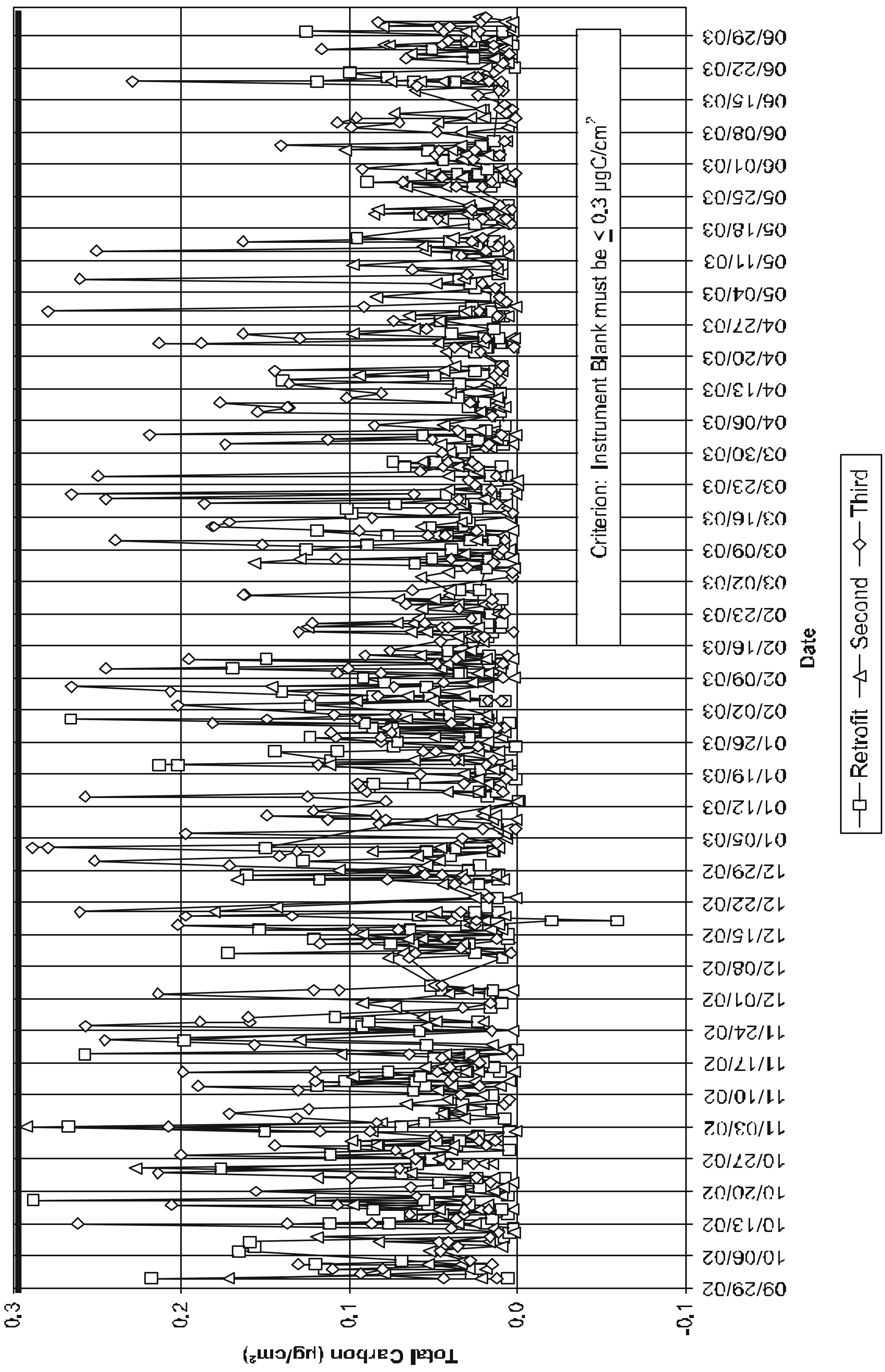


Figure 6. OC/EC Instrument Blanks

Figure 7 shows linearity (as R^2, forced-fit through the origin) for all three-point calibrations run on all three instruments during the reporting period. All three instruments met the $R^2 \geq 0.99$ (heavy line in Figure 7) requirement for every three-point calibration.

Percent recovery of standards is used to make sure the instruments are functioning properly and are still calibrated correctly. **Figures 8a, 8b, and 8c** show percent recovery on the Retrofit, Second, and Third analyzers, respectively, for each of the three (low, middle, and high) calibration standards, as well as the average percent recovery for the three, used for each three-point calibration. All three instruments met the 90-110% criterion (heavy lines in figures) for recovery for all three standards in every three-point calibration during the reporting period.

Response factors for the flame ionization detector (FID) are used to monitor FID performance. **Figures 9a, 9b, and 9c** show FID response factors for each of the three calibrations standards and the average FID response factor for each three-point calibration on the Retrofit, Second, and Third instruments, respectively, during the reporting period. FID response is affected by slight changes in flow rate for hydrogen and other gases, but use of the internal methane standard at the end of every analysis compensates for such changes. All three-point calibrations on all three analyzers met the acceptance criteria in Section 1.3.1. The ratio of FID area counts for the internal standard to the known mass of carbon in the internal standard injection loop is calculated separately for each analysis and used to calculate the mass of carbon volatilized from the filter punch during that analysis as shown in the following equation.

$$\text{mass } C_{\text{punch}} = \frac{\text{FID area counts}_{\text{punch}}}{\left[\dfrac{\text{FID area counts}_{\text{internal standard}}}{\text{mass } C_{\text{internal standard loop}}}\right]}$$

Figure 10 shows the slopes of three-point calibration plots with force-fit through the origin for all three OC/EC analyzers during the reporting period.

Figure 11 shows percent recovery for all daily calibration checks run on all three instruments during the reporting period. All daily calibration checks met the acceptance criterion of 90% to 110% recovery.

Duplicate measurements are used to monitor the uniformity of filter loading and to indicate instrument stability. The acceptance criteria for duplicate measurements (in the Table above) are based on a significant absolute uncertainty at low (< 5 μg C/cm^2) TC loadings and the relative uncertainty at higher TC loadings. **Figures 12a, 12b, and 12c** show relative percent difference of duplicate measurements versus filter concentration (μg C/cm^2) for the Retrofit, Second, and Third instruments, respectively, during the reporting period. Text boxes beside each figure show total number of duplicates run on that instrument and the numbers of filters that passed and that failed the appropriate duplicate criterion. Filters that failed to meet the appropriate duplicate acceptance criterion were flagged as having a nonuniform filter deposit (LFU).

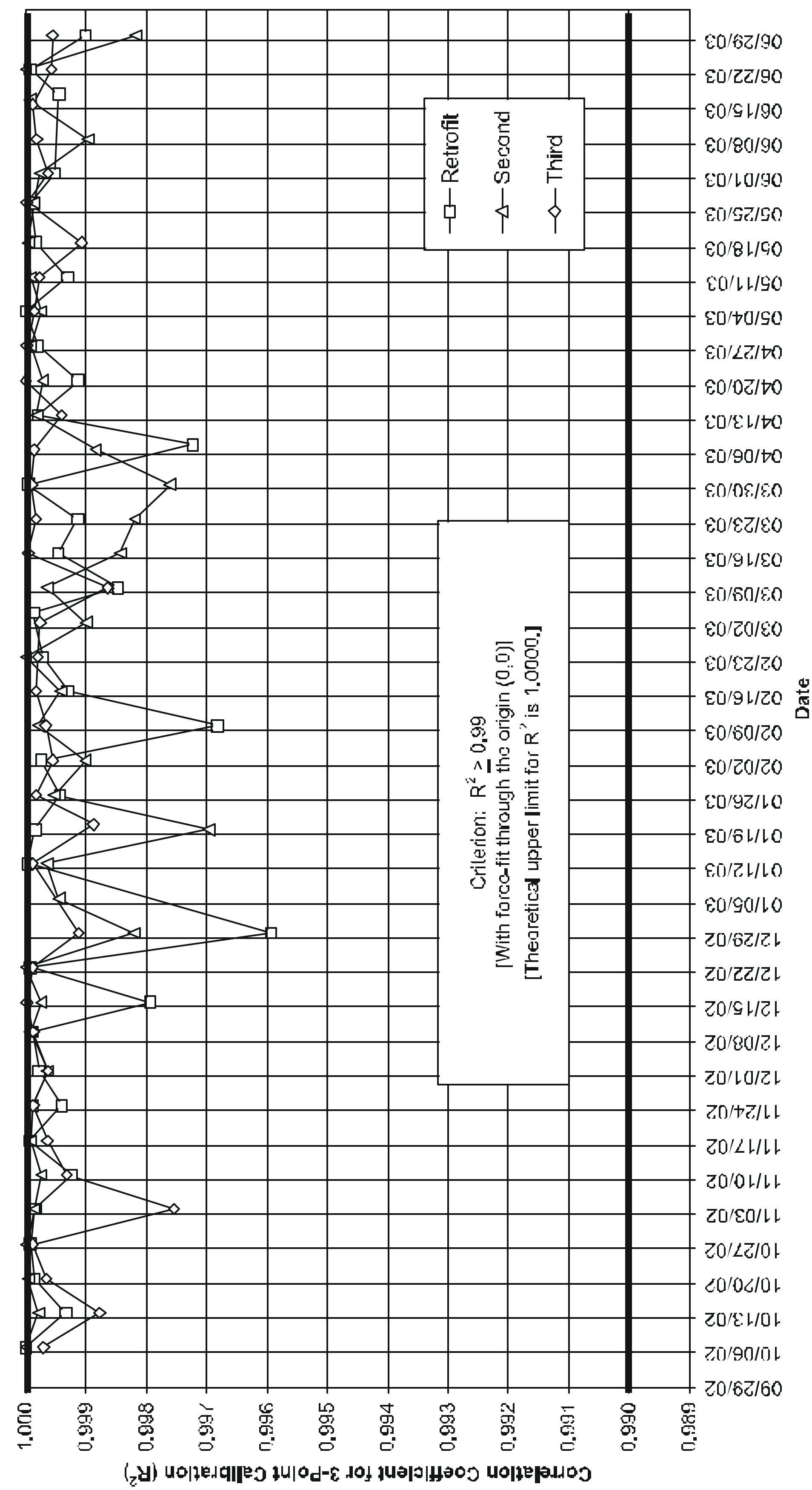


Figure 7. Linearity of Three-Point Calibrations

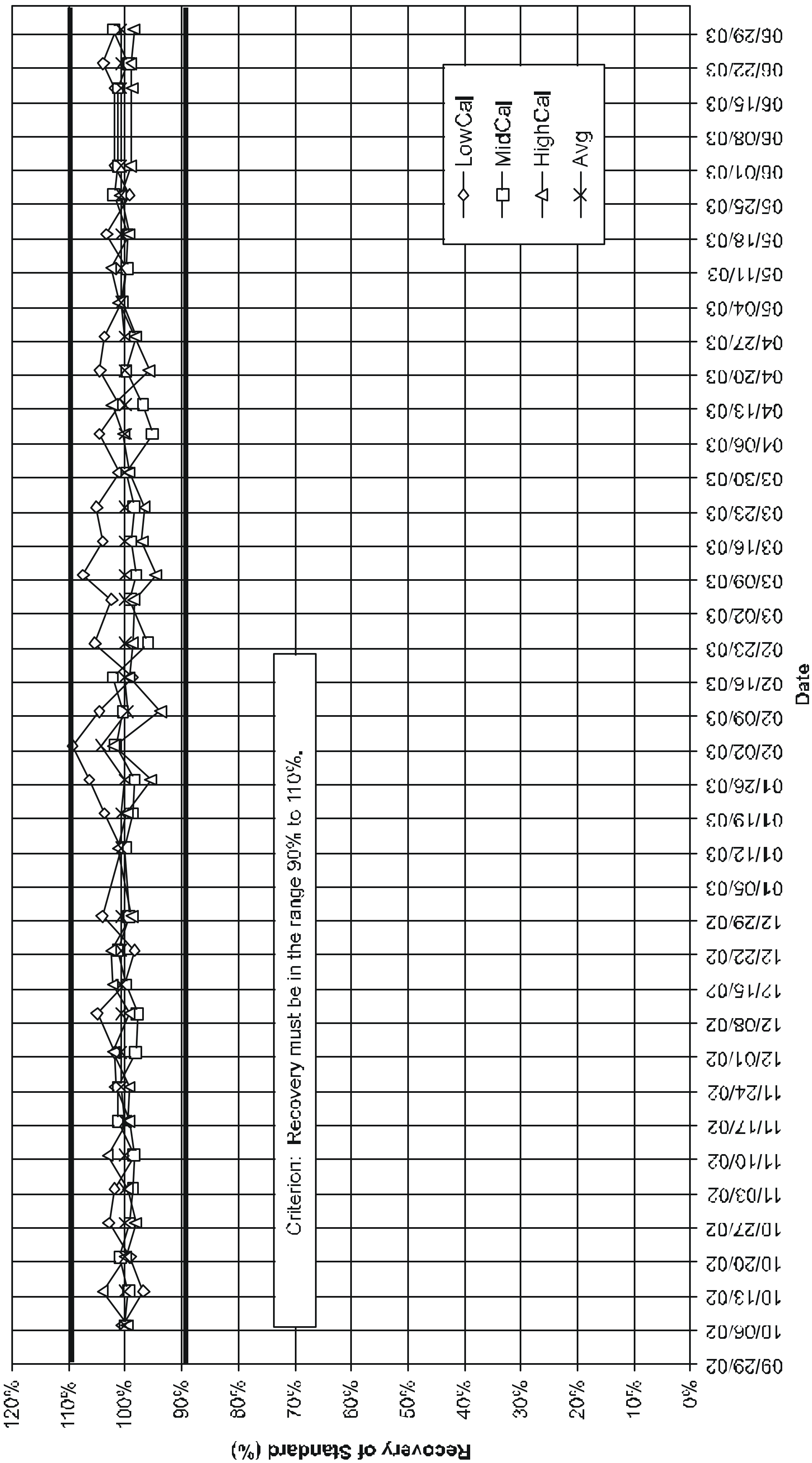


Figure 8a. Percent Recoveries for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

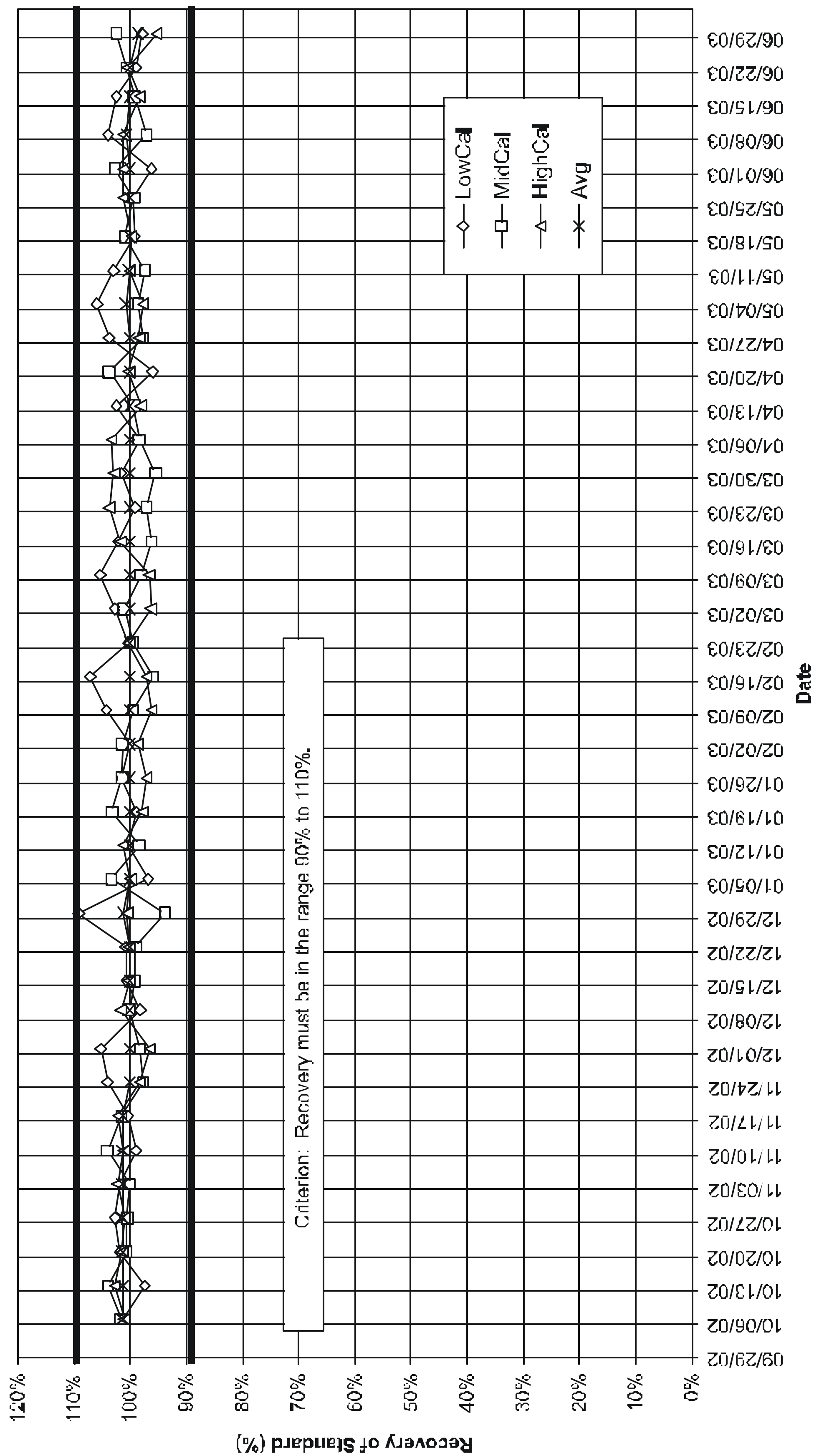


Figure 8b. Percent Recoveries for Three-Point Calibration Standards on the Second OC/EC Analyzer

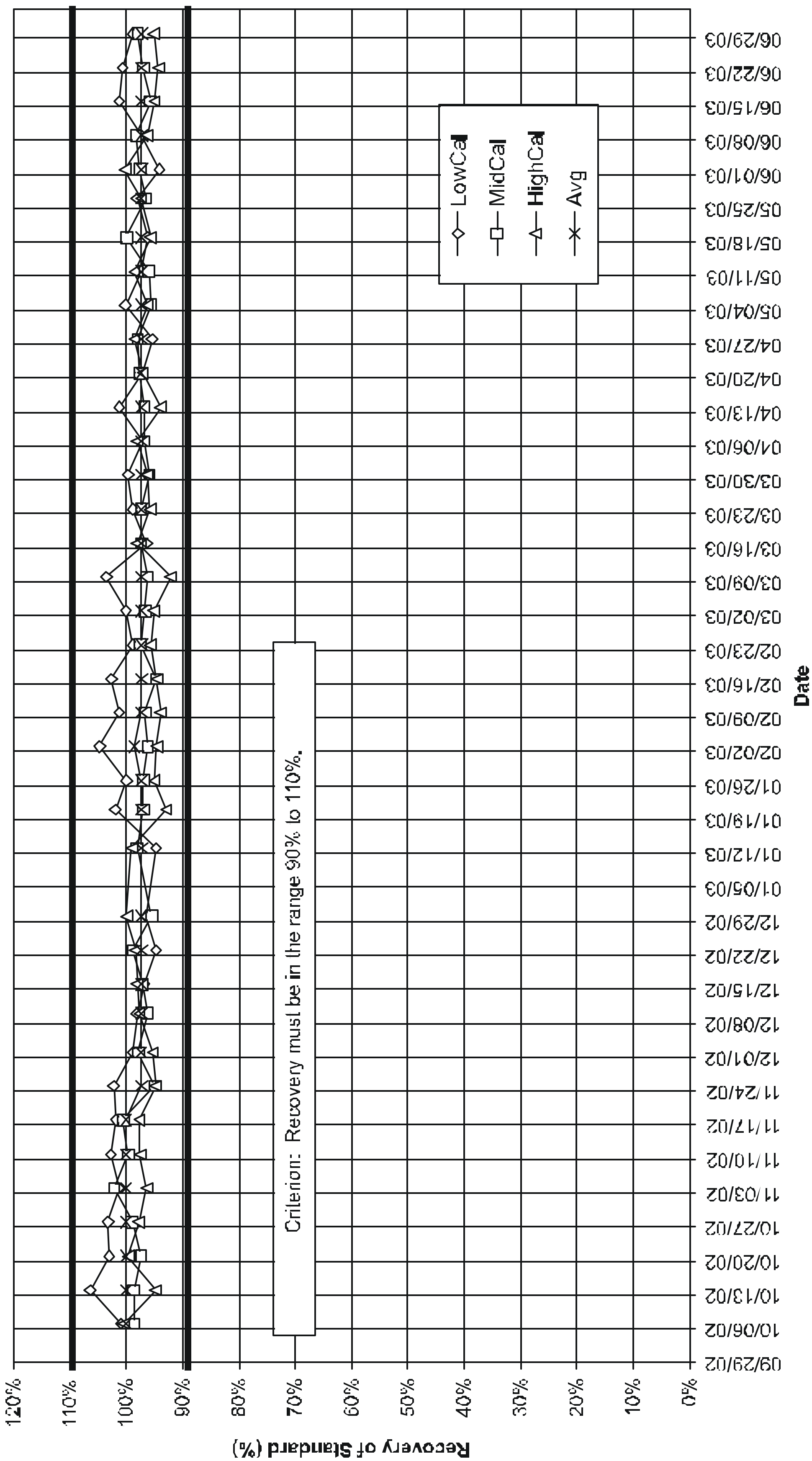


Figure 8c. Percent Recoveries for Three-Point Calibration Standards on the Third OC/EC Analyzer

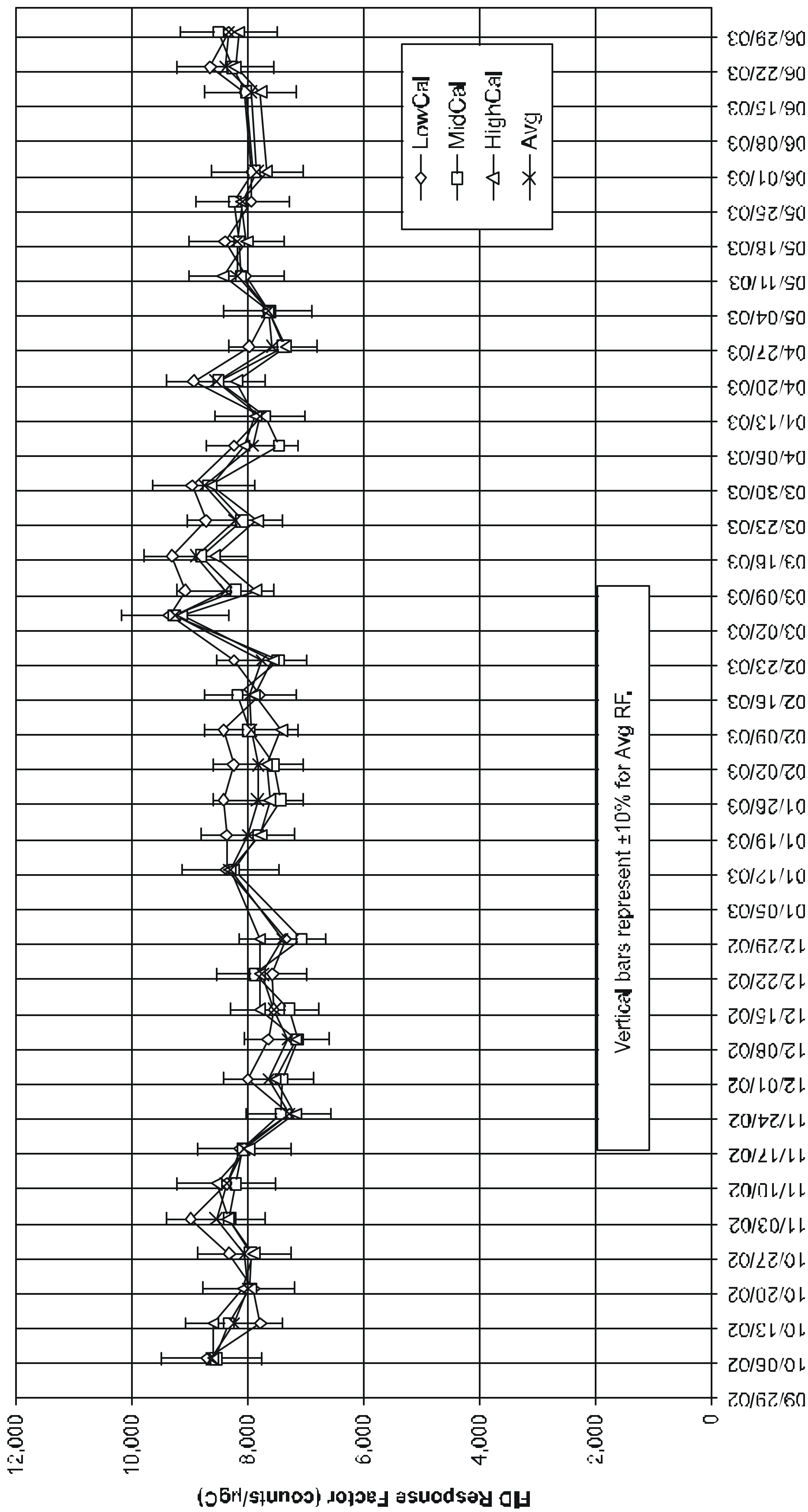


Figure 9a. FID Response Factors for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

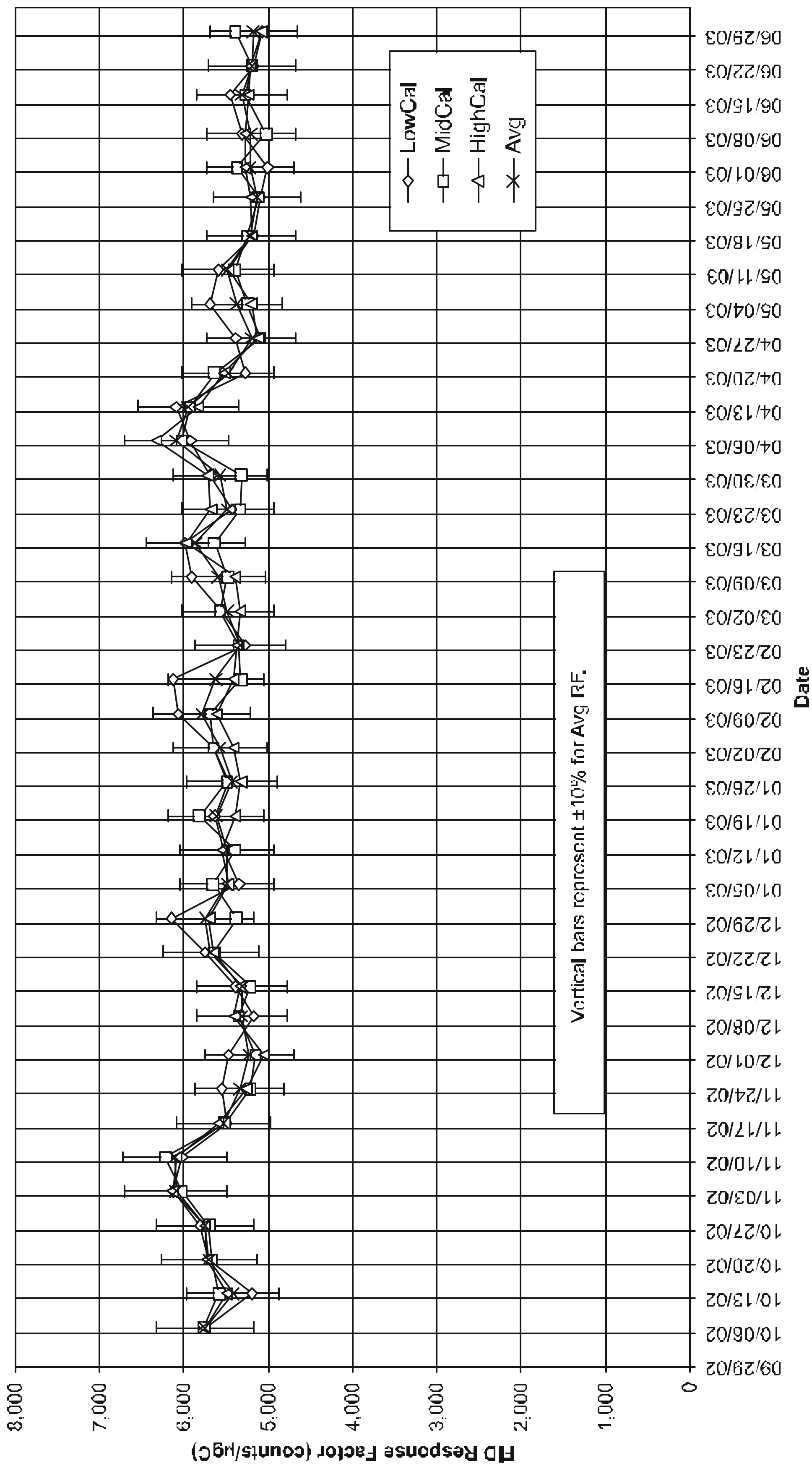


Figure 9b. FID Response Factors for Three-Point Calibration Standards on the Second OC/EC Analyzer

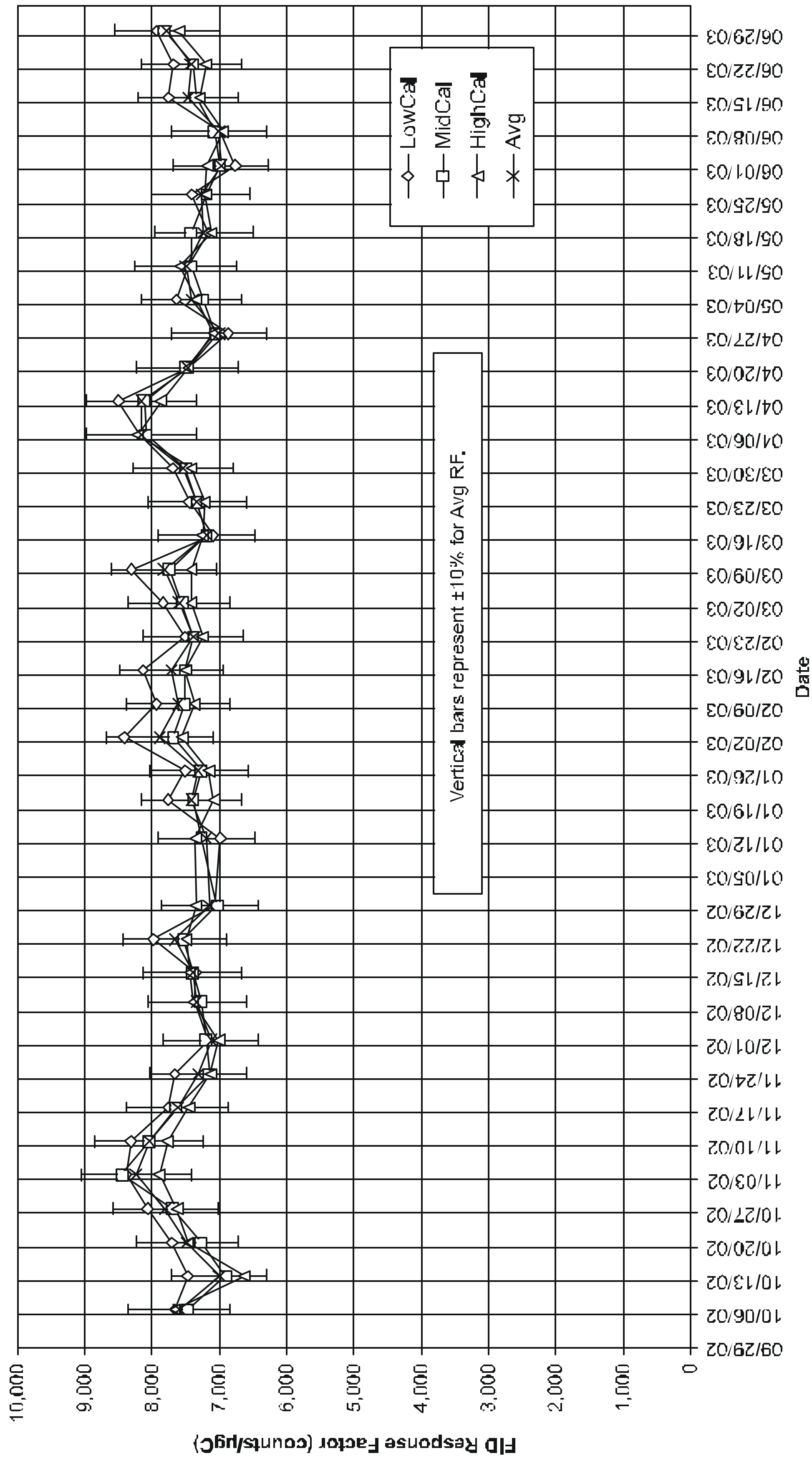


Figure 9c. FID Response Factors for Three-Point Calibration Standards on the Third OC/EC Analyzer

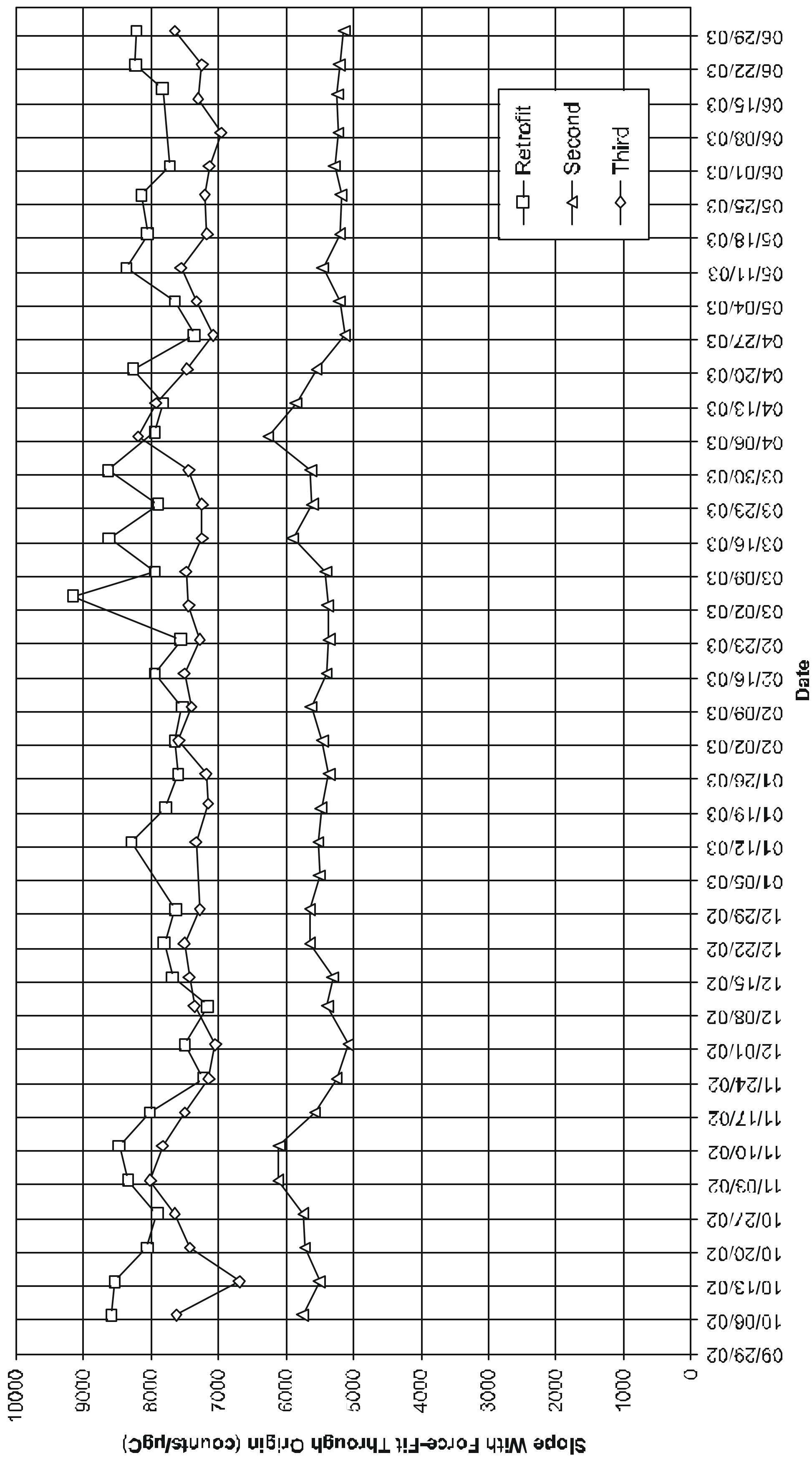


Figure 10. Slopes of Calibration Plots for Three-Point Calibrations With Force-Fit Through Origin (0,0)

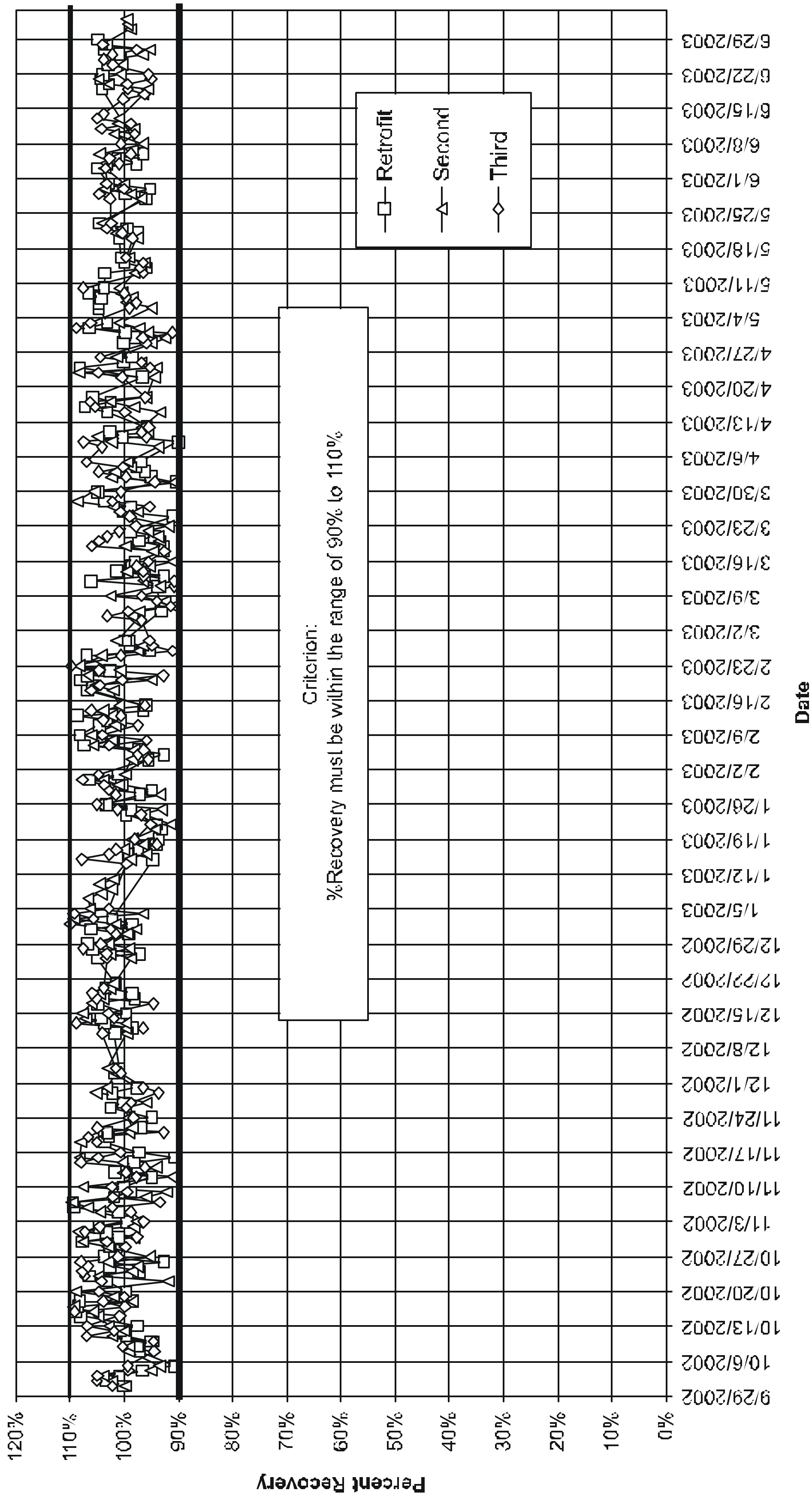


Figure 11. Daily Calibration Checks

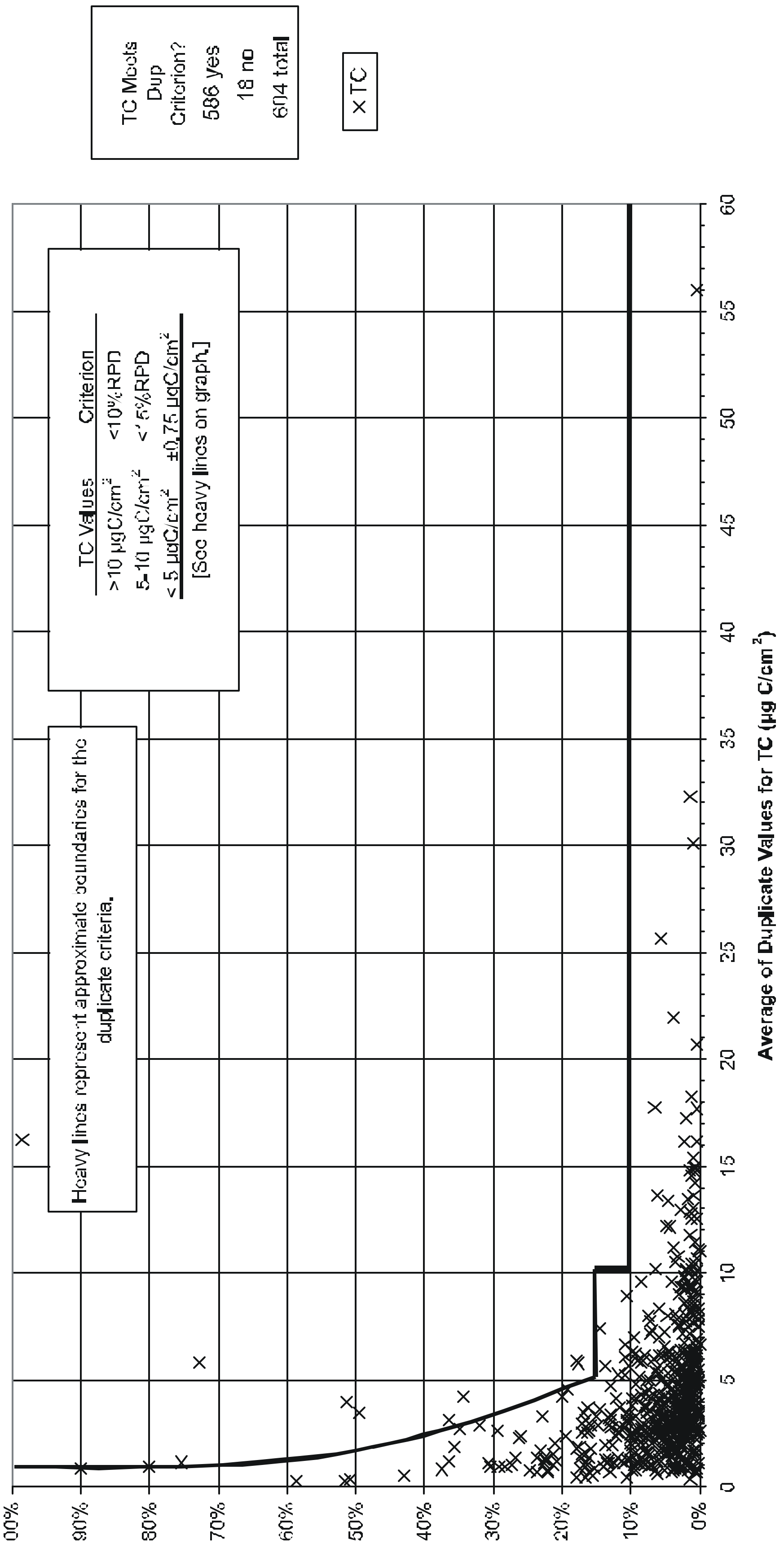


Figure 12a. Relative Percent Difference of Duplicates vs. Average Value for TC on Retrofit OC/EC Analyzer

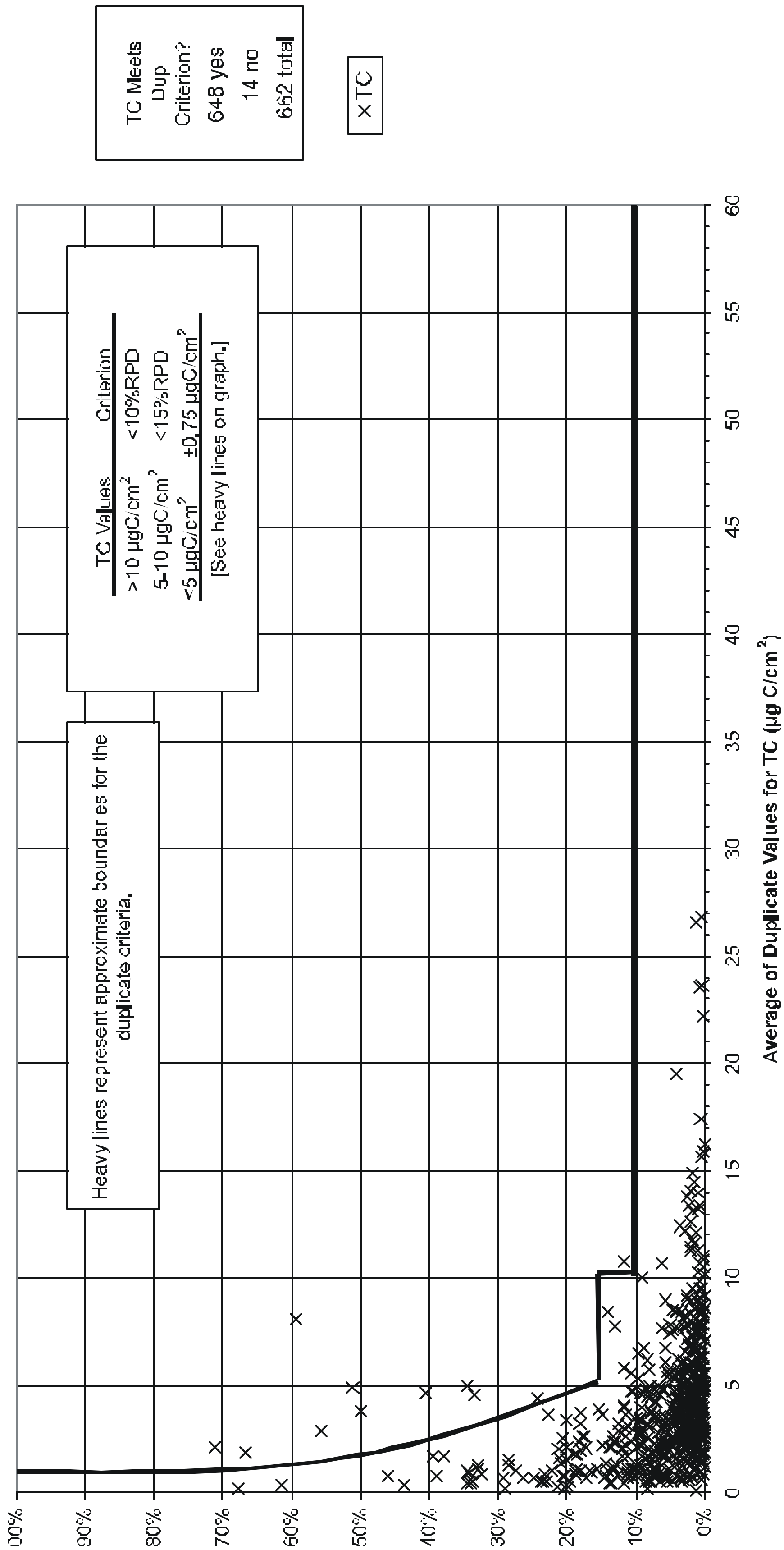


Figure 12b. Relative Percent Difference of Duplicates vs. Average Value for TC on Second OC/EC Analyzer

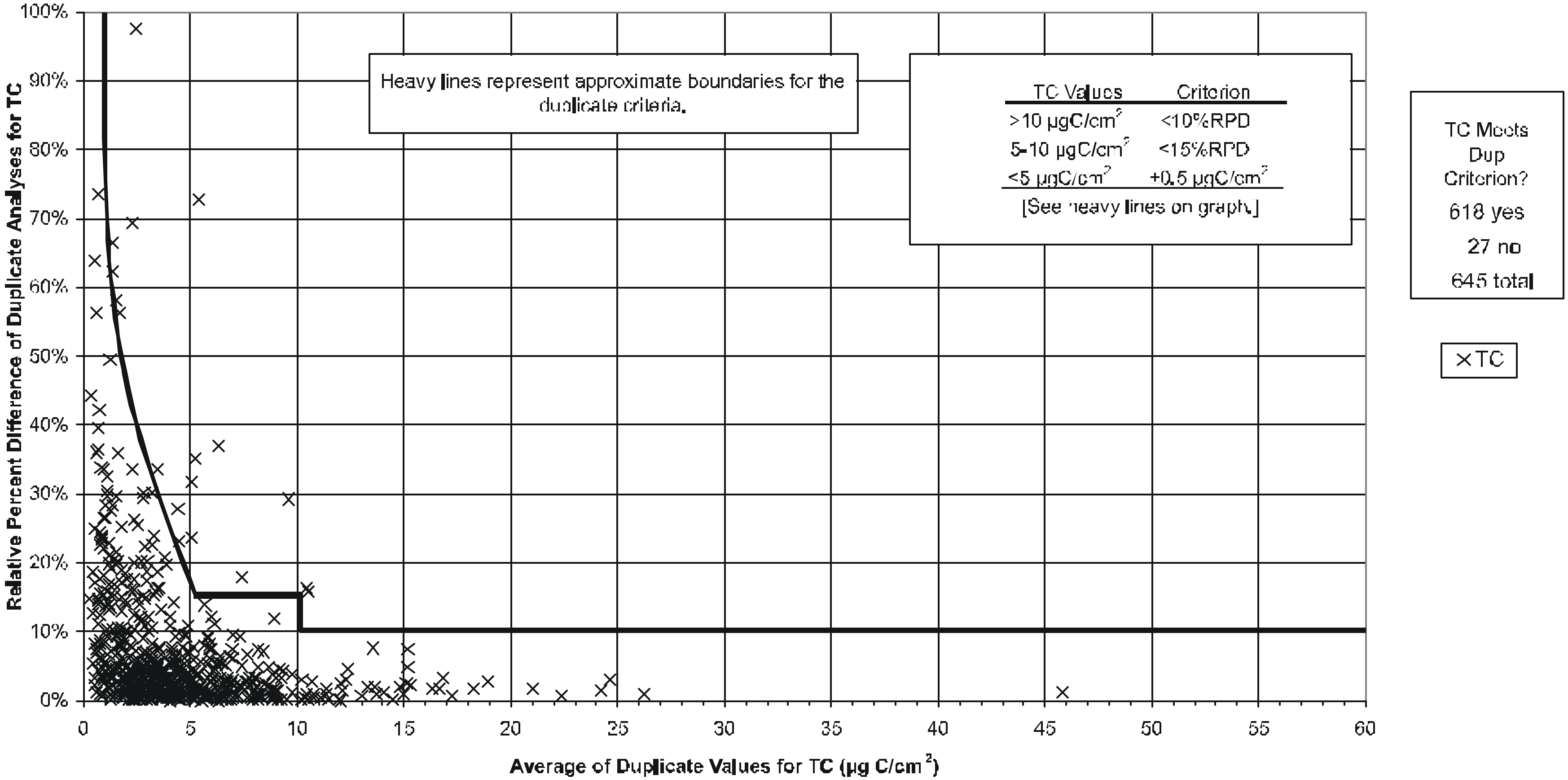


Figure 12c. Relative Percent Difference of Duplicates vs. Average Value for TC on Third OC/EC Analyzer

2.3.3 Data Validity Discussion

Invalid Data Due to OC/EC Laboratory Errors. The ability to take a second or third punch from a quartz filter for analysis allows the OC/EC analyst to avoid invalidating data due to OC/EC Laboratory error except in extreme cases when an entire filter (or half-filter aliquot) is involved in an error. So far, this has occurred only when a filter or half-filter aliquot arrived at the OC/EC Laboratory in pieces so small that a full punch could not be taken as a single piece. Quartz filters are almost always torn around the edges during removal from the cassette filter holder in the SHAL but are only flagged as torn (1) by SHAL personnel if they arrive at RTI damaged or (2) by the OC/EC analyst if there is no portion of the filter large enough for the removal of a full punch for analysis as a single piece. The second occurrence is extremely rare.

Invalid Data Due to Other Causes. The OC/EC Laboratory simply analyzes filters that are delivered from the SHAL without any knowledge of the sampling or other field and transport data associated with those filters. OC/EC Laboratory personnel do not know if data for a filter will be invalidated for causes other than those associated with the OC/EC analysis.

2.3.4 Summary of Audit Findings and Recommendations

The RTI OC/EC Laboratory was not audited during the reporting period.

2.3.5 Corrective Actions Taken

No corrective actions were required during the reporting period.

2.4 X-ray Fluorescence Laboratories

During the reporting period, four XRF instruments were in use. Included were one at RTI, two at Chester LabNet, and one at Cooper Environmental Services. Each had been tested and accepted by the EPA for use in the PM2.5 Speciation Program.

Section 2.4.1 describes the checks common to all laboratories (and instruments within each laboratory). Sections 2.4.2, 2.4.3, and 2.4.4, respectively, describe the specific QC results for Chester, CES, and RTI.

2.4.1 Description of QC Checks Applied

QC elements for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions are shown in **Table 19**.

Table 19. QC Procedures Used to Analyze EDXRF Elements

QC Element	Frequency	Control Limits	Corrective Action
Calibration	as needed	--	--
Calibration verification	weekly	within NIST uncertainties	recalibrate
Instrument precision	once per batch of $\leq$ 15	95–105% recovery	batch reanalysis
Excitation condition check	every sample	within analysis uncertainty	sample reanalysis
Sample replicate precision	10%	± 5 RPD	batch reanalysis

The two-sigma (95 percent confidence level) detection limits in units of µg/cm^2 are calculated from the analysis of a blank Teflon filter as follows:

$$\text{detection limit for element } i = 2\delta_i = \frac{2(2B_i)^{1/2}}{s_i t}$$

where,

B_i is the background counts for element i,
s_i is the sensitivity factor for element i,
and t is the counting lifetime.

Theoretically, detection limits may be decreased by simply increasing the counting lifetime. In practice, a point of diminishing returns is reached for real-world samples in which the background increases along with the analyte signal. At this point, further improvement in detection limits by increasing the counting time is not possible.

2.4.2 Chester LabNet

Chester LabNet was the original XRF subcontractor laboratory used for the STN program. During this period, Chester operated two Kevex XRF instruments which have been designated 770 and 771.

2.4.2.1 Statistical Summary of QC Results –

Precision

Precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for select elements are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of reproducibility or precision. The data used to monitor precision are presented in **Figures 13 through 25**. **Tables 20a and 20b** provide summaries of the precision data. The last three columns, R and Slope/Year: Current and Previous indicate the uncorrected systematic drift that took place during the reporting period. Comparison of the annualized slopes of the current vs. period in the previous semiannual STN QC report shows whether or not there was a continuing trend across reporting periods. Based on the R values for the regression of recovery vs. time and the current slopes, the 771 instrument appears to have somewhat less calibration drift than the 770 instrument.

Table 20a. Summary of Chester QC Precision Recovery Data, Kevex 770, 10/01/2002 - 06/30/2003.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(0)	99.53	2.82	2.83	106.4	92.3	-0.31839	-4.05	11.58
Si(1)	99.02	2.57	2.60	106.5	91.3	-0.59735	-6.94	1.50
Ti(2)	99.66	2.70	2.71	105.9	93.6	-0.76000	-9.28	1.12
Fe(3)	99.54	1.86	1.87	104.7	94.0	-0.34711	-2.91	0.90
Se(4)	102.03	2.31	2.26	107.3	95.6	-0.34631	-3.61	2.40
Pb(4)	102.12	2.47	2.42	108.4	96.9	-0.30051	-3.35	2.40
Cd(5)	98.67	2.79	2.83	108.7	91.7	-0.63165	-7.96	3.08

N=293 for all elements.

Figure 13. Recovery Precision for Chester Kevex 770 XRF
Si(0) - Rh L/7.5kV/0.1mA

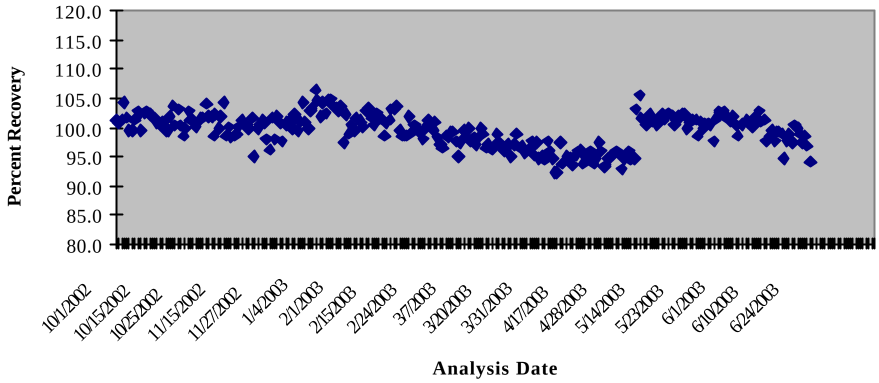


Figure 14. Recovery Precision for Chester Kevex 770 XRF
Si(1) - Ti target/25kV/1.0mA

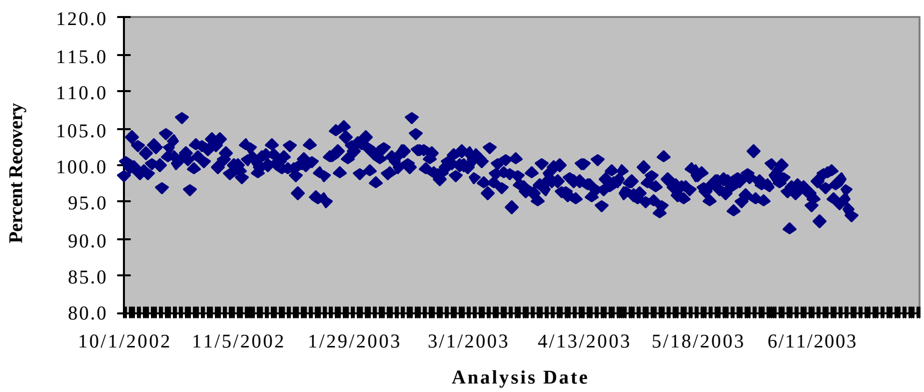


Figure 15. Recovery Precision for Chester Kevex 770 XRF
Se(4) - Rh K/35kV/0.25mA

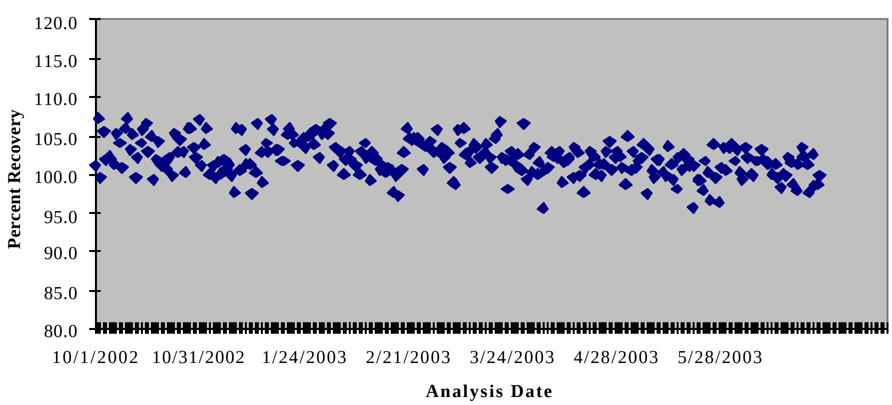


Figure 16. Recovery Precision for Chester Kevex 770 XRF
Pb(4) - Rh K/35kV/0.25mA

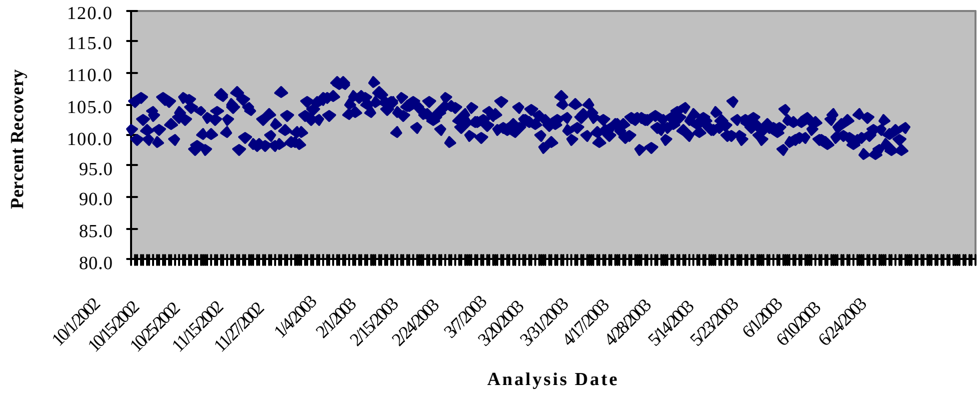


Figure 17. Recovery Precision for Chester Kevex 770 XRF
Cd(5) - Rh K/W filter/55kV/0.25mA

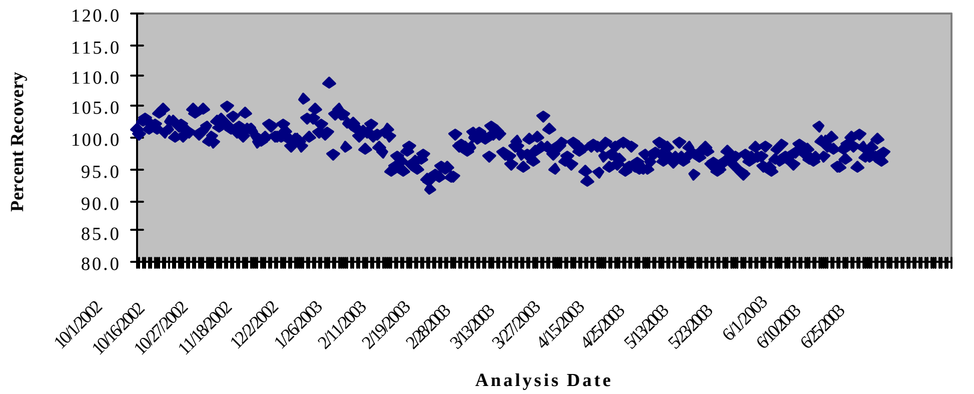


Figure 18. Recovery Precision for Chester Kevex 770
Fe(3) - Ge target/35kV/0.5mA

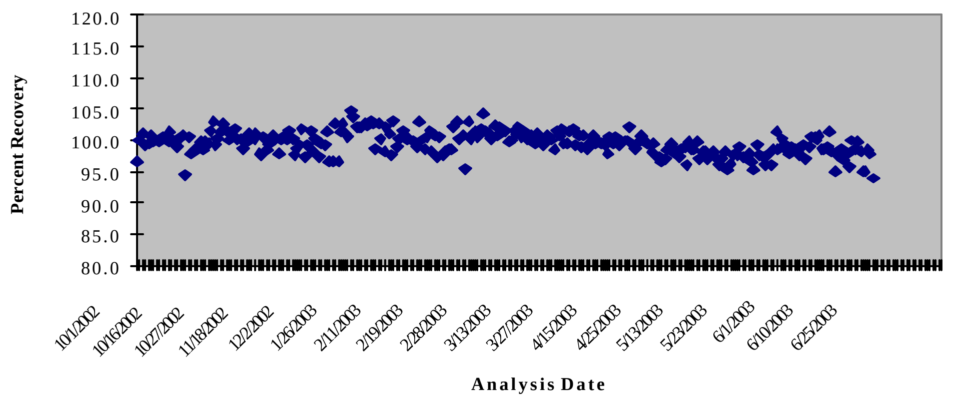


Figure 19. Recovery Precision for Chester Kevex 770 XRF
Ti(2) - Fe target/35kV/0.5mA

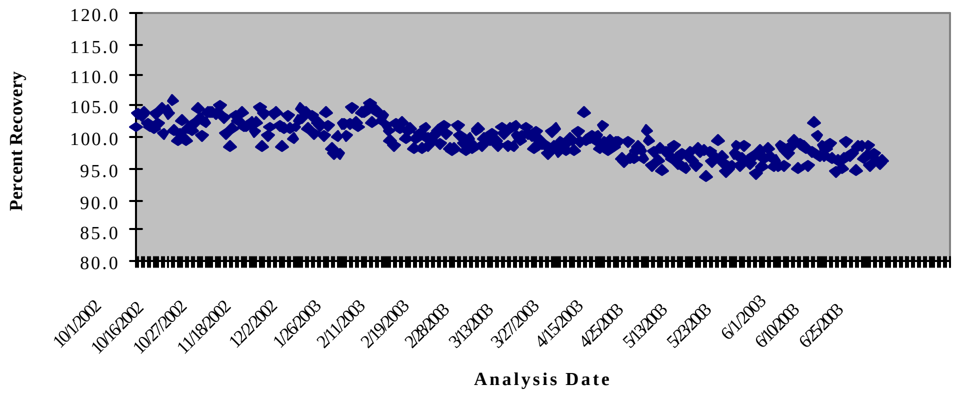


Figure 20. Recovery Precision for Chester Kevex 771 XRF
Si(1) - Rh L-alpha 6.0kV

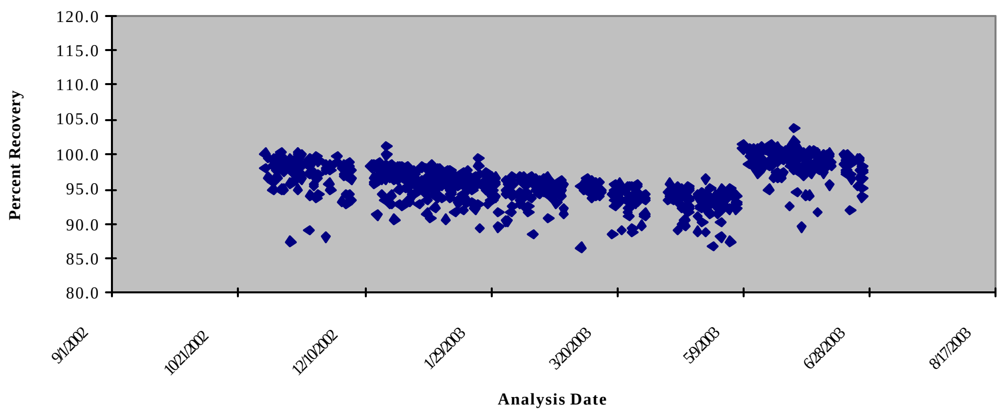


Figure 21. Recovery Precision for Chester Kevex 771 XRF
Se(4) - Rh K-alpha 35kV

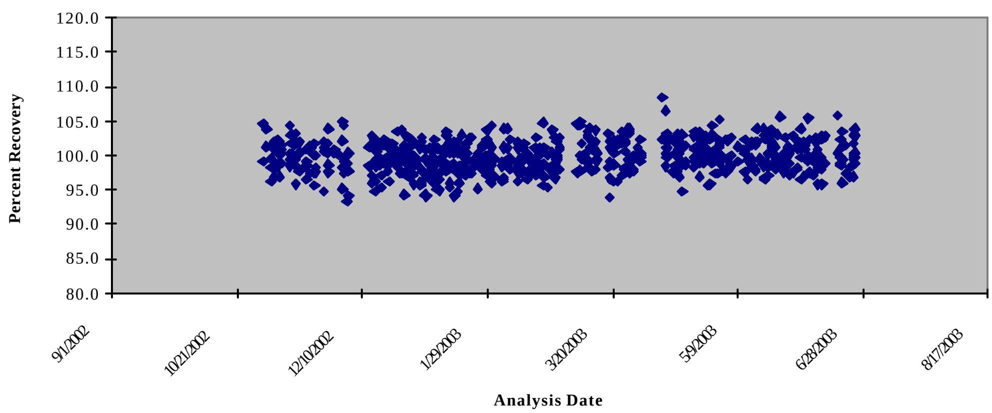


Figure 22. Recovery Precision for Chester Kevex 771 XRF
Pb(4) Rh K-alpha 35kV

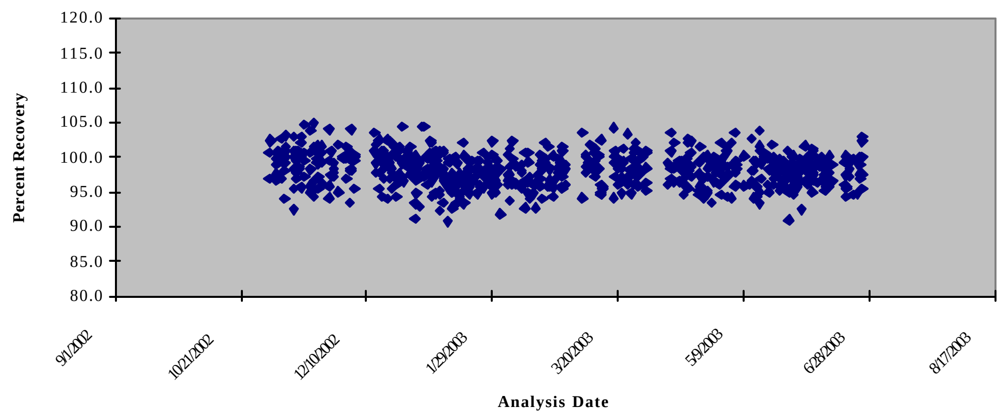


Figure 23. Recovery Precision for Chester Kevex 771 XRF
Cd(5) W filter 55kV

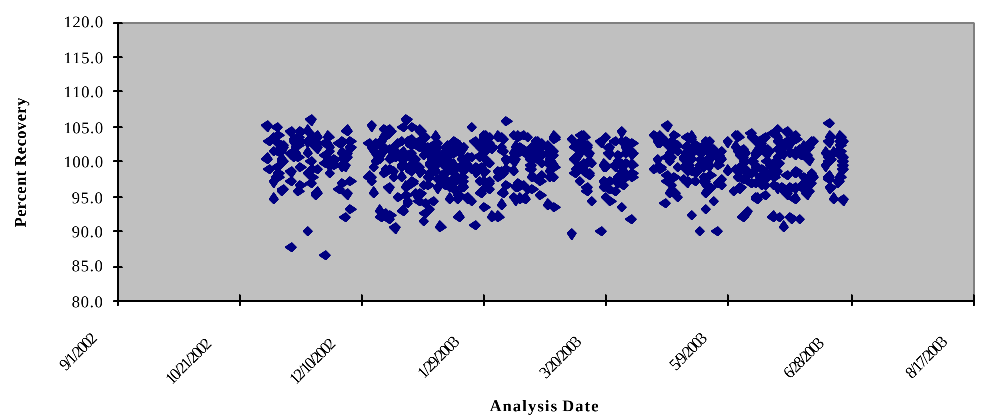
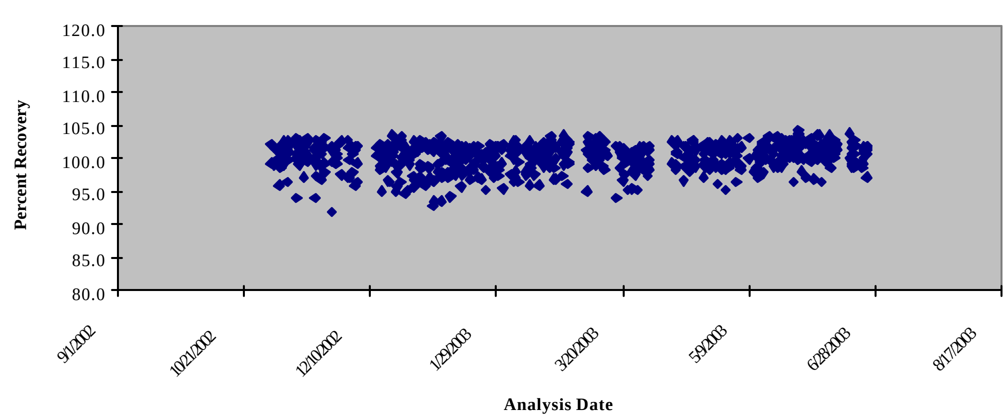


Figure 24. Recovery Precision for Chester Kevex 771 XRF
Fe(3) - Ge target 45kV



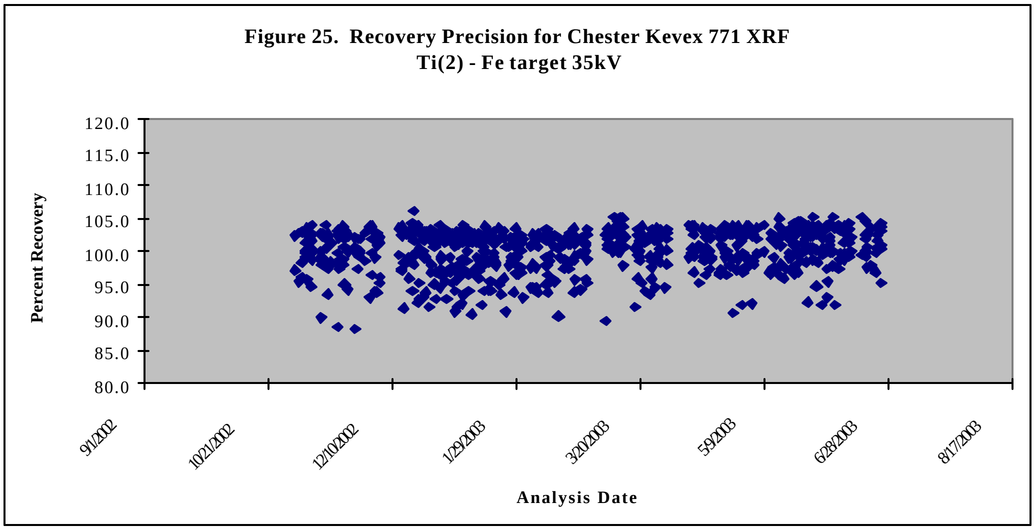


Table 20b. Summary of Chester QC Precision Recovery Data, Kevex 771, 10/01/2002 - 06/30/2003.

Element	Avg.	Std Dev	RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(1)	95.96	2.79	2.91	103.8	86.4	0.06336	0.94	-7.27
Ti(2)	100.15	3.21	3.20	106.1	88.4	0.15947	2.72	2.39
Fe(3)	100.28	2.02	2.02	104.4	92.0	0.13933	1.50	1.99
Se(4)	99.87	2.22	2.23	108.4	93.2	0.13637	1.61	3.31
Pb(4)	98.16	2.39	2.43	104.9	90.6	-0.11128	-1.41	2.24
Cd(5)	99.48	3.22	3.24	106.0	86.5	-0.03475	-0.60	2.25

N=696 for all elements.

Recovery

Recovery (accuracy) is determined based on periodic analysis of NIST standards. These results are tabulated in Table 21 for both the Kevex 770 and 771 instruments.

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of measured and expected values. **Figures 26 through 51** show recovery for 12 select elements spanning the range of the 48 elements normally measured. The recovery values for all elements ranged between 90.0 and 114.5 percent for the 770 and between 90.7 and 112.4 percent for the 771, as shown in **Table 21**. For the 770 instrument, the high value of 114.5% was for Si-1832; and two additional values for Si-1832 above the 110% upper limit were also seen. One point each for aluminum and calcium exceeded the 110% upper limit. For the 771 instrument, the high value of 112.4% was for sulfur, which had several points above the 110% limit. All other elements were in control (> 90%, < 110%) at all times.

Table 21. Recovery Determined from Analysis of NIST Standard Reference Material Filters, Kevex 770 and 771.

Element	Kevex 770	Kevex 771
	Range % Recovery	Range % Recovery
Al	92.4 - 112.4	97.3 - 107.3
Si*	94.1 - 114.5	99.1 - 107.7
Si**	90.2 - 102.8	92.5 - 102.5
S	90.0 - 106.7	93.2 - 112.4
K	93.3 - 101.6	95.5 - 107.2
Ca	92.9 - 112.1	99.4 - 109.8
Ti	94.3 - 101.9	90.7 - 99.0
V	91.7 - 104.8	97.1 - 107.7
Mn	96.5 - 108.4	96.6 - 105.4
Fe	94.3 - 101.8	95.7 - 101.4
Cu	97.3 - 104.4	94.3 - 103.0
Zn	94.7 - 102.0	96.5 - 101.5
Pb	96.5 - 105.4	96.5 - 105.0

*SRM 1832. **SRM 1833.

Replicates

Ten percent of the filters are reanalyzed and the results for select elements are compared. **Figures 52 through 63** compare replicate values for six elements through regression analysis.

2.4.2.2 Data Validity Discussion – The data presented in Section 2.4.2 indicate no problems with the XRF data.

2.4.2.2 Corrective Actions – No changes were made in the analytical procedures used by the Chester LabNet XRF laboratory.

Figure 26. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester Kevex 770

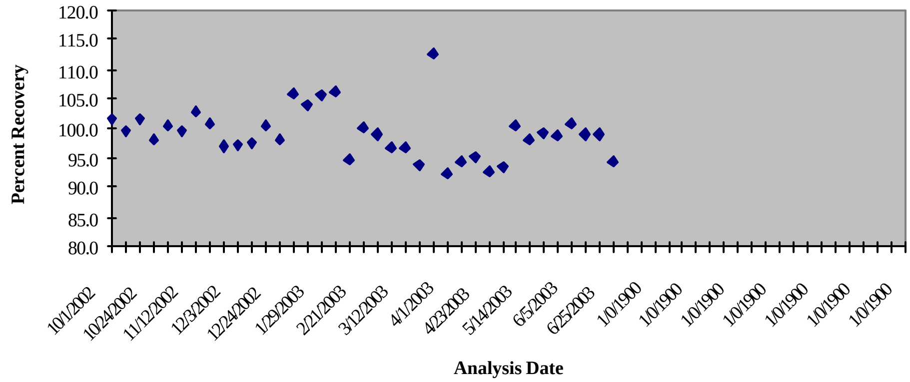


Figure 27. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 770

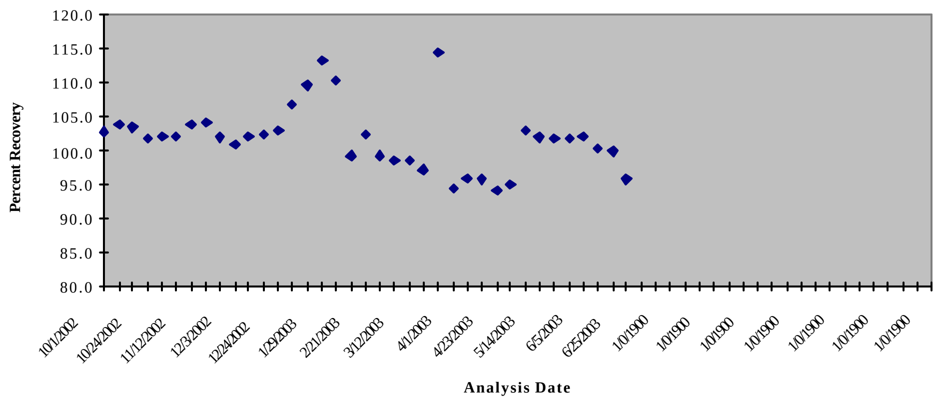


Figure 28. Recovery of Silicon (Si) in NIST SRM 1833 with Chester Kevex 770

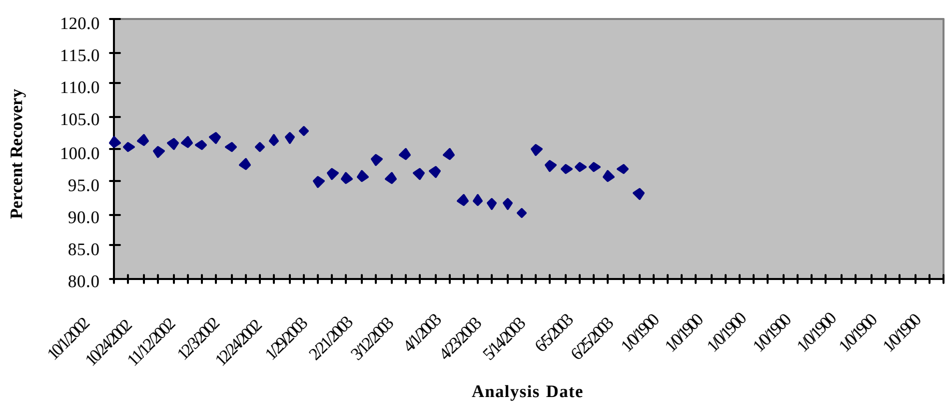


Figure 29. Recovery of Sulfur (S) in NIST SRM 2708 with Chester Kevex 770

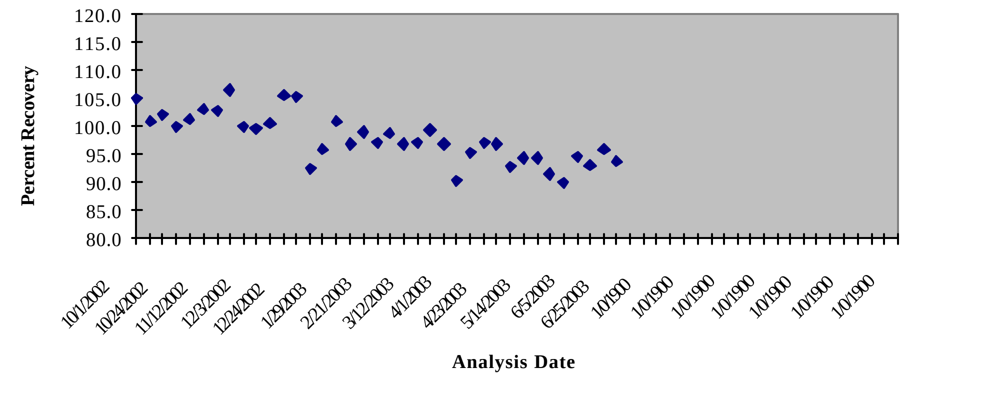


Figure 30. Recovery of Potassium (K) in NIST SRM 1833 with Chester Kevex 770

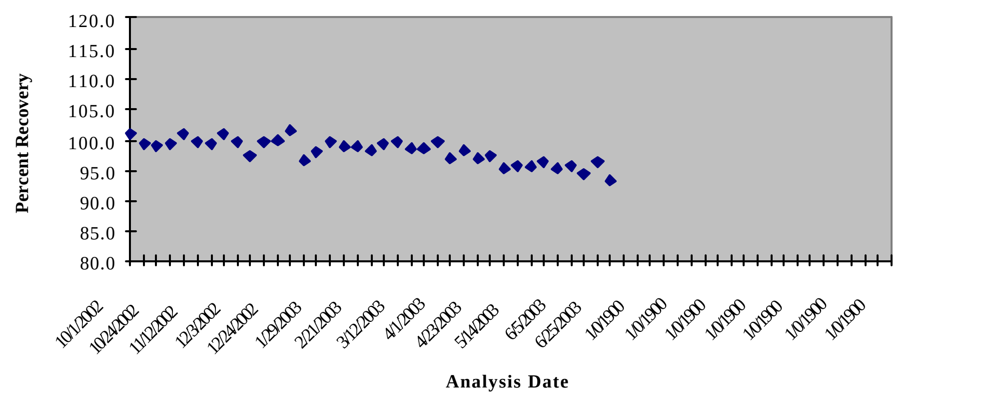


Figure 31. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester Kevex 770

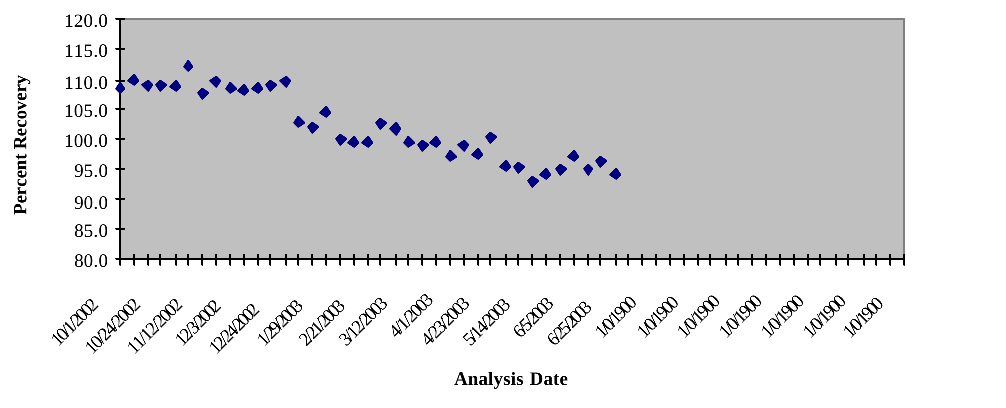


Figure 32. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester Kevex 770

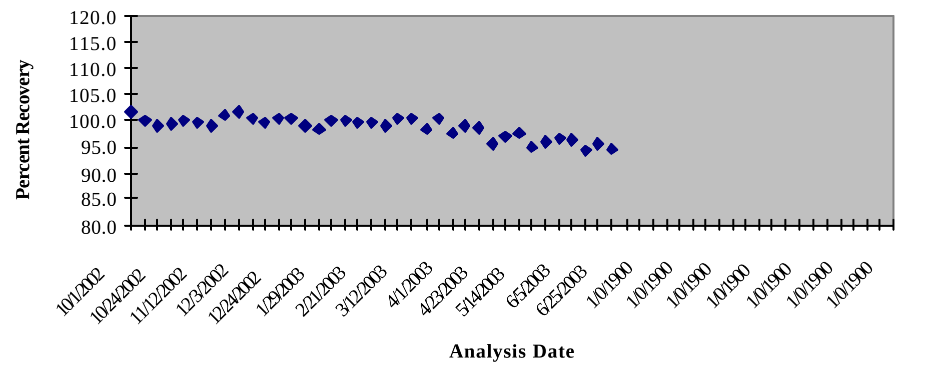


Figure 33. Recovery of Vanadium (V) in NIST SRM 1832 with Chester Kevex 770

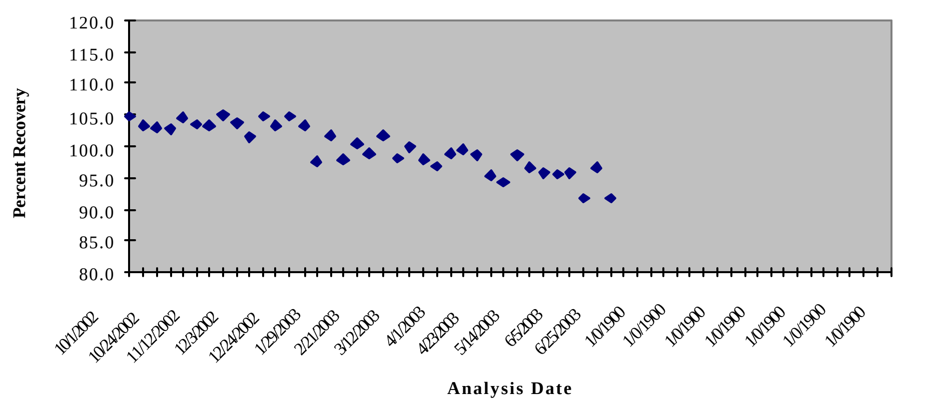


Figure 34. Recovery of Manganese (MN) in NIST SRM 1832 with Chester Kevex 770

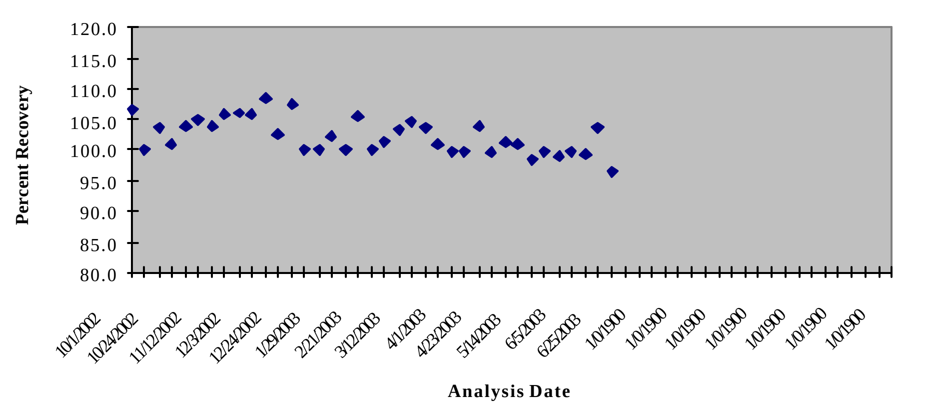


Figure 35. Recovery of Iron (Fe) in NIST SRM 1833 with Chester Kevex 770

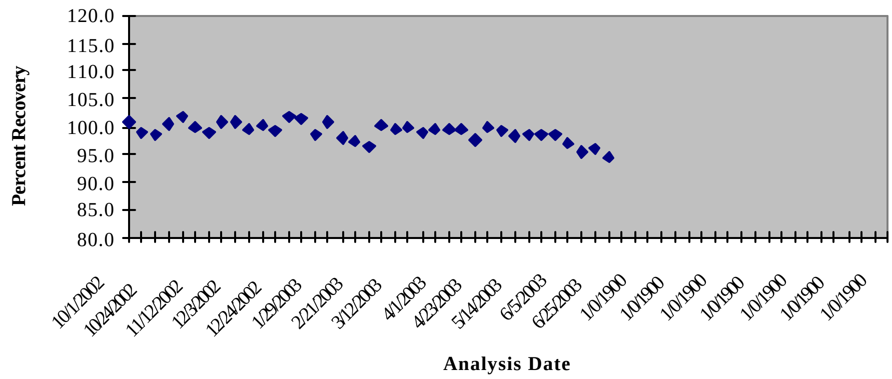


Figure 36. Recovery of Copper (Cu) in NIST SRM 1832 with Chester Kevex 770

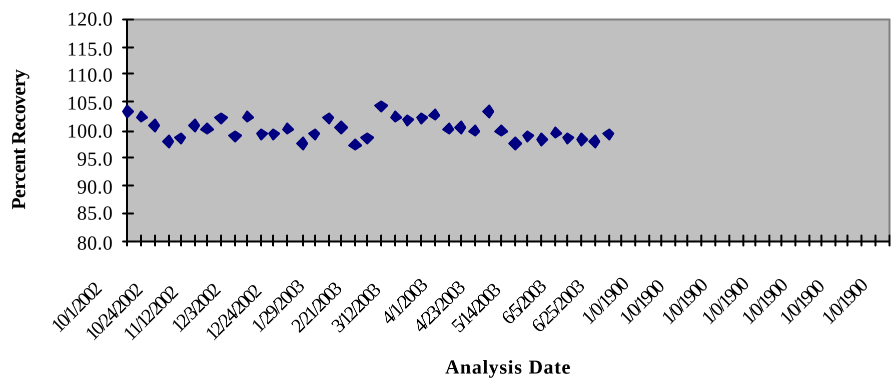


Figure 37. Recovery of Zinc (Zn) in NIST SRM 1833 with Chester Kevex 770

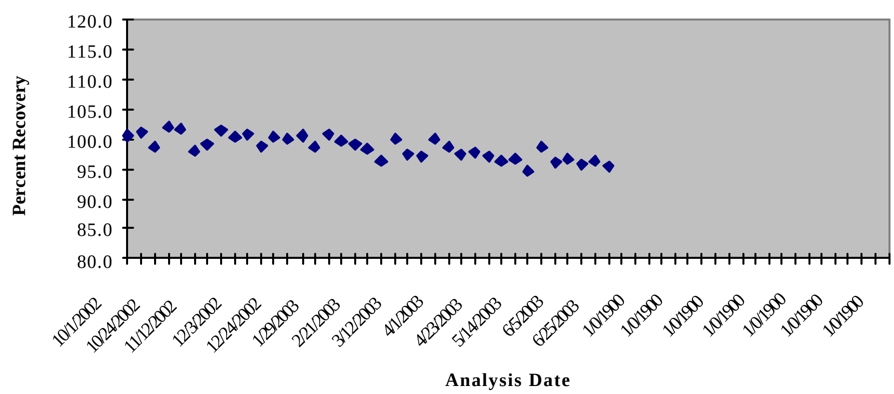


Figure 38. Recovery of Lead (Pb) in NIST SRM 1833 with Chester Kevex 770

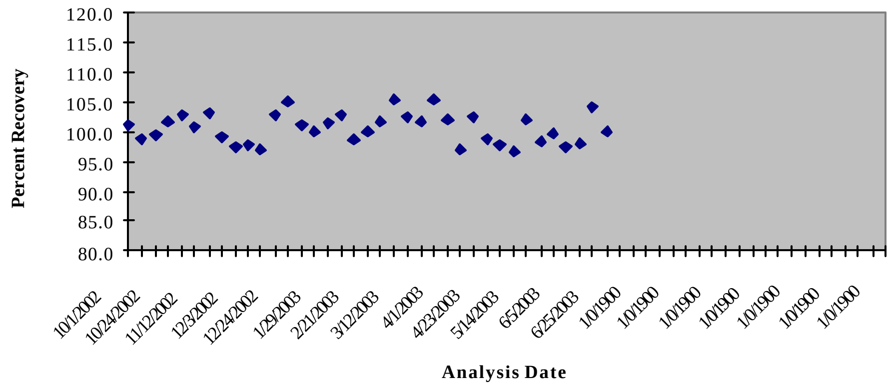


Figure 39. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester 771 XRF

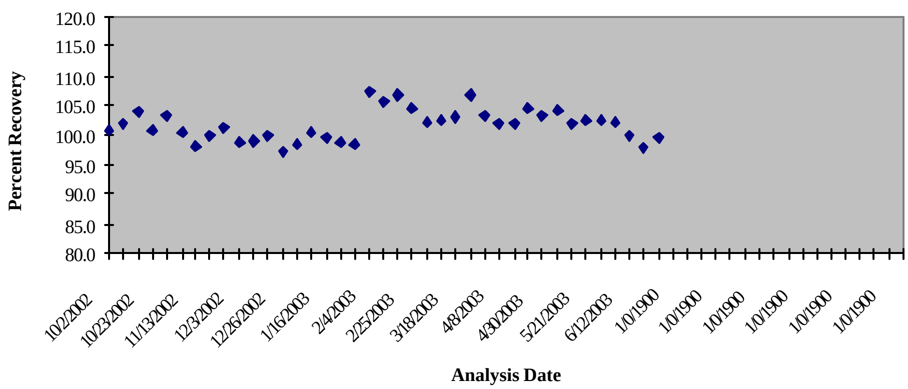


Figure 40. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 771 XRF

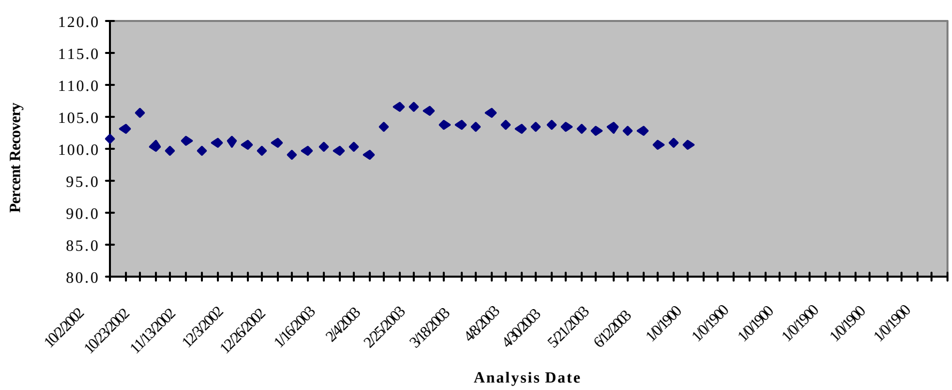


Figure 41. Recovery of Silicon (Si) in NIST SRM 1833 with Chester 771 XRF

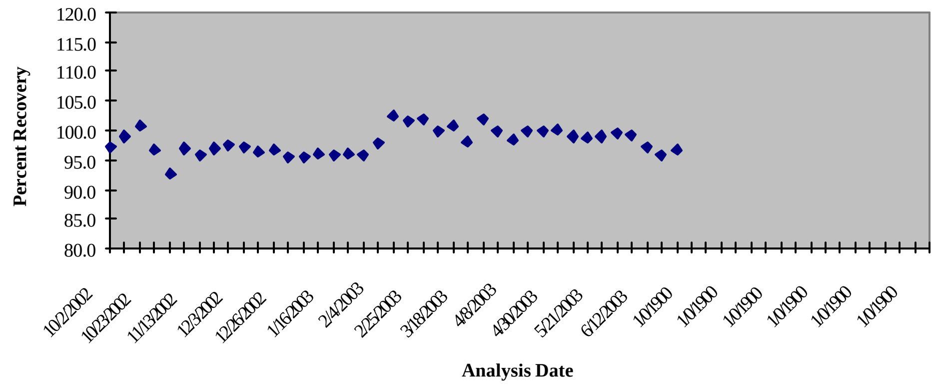


Figure 42. Recovery of Sulfur (S) in NIST SRM 2708 with Chester 771 XRF

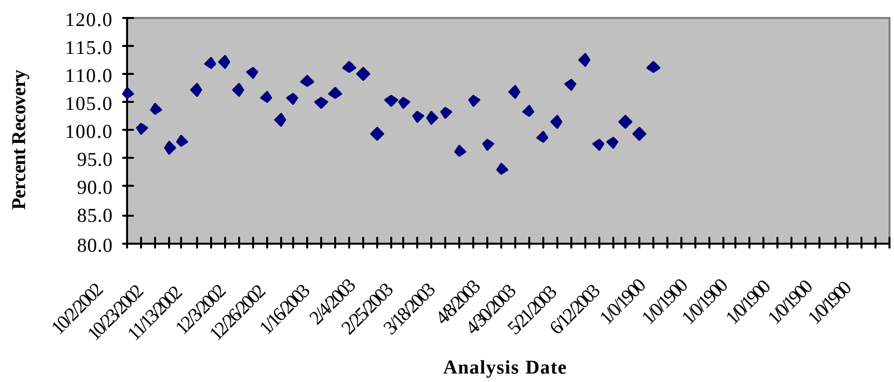


Figure 43. Recovery of Potassium (K) in NIST SRM 1833 with Chester 771 XRF

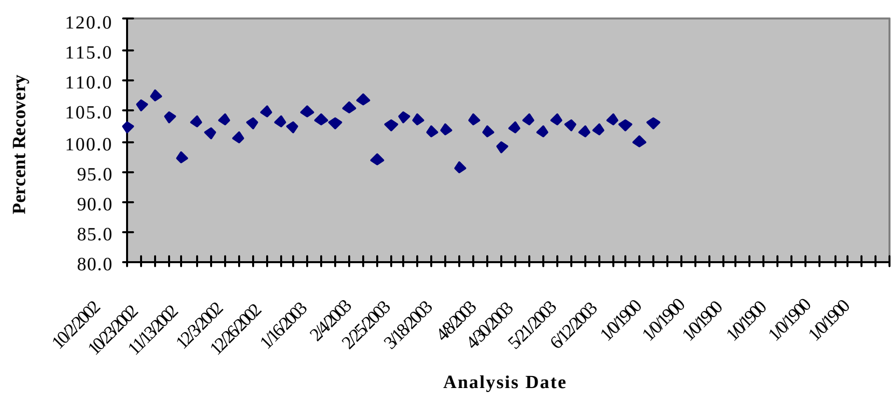


Figure 44. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester 771 XRF

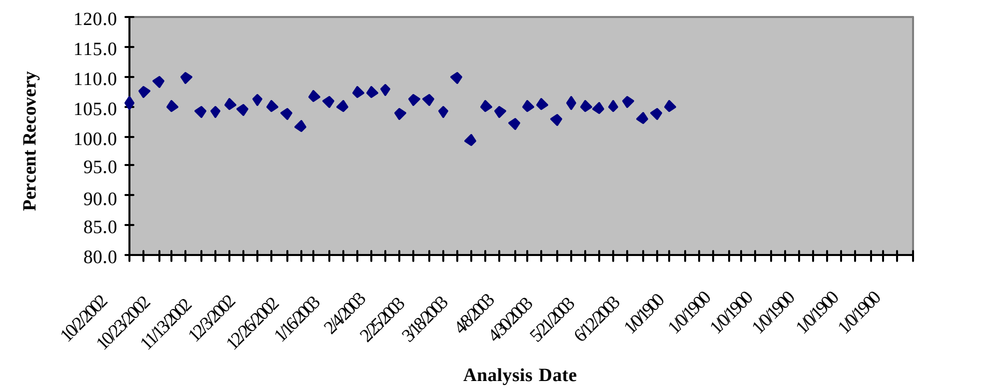


Figure 45. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester 771 XRF

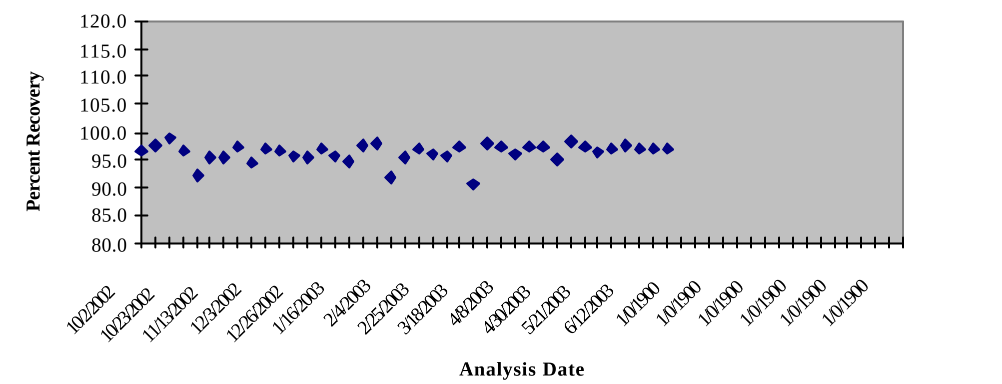


Figure 46. Recovery of Vanadium (V) in NIST SRM 1832 with Chester 771 XRF

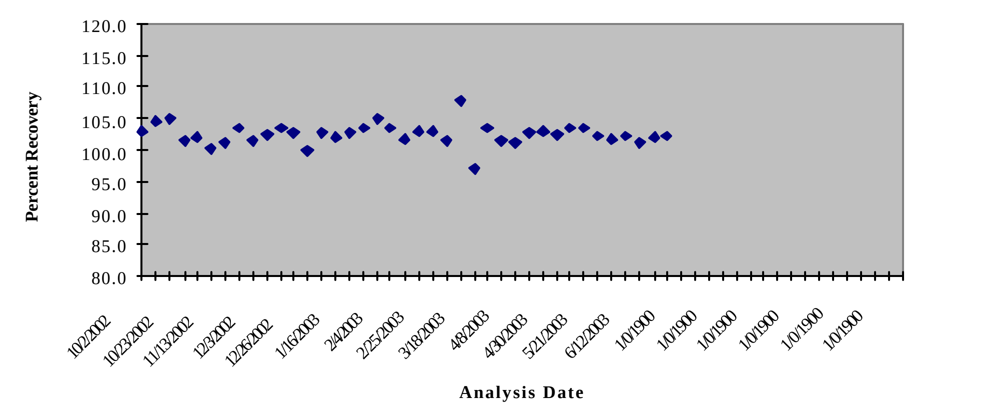


Figure 47. Recovery of Manganese (Mn) in NIST SRM 1832 with Chester 771 XRF

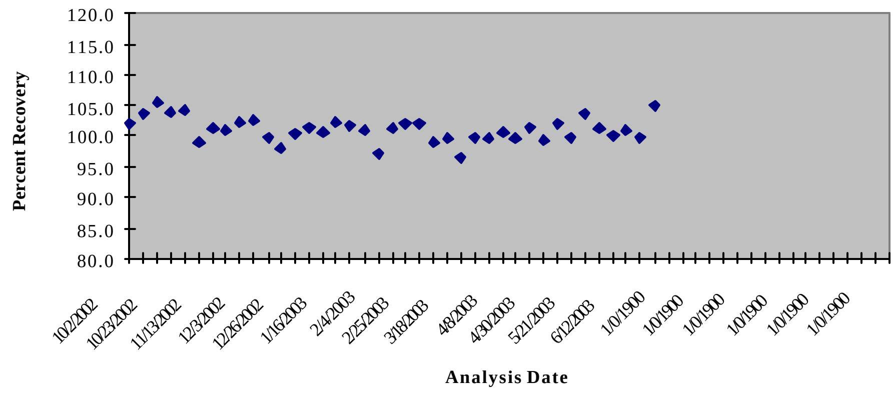


Figure 48. Recovery of Iron (Fe) in NIST SRM 1833 with Chester 771 XRF

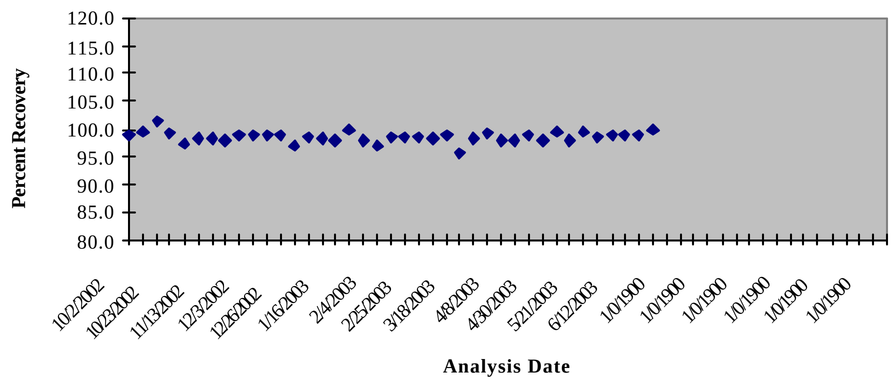
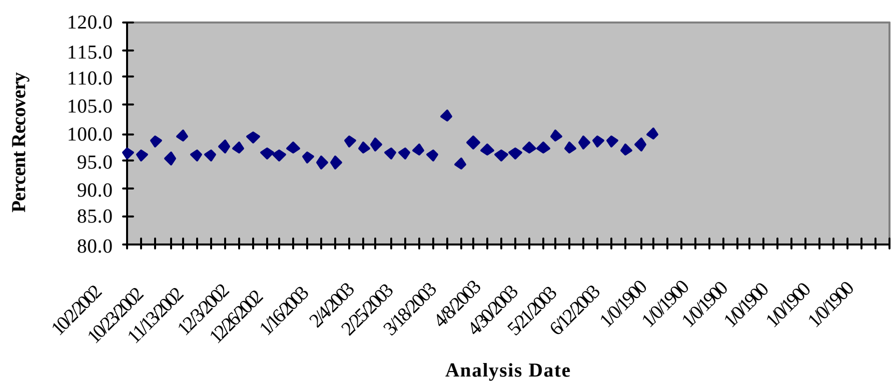


Figure 49. Recovery of Copper (Cu) in NIST SRM 1832 with Chester 771 XRF



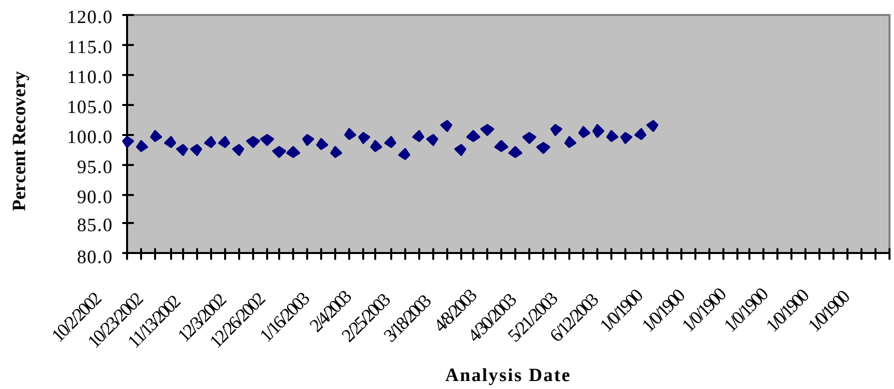


Figure 50. Recovery of Zinc (Zn) in NIST SRM 1833 with Chester 771 XRF

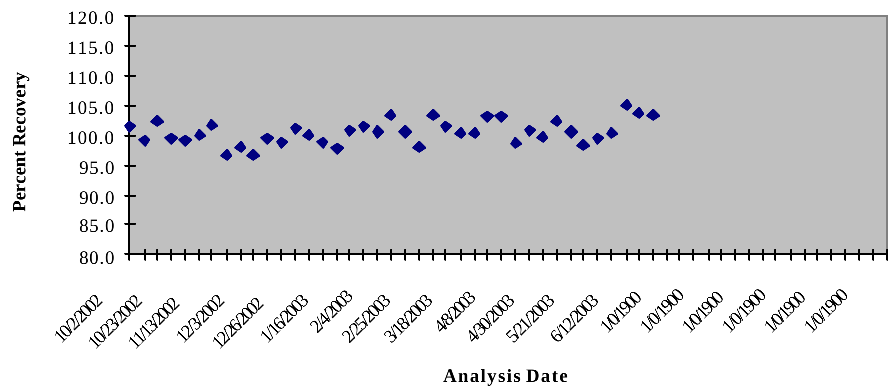


Figure 51. Recovery of Lead (Pb) in NIST SRM 1833 with Chester 771 XRF

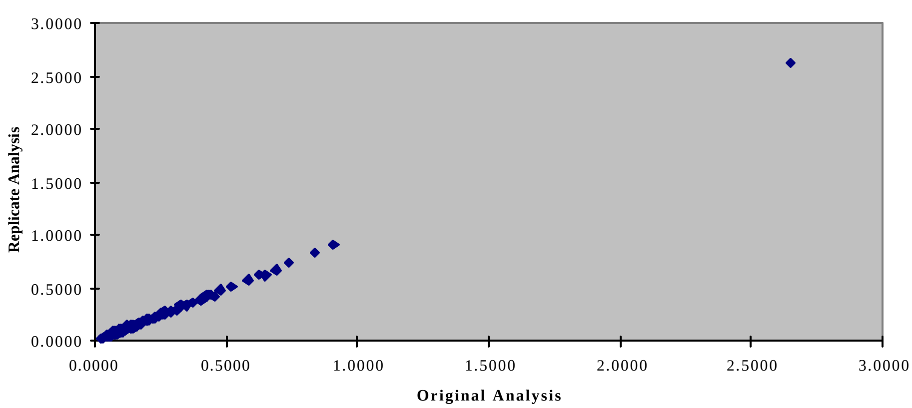


Figure 52. Results of Replicate Silicon (Si) Analysis with Chester 770 XRF

Figure 53. Results of Replicate Sulfur (S) Analysis with Chester 770 XRF

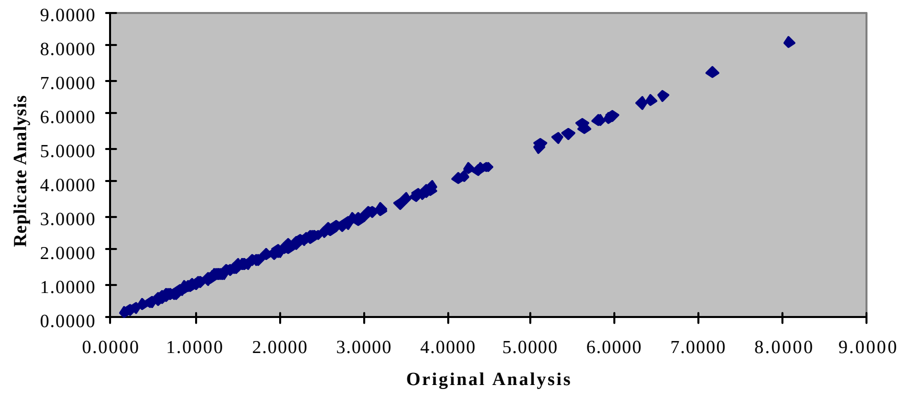


Figure 54. Results of Replicate Potassium (K) Analysis with Chester 770 XRF

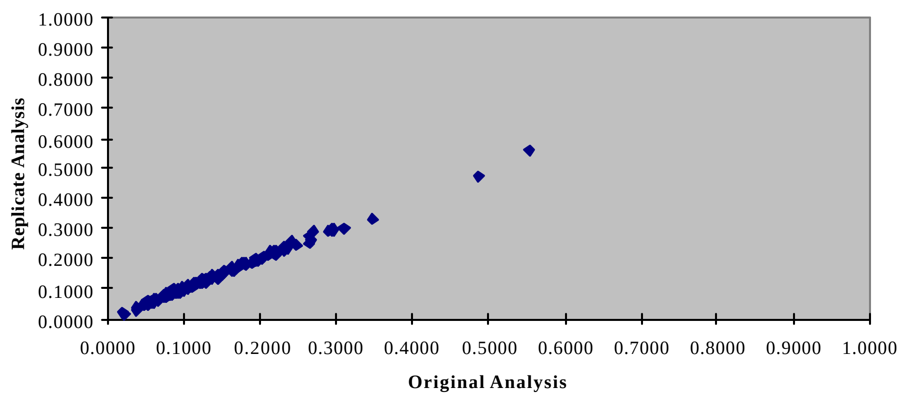


Figure 55. Results of Replicate Calcium (Ca) Analysis with Chester 770 XRF

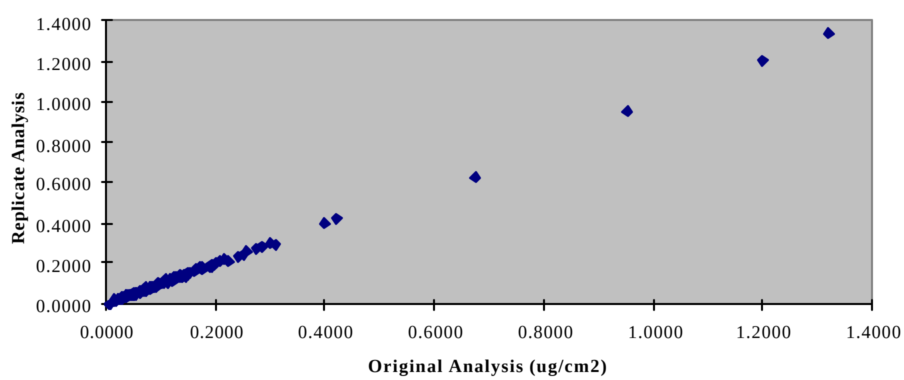


Figure 56. Results of Replicate Iron (Fe) Analysis with Chester 770 XRF

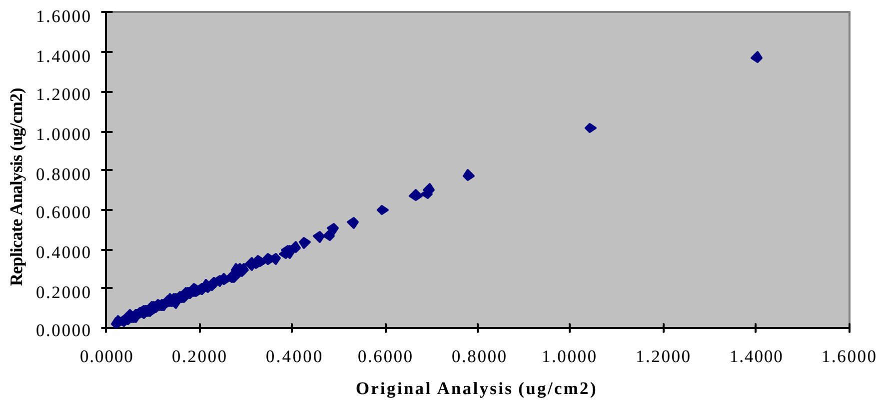


Figure 57. Results of Replicate Zinc (Zn) Analysis with Chester 770 XRF

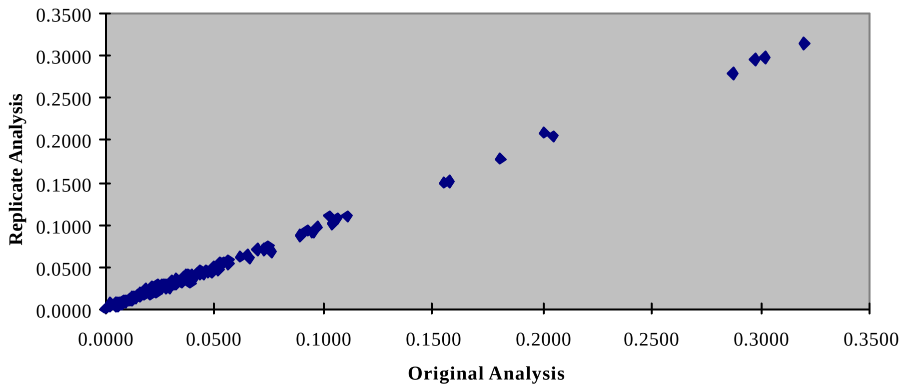


Figure 58. Results of Replicate Silicon (Si) Analysis with Chester 771 XRF

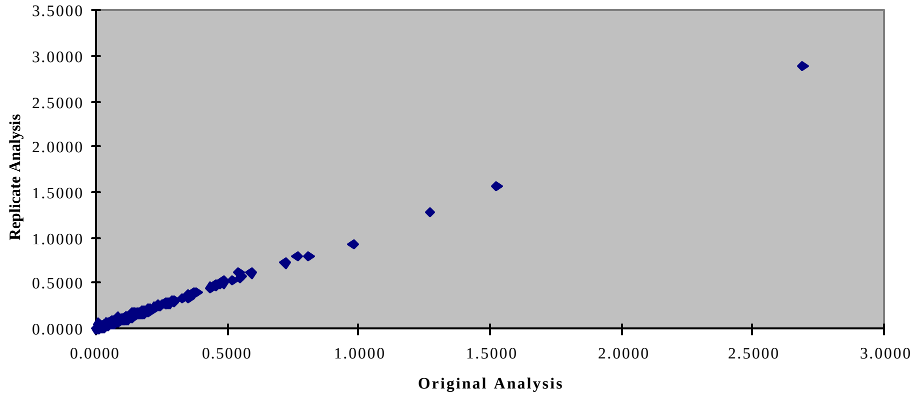


Figure 59. Results of Replicate Sulfur (S) Analysis with Chester 771 XRF

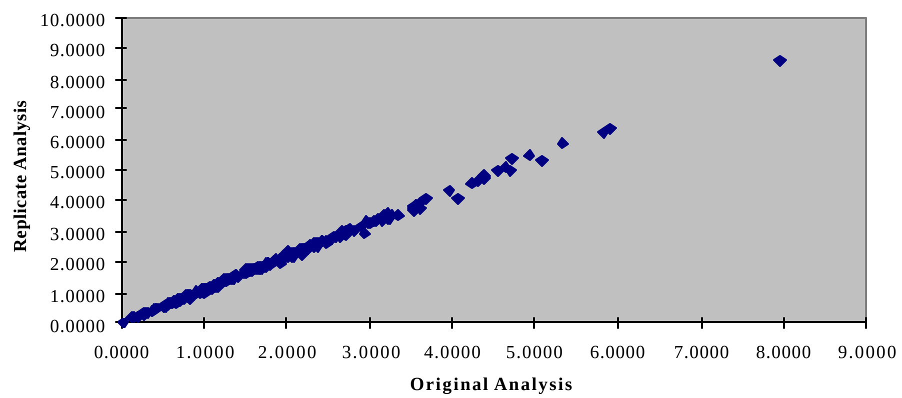


Figure 60. Results of Replicate Potassium (K) Analysis with Chester 771 XRF

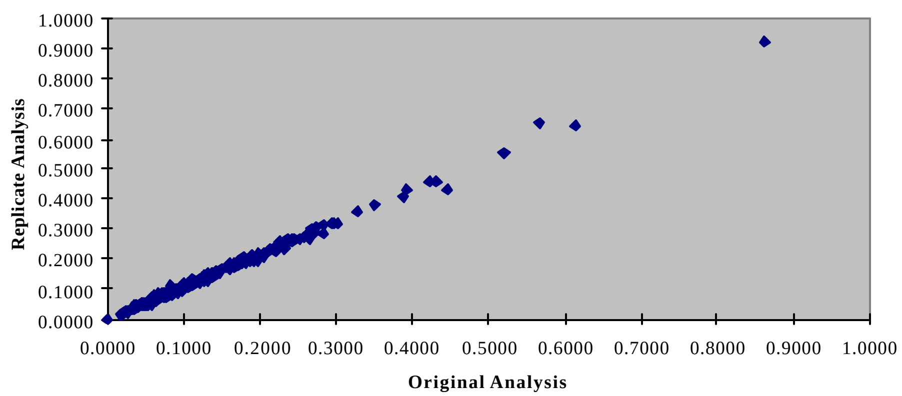


Figure 61. Results of Replicate Calcium (Ca) Analysis with Chester 771 XRF

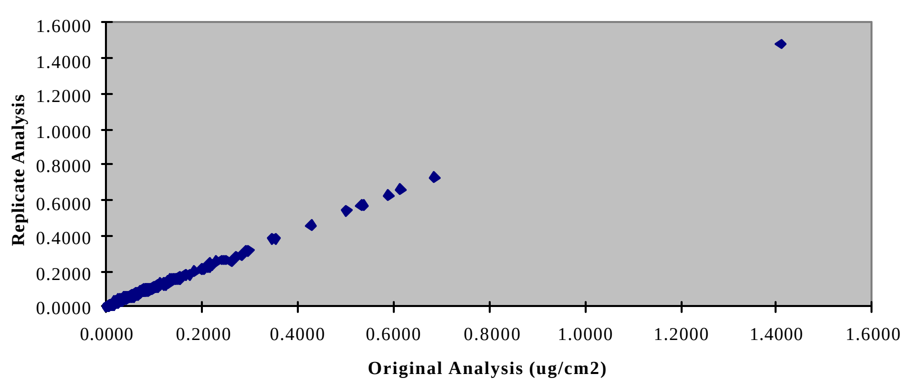


Figure 62. Results of Replicate Iron (Fe) Analysis with Chester 771 XRF

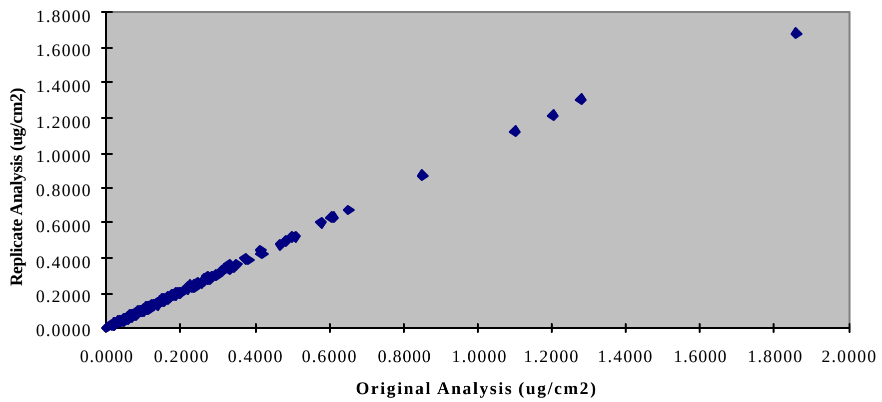
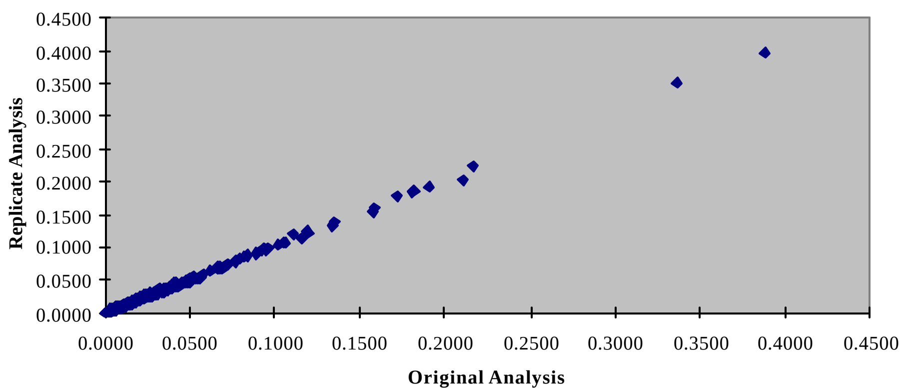


Figure 63. Results of Replicate Zinc (Zn) Analysis with Chester 771 XRF



2.4.3 Cooper Environmental Services (CES)

During this period, turn-around–time has ranged between 10 and 20 calendar days. The RTI turn-around-time goal is 20 calendar days. It is recommend that a maximum of 18 calendar days be allowed in order to meet RTI's turnaround time.

The following summarizes the QA/QC and XRF maintenance requirements for CES October 1, 2002 through June 30, 2003.

2.4.3.1 Statistical Summary of QC Results –

The CES QAPP requires the daily analysis of a QA/QC Multi-Metal standard to monitor instrument precision over time, monthly analysis of NIST standards to monitor instrument recovery or accuracy, and daily replicate analysis to monitor precision of unknown analyses.

Precision

The results of each multi-metal standard analysis are compared with the results of the same standard performed after the last instrument calibration. The QAPP dictates that each daily measurement of the QA/QC Multi-Metal Standard must be within 5% of the calibrated values or the instrument must be recalibrated to account for instrument drift. During the nine month period, the daily analysis of the QA/QC standard never indicated instrument drift. The plots of the Multi-Metal analyses are shown in **Figures 64 through 69**. **Table 22** shows the results of daily precision checks.

Table 22. Daily Replicate Measurement Results CES

	Si	V	Ni	Pb	Cd	Se
Initial Calibration Value	9.110	10.170	10.20*	20.530	5.150	3.860
Average Daily Value	9.196	10.648	10.66	21.391	5.267	3.972
Standard Deviation	0.098	0.059	0.038	0.066	0.047	0.018
Rel Std Dev, percent	1.1%	0.6%	0.4%	0.3%	0.9%	0.5%
Percent Recovery						
Average	100.9	100.8	101.9	104.2	100.7	102.9
Standard Deviation	1.076	0.667	2.073	0.323	0.868	0.473
Rel Std Deviation	1.1%	0.7%	2.0%	0.3%	0.9%	0.5%

*Ni was recalibrated to 10.65 on 1/19/03.

Figure 64. Recovery Precision for Silicon (Si) with CES QuanX XRF

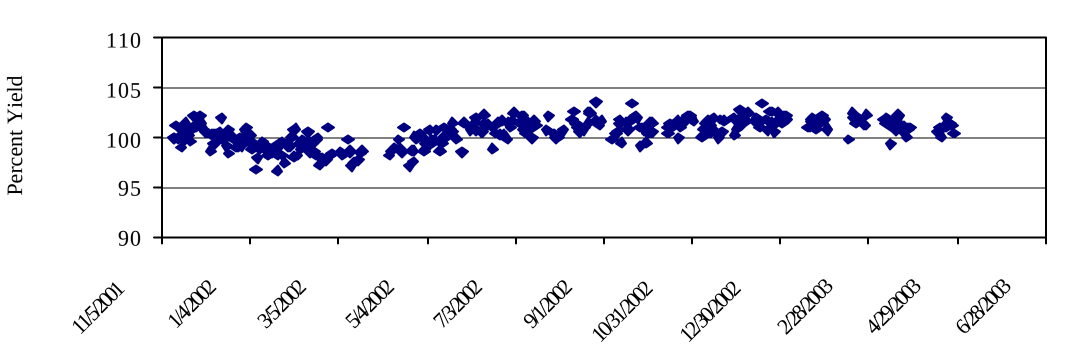


Figure 65. Recovery Precision for Vanadium (V) with CES QuanX XRF

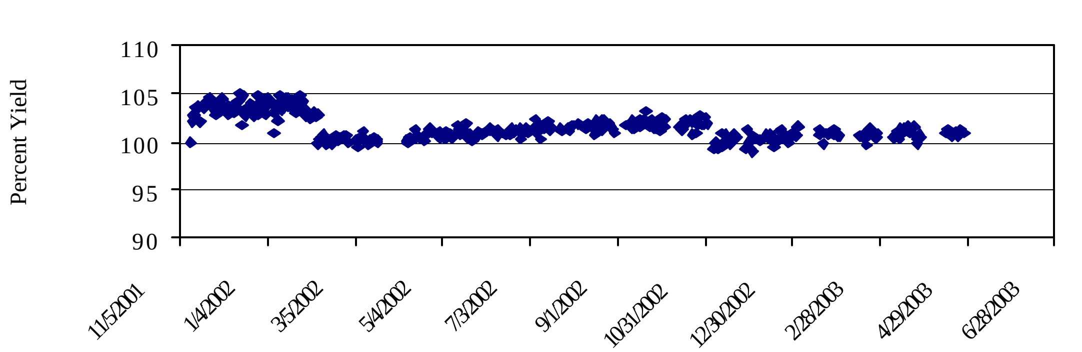


Figure 66. Recovery Precision for Nikel (Ni) with CES QuanX XRF

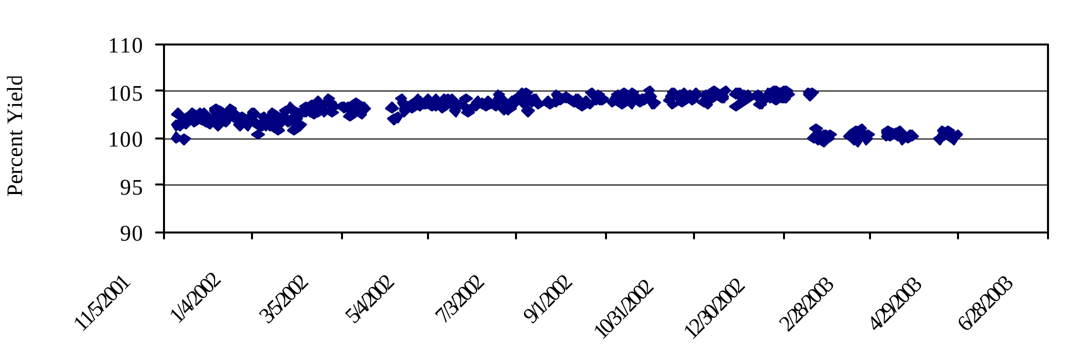


Figure 67. Recovery Precision for Lead (Pb) with CES QuanX XRF

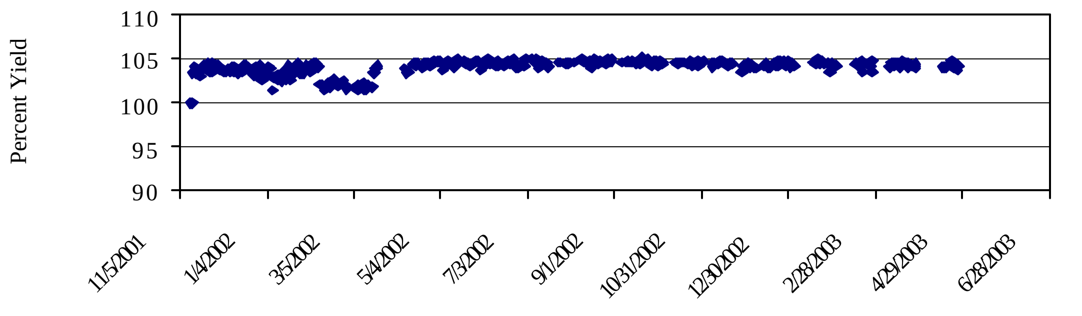


Figure 68. Recovery Precision for Cadmium (Cd) with CES QuanX XRF

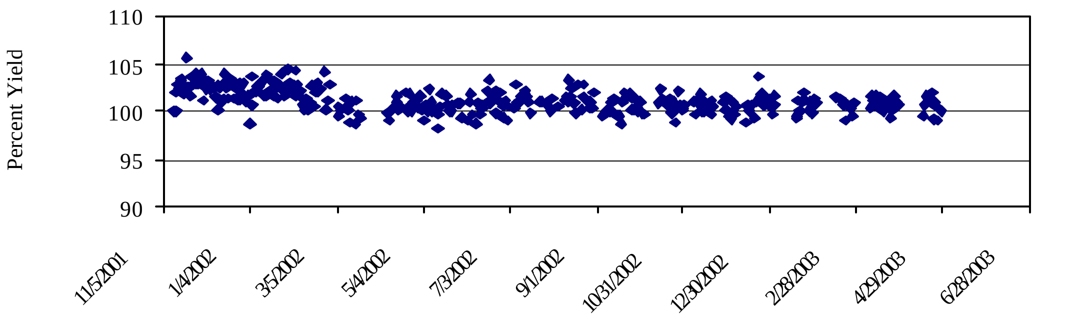
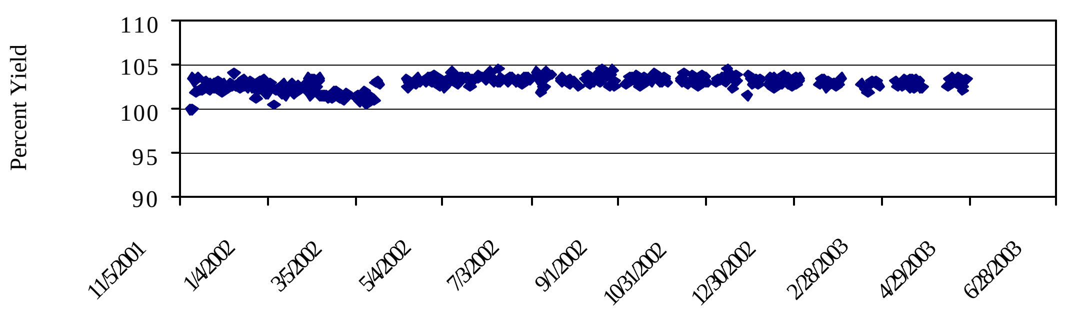


Figure 69. Recovery Precision for Selenium (Se) with CES QuanX XRF



Recovery

NIST Standard Reference Materials 1832 1228 and 1833 987 were analyzed to insure accuracy. The NIST standards were analyzed eight times during the period. The QAPP requires that NIST values be within 3 sigma of the certified values for the calibration to be considered accurate. All values except copper were within these boundaries. The NIST analysis results are plotted below. The copper consistently measures about 12% low. NIST and Dr. Cooper have acknowledged that the Copper certified values are suspect and are investigating the issue. On October 31, the NIST standard 1832 Calcium value was 110.8% above the certified value. Although this does not violate the QAPP specified limit of 3 sigma (or 4.32 µg/cm²), a recalibration of the procedure was performed in order to maintain the highest level of quality assurance. When the last calibration was investigated, it was observed that the Ca NIST analysis just after the previous calibration was 108.8% of the certified value. The 2% variance of the Ca could be attributed to a very slight instrument drift over an 8 month period. After the calibration was performed, the Ca value was 106.6% of the certified NIST value. **Figures 70 through 82** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 86.2 and 109.1 percent as shown in **Table 23**.

Table 23. Recovery Determined from Analysis of NIST Standard Reference Material Filters, QuanX

Date	NIST-1228 - Percent of Standard Value						
	Al	Si	Ca	V	Mn	Co	Cu
10/31/2002	93.7	99.9	110.6	108.0	109.1	104.8	91.4
11/25/2002	97.7	100.9	107.1	106.5	107.7	99.9	91.8
12/24/2002	94.4	99.9	107.8	107.2	107.7	100.9	91.4
1/20/2003	96.6	99.9	107.4	107.6	107.8	99.2	87.7
2/28/2003	95.9	99.7	107.4	107.0	108.0	100.7	87.3
3/31/2003	91.3	97.4	106.7	106.3	107.2	100.1	86.8
5/13/2003	92.1	97.6	107.1	105.8	107.6	100.1	87.6
6/3/2003	93.5	95.7	106.6	107.1	107.5	98.9	87.5

Date	NIST-987 - Percent of Standard Value					
	Si	K	Ti	Fe	Zn	Pb
10/31/2002	103.1	98.1	104.3	103.9	104.2	101.5
11/25/2002	101.8	96.8	100.8	103.3	104.9	102.3
12/24/2002	101.9	97.9	103.0	102.9	103.8	100.2
1/20/2003	100.9	97.2	101.8	100.9	102.8	101.5
2/28/2003	101.1	98.3	102.8	102.0	103.1	102.2
3/31/2003	100.5	97.9	102.2	101.6	102.6	100.1
5/13/2003	97.4	95.8	101.4	99.9	100.5	99.4
6/3/2003	98.5	96.5	101.7	101.2	102.9	100.4

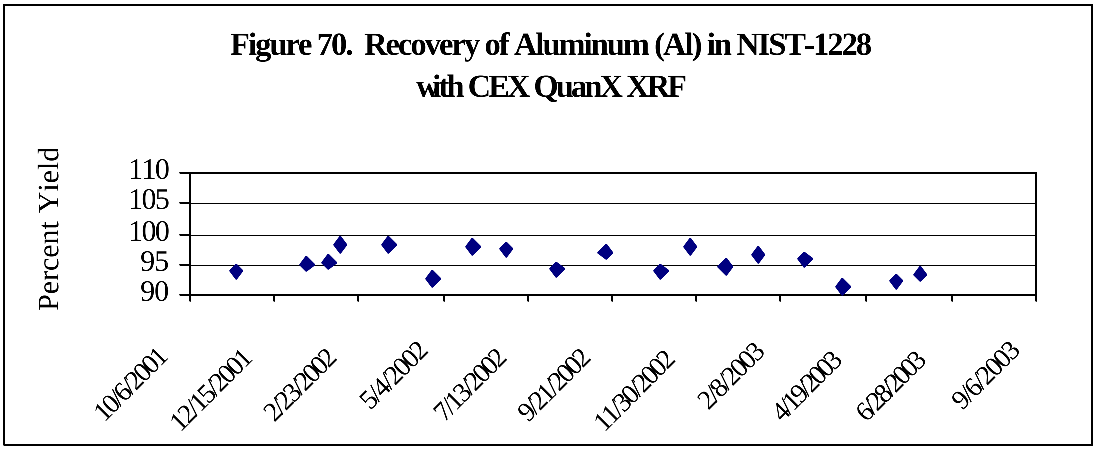


Figure 70. Recovery of Aluminum (Al) in NIST-1228
with CEX QuanX XRF
Percent Yield
110
105
100
95
90
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

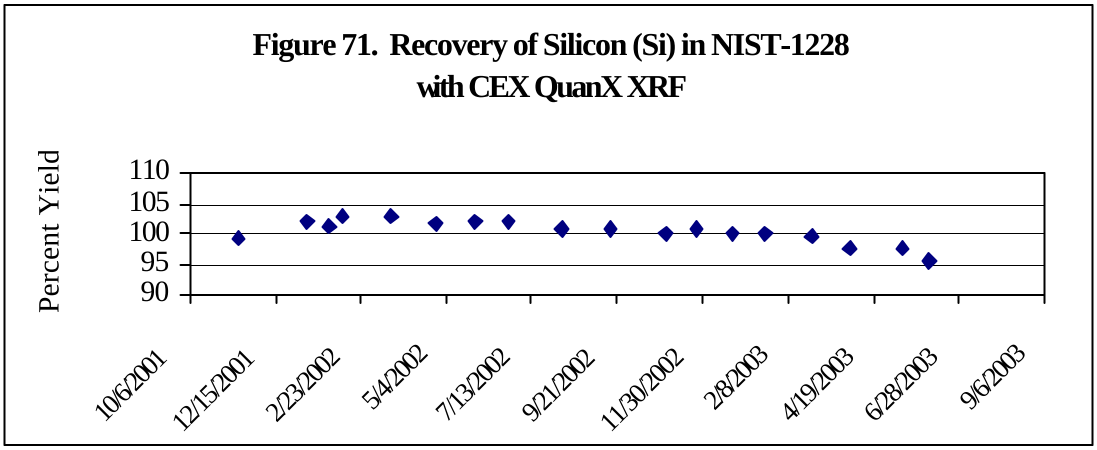


Figure 71. Recovery of Silicon (Si) in NIST-1228
with CEX QuanX XRF
Percent Yield
110
105
100
95
90
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

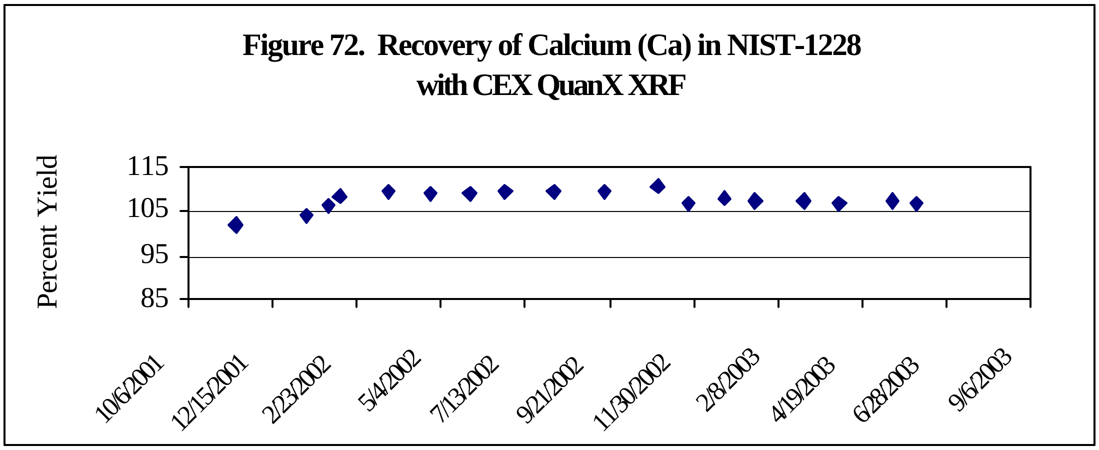


Figure 72. Recovery of Calcium (Ca) in NIST-1228
with CEX QuanX XRF
Percent Yield
115
105
95
85
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

Figure 73. Recovery of Vanadium (V) in NIST-1228 with CEX QuanX XRF

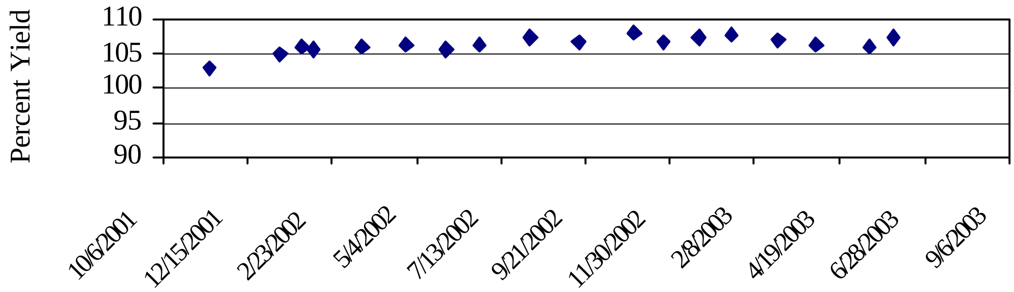


Figure 74. Recovery of Manganese (Mn) in NIST-1228 with CEX QuanX XRF

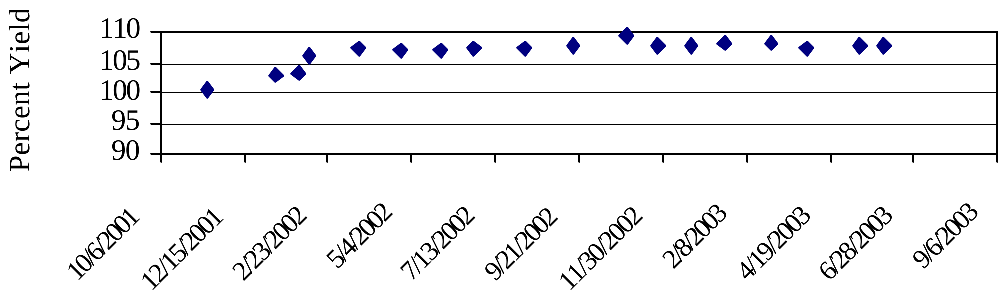
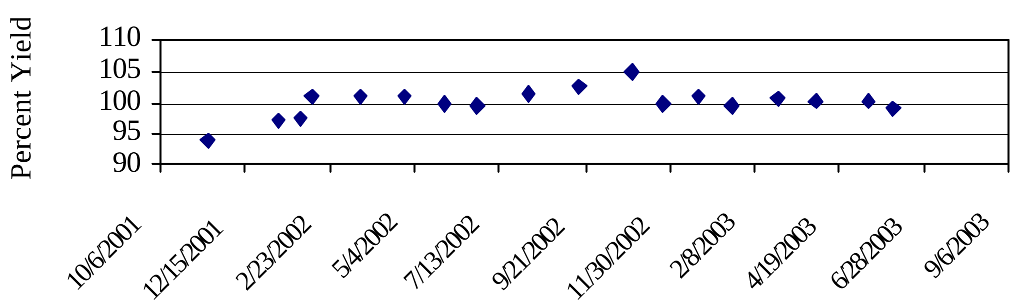


Figure 75. Recovery of Cobalt (Co) in NIST-1228 with CEX QuanX XRF



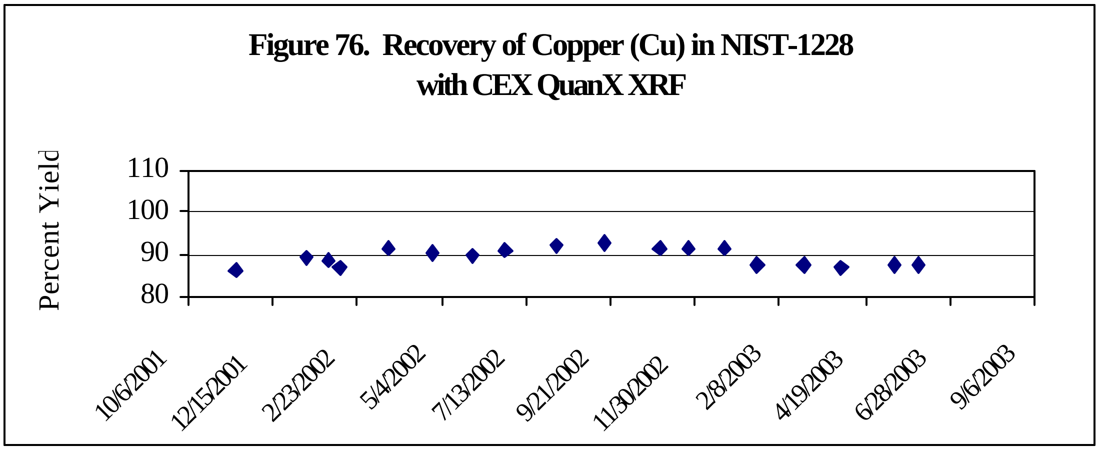


Figure 76. Recovery of Copper (Cu) in NIST-1228
with CEX QuanX XRF
Percent Yield
110
100
90
80
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

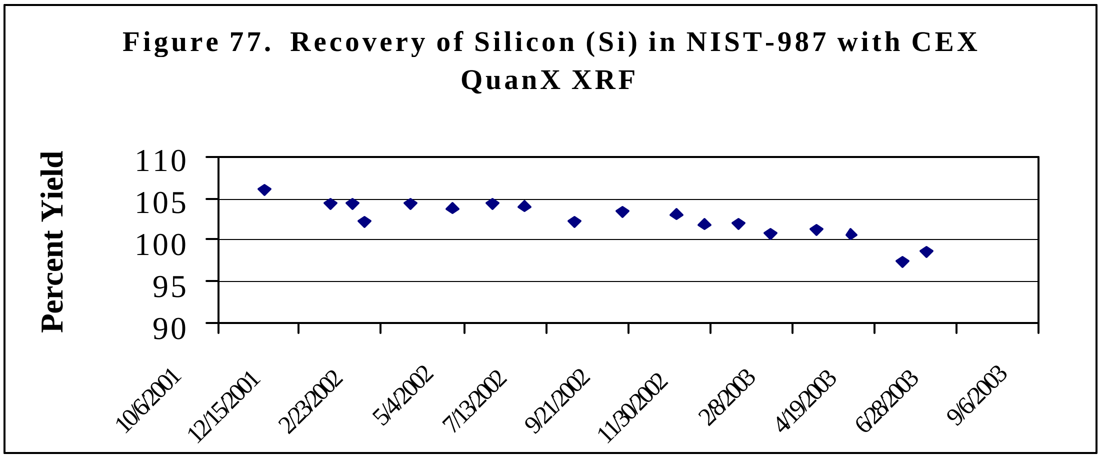


Figure 77. Recovery of Silicon (Si) in NIST-987 with CEX
QuanX XRF
Percent Yield
110
105
100
95
90
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

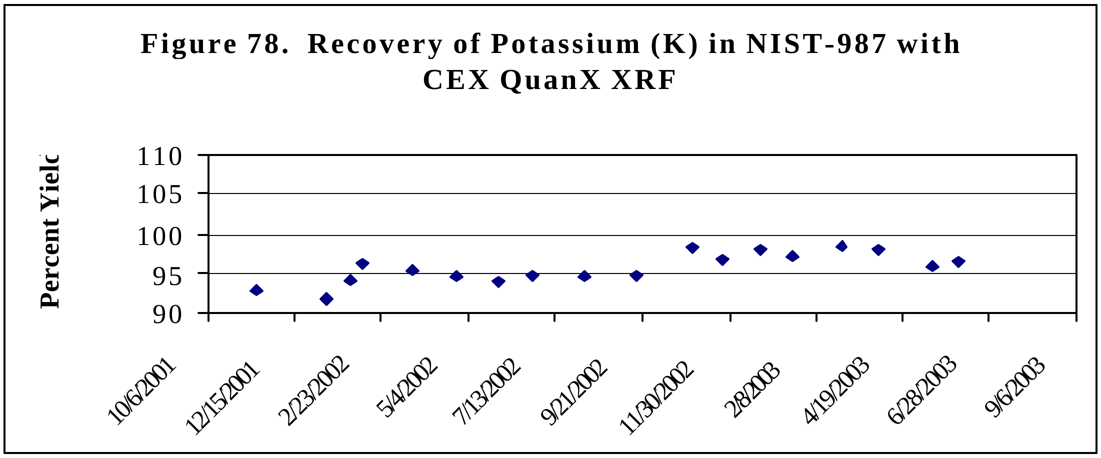


Figure 78. Recovery of Potassium (K) in NIST-987 with
CEX QuanX XRF
Percent Yielc
110
105
100
95
90
10/6/2001
12/15/2001
2/23/2002
5/4/2002
7/13/2002
9/21/2002
11/30/2002
2/8/2003
4/19/2003
6/28/2003
9/6/2003

Figure 79. Recovery of Titanium (Ti) in NIST-987 with CEX QuanX XRF

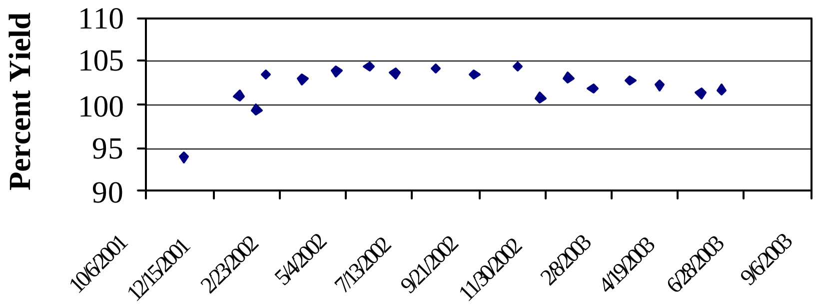


Figure 80. Recovery of Iron (Fe) in NIST-987 with CEX QuanX XRF

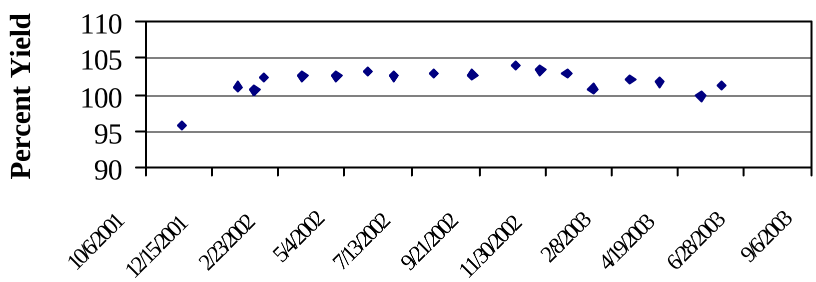


Figure 81. Recovery of Zinc (Zn) in NIST-987 with CEX QuanX XRF

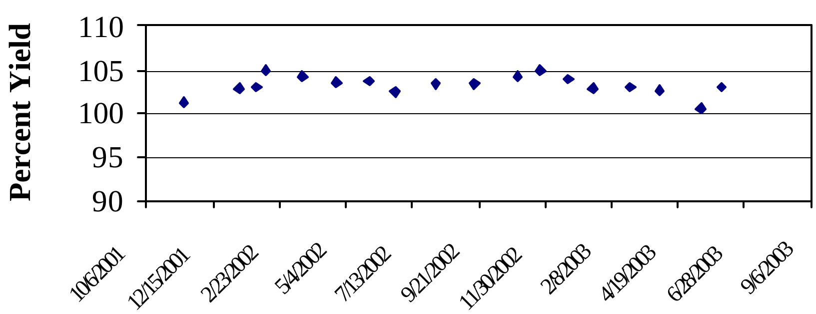
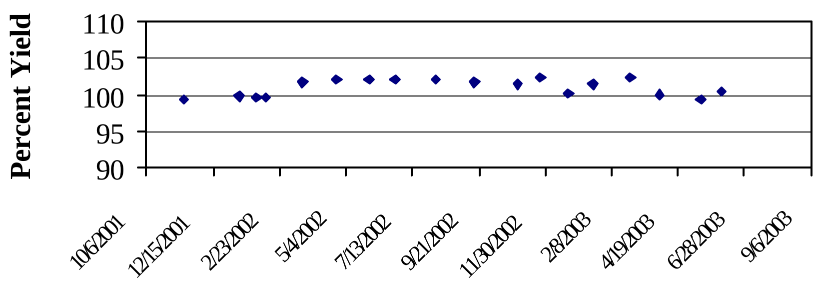


Figure 82. Recovery of Lead (Pb) in NIST-987 with CEX QuanX XRF



Replicates

Daily replicates have been run in order to assure good reporting consistency for STN samples under realistic concentrations and matrices. During the past nine months, 149 replicates were run representing each of the days of XRF operation. These replicates represent about five percent of the total filters analyzed. Replicate results are analyzed for reported concentrations with greater than 10 times the uncertainties. Typically, 4 to 10 elements per filter are present in abundant enough concentrations for QA analysis. Daily replicates are considered to be satisfactory if the abundant elements fall within 10% of each other. If an element is not within the 10% criteria, the Quality Assurance Manager makes a comparison to propagated uncertainty. Results are shown in **Figures 83 through 88**.

In general, daily replicates have demonstrated that, at concentrations of 10 times the uncertainty, good replication of results is occurring. On most days, a few of the elements that are more than 10 times the uncertainty have RPDs of greater than 10%; however, these elements typically have high propagated uncertainties and do not show consistent quality concerns.

2.4.3.2 Data Validity Discussion – The data presented in Section 2.4.3 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters. These were minor, and not considered to have a significant impact on the analysis results.

2.4.3.3 Corrective Actions – On 10/1/02, the XRF stopped and produced an error message reading “ADC Failed to Respond.” There was no obvious cause as analysis of the MultiMetal QA standard produced intensities within the acceptable range. This occurred again on 10/2/02. On 10/04/02, the PC was vacuumed out and the ADC interface board was reseated. The previous day’s samples were run in order to replicate the error message. The error did not occur thereafter and is therefore attributed to a short caused by dust on the ADC board. It may be desirable to install a prefilter for the PC cover to minimize dust contamination. The details of each error and subsequent maintenance can be found in the CES XRF Maintenance Log.

On December 19, 2002 the nickel concentration was 105.2%. This is slightly above the acceptable threshold of 105%. When the standard was retested, the nickel concentration was within the 5% threshold of acceptability (104.6%). The nickel concentration was within bounds until Jan. 16, 2003, when the value was 105.1%. Reanalysis of the QA standard gave a value of 104.2%. After reviewing the QuanX manual, it was determined that a 30 minute warm-up is recommended. This allows the filament in the x-ray tube to heat up to operating temperature. In both of the cases where the nickel was out of bounds, the instrument was not warmed up first. Since the nickel was within bounds following warm up, the nickel did not need to be recalibrated, but, in order to ensure high quality nickel results, the instrument was recalibrated for nickel to establish a new baseline value. Since cadmium was also approaching the 105% threshold, it was recalibrated at this time as well.

Figure 83. Results of Replicate Silicon (Si) Analyses with CES QuanX XRF

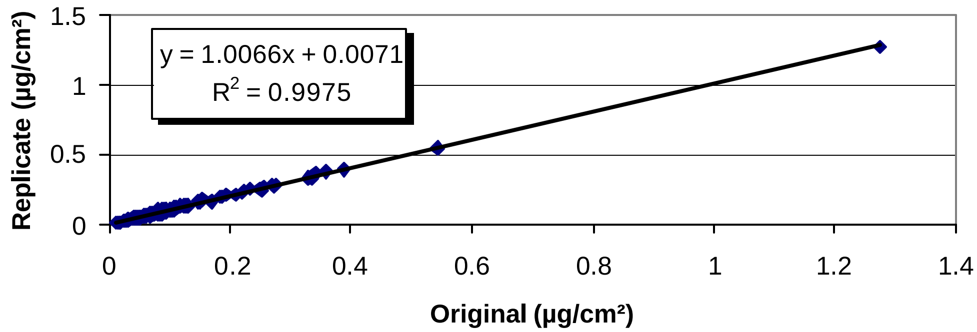


Figure 84. Results of Replicate Sulfur (S) Analyses with CES QuanX XRF

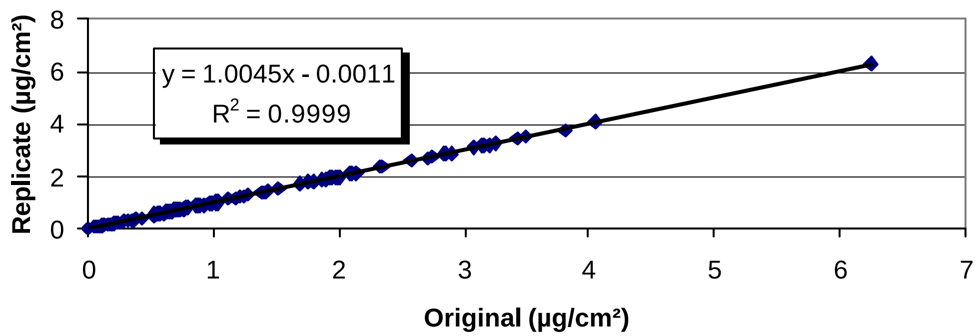


Figure 85. Results of Replicate Potassium (K) Analyses with CES QuanX XRF

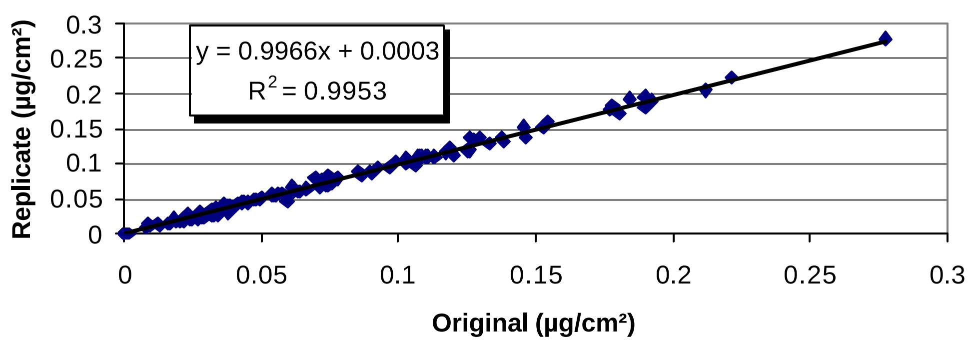


Figure 86. Results of Replicate Calcium (Ca) Analyses with CES QuanX XRF

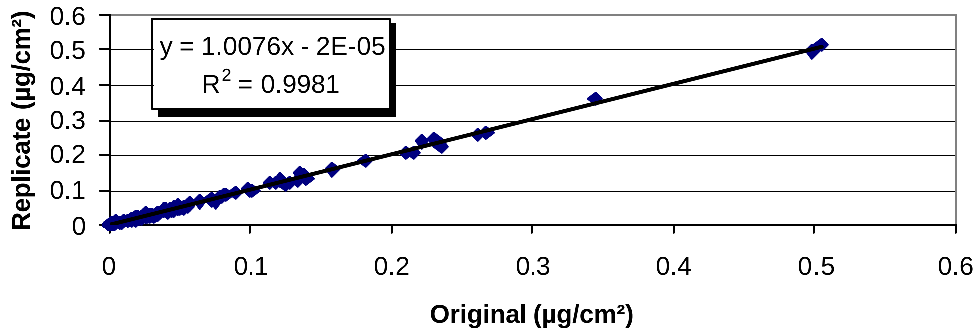


Figure 87. Results of Replicate Iron (Fe) Analyses with CES QuanX XRF

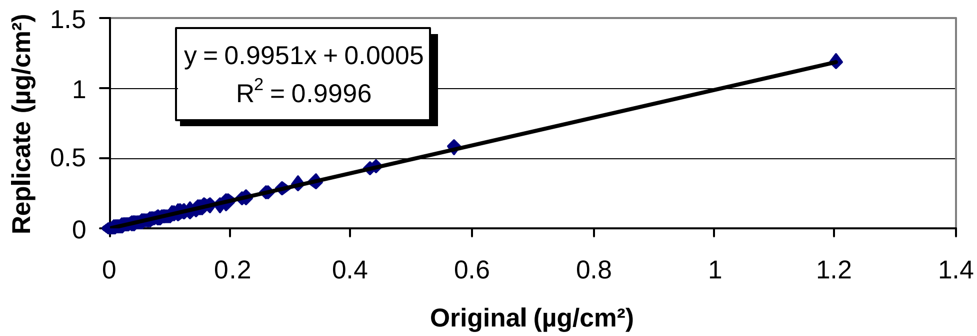
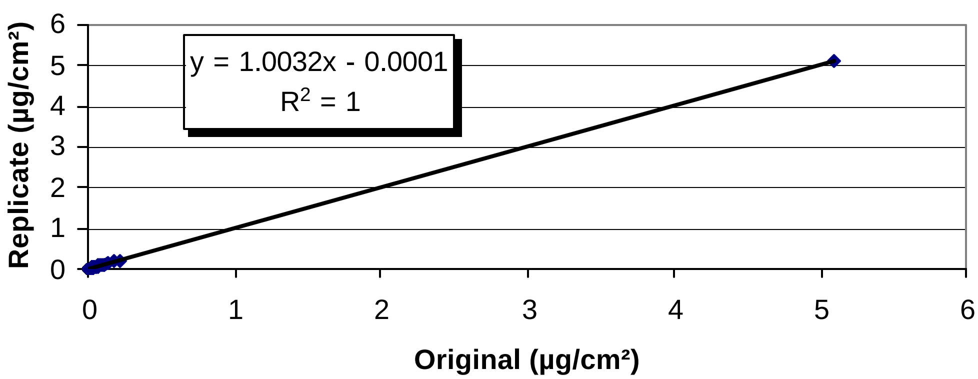


Figure 88. Results of Replicate Zinc (Zn) Analyses with CES QuanX XRF



At 9:30 AM on March 15, 2003, the analysis of 9 filters from Batch CY as well as a replicate from the previous day's analysis (A226305M) was begun. At 4:00 PM that day, an "ADC Failed to Respond" message was discovered. The analysis was immediately restarted without performance of an energy calibration or the analysis of the multi-metal standard. Later that night, another group of filters was analyzed. Five of these filters were from Batch CZ. The next morning, an energy calibration was performed and the multi-metal standard was analyzed. Both QA events indicated that the instrument was performing within specifications. The analysis of 19 new filters and replicate A2329622 was performed without recurrence of the ADC Failure. On 3/17/03, the energy calibration showed a dead time > 77%. The computer was restarted and the energy calibration and analysis of the multi-metal QC was within spec. The replicate report for filter A226305M from Batch CY indicated no significant difference between the original and replicate results. The replicate report for filter A2329622 indicated a 91.7% relative percent difference between the original and replicate values for phosphorus. It is thought that the original analysis of filter A2329622 may have been performed under erroneous instrumental conditions. The ADC failure may have changed the Gain DAC setting and therefore attributed sulfur counts to the nearby phosphorus peak. Without the analysis of an energy calibration or a multi-metal standard, there is no way to ensure that the instrument was performing properly during this time. The five filters from Batch CZ were reanalyzed 3/28/03 after the daily QA events to eliminate uncertainty in accuracy of data from 3/15/03. In the future, if an ADC failure occurs, it is recommended that an energy calibration and multi-metal standard analysis be run before analysis of any samples to ensure that the instrument remains within specifications.

2.4.4 RTI XRF Laboratory

2.4.4.1 Statistical Summary of QC Results –

<u>Precision</u>

The precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for a select element are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of reproducibility or precision (**Table 22**). The data used to monitor precision are presented in **Figures 89 through 94**.

<u>Recovery</u>

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of measured and expected values. **Figures 95 through 107** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 90 and 106 percent as shown in **Table 23**.

Figure 89. Recovery Precision for RTI QuanX XRF with Silicon (Si)

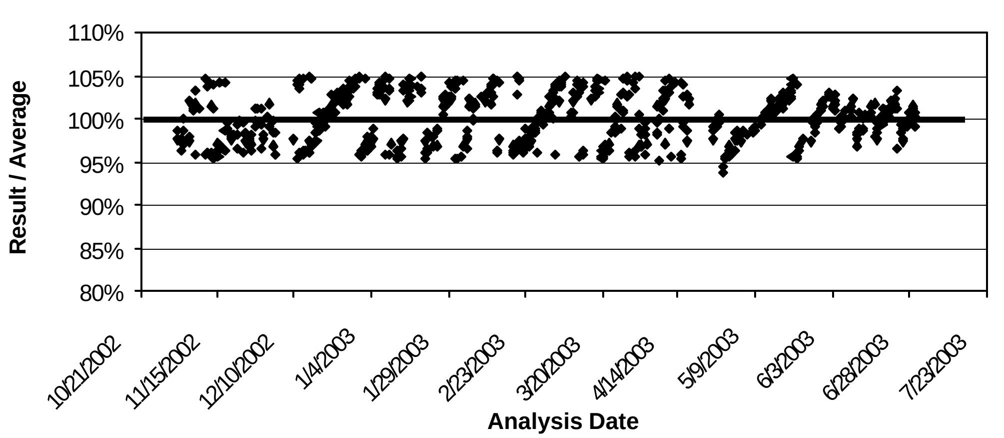


Figure 90. Recovery Precision for RTI QuanX XRF with Titanium (Ti)

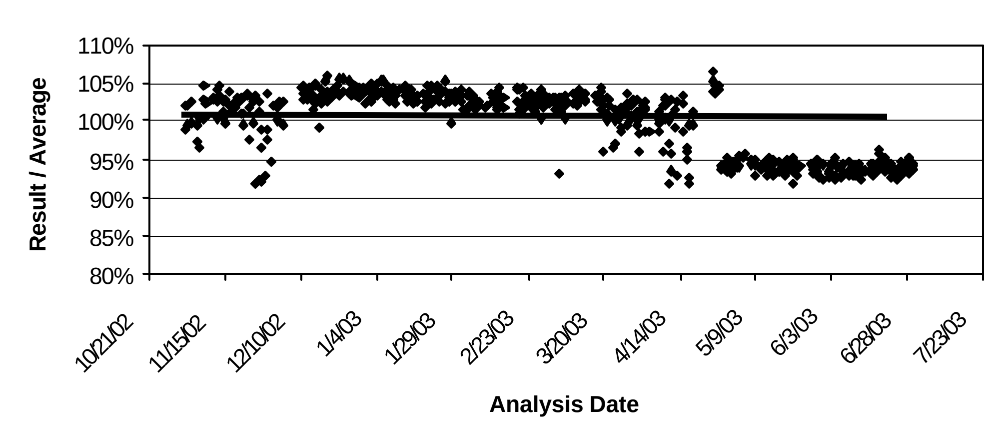
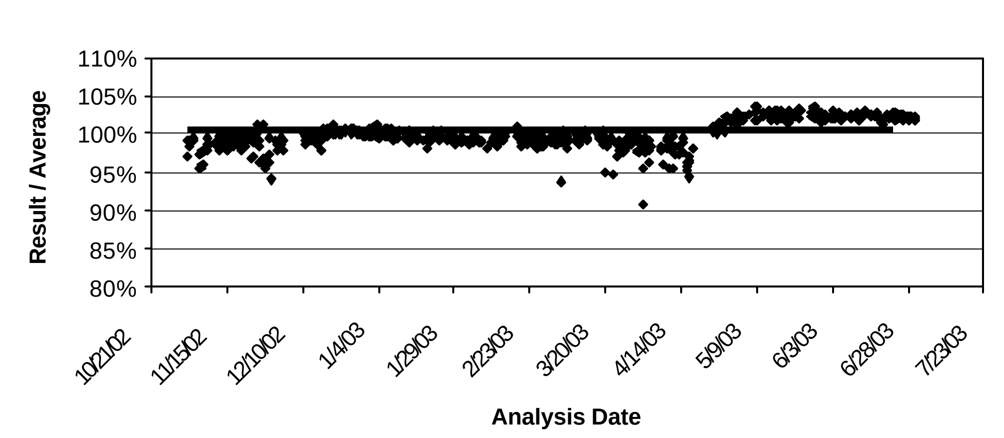


Figure 91. Recovery Precision for RTI QuanX XRF with Iron (Fe)



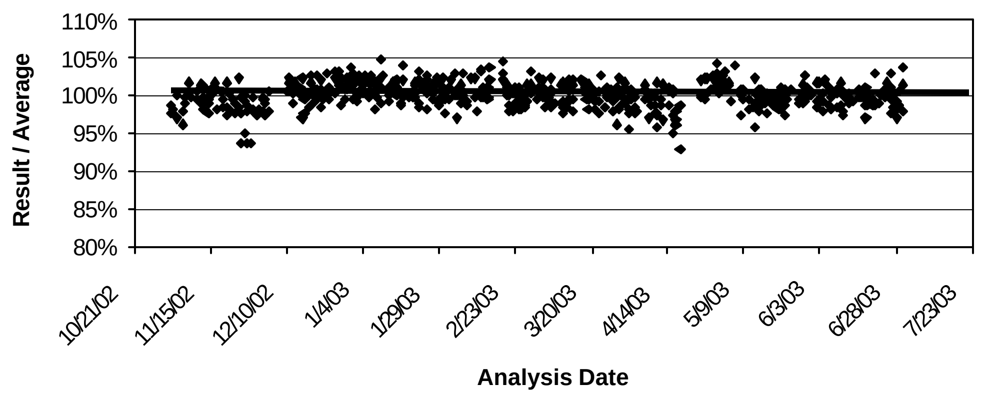


Figure 93. Recovery Precision for RTI QuanX XRF with Cadmium (Cd)

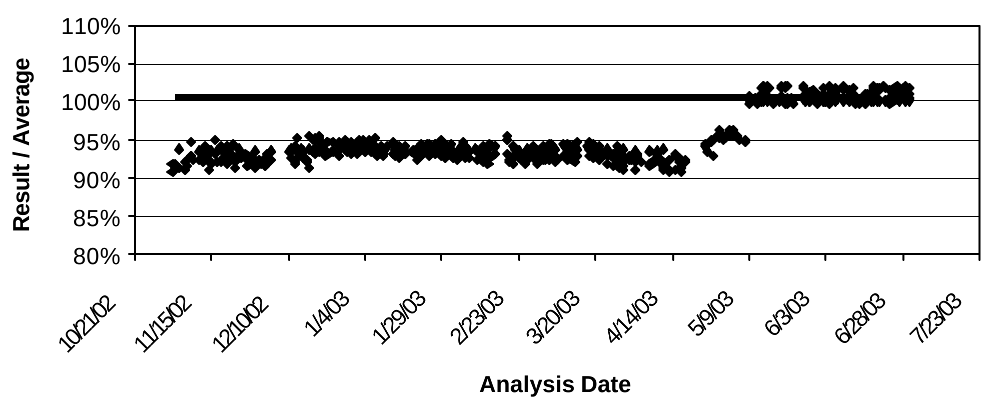


Figure 92. Recovery Precision for RTI QuanX XRF with Selenium (Se)

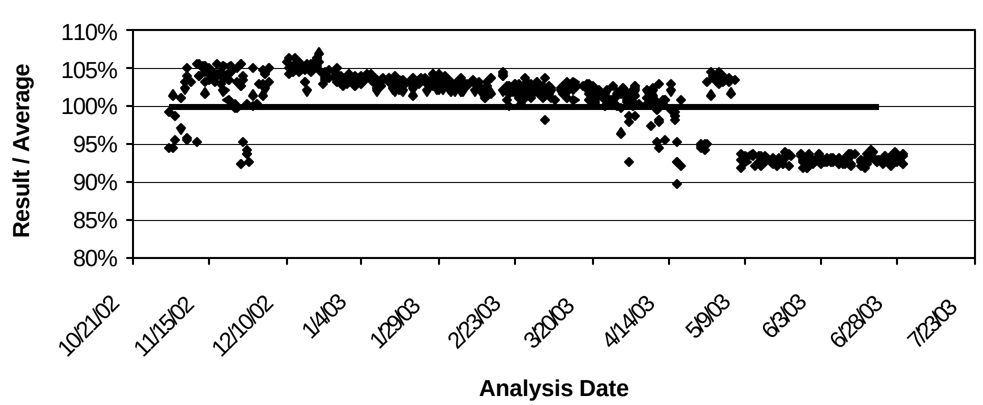


Figure 94. Recovery Precision for RTI QuanX XRF with Lead (Pb)

Figure 95. Recovery Precision of Aluminum (Al) in NIST SRM 1832 with RTI QuanX XRF

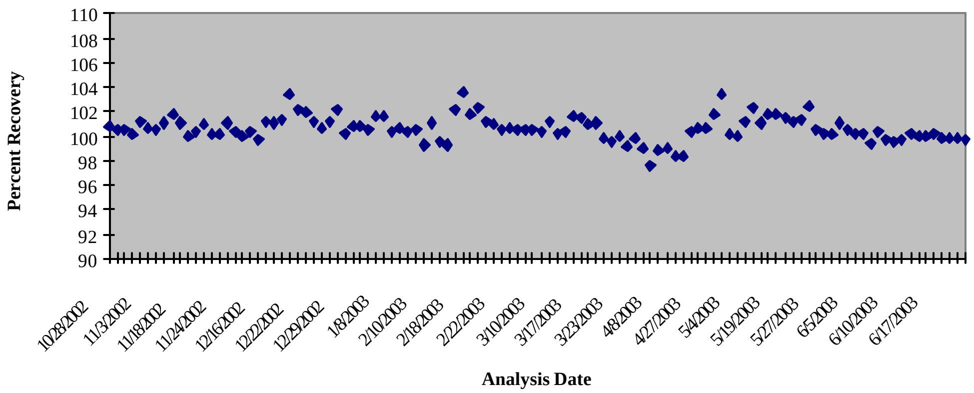


Figure 96. Recovery Precision of Silicon (Si) in NIST SRM 1832 with RTI QuanX XRF

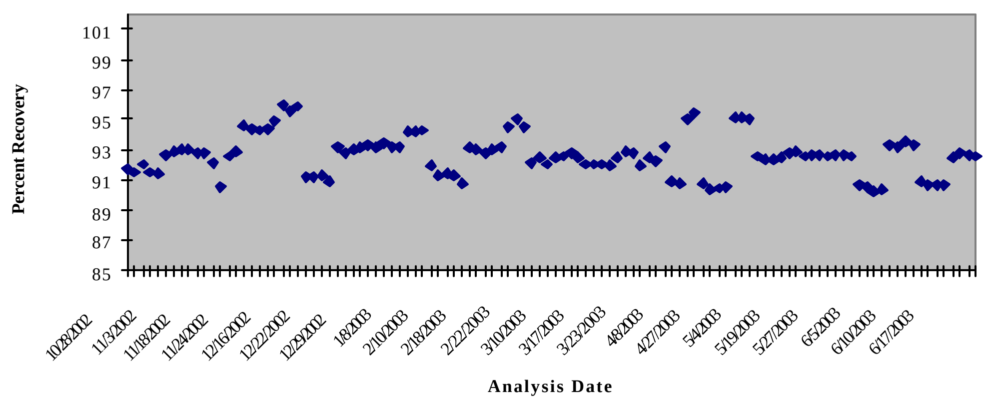


Figure 97. Recovery Precision of Silicon (Si) in NIST SRM 1833 with RTI QuanX XRF

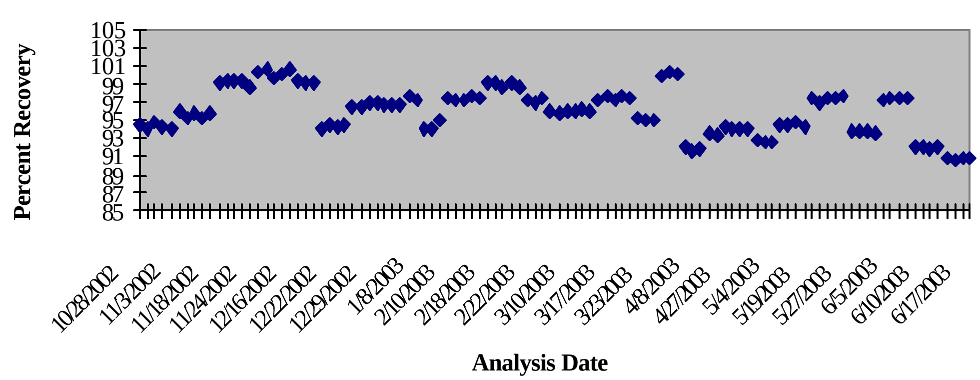


Figure 98. Recovery Precision of Potassium (K) in NIST SRM 1833 with RTI QuanX XRF

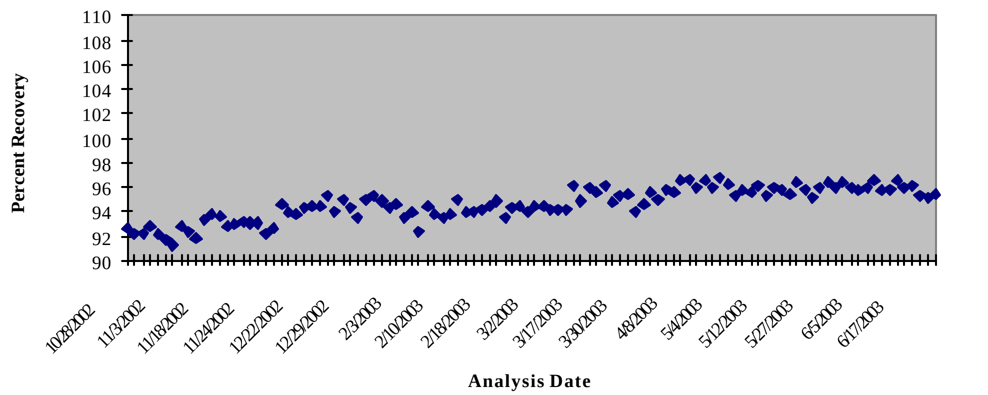


Figure 99. Recovery Precision of Calcium (Ca) in NIST SRM 1832 with RTI QuanX XRF

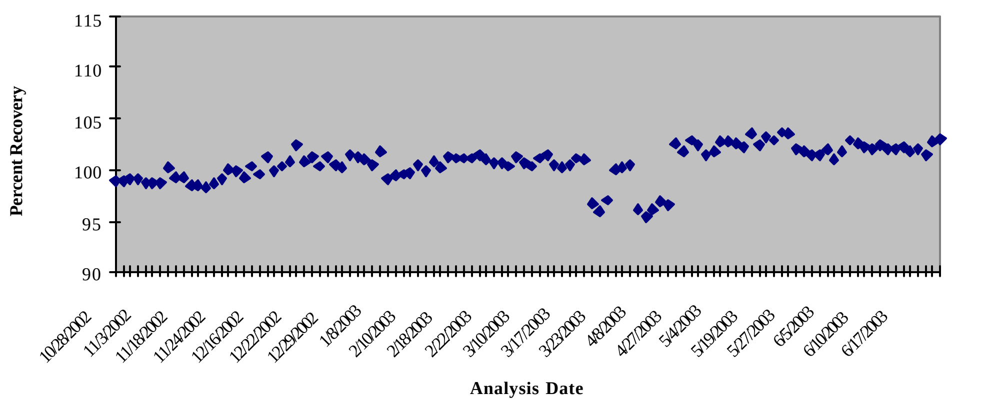


Figure 100. Recovery Precision of Titanium (Ti) in NIST SRM 1833 with RTI QuanX XRFSRM 1833 - Titanium

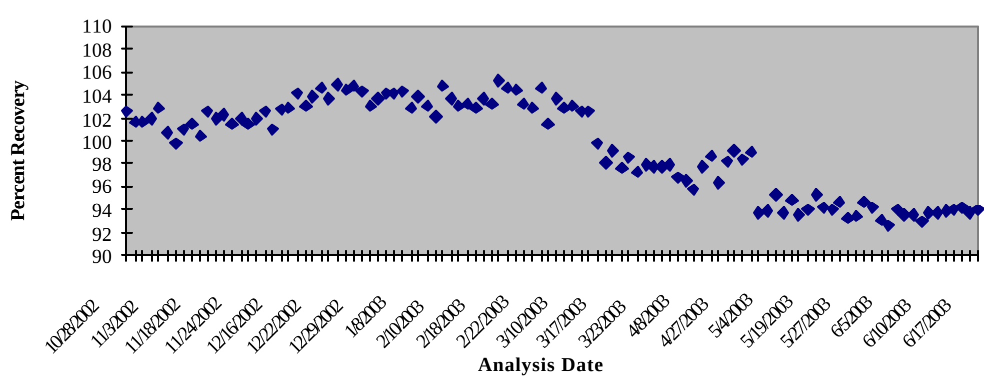


Figure 101. Recovery Precision of Vanadium (V) in NIST SRM 1832 with RTI QuanX XRF

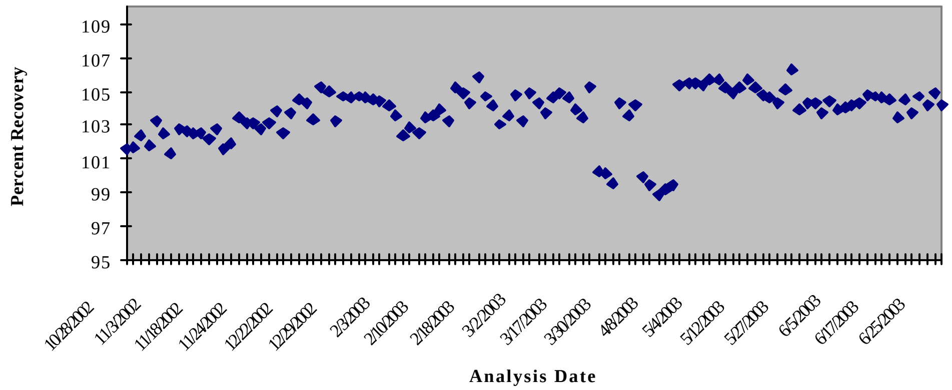


Figure 102. Recovery Precision of Manganese (Mn) in NIST SRM 1832 with RTI QuanX XRF

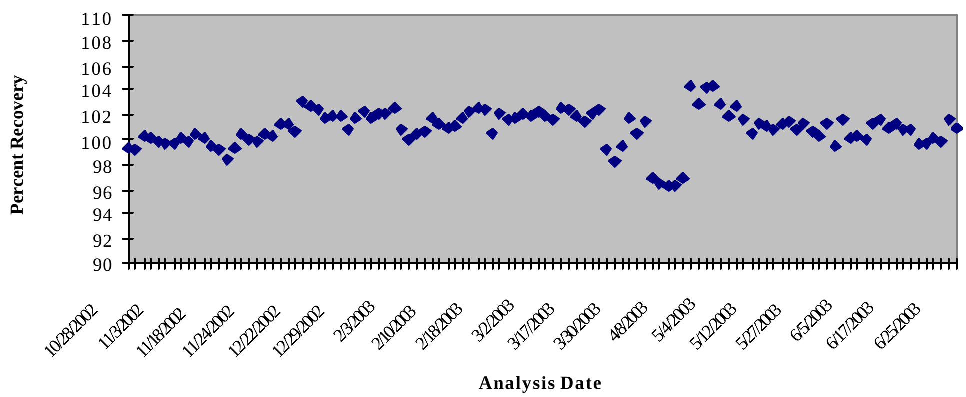


Figure 103. Recovery Precision of Cobalt (Co) in NIST SRM 1832 with RTI QuanX XRFSRM 1832 - Cobalt

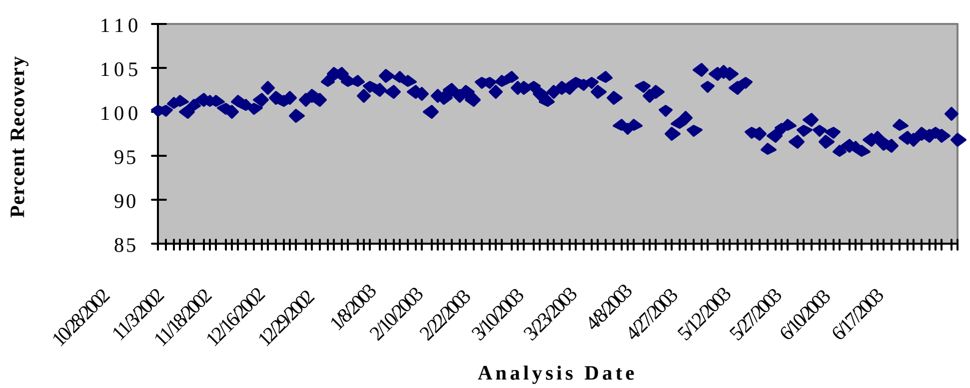


Figure 104. Recovery Precision of Iron (Fe) in NIST SRM 1833 with RTI QuanX XRF

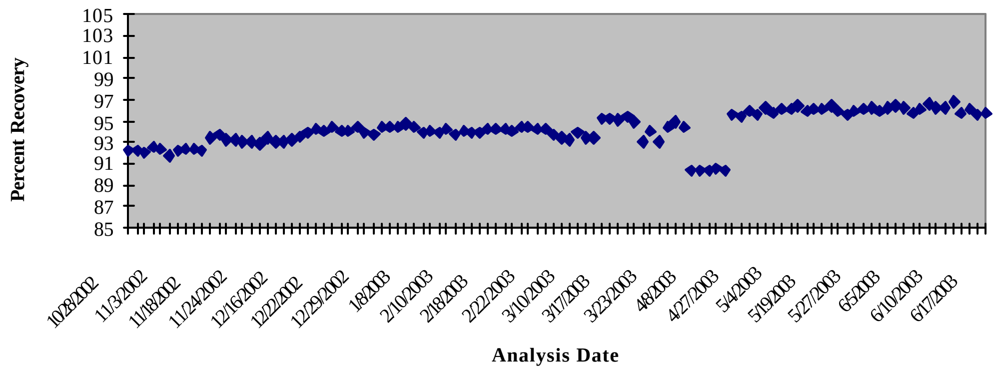


Figure 105. Recovery Precision of Copper (Cu) in NIST SRM 1832 with RTI QuanX XRF

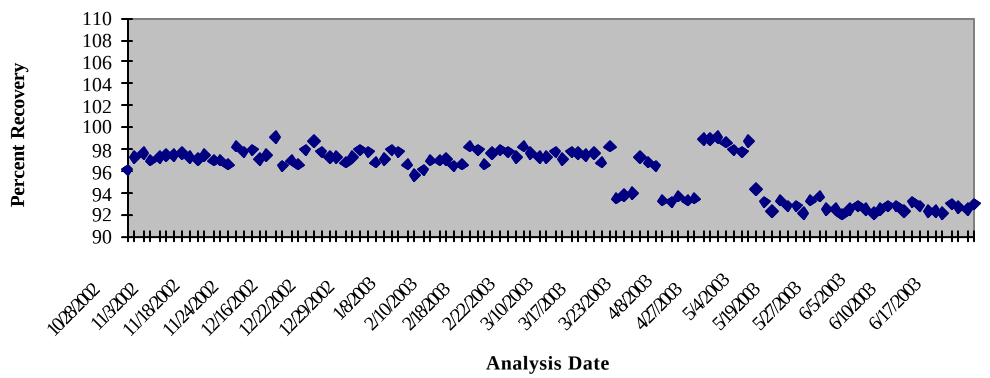


Figure 106. Recovery Precision of Zinc (Zn) in NIST SRM 1833 with RTI QuanX XRF

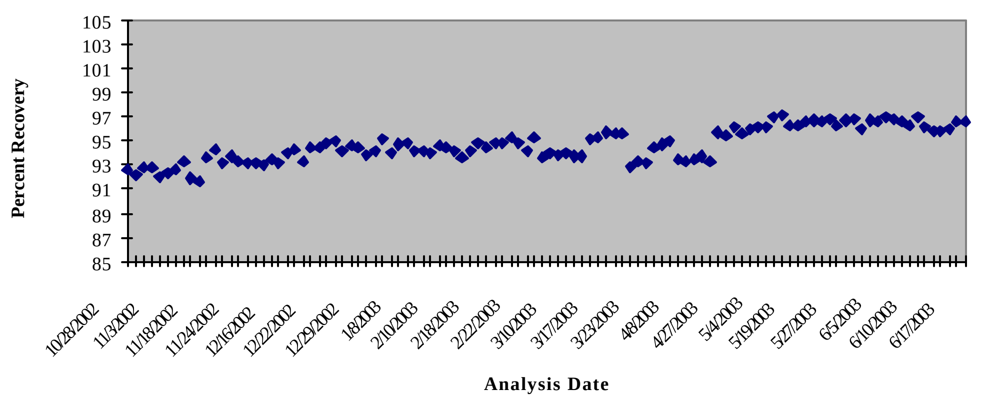


Figure 107. Recovery Precision of Lead (Pb) in NIST SRM 1833 with RTI QuanX XRF

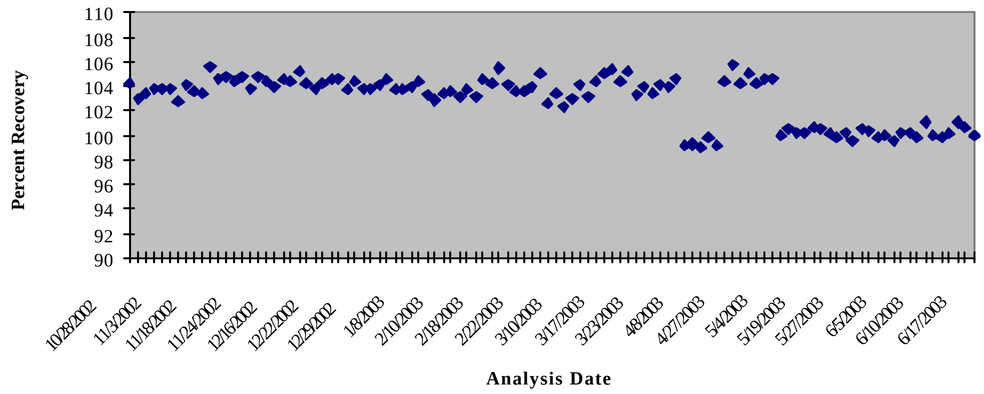


Table 22. Summary of RTI XRF Laboratory QC Precision Recovery Data, 10/1/02 through 6/30/03

Element	n	Min	Max	Average	Std Dev	%CV
Si	542	9.82	11.0	10.5	0.30	2.85
Ti	542	9.09	10.5	9.91	0.42	4.23
Fe	542	9.65	11.0	10.6	0.19	1.76
Se	542	5.35	6.03	5.76	0.10	1.68
Cd	542	4.00	4.50	4.41	0.15	1.02
Pb	542	9.57	11.4	10.7	0.48	4.54

n = number of observations
Min = minimum value observed
Max = maximum value observed
Std Dev = standard deviation
%CV = percent coefficient variation (Std Dev/Average*100)

Table 23. Recovery Determined from Analysis of NBS SRMs 1832 and 1833.

Element	Range % Recovery
Al	98 - 104
Si*	90 - 96
Si**	91 - 101
K	91 - 97
Ca	95 - 104
Ti	93 - 105
V	99 - 106
Mn	96 - 104
Fe	90 - 97
Co	96 - 105
Cu	92 - 99
Zn	92 - 97
Pb	99 - 106

*SRM 1832 **SRM 1833

Replicates

Ten percent of the filters are re-analyzed and the results for select elements are compared. **Figures 108 through 113** compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.9922 and correlation coefficients range from 0.9976 to 0.9999, indicating acceptable replication.

2.4.4.2 Data Validity Discussion – The data presented in Section 2.4.4 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters and a problem with the stability of the tube April 2003. A drift for silicon is also indicated in the QC data, but the data never exceeded the QC requirements. These were minor, and not considered to have a significant impact on the analysis results.

2.4.4.3 Corrective Actions – The XRF experienced some tube stability problems, in which the instrument would arc during analysis. In April 2003, the system was serviced, a full calibration was performed, and samples were re-analyzed where necessary. The new calibration caused a shift in the graphs for each element, but the data never exceeded the QC requirements and each element is showing to be stable.

The XRF showed a slight upward drift with silicon, but the values for the SRMs and the Micromatter QC never exceeded the QC requirements. The instrument was re-calibrated April 2003 to correct the drift and the calibration for silicon is checked weekly.

2.4.5 Round-Robin Intercomparison Results

Four different XRF instruments have been approved for use with this program. Before being accepted for use by the STN Program, each instrument was put through a series of acceptance tests using NIST reference materials and exposed STN filters. The Round-Robin program is a filter exchange whose purpose is to verify equivalency of the four instruments on an ongoing basis. To do this, a set of filters exposed filters from the STN archive is being circulated among the laboratories by RTI. Ninety-six (96) round-robin filters were used during the reporting period.

Figure 114 presents the results for each round-robin analysis vs. the original measurement value. All elements are plotted on the same graph. The majority of the "original values" were generated using the Chester 770 instrument, which might introduce some bias into the regression line. The apparent lack of bias demonstrates the lack of drift from the original analysis of the filter and the round robin analyses.

Figure 115 shows the round-robin analyses vs. the median of all observations (original and round-robin measurements). The Median is used in an effort to get the best consensus value for each filter/element combination. In a few cases, the same filter has been analyzed more than once by the same laboratory. Linear correlation equations for each instrument vs. the median value are shown on Figure 115, along with correlation coefficients (R-square). All four instruments have a slope greater than 0.99, which indicates good agreement between the instruments.

Figure 108. Results of Replicate Silicon (Si) Analysis with RTI QuanX XRF

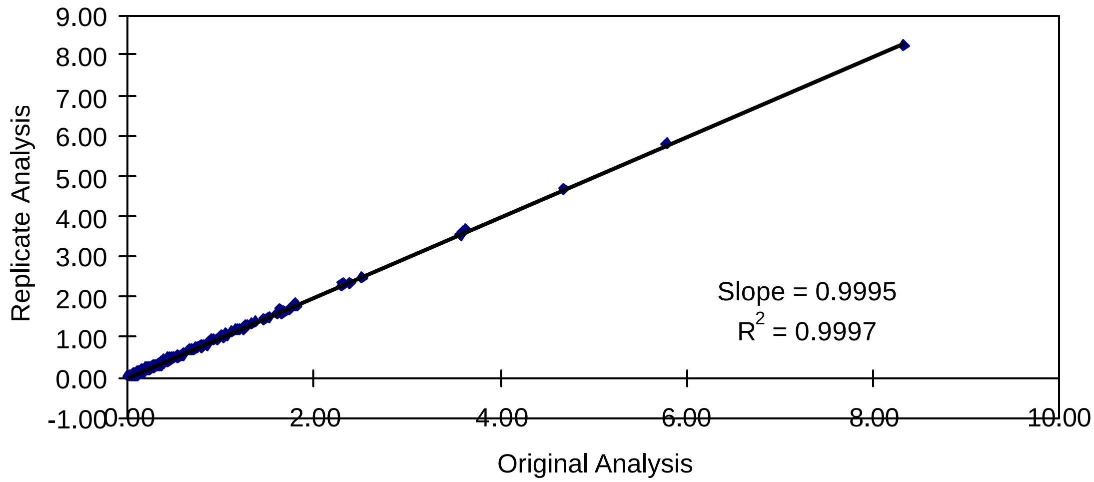


Figure 109. Results of Replicate Sulfur (S) Analysis with RTI QuanX XRF

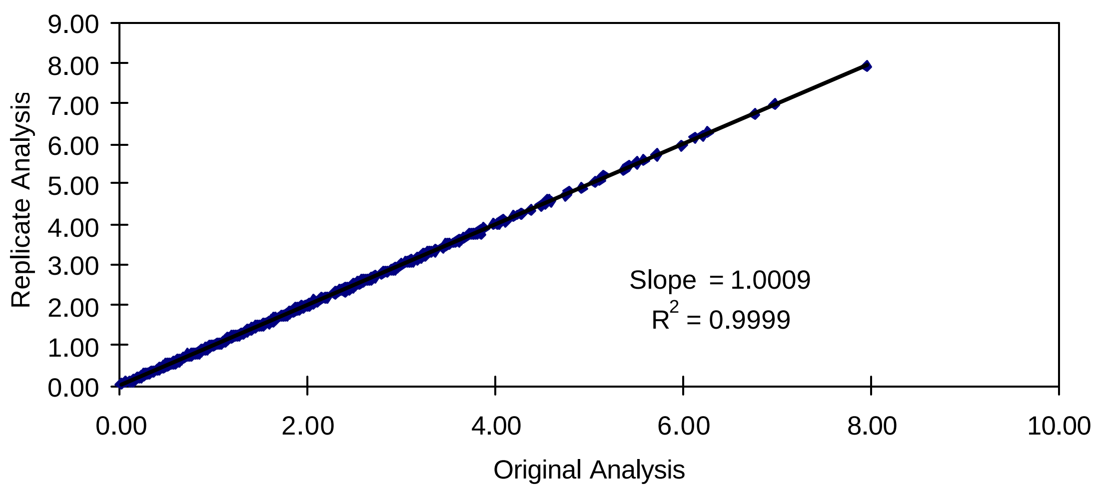


Figure 110. Results of Replicate Potassium (K) Analysis with RTI QuanX XRF

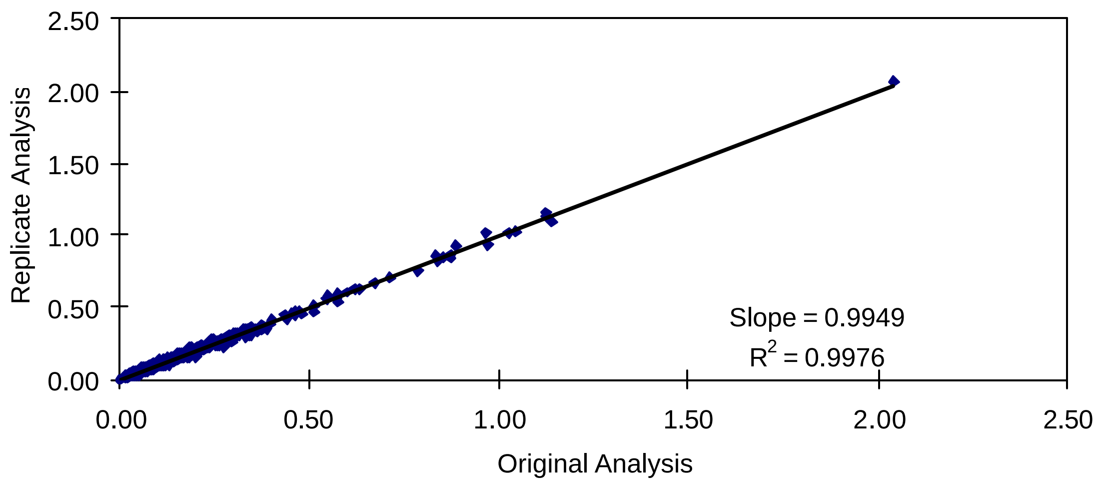


Figure 111. Results of Replicate Calcium (Ca) Analysis with RTI QuanX XRF

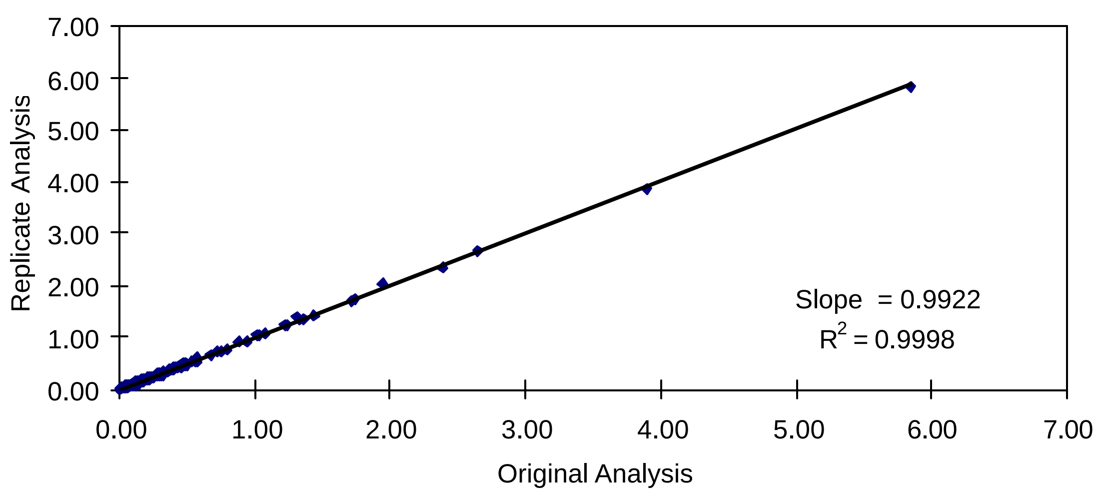


Figure 112. Results of Replicate Iron (Fe) Analysis with RTI QuanX XRF

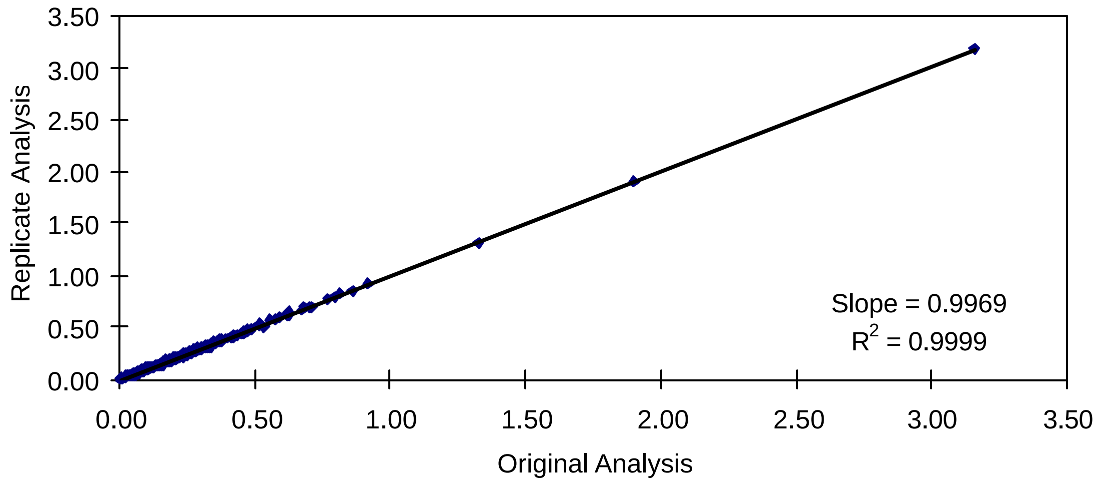


Figure 113. Results of Replicate Zinc (Zn) Analysis with RTI QuanX XRF

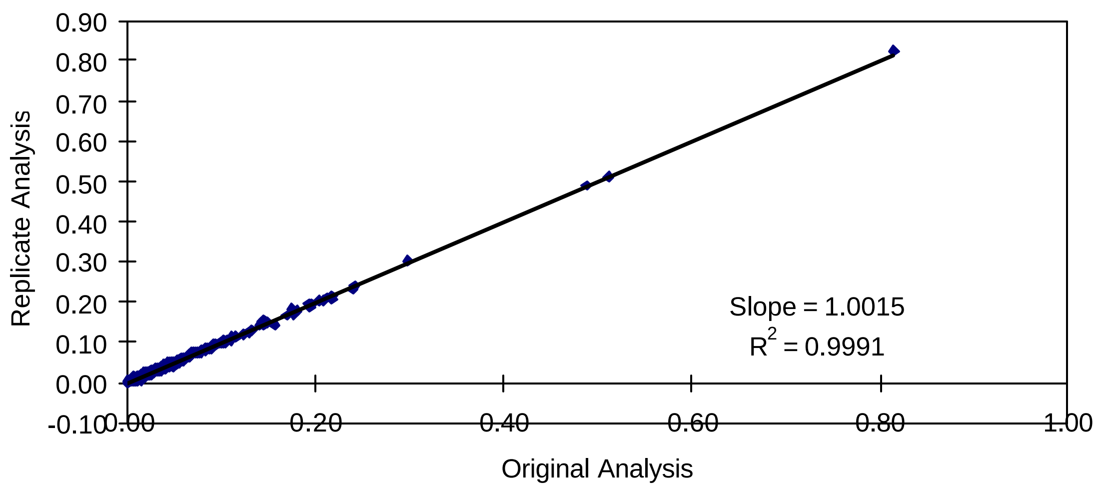


Figure 114. Round Robin Results vs Originally Reported Values
all elements plotted

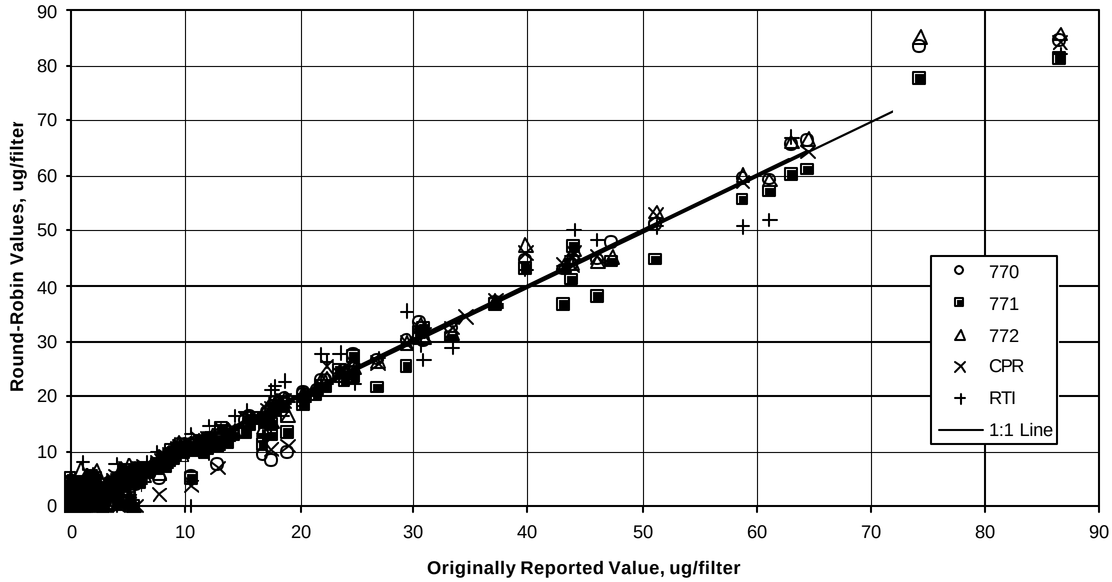
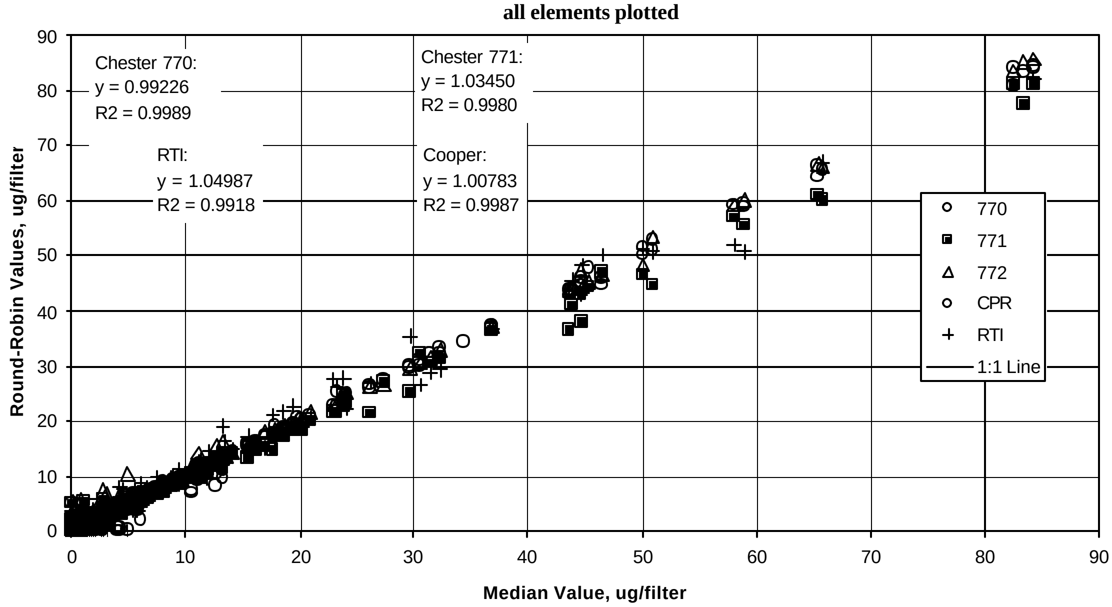


Figure 115. Round Robin Results vs Median of all Reported Values
all elements plotted



2.5 Sample Handling and Archiving Laboratory (SHAL)

2.5.1 Description of QC Checks Applied

Numerous QC checks are built into the SHAL procedures. These include:

- Bar-code readers are used to input identification numbers from modules, bins, containers, and data forms to virtually eliminate data transcription errors.
- Barcoded labels with identification numbers are generated by computer and the ID numbers include a check-digit.
- The training of new employees includes a reciprocal check procedure, in which other SHAL technicians check the contents of each other's coolers before they are closed for shipment. This cross-checking procedure is used by all personnel for all coolers processed.
- Periodically all SHAL personnel review the latest version of the Standard Operating Procedure. A record of the review is included in the person's training file.
- The SHAL supervisor or his designee will observe a SHAL worker performing the handling of filter modules. A checklist of correct tasks has been prepared for each type of module. The checklist is used by the supervisor during the observation of the worker handling the filters and modules. Completed checklists are kept by the SHAL supervisor. Workers are briefed following the observation of any findings.

2.5.2 Corrective Actions Taken

Problem: Severe ice storm hits Raleigh-Durham, NC area on Wednesday December 4, 2002. Power is lost to almost the entire area.

Corrective Action: The SHAL supervisor sent an e-mail to the three EPA DOPO's informing them of the ice storm and situation at RTI and asked them to distribute to all network operators. Over the next few days the SHAL supervisor kept the EPA and the EPA DOPO's informed of the current status of outgoing shipments to the sites. The shipment of filters scheduled to be shipped from the SHAL on Thursday December 5 was delayed one day. It was sent to the sites from RTI on Friday December 6. The next shipment was sent from RTI on Monday December 9. In order to recover from the ice storm and get back on the STN shipping scheduled it was decided that all sites in the STN would not sample on December 22, 2002. All sampling events for this date were flagged as "Invalid" and "Scheduled But Not Collected". Sites were informed of this change through the EPA and EPA DOPO's.

Problem: For the period October 1, 2002 through June 30, 2003 there were 16,643 scheduled events in the STN. In this same period there were 465 late arriving coolers at RTI. Approximately 2.8% of the return shipments arrived at RTI past the scheduled return date. These late arrivals were typically due to late returns by the site or delays in transit by the carrier.

Corrective Action: RTI has continued to track late arriving coolers. RTI will inform the EPA DOPO's of events which cannot be shipped due to late arriving coolers at RTI. The SHAL supervisor has also been sending EPA a listing of all coolers arriving on Monday. These coolers are either delayed in transit by the carrier or were shipped on Friday from the site which is not the preferred shipping day.

Problem: In a continuing effort to improve overall quality, the SHAL performed a limited experiment to investigate blank levels of OC on the quartz filters.

Experiment Description and Results: On February 19, 2003 the SHAL was preparing a shipment of Field Blank samples to be sent to the sampling locations. As this set was being prepared in the SHAL laboratory, 16 quartz filters were removed from the same batch of quartz filters being sent out. Eight quartz filters were kept in the SHAL freezer in their petrislide containers and eight quartz filters were kept in their petrislide containers but placed on a desktop at room temperature. When the Field Blank filters were returned from the sampling locations, all sixteen of the experimental filters were sent to the OC/EC lab along with the Field Blank filters on March 4, 2003. The results of the analysis are presented here:

Field Blanks					
Sampler	Avg Total Carbon ug/filter	Std Dev	Min	Max	Count
MASS	7.238	2.128	4.217	10.057	8
RAAS	9.282	2.617	4.969	15.638	26
RPFRM	14.110	14.405	6.762	52.329	9
RPSPEC	14.995	8.723	8.021	37.621	13
SASS	9.820	4.176	4.215	38.179	153
Overall Average = 11.089					
SHAL Blank Quartz Filters					
	Avg Total Carbon ug/filter	Std Dev	Min	Max	Count
Freezer	3.362	1.861	1.040	6.328	8
Desktop	6.553	1.913	4.452	9.417	8

Results of this limited experiment indicate that storage of the SHAL Blank QC filters should be in a freezer as those stored at room temperature for two weeks showed almost twice the Total Carbon as those stored in the freezer for the same time. The Field Blank filters picked up more Total Carbon (overall average of 11.089 ug) than the filters kept in the SHAL over the same two week period. This is most likely due to the cassette rings in the filter modules. These results agree with the EPA Technical Memorandum "PM2.5 Quartz Filter/Cassette Experiments" dated March 24, 2003 form Michael S. Clark at NAREL. In those experiments, 20 quartz filters held in MET ONE modules with delrin cassettes for two weeks averaged 13.6 ug/filter of OC.

2.6 Denuder Refurbishment Laboratory

The Denuder Refurbishment Laboratory is located in RTI Building No. 3, laboratory 220. The purpose of the laboratory is to clean and refurbish the coatings on acid-gas-removing denuders used in samplers of chemical speciation networks operated by EPA and various State and local agencies which utilize the RTI/EPA contract. The laboratory follows these protocols:

- Procedure for Coating Annular Denuders with Magnesium Oxide
- Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate
- Procedures for Coating R & P Speciation Sampler "ChemComb" Denuders with Sodium Carbonate
- Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin.

Denuders for the Andersen and URG speciation samplers are being cleaned and then re-coated with magnesium oxide. They are replaced at the sites at 3-month intervals. The last denuder replacement cycle was in April 2003; the next scheduled change-out will occurr in mid-July 2003.

MetOne speciation sampler aluminum honeycomb denuders are also coated with magnesium oxide. Because the MetOne denuders are part of the sampling module and six sets of modules are in circulation to each site, these denuders are refurbished at 18-month intervals. RTI is able to remove MgO from denuders using a dilute hydrochloric acid solution. As needed, RTI orders uncoated aluminum honeycomb denuder substrates from MetOne, cleans them with solvent and deionized water, and then coats them with magnesium oxide. Several other 18-month interval change-outs occurred in the period October 2002 through June 2003. The change-out occurs whenever the MetOne denuder assembly has been in use for 18 months.

R & P ChemComb™ glass honeycomb denuders are cleaned and coated with sodium carbonate/glycerol. R & P denuders are replaced after each 24-hour sampling use.

No XAD-4 resin coated denuders (for removal of organic vapors) were ordered by EPA/OAQPS during the reporting interval.

The only significant problem encountered in the reporting period of operation has been the occasional receipt of broken or loose glass denuders.

2.7 Data Processing

2.7.1 Operational Summary

The data processing system has continued to operate with minimal problems, although minor improvements and modifications continue to be made. Problems, Corrective Actions and Operational Improvements are discussed in Section 2.7.2, below.

2.7.2 Problems, Corrective Actions and Operational Improvements

2.7.2.1 Problems with long runtimes in EPA's Stats_CR – Starting in July 2002, we noticed that the Stats_CR step in posting AQS data was taking excessive time. By August 2002, the Stats_CR job had slowed to over 8 hours per batch (six batches were required to post each RTI monthly AQS report). Often the time required to run Stats_CR was so long that we would time out and have to resubmit the job (with an additional 8 to 12 hour wait). EPA was notified of the problem and was able to revise their procedures to fix the delays.

2.7.2.2 Additional Automated QA reports as part of monthly reporting procedures – We have continued to add to our monthly outliers report. Items added include reports to detect:

- Field data with unreasonable temperatures and barometric pressures
- Samples run on dates other than those scheduled. (This is not always an error; however, reviewing this helps to find data entry and blank substitution errors).

In addition we have added a revised blank report, that better helps us track elevated blank values.

2.7.2.3 New AQS data review procedures – As we have gained more experience with AQS processing and review procedures, we have developed a number of checks that are applied before posting data to AIRS. Many of these checks were developed and performed by our QA officer as part of his monthly review. We have now prepared a formal checklist of these items and delegated these checks to our RTI data processing staff. This permitted the QA officer to focus on a higher-level data review, while ensuring that all routine checks are performed and their results documented.

2.7.2.4 Modifications to double-entry comparison procedures to prevent loading of incomplete data – All field channel data are double entered by two different operators. Each enters data into a different table. The results in each table are compared to the data in the other table before any matching data is copied into the main table (and then deleted from the individual tables). Additionally, we have checks that require all channels for a routine (non-blank) have data before that data is approved for reporting. As the number of field events grew, we noticed that we were seeing several events that were not getting all channels entered in the main table. As these events had incomplete data entry, they were not approved for reporting. Although our normal check procedures were detecting this problem, we were spending time to track down and correct each missing entry.

The incomplete field entry problem was traced back to the double-entry comparison routine, which was ignoring any channels entered only in the second table. Modifications were made to the comparison routine to fix this problem.

2.7.2.4 Addition of new automated remote backup procedures – We have been routinely (nightly) backing-up server data to tape and removing the tapes to an offsite location on a weekly basis. Although this provides a high level of protection against server failure, there was still the potential for data loss in case of catastrophic site failure (such as fire or flood). In addition, the time to restore a new system from backup tape could exceed a full day. To provide greater protection against data loss and service interruption, we have developed a program that automatically copies the most recent SQL Server backup and transaction files to a server located at RTI's 800 Park facility (approximately 1 mile from the main campus). The remote server also contains the same version of SQL Server and could be quickly converted to the primary server in case of major site or hardware malfunction. The new program is scheduled to run each business day on the half-hour (transaction logs are generated on the hour) during business hours. This is in addition to the automated nightly tape backups.

2.8 Quality Assurance and Data Validation

2.8.1 QA Activities

QA activities directly related to data validation are described in the PM2.5 Chemical Speciation Laboratory QAPP (January 2003), and include the following:

- Review of monthly data reports sent to the state monitoring agencies and EPA
  - Verification of data attribution to the correct site, POC, and date
  - Review of report formats
  - Troubleshooting when discrepancies are found
  - Running manual and partially-automated range checks
  - Reviewing the results of fully-automated validation checks
  - Application of Level 1 outlier screening criteria.
- Review of each data batch before it is sent to AIRS
  - Verification of data attribution to the correct site, POC, and date
  - Verification that changes requested by the state monitoring agencies have been correctly made by the Data Processing personnel
  - Review of data format to be sure that records and individual fields are of the correct length.
- Troubleshooting of sample and data problems that cross the boundaries between laboratories, the SHAL, and/or the data processing function.

2.8.2 Data Validation Procedures

The full scope of the Level 0 and Level 1 procedures carried out by RTI before data are delivered to the state monitoring agencies each month are described in the Laboratory QAPP (January 2003).

The data validation procedures described in previous QA Reports continue to be performed as described there and in the Laboratory QAPP. Some of the screening procedures have been automated to speed the monthly review process; however all questionable data identified by automated screening continue to be reviewed by a data validation staff member.

2.8.3 Internal Assessments

In October 2002, with the collaboration of the RTI QAO, the RTI Deputy QAO performed an internal assessment of the program. The purpose was to assess and improve the quality and efficiency of multiple complex processes. The focus of the assessment was on identifying the potential for improving processes for generating data of known and documented quality. These processes require the interactions of physical processes and data management across a large team of RTI, EPA, and state team members. Several incremental opportunities were identified; no significant problems were noted.

2.8.4 Corrective Actions

Issue: MetOne Date/Clock Problem March 2003

On March 7, 2003, RTI became aware of a problem affecting the internal date for the MetOne SASS units that sampled on March 1, 2003. Fourteen of the 50 SASS units that sampled on that date reported elapsed sample times of 48 hours instead of the normal 24. In addition, several of the operators recorded comments that the system's date was one day behind. Thus, it appeared that March 1 happened twice, and now the sampler's internal clock was reading one day early. MetOne was contacted and confirmed that there was a bug in the sampler's leap year software and that not all samplers were affected.

The software bug resulted in problems with subsequent sampling events as well. A brief summary of the problems is presented here:

- March 1 -A 48 hour sample was taken by affected samplers. March 1 was a 1-in-3 day sample, so a relatively small number of runs were affected (**Table 24**).
- March 4 - Affected samplers sampled one day late -- March 5 instead of March 4. March 4 was both a 1-in-3 and a 1-in-6 sample day, so that many additional sites were involved in this event (**Table 25**).

Some samplers were stopped early by the site operator when the operator went to retrieve the sample, but the sample was still running when the actual sampling event should have been completed (**Table 26**).

March 7 was another 1-in-3 sampling day. Any of the 1-in-3 samplers that were not corrected earlier in the week, sampled one day late (Table 25). Again, some samplers were stopped early by the site operator when the operator went to retrieve the sample, but the sample was still running when the actual sampling event should have been completed (Table 26).

March 10 was a 1-in-6 and 1-in-3 sampling day. Any samplers with uncorrected dates sampled one day late (Table 25). Again, some samplers were stopped early by the site operator when the operator went to retrieve the sample, but the sample was still running when the actual sampling event should have been completed (Table 26).

Corrective Action:

RTI notified EPA on Friday March 7, 2003, and requested that they immediately contact all sites with SASS samplers, asking the operators to check and if necessary, reset the date on all of their units.

A notice was sent to all MetOne sites inside a cooler containing sampling filters alerting them to the problem and asking them to check and reset their instrument clocks if necessary (**Figure 116**). Site operators were asked to inform RTI of any corrections that were necessary due to the date problem. Where necessary, RTI reassigned data to the correct dates.

MetOne was contacted and agreed to supply new software to SASS operators within 60 days.

Table 24. Samples With 48-Hour Sample Times

Sampling Request	Location	Sample Date	Sample Time
Q46914H	Washington Park	01-Mar-03	47.59
Q47159A	SER-DNR Headquarters	01-Mar-03	47.59
Q47706F	El Cajon	01-Mar-03	47.59
Q47776T	Bakersfield-California Ave	01-Mar-03	47.59
Q47811F	Bakersfield-California Ave (Collocated)	01-Mar-03	47.59
Q48196J	Riverside-Rubidoux (Collocated)	01-Mar-03	47.59
Q48922P	Arnold	01-Mar-03	47.59
Q49077H	Sault Ste Marie	01-Mar-03	48
Q49287P	Tonto National Monument	01-Mar-03	47.59
Q49531I	Canal St. Post Office	01-Mar-03	47.59
Q501026	Burlington	01-Mar-03	47.59
Q50382S	Sherwood Is. St. Pk.	01-Mar-03	47.59
Q504870	Chester	01-Mar-03	47.59
Q505920	Gulfport	01-Mar-03	47.59

Table 25. Events Sampled One Date Late Due to Sampler Clock Being Off by One Day

Sampling Request	Location	Sample Date	Start Date	Sample Time
Q471603	SER-DNR Headquarters	04-Mar-03	05-Mar-03	24
Q47195E	Chiwaukee Prairie Site	04-Mar-03	05-Mar-03	24
Q472719	Grand Rapids	10-Mar-03	11-Mar-03	24
Q47365E	Manitowoc, Woodland Dunes site	04-Mar-03	05-Mar-03	24
Q47707G	El Cajon	04-Mar-03	05-Mar-03	24
Q482508	Bismarck Residential	04-Mar-03	05-Mar-03	24
Q48258G	Bismarck Residential	10-Mar-03	11-Mar-03	24
Q48386N	Mesa County Health Department	04-Mar-03	05-Mar-03	24
Q48454I	Simi Valley	04-Mar-03	05-Mar-03	23.9
Q490357	OCUSA Campus	10-Mar-03	11-Mar-03	24
Q49532J	Canal St. Post Office	04-Mar-03	05-Mar-03	13.15
Q498957	Guthrie	10-Mar-03	11-Mar-03	24
Q49930T	Portsmouth	10-Mar-03	14-Mar-03	23.95
Q50208F	Lawrenceville	04-Mar-03	03-Mar-03	24
Q50702O	Covington - University College	04-Mar-03	05-Mar-03	24
Q507700	London-Laurel County	04-Mar-03	05-Mar-03	24
Q51071K	Florence	04-Mar-03	05-Mar-03	24
Q51130E	Grenada	10-Mar-03	11-Mar-03	24
Q51190Q	Hazelwood	04-Mar-03	05-Mar-03	24
Q514794	State College	04-Mar-03	05-Mar-03	24
Q51598A	Pearl City	04-Mar-03	05-Mar-03	24

Table 26. Events Stopped Early by Site Operators Due to Sampler Running One Day Late

Sampling Request	Location	Sample Date	Sample Time
Q46915I	Washington Park	04-Mar-03	14.58
Q472639	Grand Rapids	04-Mar-03	7.48
Q47297J	Head Start	04-Mar-03	11.23
Q47348D	Luna Pier	04-Mar-03	13.32
Q489763	Crossett	04-Mar-03	12.32
Q49532J	Canal St. Post Office	04-Mar-03	13.15
Q504881	Chester	04-Mar-03	11.53
Q505931	Gulfport	04-Mar-03	13.63
Q509433	Chester (PA)	10-Mar-03	9.57
Q51037I	Elmwood	04-Mar-03	9.33
Q51207I	Hendersonville	04-Mar-03	15.95
Q51215I	Hendersonville	10-Mar-03	4.54
Q515811	York	04-Mar-03	12.38
Q515899	York	10-Mar-03	9.2

The affected data was dealt with as follows:

- For events scheduled on March 1, 2003 that were sampled for 48 hours: All data was invalidated with the "AN" AIRS null value code (Machine Malfunction) The data was reported on the scheduled date.
- For events scheduled after March 1, 2003 (e.g. 3/4/03, 3/7/03, etc), which were sampled one day later than scheduled, but sampled for a full 24 hours: Data was reported as valid to AIRS on the date it actually ran.
- For events scheduled after March 1, 2003, which sampled one day later than scheduled, but sampled less than 24 hours because the operator retrieved the filters while the sampler was still running: All data was invalidated with the "AN" AIRS null value code. These events were reported to AIRS on the scheduled date.

Note to Operators about the MetOne SASS Date Problem:

On approximately March 1, 2003, many of the MetOne SASS samplers experienced a problem with their internal clocks. As a result, several samplers ran for 48 hours on their March 1 sample. (Note that only samplers on the 1-in-3 day schedule ran on March 1.)

Many samplers' internal clocks read one day slow after March 1, so that samples scheduled for March 4 actually ran on March 5, etc. As a result of this date discrepancy, some operators retrieved filters before a full 24-hour sample had been completed.

MetOne has identified the problem in their software, and has proposed to distribute revised software to all the sites in the next 60 days. In the meantime, simply resetting the internal clock will insure that future samples are run on the correct date.

If you have not already checked and reset the clock on your MetOne SASS sampler, please do so as soon as possible. Note that not all samplers were affected by the problem, so some clocks may not need to be reset.

Since EPA's criteria for valid samples require that filters must sample for between 23 and 25 hours, RTI will automatically invalidate any filters that were sampled for 48 hours on March 1. In addition, data will be invalidated if filters were retrieved before being sampled for at least 23 hours.

Please record the actual run date and time on the PM2.5 STN Custody and Field Data Form Section D. RTI will attempt to report all valid data on the date that the filters actually ran, not on the date scheduled. This will be reflected in the data reports for the events scheduled during early March, which will be posted on April 15. We may have to contact individual sites if it is unclear from the Custody form which day a sample actually ran.

Please call or e-mail me if you have any questions regarding RTI's handling of the data. Contact MetOne for specific questions about the planned software update or for assistance resetting the internal clock.

Thanks,

Jessie Deal
Research Triangle Institute
1000 Parliament Court
Suite 100 Room 152
Durham, NC 27703

Figure 116. Sampler notice sent to sites in coolers.

3.0 Data Validity and Completeness

3.1 Summary of Scheduled Samples

Routine samples were scheduled on 1-in-6 and 1-in-3 day schedules during the reporting period for this report, delivery batches 29 through 42. **Table 27** summarizes the delivery batch by delivery date covered by this report. To avoid confusion, RTI does not report partial results for any exposure session, but waits until all the analysis results are complete before an event is reported.

Table 27. Delivery Batches by Delivery Date

Delivery Batch ID	Report Date	Earliest Sample	Latest Sample	Number of Samples
29	06/14/2002	02/25/2002	05/08/2002	2066
30	07/16/2002	04/02/2002	06/10/2002	2001
31	08/14/2002	04/29/2002	07/10/2002	1768
32	09/15/2002	06/25/2002	08/12/2002	1831
33	10/14/2002	08/09/2002	09/11/2002	1885
34	11/13/2002	09/08/2002	10/14/2002	1908
35	12/14/2002	09/26/2002	11/13/2002	1896
36	01/14/2003	11/07/2002	12/10/2002	1793
37	02/14/2003	12/07/2002	01/12/2003	1939
38	03/14/2003	01/09/2003	02/14/2003	1865
39	04/14/2003	12/10/2002	03/16/2003	1859
40	05/13/2003	03/10/2003	04/12/2003	1629
41	06/12/2003	04/03/2003	05/12/2003	2118
42	07/11/2003	05/15/2003	06/14/2003	1729

Turnaround times from sample receipt continued to decline during the reporting period, as shown in **Table 28**. Turnaround time is defined as the elapsed time from receipt of a cooler at the SHAL for a completed event, and the reporting of the data from that event.

Table 28. Data Turnaround Times

Delivery Batch	Date	Turnaround Time (days)
35	Dec-02	42
36	Jan-03	44
37	Feb-03	42
38	Mar-03	39
39	Apr-03	41
40	May-03	41
41	Jun-03	40
42	Jul-03	39

3.2 Trip and Field Blanks

The number of blanks run during this period are summarized in **Table 29**. Blank data are not submitted to AIRS, but are reported to the state monitoring agencies and to EPA for statistical analysis. As required by the QAPP, trip blanks are being scheduled at a frequency of one per 30 regular exposure events, and field blanks are scheduled at a rate of one per 10 regular exposures. However, use of the "alternate schedule" at sites where operators do not work on weekends has resulted in a larger proportion of Trip Blanks than required by the QAPP. Some routine samples that are not run are converted to additional Trip Blanks or Field Blanks provided that the site operator indicates that the correct SOP has been followed. Other unexposed samples are designated "unsampled blanks" when it is not clear what protocol the operator followed.

Table 30 summarizes the Trip and Field Blank results for the reporting period. High average sodium blank values that were seen in Batches 36 and 37 have been attributed to the cleaning procedure for centrifuge tubes. RTI instituted a new tube washing procedure early in 2003 that effectively reduced the background levels of sodium. The comparatively high values for Organic Carbon, which are typically above 10 micrograms per filter, are thought to be due to adsorption of VOCs from the air.

Table 29. Number of Blanks Reported in Batches 35 through 42

Delivery Batch ID	Sample Type	Number of Samples
35	FIELD BLANK	281
35	ROUTINE	1524
35	TRIP BLANK	24
35	UNSAMPLED_BLANK	23
36	FIELD BLANK	129
36	ROUTINE	1365
36	TRIP BLANK	237
36	UNSAMPLED_BLANK	26
37	FIELD BLANK	279
37	ROUTINE	1558
37	TRIP BLANK	41
37	UNSAMPLED_BLANK	33
38	FIELD BLANK	155
38	ROUTINE	1517
38	TRIP BLANK	135
38	UNSAMPLED_BLANK	35
39	FIELD BLANK	283
39	ROUTINE	1501
39	TRIP BLANK	41
39	UNSAMPLED_BLANK	20
40	FIELD BLANK	157
40	ROUTINE	1419
40	TRIP BLANK	18
40	UNSAMPLED_BLANK	35
41	FIELD BLANK	282
41	ROUTINE	1547
41	TRIP BLANK	254
41	UNSAMPLED_BLANK	35
42	FIELD BLANK	160
42	ROUTINE	1492
42	TRIP BLANK	42
42	UNSAMPLED_BLANK	35

Table 30. Trip and Field Blanks Average for the Reporting Period (µg/filter)

Trip Blanks

Analysis	Analyte	35	36	37	38	39	40	41	42
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.14	0.04	0.02	0.08	0.07	0.04	0.00	0.01
Cations - PM2.5 (NH4, Na, K)	Sodium	0.80	1.21	1.06	0.62	0.68	0.87	0.42	0.63
Mass - PM2.5	Particulate matter 2.5u	8.74	6.83	7.12	8.59	15.80	7.41	7.81	7.60
Nitrate - PM2.5	Nitrate	1.06	0.99	0.75	0.86	0.83	0.82	0.81	0.67
Sulfate - PM2.5	Sulfate	1.16	1.64	2.16	1.20	1.48	1.26	0.79	1.06
OC/EC	Elemental carbon	1.63	1.82	1.43	1.76	1.31	1.46	1.50	0.91
OC/EC	Organic carbon	10.49	14.11	8.68	10.15	11.27	8.39	10.22	11.20

Field Blanks

Analysis	Analyte	35	36	37	38	39	40	41	42
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.07	0.01	0.04	0.03	0.03	0.02	0.00	0.01
Cations - PM2.5 (NH4, Na, K)	Sodium	0.57	1.10	0.45	0.28	0.20	0.51	0.33	0.27
Mass - PM2.5	Particulate matter 2.5u	7.35	9.28	7.69	6.20	7.76	7.24	13.17	5.78
Nitrate - PM2.5	Nitrate	0.73	0.91	0.61	0.78	0.57	1.20	0.53	0.78
Sulfate - PM2.5	Sulfate	0.62	2.09	0.85	0.64	0.55	0.78	0.54	0.61
OC/EC	Elemental carbon	2.10	1.64	2.10	2.08	1.66	2.10	1.89	1.82
OC/EC	Organic carbon	12.38	10.85	12.29	12.23	9.38	11.15	11.73	12.59

3.3 Data Completeness

Table 31 shows the percentage of routine exposure records in each delivery batch group that were valid (i.e., not invalidated with an AIRS Null Value Code). Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval.

Table 31. Summary of Percent Valid AIRS Data by Delivery Batch

Location	AIRS Code	POC	Percent by Delivery Batch					
			35	36	37	38	39	40
20th St. Fire Station	120861016	5	100	90	90	91	100	100
5 Points	391530023	5			96	20	96	100
Air Monitoring, VA DEQ	517600020	5	99	99	88	89	98	100
Aldine	482010024	5	79	93	91	92	91	100
Allen Park	261630001	5	92	60	90	83	83	100
Alpine	480430002	5	99	100	100	100	100	100
Alton	171192009	5	100	100	83	100	100	75
APCD (Barret)	211110048	5	100	100	83	100	100	100
Arendtsville	420010001	5	100	77	54	79	100	100
Army Reserve Center	191130037	5	100	100	83	100	100	100
Arnold	290990012	5	100	100	90	100	90	100
Ashland Health Department	210190017	5	100	81	83	82	100	100
Athens	130590001	5	100	80	53	80	100	100
Augusta	132450091	5	80	100	33	65	100	80
Bakersfield-California Ave	060290014	5	89	100	72	80	70	90
Bakersfield-California Ave (Collocated)	060290014	6	72	89	70	82	70	89
Bates House (USC)	450790019	5	100	100	80	100	100	100
Bayland Park	482010055	5	85	84	89	99	90	100
Beacon Hill	530330080	6	100	100	82	100	100	100
Bethune School	040138006	5						12
Big Bend National Park	480430101	5	86	76	71	79	86	99
Bismarck Residential	380150003	5	100	100	83	100	100	100
Blair Street	295100085	6	66	88	70	100	100	100
Blair Street	295100085	6	66	88	70	100	100	100
Bonne Terre	291860006	5					53	52
Bountiful	490110001	5	100	100	83	82	100	100
Bowling Green-Kereiakes Park	212270007	5	100	100	83	100	80	100
Bristol	515200006	5	85	100	83	100	100	100
Buffalo	360290005	6	100	100	80	100	100	100
Buncombe County Board of Education	370210034	5	100	100	80	100	100	100
Burlington	500070012	5	100	100	90	100	90	100
Camden	340070003	5	100	69	75	89	88	100
Canal St. Post Office	360610062	5	100	100	90	100	82	87
Canton Health Dept.	391510020	5	82	100	83	100	100	100
Capitol	220330009	5	73	99	73	89	88	70
Chamizal	481410044	5	100	100	83	82	90	80
Channelview	482010026	5	65	100	85	83	60	100
Cherry Grove	370330001	5	85	100	83	100	100	100
Chester	340273001	5	90	78	88	44	20	100
Chester (PA)	420450002	5	82	81	83	99	58	100
Chesterfield	450250001	5	100	100	82	100	78	97
Chickasaw	010970003	5	100	100	60	100	100	100
Chicopee	250130008	5	100	89	27	20		

Table 31. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch					
			35	36	37	38	39	40
Children's Park	040191028	5	100	100	80	100	100	100
Chiwaukee Prairie Site	550590019	5	100	100	83	100	100	80
Columbus	132150011	5	82	100	52	95	98	80
Com ED	170310076	5	100	100	89	88	75	76
Commerce City	080010006	5	100	88	88	100	100	43
Conroe Airport	483390078	5	99	99	59	91	82	100
Cornell Elementary	191532520	5	99	100	60	65	100	100
Courthouse Annex-Libby	300530018	5	100	100	80	100	100	100
Covington - University College	211170007	5	100	100	83	100	100	100
CPW	450190049	5	100	100	90	100	90	100
Crossett	050030005	5	60	100	83	100	80	78
Dallas Convention Center	481130050	5	87	100	99	100	99	91
Dearborn	261630033	5	100	100	83	100	83	100
Decatur	011030011	5	100	100	82	100	100	80
Deer Park	482011039	6				69	100	100
Deer Park (Collocated)	482011039	7	74	70	64	92	74	45
Dona Park	483550034	5	84	99	100	100	99	99
Douglas	130690002	5	94	100	40	72	100	80
Dover	100010003	5	80	100	80	100	77	100
Durango - Park School	080670008	5	80		33	100	83	75
Duwamish	530330057	6	100	100	80	67	75	100
East Charleston	320030560	5	100	100	83	100	100	100
El Cajon	060730003	5	80	75	88	89	89	100
Elizabeth Lab	340390004	5	100	89	75	89	100	88
Ellis County WMA	400450890	5	100	97	80	100	100	100
Ellyson	120330004	6	80	100	83	80	100	100
Elmwood	421010136	5	83	100	83	100	80	100
Erie	420490003	5	100	100	67	80	100	100
Essex	240053001	5	100	89	88	78	75	100
Evansville - Mill Road	181630012	5	100	100	80	100	100	100
Fargo NW	380171004	5	100	100	80	100	100	99
Florence	421255001	5	80	100	83	100	100	100
Florence Special	421255001	5	80	100	83	100	100	100
Fort Meade	240030019	5	100	100	75	100	82	100
Fort Wayne CAAP	180030004	5						100
Francis Elementary School	440071010	5	100	80	80	80	100	100
Freemansburg	420950025	5	100	100	80	100	100	100
Fresno - First Street	060190008	5	91	99	84	100	100	87
G.T. Craig	390350060	5	100	100	67	78	80	90
G.T. Craig - Collocated	390350060	6	100	100	78	100	80	67
Galveston Airport	481670014	5	92	98	65	92	75	100
Garden St.	020200018	5	100	100	82	90	100	100
Garinger High School	371190041	5	100	50	88	90	100	85
Gary Iitri	180890022	5						100
General Hospital	390870010	5	97	100	82	100	100	100
Georgetown (Andersen)	530330032	6	100	100	50	100	100	100
Grand Rapids	260810020	5	99	99	80	100	80	99
Greensburg	421290008	5	80	100	83	100	80	100
Greensburg Special	421290008	5	80	100	83	100	80	100

Table 31. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch					
			35	36	37	38	39	40
Grenada	280430001	5	100	100	83	100	100	100
Guaynabo	720610005	5	100	100	90	100	91	100
Guiding Hands School	390530003	5	97	100	83	80	54	75
Gulfport	280470008	5	80	88	88	100	75	100
Guthrie	471570047	5	91	90	90	100	100	100
Hamshire	482450022	5	92	92	100	100	100	91
Harrisburg	420430401	5	100	100	83	82	80	100
Hattie Avenue	370670022	5	100	100	83	100	82	100
Hattiesburg	280350004	5	100	100	67	100	100	100
Hawthorne	490353006	5	100	89	90	82	90	100
Hazard - Perry County Horse Park	211930003	5	100	100	83	100	100	100
Hazelwood	420030021	5	100	100	80	100	77	100
Hazelwood Special	420030021	5	100	100	80	100	77	100
Head Start	390990014	5	100	100	83	100	80	85
Hendersonville	471650007	5	100	100	83	100	60	100
Hickory	370350004	5	100	100	83	100	100	100
Hinton	481130069	5	92	90	73	100	89	90
Holland	260050003	5				100	80	100
Houghton Lake	261130001	5	100	100	62	100	60	80
Huntsville Old Airport	010890014	5			23	80	98	63
IL - Decatur	171150013	5			100	100	100	100
IS 52	360050110	5	100	100	90	100	100	99
Jackson Hinds Co.	280490018	5	100	100	75	67	98	100
Jefferson Elementary (10th and Vine)	191630015	5	89	91	70	100	100	100
JFK Center	202090021	5	100	100	78	100	100	100
Kalamazoo	260770008	5				98	83	29
Karnack	482030002	5	87	100	60	100	92	75
Kaufman	482570005	5	100	100	83	83	75	83
Kelo	460990006	5	100	100	83	100	100	100
Kingsport	471631007	5	100	100	65	82	100	100
Lake Forest Park	530330024	6	79	100	40	100	100	100
Lancaster	420710007	5	100	100	80	100	100	100
Laurel	280670002	5	100	100	60	100	100	100
Lawrence County	470990002	5	74	97	80	100	100	100
Lawrenceville	420030008	6	100	100	90	91	100	100
Lawrenceville Special	420030008	6	100	100	90	91	100	100
Lenoir Community College	371070004	5	100	100	54	100	100	77
Lewis	120571075	5	100	100	90	99	100	89
Lexington Health Department	210670012	5	83	100	65	100	100	100
Liberty	290470005	5	100	100	79	100	100	100
Lindon	490494001	5	100	100	83	100	100	100
Lockeland School	470370023	5	100	100	83	100	100	100
London-Laurel County	211250004	5	100	100	80	100	100	100
Lorain	390933002	5	83	80	80	80	60	100
LPH	390610042	5	80	99	78	100	80	100
Lubbock	483030001	5			100	99	100	83
Luna Pier	261150005	5	100	77	83	100	83	100
Macon	130210007	5	100	50	66	100	100	100
Mae Drive	482011034	5	100	100	100	100	83	100

Table 31. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch					
			35	36	37	38	39	40
Manchester	330110020	5	85	81	83	100	100	100
Manitowoc, Woodland Dunes site	550710007	5	100	100	67	100	100	100
Maple Canyon	390490081	6	99	100	83	100	100	80
Maple Leaf	530330038	6	100	100	75			
Mauriceville	483611100	5	92	100	92	83	100	99
Mayville Hubbard Township site	550270007	5	100	100	90	100	100	100
McDonald Observatory	482430004	5	68	100	100	83	100	100
McMillan Reservoir	110010043	5	100	100	88	89	88	100
Mendenhall	370810013	5	100	98	83	100	100	100
Mesa County Health Department	080770003	5	100	100	83	100	100	100
Middletown	390171004	5	100	100	83	100	100	100
Midlothian Tower	481390015	5	100	100	100	100	60	100
Millbrook	371830014	5	100	100	80	100	100	100
Mille Lacs	270953051	5	91	100	70	100	100	81
Mingo	292070001	5	90	100	90	100	100	78
Missoula County Health Dept.	300630031	5	100	100	90	99	100	100
MLK	100032004	5	60	100	83	100	62	80
MN - Rochester	271095008	5	97	100	83	52	100	100
MOMS	011011002	5	100	100	83	100	100	100
Nampa NNC	160270004	5	100	100	70	91	100	100
New Baltimore SuperSite	245100053	5	100	99				
New Brunswick	340230006	5	100	89	86	99	90	100
New Brunswick (Collocated)	340230006	6	81	75	80	100	100	100
New Garden	420290100	5	100	100	80	100	100	100
NLR Parr	051190007	5	100	100	80	79	60	100
North Birmingham	010730023	5	100	89	90	100	90	100
North Los Angeles	060371103	5	99	100	83	100	100	75
Northbrook	170314201	5	93	96	78	100	100	98
NY Botanical Gardens	360050083	6	100	100	90	100	100	63
OCUSA Campus	401091037	5	100	100	80	100	100	100
Olive Street	530330048	6			55	80	100	100
Owensboro - KY Wesleyan College	210590014	5	80	100	67	100	100	100
Padre Island National Seashore	482730314	5				100	100	82
Paducah Middle School	211451004	5	100	100	83	60	100	100
Pearl City	150032004	5			100	100	100	100
Peoria Site 1127	401431127	5	100	100	90	100	100	100
PerkinstownCASNET	551198001	5	100	100	90	100	100	100
Perry County	420990301	5	100	77	83	100	100	100
PHILA - AMS Laboratory	421010004	7	100	100	84	100	89	92
Philips	270530963	5	100	100	88	100	100	100
Phoenix Supersite	040139997	7	100	90	79	92	90	90
Pinnacle State Park	361010003	5	100	100	90	91	100	100
Platteville	081230008	5	100	100	83	100	100	98
Pleasant Green (Central MO)	290530001	5	100	50	39	62	100	
Portland N. Roselawn	410510246	6	100	100	90	91	90	99
Portsmouth	330150014	5	99	100	90	93	100	100
Providence	010731009	5	99	100	83	100	77	100
Queens College	360810124	6	78	100	90	100	90	100
RBD	080410011	5	100	100	83	85	100	100

Table 31. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch					
			35	36	37	38	39	40
Reno	320310016	5	100	100	90	83	100	89
Riverside-Rubidoux	060658001	5	100	100	90	100	100	100
Riverside-Rubidoux (Collocated)	060658001	6	100	92	90	92	91	100
Roanoke	517700014	5	100	100	80	99	100	100
Rochester Fire Headquarters	360556001	5	100	90	80	99	99	100
Rome	131150005	5	100	100	80	99	100	100
Roxbury (Boston)	250250042	5	58	18	27	100		89
Roxbury (Boston) - collocated	250250042	6	73	50	89	82	90	100
Sacramento - Del Paso Manor	060670006	5	91	99	90	100	100	100
San Jose - Jackson Street	060850005	5	100	89	88	100	100	88
Sault Ste Marie	260330901	5	100	100	90	100	90	100
Savannah	130510017	5	99	100	60	97	100	100
Scranton	420692006	5	82	100	83	100	100	100
Searcy	051450001	5	100	100	82	99	80	100
Seney NWR	261530001	5	97	100	100	85		
SER-DNR Headquarters	550790026	5	100	100	90	100	90	89
Shenandoah High School	180650003	5	100	100	67	98	100	100
Sherwood Is. St. Pk.	090019003	5	89	70	60	78	71	90
Shreveport Airport	220150008	5			100	100	100	100
Simi Valley	061112002	5	100	100	80	100	100	82
South DeKalb	130890002	5	100	90	70	100	100	100
Southwick Community Center	211110043	5	100	100	83	100	100	100
Spring Hill Elementary School	470931020	5	100	100	82	85	100	100
Springfield Pumping Station	170310057	5	100	100	83	100	100	100
St Theo	390350038	6	100	100	83	100	80	100
St. Paul Harding	271230871	5	100	100	83	100	100	100
State College	420270100	5	100	80	60	64	100	65
Sun Metro	481410053	5	100	100	100	83	100	100
Tallahassee Community College	120730012	5	100	100	83	100	100	80
Taylors Fire Station	450450009	5	100	100	83	100	98	98
Toledo Airport	390950026	5	100	100	40	100	100	99
TRNP - NU	380530002	5	97	100	83	87	62	82
Urban League	440070022	5	100	100	80	100	100	96
UTC	470654002	5	100	100	68	62	98	100
Washington Park	180970078	5	100	100	88	100	75	100
Waukesha, Cleveland Ave. Site	551330027	5	100	100	83	100	100	100
West 43rd Ave	040134009	5						100
Whiteface	360310003	5	100	100	90	82	100	78
Wilbur Wright Middle School	391130031	5	82	100	52	44	82	80
William Owen Elem. School	370510009	5	85	100	83	100	100	100
Woolworth St	310550019	5	89	97	76	65	97	73
Wylam	010732003	5	100	100	83	100	100	100
York	421330008	5	80	97	76	100	59	98