RTI/08858/01QAS March 25, 2004

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

July 8, 2003 through December 31, 2003

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

EPA Contract No. 68-D-03-038

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RTI INTERNATIONAL

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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 240-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 186 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 December 31, 2003, RTI is providing support for 240 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 December 31, 2003, we were providing support to 240 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples from July 8 through December 31, 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 during the time period of this request. 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, total carbon, and five new peaks (PK1C, PK2C, PK3C, PK4C, and PyrolC) 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 – No significant corrective actions have been taken.
- Elemental Analysis – Currently four XRF instruments are used for elemental analysis. Corrective actions taken for the RTI XRF instruments are described in Section 2.4.3.3.
- Ion Analysis – No significant corrective actions have been taken.
- OE/EC Analysis – No significant corrective actions have been taken.
- Sample Handling and Archiving Laboratory (SHAL) – No significant corrective actions have been taken; however, the problem of late shipments is discussed.
- Data Processing – A problem with blank reporting in the text files used by some states for their monthly review is discussed in Section 2.7.3.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

The laboratory's two weigh chambers were used to tare 11,477 filters between June 2003 and November 2003 (5,296 in Chamber 2, 6,181 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 **Table 1**.

Table 1. 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
11/24/03	High humidity	Humidity control system failed due to a damaged actuator. RTI HVAC personnel manually opened actuator and roughly positioned it to allow laboratory staff to continue working. RTI HVAC personnel installed new actuator on 12/01/03. Note: Due to low ambient winter relative humidity, impact on filters in the laboratory was minimal.

For the most part the Grav Lab humidity problem was limited to 11/24. Chamber 2 "alarmed out" around noon on 11/24. There were RH excursions above 40%, each lasting approximately 45 minutes-1 hour, that afternoon, but RH did not stay consistently above 40% that afternoon. Chamber RH peaked at 48% around 8:00 p.m. on 11/24. RH did not exceed 40% for the remainder of the work week. This was the short work week before the Thanksgiving holiday and no filters were weighed 11/27-30/2003. The actuator was replaced by RTI HVAC staff on Monday, 12/1/04.

The moisture pickup tests that we perform each year on the Teflon filter media for use in EPA's PM program (under subcontract to TRC Environmental) lead us to believe that the Teflon filters are not substantially affected by humidity increases (i.e., less than 10 μg weight gain after 24-hour exposure to air of 40% relative humidity, relative to its weight after 24-hour exposure to air of 35% relative humidity). Based on this finding, we were not concerned about any filters that were tared on 11/24. No sampled filters were weighed after 10:00 a.m. on 11/24; therefore, there need not be any concern about hydration of deposited material.

2.1.2 Description of QC Checks Applied

QC data for the laboratory (types and frequency as recommended in Guidance Document 2.12) are summarized in **Table 2**. PM2.5 STN sample throughput data for the Gravimetry Laboratory are summarized in **Table 3**.

2.1.3 Statistical Summary of QC Results

PM2.5 STN sample throughput data for the Gravimetric Laboratory are summarized in Table 2. QC data for the laboratory (types and frequency as recommended in Guidance Document 2.12) are summarized in Table 3.

Table 2. 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 S/N 41145 (Chamber 1) 10/25/02 Class 1 Calibration: 100.0008 mg ± 0.0024	99.998 mg ± 0.001 for 1128 weighings	Lab mean falls within tolerance interval.
		200-mg S/N 41147 (Chamber 1) 10/25/02 Class 1 Calibration: 200.0066 mg ± 0.0024	200.008 mg ± 0.001 for 1144 weighings	Lab mean falls within tolerance interval.
		100-mg S/N 41144 (Chamber 2) 10/25/02 Class 1 Calibration: 100.0068 mg ± 0.0024	100.002 mg ± 0.001 for 1015 weighings	Lab mean falls within tolerance interval.
		200-mg S/N 41148 (Chamber 2) 10/25/02 Class 1 Calibration: 200.0076 mg ± 0.0024	200.008 mg ± 0.001 for 1074 weighings	Lab mean falls within tolerance interval.
		New NIST-traceable Standard Reference Weights with Troemner Traceability Certificate - Certified 10/12/03: 100-mg S/N 58096 100-mg S/N 58097 200-mg S/N 58098 200-mg S/N 58099	N/A	New Purchase
Laboratory (Filter) Blanks	Initial weight ± 15 µg	376 total replicate weighings of 45 lab blanks	Mean difference between final and initial weight: 2 µg ± 3 µg	None of the 376 replicate weighings exceeded the 15 µg limit.

Table 2. Continued.

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Replicates	Initial weight ± 15 µg	1143 Pre-sampled (Tared) Replicates (5/28/03-11/18/03)	1 µg	Max = 4 µg; within required range
		1179 Post-sampled Replicates (6/23/03-12/31/03)	1 µg	Max = 3 µg; within required range
Polonium Strips	Each filter placed near strips for minimum of 60 seconds to minimum electrostatic charge	Replace strips every six months	N/A	New polonium strips placed in service 10/28/03. Manufacture date provided by vendor ranged from April 2003 to July 2003. RTI Radiation Safety Technician in RTI Office of Risk Management is working with Laboratory Manager to identify vendor who will provide strips with appropriately recent manufacture date.

Table 2. 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 2214004 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 1 µg 48 hours = 2 µg 72 hours = 1 µg 96 hours = -1 µg	Fall well within required range.
		Whatman Lot 3065003 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = -1 µg 96 hours = -1 µg	
		Whatman Lot 3085001 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -2 µg 72 hours = 0 µg 96 hours = 2 µg	
		Whatman Lot 3148691 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -1 µg 72 hours = -1µg 96 hours = 1 µg	
		Whatman Lot 1256009 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	
		Whatman Lot 3183001 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	
		Whatman Lot 3182001 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	
Calibrations Balances (Chamber 2, Balance B- S/N 1118311244 and Chamber 1, Balance C - S/N 1118252777)	Auto (internal) calibration daily	Daily	N/A	
	External calibration annually or as needed	Balance B last inspected and calibrated by Mettler Toledo on August 11, 2003 using NIST-traceable weights. Balance C last inspected and calibrated by Mettler Toledo on July 16, 2003 using NIST-traceable weights.	N/A	Inspection and calibration scheduled for July 2004

Table 3. Sample Throughput for the Gravimetry Laboratory

Number of Filters	Previous QA Report	This QA Report
Tared	17241 (8/28/02-5/27/03)	11477 (5/28/03-11/18/03)
Tared in Weigh Chamber 1	8964	6181
Tared in Weigh Chamber 2	8277	5296
Retained by Grav Lab for use as Lab Blanks	56 (0.32%)	45 (0.39%)
Not Transferred to SHAL; does not include lab blanks	0	0
Total Transferred to and Retained by SHAL for Sampler Modules	17185	11432
Returned to Grav Lab by SHAL for Final Weighing	16292 (94.8% return rate) (9/10/02-6/30/03)	11000 (96.2% return rate) (6/23/03-12/31/03)
Voided by SHAL and Grav Lab (% of samples returned)	1 (0.01%)	6 (0.05%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab (% of samples returned)	0	0
Flagged by Grav Lab for Laboratory Environmental Criteria Being Out of Limits (% of samples returned)	1366 (8.4%)	0
Filters reweighed at request of SHAL (% of samples returned)	13 (0.08%)	6 (0.05%)

The Gravimetric Laboratory's MDL and uncertainty were calculated in 2003 using data from lot acceptance blank batches run in 2001 and 2002. A 3-sigma MDL for gravimetry of 7.2 µg per filter was calculated, with a corresponding 1-sigma laboratory uncertainty of 2.4 µg per filter.

The laboratory also performed a study to determine the repeatability of measurements on exposed (sampled) filters. FRM program filters in five sample loading ranges (50-100 µg, 100-300 µg, 300-500 µg, 500-1000 µg, and >1000 µg) were selected for the study. FRM program filters were selected for the study because STN program filters are sent to other RTI laboratories for chemical analyses. The FRM filters selected are comparable to STN filters in that they are Teflon filters from the same manufacturer conditioned and weighed in the same chamber on the same balance by the same laboratory personnel following the same weighing SOP. Initial results indicate that the random variation for loaded filters does not differ greatly from blanks. However, there is a downward trend in sample weight over time. The Gravimetric Laboratory will continue this investigation in coordination with the RTI QA Officer.

2.1.4 Data Validity Discussion

The mean weight recorded for one of the 100-mg reference weights routinely weighed by the laboratory (S/N 41144) falls near the lower limit of its calculated tolerance interval. In response, the laboratory recently purchased new NIST-traceable Class 1 reference weights for use in both chambers. The new weights will replace the reference weights currently in use so that existing weights can be sent to the North Carolina Department of Agriculture (NCDA) Standards Laboratory for verification.

2.1.4.1 Invalidated Data – Six (0.05%) of the filters analyzed were invalidated by SHAL. Three of the six filters were invalidated because they had illegible filter ID numbers and anomalous loadings. One of the filters had not been analyzed. One filter had been placed in the wrong batch, and another filter had been sampled twice resulting in an anomalously high net mass loading.

2.1.5 Audits, Performance Evaluations, Training, and Accreditations

2.1.4.1 Audit by EPA NAREL/OAQPS – On September 16, 2003, a technical systems audit of the Gravimetry Laboratory was performed by personnel from the EPA National Air and Radiation Environmental Laboratory (NAREL) in order to inspect RTI's laboratory systems and operations for the analysis of air samples collected for the PM2.5 Speciation Trends Network (STN). System checks of the Gravimetry Laboratory included duplicate weighings of metallic reference weights supplied by NAREL and a duplicate weighing of a sampled STN filter pulled at random from the analysis queue by the NAREL auditor. In each case, good agreement was observed between NAREL reference values and RTI values.

A second part of the audit of the RTI Gravimetry Laboratory was the placement of a Dickson data logger provided by NAREL near the RTI Dickson data logger in order to judge the accuracy of the RTI data logger. It was determined that the average relative humidity (RH) recorded by the RTI data logger was consistently lower than that measured by the NAREL data logger, with the average for the RTI data logger being 35.3% and the average RH for the NAREL data logger being 37.1%. Good agreement for temperature recordings was observed between the two data loggers.

A third component of the audit consisted of the reweighing of seven RTI-tared filters at the NAREL facility in Montgomery Alabama. Good agreement was observed between the RTI tare weights and the NAREL duplicate weights. The audit concluded that the operation of the RTI Gravimetry Laboratory is continually improving, citing the addition of procedures to the SOP for monthly weigh chamber cleaning and the implementation of a new procedure for removing "nuisance" dust from filters by using a stream of air from a rubber pipet bulb.

2.1.4.2 EPA Performance Evaluation – Performance Evaluation (PE) samples consisting of Teflon filters and metallic reference weights were provided to the RTI Gravimetry Laboratory by EPA NAREL in mid-summer 2003. The filters were tared at RTI, sent to NAREL in Montgomery, Alabama, re-tared at the NAREL facility, and used for sampling in Montgomery. The sampled filters were reweighed at the NAREL facility and then returned to RTI for reweighing. RTI's final PE sample results were submitted to NAREL for evaluation in the fall of 2003. The results of the performance evaluation had not yet been received as of this writing.

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 4**. The use of these six systems was determined by the workload.

Table 4. 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 QA/QC Checks Applied

QA/QC checks for ion analyses are summarized in **Table 5**. 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) an RTI-prepared QC sample containing concentrations of each ion in the mid- to high-range of the calibration standard concentrations, (2) an RTI-prepared 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 5. 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 6 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 98.3 to 102.0% over the six month period; average recoveries for the two QA samples ranged from 98.2% to 101.2%.

Table 7 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 98.7% to 102.2% over the six month period; average recoveries for the two QA samples ranged from 97.3% to 101.1%.

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 8 shows percent recovery for nitrate and sulfate spikes for the six month period. The average recoveries of nitrate for ranged from 97.1% to 101.0%, while the average recoveries for sulfate ranged from 97.9% to 100.5%.

Table 9 presents filter blank (N BLANK) and reagent blank values for nitrate and sulfate over the six month period. The highest average value for filter blanks was 0.009 ppm (25 mL extract) for nitrate and 0.003 ppm for sulfate; the highest average reagent blank was 0.002 ppm for nitrate and 0.008 ppm for sulfate.

Table 6. Average Percent Recovery for Nitrate QA and QC Samples

Inst	Sample ID	Count	NO3 Conc., ug/mL	Av NO3 Rec	SD NO3	Min NO3	Max NO3
D6A	CPI QA-LOW	101	0.6	98.8%	1.2%	0.577	0.607
D6A	CPI QA-MED-HI	68	3.0	100.6%	1.2%	2.946	3.072
D6A	RTI QC-HIGH	91	6.0	101.4%	0.7%	5.970	6.233
D6A	RTI QC-LOW	124	0.6	98.9%	0.9%	0.583	0.613
D6A	RTI QC-MED	174	1.5	98.8%	1.8%	1.454	1.723
S1A	CPI QA-LOW	52	0.6	98.2%	1.8%	0.566	0.611
S1A	CPI QA-MED-HI	32	3.0	99.5%	1.7%	2.866	3.074
S1A	RTI QC-HIGH	38	6.0	101.1%	1.3%	5.939	6.279
S1A	RTI QC-LOW	63	0.6	98.5%	1.7%	0.560	0.630
S1A	RTI QC-MED	86	1.5	98.3%	1.7%	1.386	1.534
S2A	CPI QA-LOW	41	0.6	99.6%	0.6%	0.591	0.611
S2A	CPI QA-MED-HI	27	3.0	101.2%	0.8%	2.971	3.088
S2A	RTI QC-HIGH	32	6.0	102.0%	0.7%	6.044	6.221
S2A	RTI QC-LOW	51	0.6	100.1%	1.4%	0.585	0.649
S2A	RTI QC-MED	68	1.5	99.5%	0.9%	1.465	1.556
S3A	CPI QA-LOW	72	0.6	99.3%	1.7%	0.577	0.625
S3A	CPI QA-MED-HI	52	3.0	101.1%	1.3%	2.949	3.132
S3A	RTI QC-HIGH	61	6.0	101.7%	0.7%	6.034	6.217
S3A	RTI QC-LOW	100	0.6	99.6%	1.4%	0.584	0.629
S3A	RTI QC-MED	134	1.5	99.2%	0.9%	1.463	1.543

Table 7. Average Percent Recovery for Sulfate QA and QC Samples

Inst	Sample ID	Count	SO4 Conc., ug/mL	Av SO4 Rec	SD SO4	Min SO4	Max SO4
D6A	CPI QA-LOW	101	1.2	98.4%	1.1%	1.162	1.251
D6A	CPI QA-MED-HI	68	6.0	100.7%	0.8%	5.965	6.148
D6A	RTI QC-HIGH	91	12.0	101.6%	1.0%	11.830	12.446
D6A	RTI QC-LOW	124	1.2	99.5%	1.5%	1.161	1.286
D6A	RTI QC-MED	174	3.0	99.9%	1.2%	2.935	3.175
S1A	CPI QA-LOW	52	1.2	97.3%	1.3%	1.125	1.205
S1A	CPI QA-MED-HI	32	6.0	99.8%	1.5%	5.770	6.182
S1A	RTI QC-HIGH	38	12.0	101.5%	1.0%	11.866	12.443
S1A	RTI QC-LOW	63	1.2	98.7%	1.5%	1.128	1.227
S1A	RTI QC-MED	86	3.0	99.4%	1.6%	2.840	3.129
S2A	CPI QA-LOW	41	1.2	98.6%	0.6%	1.172	1.211
S2A	CPI QA-MED-HI	27	6.0	100.8%	0.5%	5.991	6.120
S2A	RTI QC-HIGH	32	12.0	102.0%	0.6%	11.958	12.367
S2A	RTI QC-LOW	51	1.2	100.0%	0.9%	1.172	1.227
S2A	RTI QC-MED	68	3.0	100.3%	0.8%	2.956	3.073
S3A	CPI QA-LOW	72	1.2	98.8%	1.0%	1.150	1.230
S3A	CPI QA-MED-HI	52	6.0	101.1%	0.9%	5.968	6.247
S3A	RTI QC-HIGH	61	12.0	102.2%	0.8%	11.967	12.525
S3A	RTI QC-LOW	100	1.2	100.1%	1.1%	1.170	1.243
S3A	RTI QC-MED	134	3.0	100.6%	0.9%	2.959	3.107

Figure 1. Nitrate Duplicate Analyses (ug/mL)

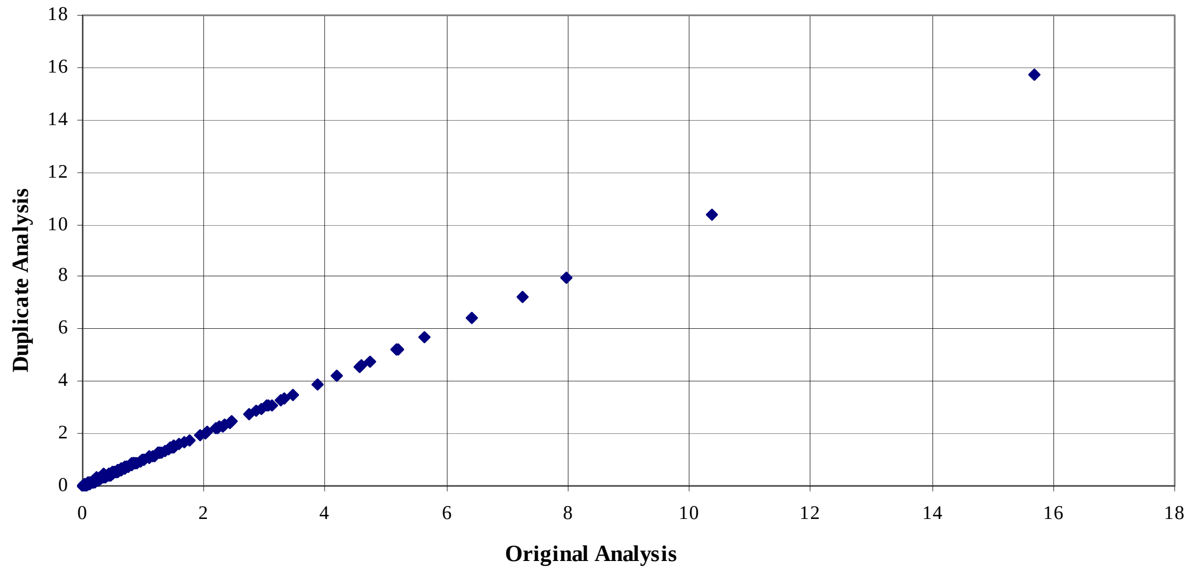


Figure 2. Sulfate Duplicate Analyses (ug/mL)

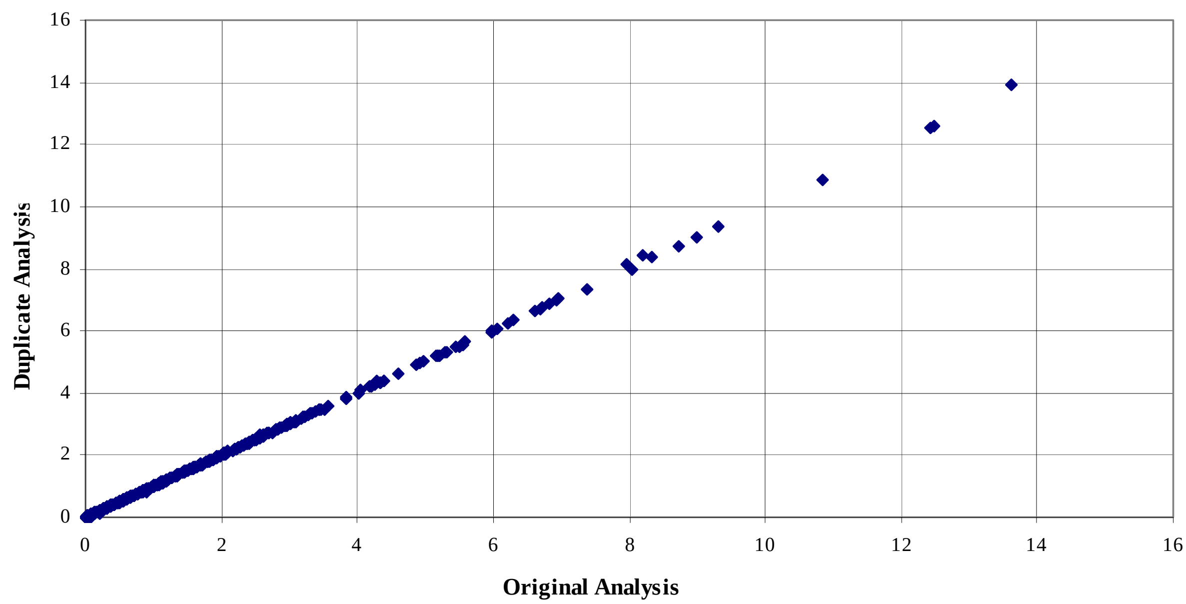


Table 8. Average Percent Recovery for Nitrate and Sulfate Spikes

Inst	D6A					
Analyte	Nitrate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.1%	99.0%	99.1%	97.7%	100.2%	99.3%
St Dev:	1.6%	1.1%	2.3%	1.0%	1.1%	1.9%
Count:	47	40	50	4	15	38
Min Recovery:	95.9%	96.6%	96.4%	96.8%	97.9%	91.0%
Max Recovery:	102.5%	100.9%	113.4%	99.1%	101.9%	102.2%
Inst	D6A					
Analyte	Sulfate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.5%	98.8%	98.4%	98.2%	100.5%	99.5%
St Dev:	1.6%	1.4%	2.9%	1.6%	0.7%	1.7%
Count:	47	40	50	4	15	38
Min Recovery:	94.9%	96.1%	83.6%	96.8%	98.6%	90.6%
Max Recovery:	102.4%	102.7%	102.2%	100.1%	101.5%	101.3%
Inst	S1A					
Analyte	Nitrate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	98.7%	99.3%	99.2%	99.0%	97.1%	
St Dev:	2.5%	1.6%	1.1%	1.4%	1.9%	
Count:	7	6	8	40	31	
Min Recovery:	96.1%	96.2%	97.9%	96.6%	93.2%	
Max Recovery:	101.8%	100.3%	101.1%	102.6%	99.7%	
Inst	S1A					
Analyte	Sulfate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	100.4%	100.2%	99.3%	99.5%	97.9%	
St Dev:	0.8%	1.0%	1.0%	1.4%	1.9%	
Count:	7	6	8	40	31	
Min Recovery:	99.3%	98.5%	97.9%	96.6%	93.6%	
Max Recovery:	101.3%	101.1%	100.6%	103.3%	100.6%	
Inst	S2A					
Analyte	Nitrate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	100.4%	98.9%		100.1%	99.9%	
St Dev:	0.7%	0.2%		2.6%	0.9%	
Count:	7	3		38	22	
Min Recovery:	99.5%	98.7%		97.3%	98.1%	
Max Recovery:	101.3%	99.0%		109.9%	101.9%	
Inst	S2A					
Analyte	Sulfate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	100.3%	99.6%		99.3%	99.4%	
St Dev:	0.8%	1.1%		1.1%	1.1%	
Count:	7	3		38	22	
Min Recovery:	99.0%	98.4%		96.0%	96.8%	
Max Recovery:	101.2%	100.6%		101.0%	100.8%	

Table 8. (Continued.)

Inst	S3A					
Analyte	Nitrate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.6%	101.0%	99.8%	99.2%	99.5%	99.0%
St Dev:	1.2%	4.7%	1.3%	1.3%	1.3%	1.0%
Count:	28	29	34	3	14	28
Min Recovery:	97.4%	98.8%	97.4%	98.3%	96.6%	97.5%
Max Recovery:	103.0%	124.8%	102.0%	100.7%	101.8%	101.2%
Inst	S3A					
Analyte	Sulfate					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.7%	100.1%	100.2%	100.2%	99.8%	99.6%
St Dev:	1.3%	1.2%	1.2%	0.5%	1.3%	1.0%
Count:	28	29	34	3	14	28
Min Recovery:	96.7%	97.2%	97.0%	99.7%	97.9%	97.0%
Max Recovery:	101.4%	103.3%	102.2%	100.5%	101.3%	101.0%

Table 9. Filter Blank (N) and Reagent Blank Values (ppm) for Nitrate and Sulfate

Inst	Blank Type	Count	Av NO3	STD NO3	Min NO3	Max NO3
D6A	N QC	64	0.008	0.011	0.000	0.037
D6A	REAGENT	174	0.002	0.006	0.000	0.024
S1A	N QC	87	0.003	0.009	0.000	0.039
S1A	REAGENT	74	0.001	0.003	0.000	0.019
S2A	N QC	12	0.008	0.013	0.000	0.039
S2A	REAGENT	68	0.000	0.003	0.000	0.018
S3A	N QC	53	0.009	0.013	0.000	0.039
S3A	REAGENT	108	0.001	0.004	0.000	0.030

Inst	Blank Type	Count	Av SO4	STD SO4	Min SO4	Max SO4
D6A	N QC	64	0.001	0.005	0.000	0.024
D6A	REAGENT	174	0.006	0.011	0.000	0.037
S1A	N QC	87	0.002	0.005	0.000	0.021
S1A	REAGENT	74	0.004	0.008	0.000	0.029
S2A	N QC	12	0.003	0.007	0.000	0.022
S2A	REAGENT	68	0.008	0.010	0.000	0.036
S3A	N QC	53	0.001	0.003	0.000	0.017
S3A	REAGENT	108	0.003	0.007	0.000	0.032

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 10 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 six month period ranged from 99.9% to 101.4%. The average recovery for the QC samples ranged from 100.0% to 100.9%.

Table 11 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 six month period ranged from 99.8% to 101.8%. The average recovery for the QC samples ranged from 100.3% to 100.8%.

Table 12 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 six month period ranged from 99.9% to 100.9%. The average recovery for the QC samples ranged from 99.6% to 100.8%.

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 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.

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

Inst	Sample	Count	Conc., ug/mL	Av NA rec	RSD NA	Min Na	Max Na
D5C	GFS 0.4 PPM QA	184	0.40	101.4%	2.5%	0.384	3.814
D5C	GFS 4.0 PPM QA	198	4.00	99.9%	0.8%	3.924	4.121
D5C	RTI 2.0 PPM QC	149	2.00	100.9%	1.2%	1.972	2.108
D5C	RTI 5.0 PPM QC	137	5.00	100.3%	1.1%	4.919	5.511
D6C	GFS 0.4 PPM QA	166	0.40	101.0%	2.8%	0.383	0.465
D6C	GFS 4.0 PPM QA	166	4.00	99.9%	0.8%	0.396	4.100
D6C	RTI 2.0 PPM QC	131	2.00	100.6%	1.2%	1.966	2.120
D6C	RTI 5.0 PPM QC	120	5.00	100.0%	0.6%	4.934	5.091

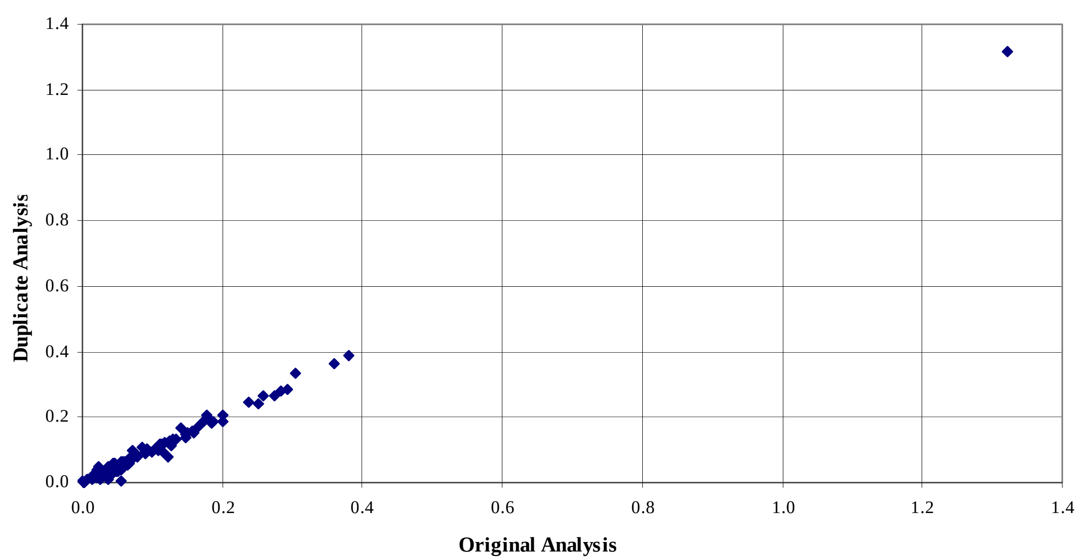
Table 11. Average Percent Recovery for Ammonium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av NH4 rec	SD NH4	Min NH4	Max NH4
D5C	GFS 0.4 PPM QA	184	0.40	101.8%	1.8%	0.383	0.752
D5C	GFS 4.0 PPM QA	198	4.00	100.1%	0.9%	3.901	4.155
D5C	RTI 2.0 PPM QC	149	2.00	100.4%	1.3%	1.935	2.079
D5C	RTI 5.0 PPM QC	137	5.00	100.8%	1.0%	4.950	5.287
D6C	GFS 0.4 PPM QA	166	0.40	100.6%	2.1%	0.381	0.433
D6C	GFS 4.0 PPM QA	166	4.00	99.8%	0.8%	0.408	4.087
D6C	RTI 2.0 PPM QC	131	2.00	100.3%	1.3%	1.909	2.170
D6C	RTI 5.0 PPM QC	120	5.00	100.5%	0.8%	4.823	5.141

Table 12. Average Percent Recovery for Potassium QA and QC Samples

Inst	Sample	Count	Conc., ug/mL	Av K rec	SDK	Min K	Max K
D5C	GFS 0.4 PPM QA	184	0.40	100.9%	3.7%	0.317	0.546
D5C	GFS 4.0 PPM QA	198	4.00	100.3%	0.8%	3.876	4.144
D5C	RTI 2.0 PPM QC	149	2.00	100.8%	1.3%	1.920	2.100
D5C	RTI 5.0 PPM QC	137	5.00	100.3%	0.8%	4.902	5.210
D6C	GFS 0.4 PPM QA	166	0.40	100.2%	1.4%	0.381	0.420
D6C	GFS 4.0 PPM QA	166	4.00	99.9%	0.6%	0.415	4.058
D6C	RTI 2.0 PPM QC	131	2.00	100.2%	1.0%	1.937	2.107
D6C	RTI 5.0 PPM QC	120	5.00	99.6%	0.7%	4.873	5.073

Figure 3. Sodium Duplicate Analyses (ug/mL)



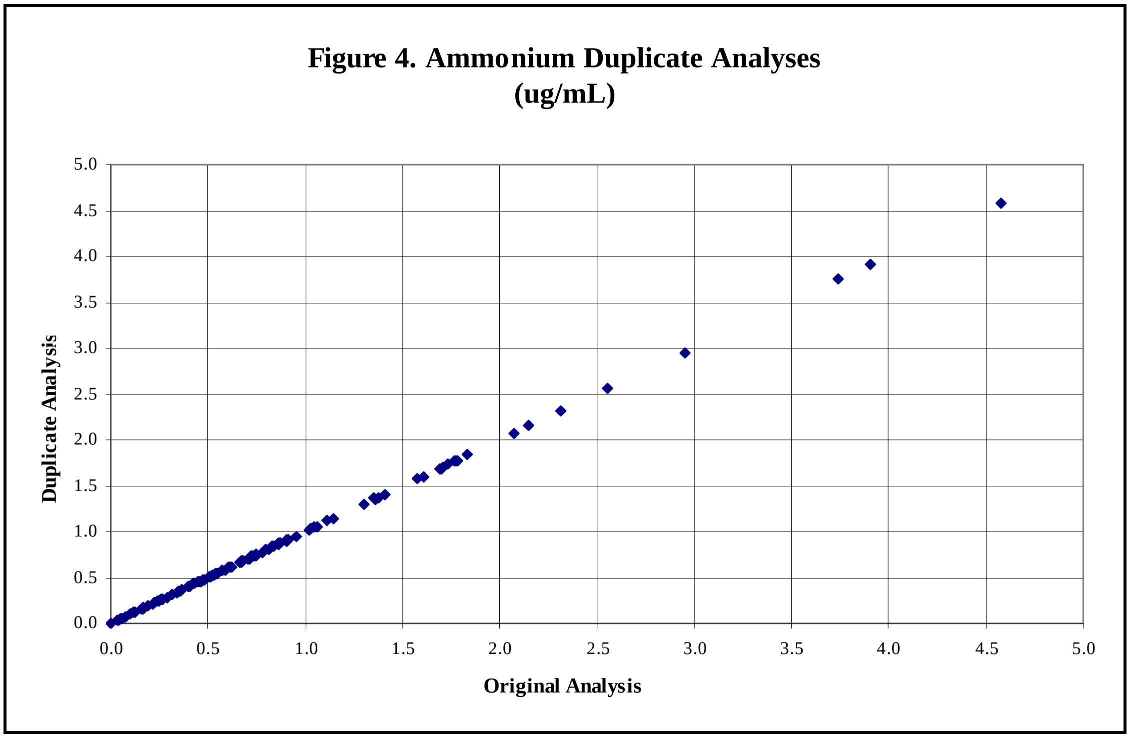


Figure 4. Ammonium Duplicate Analyses
(ug/mL)
Duplicate Analysis
Original Analysis
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

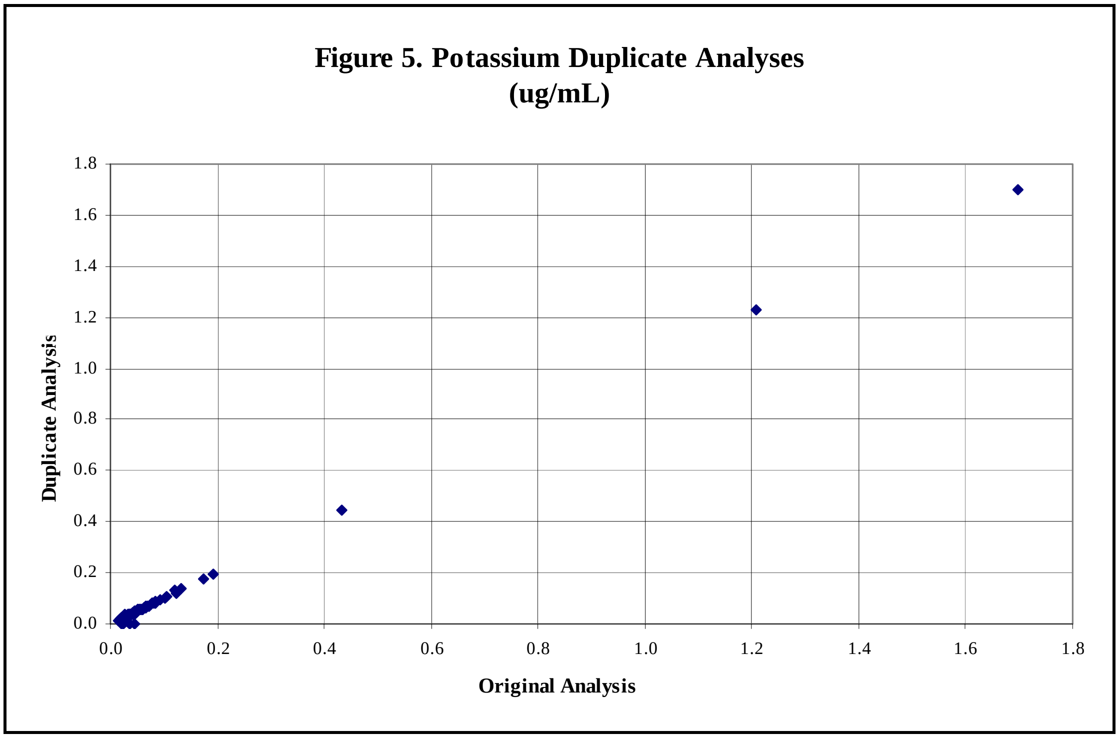


Figure 5. Potassium Duplicate Analyses
(ug/mL)
Duplicate Analysis
Original Analysis
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

Table 13 shows average percent recovery for spikes of sodium, ammonium, and potassium over the six month period. The average recovery values for ranged from 98.9% to 99.9% for sodium, 97.8% to 99.4% for ammonium, and 95.7% to 99.6% for potassium.

Table 13. Average Percent Recovery for Sodium, Ammonium, and Potassium Spikes

Inst	D5C					
Analyte	Sodium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.9%	99.3%	99.1%	99.6%	99.8%	99.3%
St Dev:	1.3%	1.4%	1.3%	1.5%	1.4%	1.3%
Count:	51	24	47	56	39	31
Min Recovery:	97.5%	95.3%	96.9%	96.5%	96.9%	97.5%
Max Recovery:	103.3%	102.1%	102.1%	103.4%	102.8%	102.0%
Inst	D5C					
Analyte	Ammonium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	98.0%	98.0%	97.8%	98.4%	99.0%	98.4%
St Dev:	2.2%	3.0%	3.1%	3.1%	2.7%	2.2%
Count:	51	24	47	56	39	31
Min Recovery:	92.3%	91.0%	91.0%	90.6%	90.1%	91.6%
Max Recovery:	105.1%	102.1%	102.7%	104.2%	106.3%	101.7%
Inst	D5C					
Analyte	Potassium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	96.0%	97.3%	96.9%	96.0%	97.3%	98.6%
St Dev:	2.2%	1.6%	1.4%	2.0%	2.4%	1.5%
Count:	51	24	47	56	39	31
Min Recovery:	89.1%	93.7%	93.7%	90.4%	88.7%	95.4%
Max Recovery:	100.8%	100.0%	98.9%	99.2%	101.2%	101.1%
Inst	D6C					
Analyte	Sodium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	99.7%	98.9%	99.4%	99.8%	99.4%	99.6%
St Dev:	1.6%	1.4%	1.6%	1.4%	1.3%	1.5%
Count:	37	38	34	27	35	37
Min Recovery:	96.6%	96.0%	93.8%	97.5%	96.9%	97.0%
Max Recovery:	104.7%	103.2%	102.3%	102.8%	101.9%	104.3%
Inst	D6C					
Analyte	Ammonium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	98.6%	98.2%	98.2%	98.4%	98.5%	99.4%
St Dev:	2.4%	2.5%	2.7%	2.2%	1.8%	2.4%
Count:	37	38	34	27	35	37
Min Recovery:	92.8%	92.0%	92.4%	92.8%	94.2%	92.0%
Max Recovery:	101.1%	100.6%	103.3%	101.1%	101.1%	103.4%
Inst	D6C					
Analyte	Potassium					
Date:	**Jul-03**	**Aug-03**	**Sep-03**	**Oct-03**	**Nov-03**	**Dec-03**
Avg Recovery:	96.5%	95.8%	95.7%	97.0%	97.2%	99.6%
St Dev:	1.5%	1.6%	2.5%	1.5%	1.2%	1.1%
Count:	37	38	34	27	35	37
Min Recovery:	92.5%	91.4%	89.1%	93.7%	95.0%	97.8%
Max Recovery:	99.2%	98.9%	99.2%	99.7%	99.6%	103.2%

Table 14 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 six month period were 0.000 ppm for the nylon filter blanks (25 mL extract) and 0.001 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.

Table 14. Filter Blank and Reagent Blank Values (ppm) for Sodium, Ammonium, and Potassium

Inst	TYPE	Count	Av Na	STD Na	Min Na	Max Na
D5C	N QC	152	0.000	0.002	0.000	0.014
D5C	Reagent Blank	157	0.001	0.004	0.000	0.030
D6C	N QC	66	0.000	0.004	-0.009	0.010
D6C	Reagent Blank	137	0.000	0.004	-0.013	0.018

Inst	TYPE	Count	Avg NH4	STD NH4	Min NH4	Max NH4
D5C	N QC	152	0.000	0.000	0.000	0.000
D5C	Reagent Blank	157	0.000	0.000	0.000	0.000
D6C	N QC	66	0.000	0.000	0.000	0.000
D6C	Reagent Blank	137	0.000	0.000	0.000	0.002

Inst	TYPE	Count	Avg K	STD K	Min K	Max K
D5C	N QC	152	0.000	0.000	0.000	0.000
D5C	Reagent Blank	157	0.000	0.000	0.000	0.000
D6C	N QC	66	0.000	0.000	0.000	0.000
D6C	Reagent Blank	137	0.000	0.000	0.000	0.000

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.

2.2.5 Corrective Actions Taken

No formal corrective actions were required during the reporting period.

2.2.6 Summary of Audit Findings and Recommendations

There were no problems identified during the annual audit of the RTI Ions Laboratory.

2.3 OC/EC Laboratory

The OC/EC Laboratory analyzed 11,241 quartz filter samples (1,833 collected under the original contract and 9,408 collected under the follow-on contract) during the period July 1, 2003, to December 31, 2003, and reported the results of those analyses to the main STN database.

Following award of the follow-on chemical speciation of $PM_{2.5}$ contract on July 7, 2003, and in accordance with RTI's proposal, two software changes were made on the STN OC/EC analyzers in the OC/EC Laboratory: the Sunset Lab OC/EC analyzer operation software was upgraded from version 81 to version 220, and the calculation software was upgraded from version 84 to version 130. The software upgrades were installed on July 16, 2003. The heating profile, which defines the STN OC/EC method, was not changed.

The last of the quartz filter samples collected under the original contract, which required reporting of OCX2, were analyzed on August 6, 2003. The OC/EC Laboratory began analyzing quartz filter samples collected under the new contract on the same day, August 6, 2003. The only changes made during the switch from old contract to new contract on August 6, 2003, were changes to the start integration times used to calculate filter loading for the four OC peaks on each analyzer. Again, the STN heating profile was not changed.

A final calculation software upgrade (from version 130 to version 132) was made on December 9, 2003. Calculation software version 130 allowed a maximum difference of 20 counts between beginning and ending FID responses in the calculation of the FID baseline, which caused an artificial enhancement of measured EC loading when the actual beginning-ending FID difference was slightly larger than 20 counts. Calculation software version 132 allows a maximum of 50 counts and provides more accurate loading measurements, especially for EC on filters with little or no EC.

Numbers of quartz filter samples analyzed during the reporting period using the analyzer operation and calculation software versions described above and under the two different contracts are as as shown in the table below.

Dates	Number of Samples	Analyzer Operation Software Version	Calculation Software Version	OC Fraction(s) Reported
7/1/03-7/15/03	534	81	84	OCX2
7/16/03-8/6/03	1,299	220	130	OCX2
8/6/03-12/31/03	9,408	220	130 & 132	OC Peaks

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	(1) Correlation Coefficient (R^2) $\geq$0.99 [with force-fit through 0,0], and (2) 93% to 107% recovery for all three standards	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) 93% to 107% 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 $\leq$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 0.09 µg C/cm^2 on March 4, 2003, (MDL at beginning of reporting period); 0.11 µg C/cm^2 on July 24, 2003 ; 0.16 µg C/cm^2 on September 8, 2003; and 0.11 µg C/cm^2 on October 7, 2003. The Second analyzer MDL was 0.13 µg C/cm^2 on June 17, 2003, (MDL at beginning of reporting period); and 0.13 µg C/cm^2 on July 22, 2003. The Third analyzer MDL was 0.09 µg C/cm^2 on March 4, 2003, (MDL at beginning of reporting period); and 0.04 µg C/cm^2 on July 22, 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.

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 (July 1, 2003, through December 31, 2003). Blanks run using the different combinations of software versions and contracts are color-coded in the figure. The instrument blank must be $\leq$0.3 µg C/cm^2 (bold line at the top of Figure OC/EC01). 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	235	248	246
Mean Response (µg C/cm^2)	0.016	0.031	0.027
Standard Deviation	0.018	0.029	0.031

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

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. Results for three-point calibrations run using the different combinations of software versions and contracts are color-coded in the figure. All three instruments met the $R^2 \geq 0.99$ (heavy line in Figure OCEC02) 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 8, 9, and 10** 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. Results for three-point calibrations run using the different combinations of software versions and contracts are color-coded in the figure. All three instruments met the 93-107% criterion (heavy lines in figures) for recovery for all three standards in every three-point calibration during the reporting period.

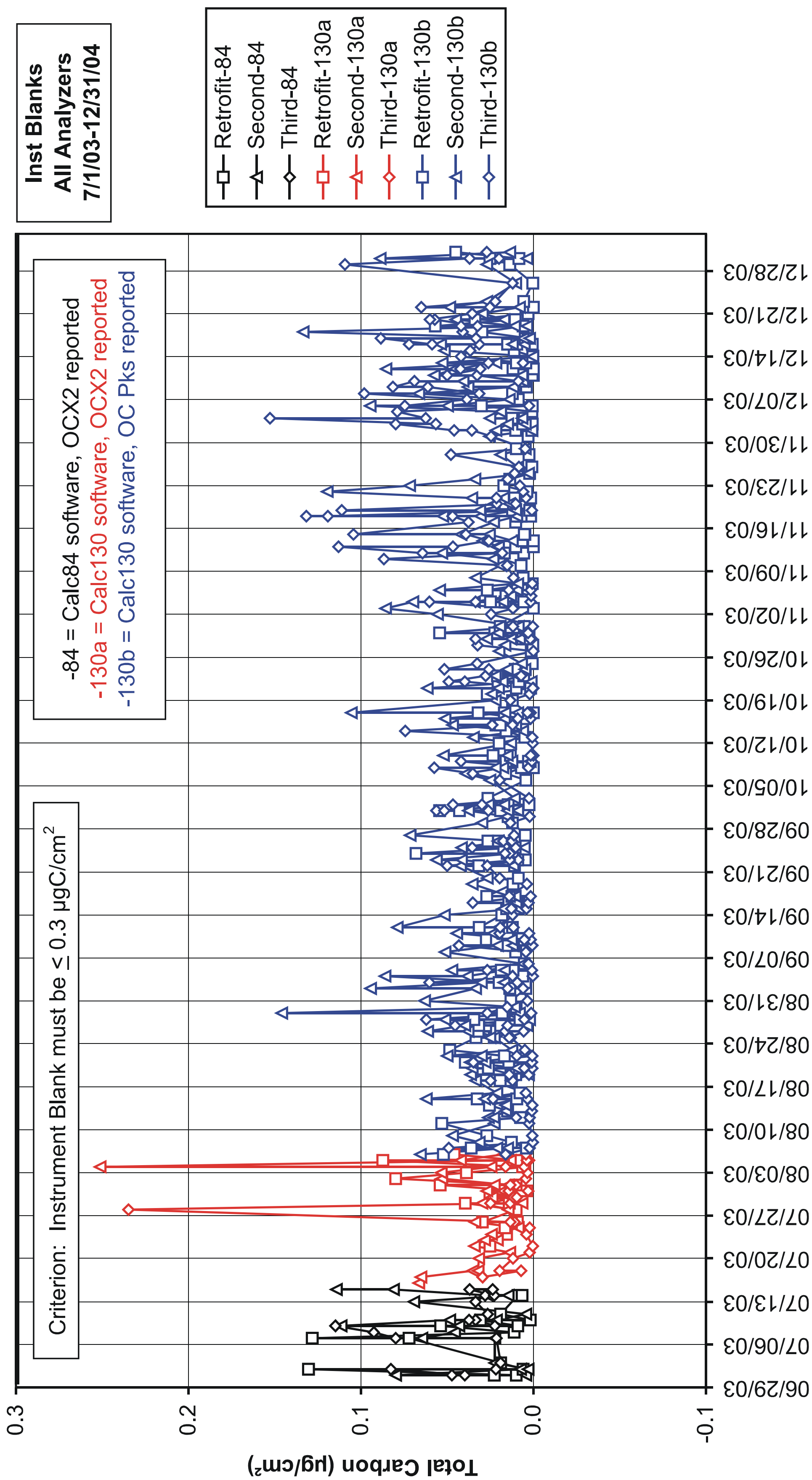


Figure 6. OC/EC Instrument Blanks: All STN OC/EC Analyzers, July 1, 2003, through December 31, 2003.

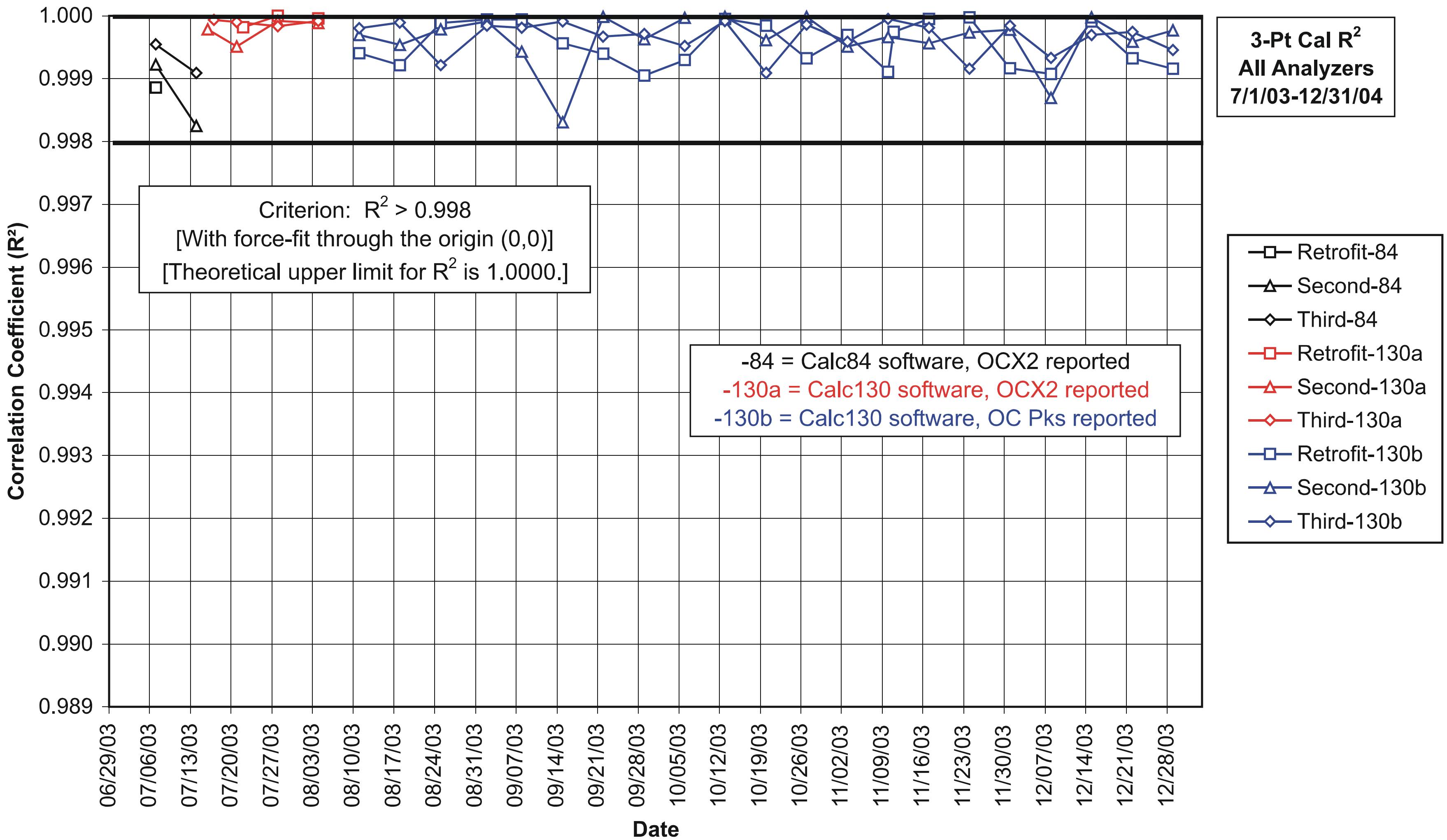


Figure 7. Linearity of Three-Point Calibration Plots: All STN OC/EC Analyzers, July 1, 2003, through December 31, 2003.

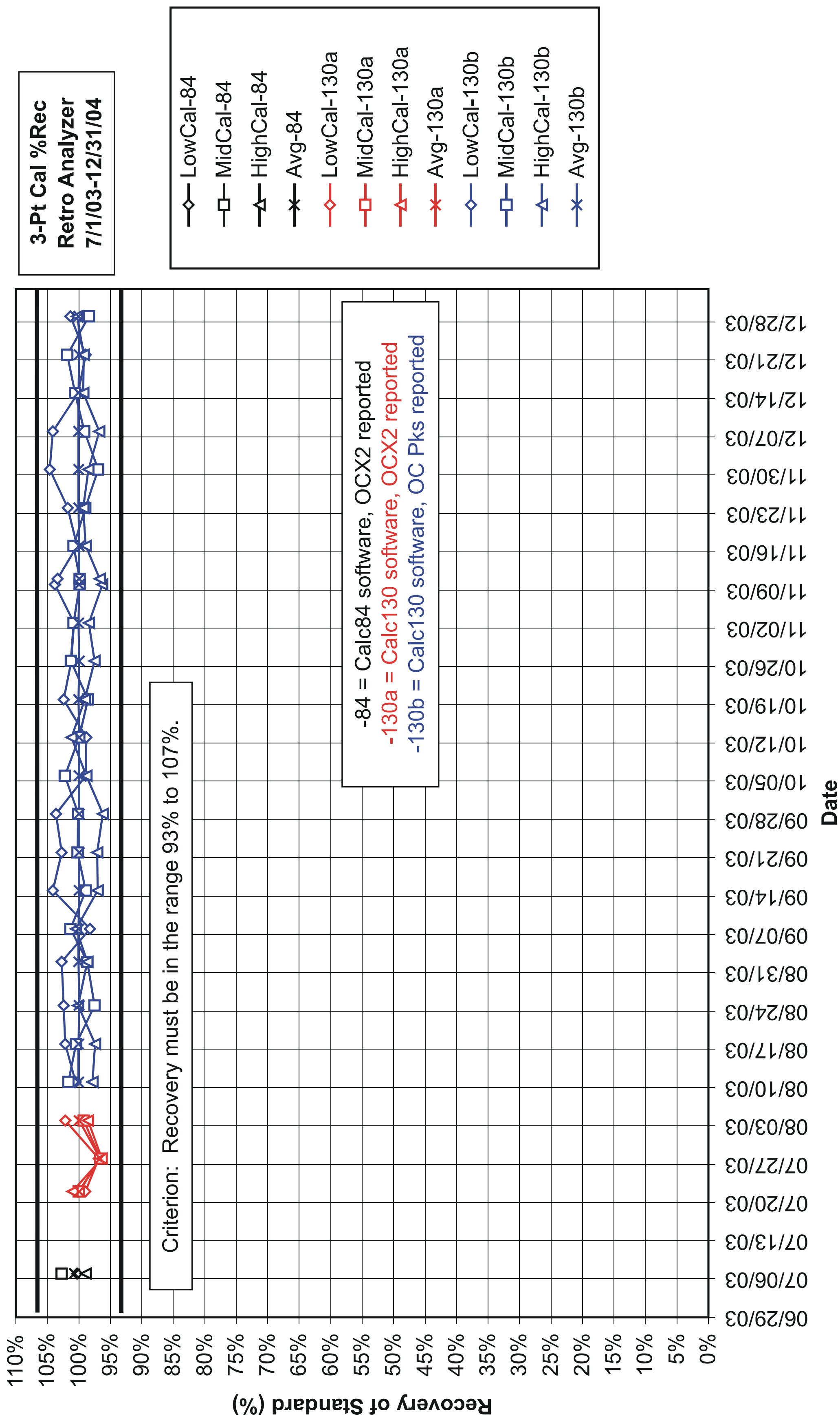


Figure 8. Percent Recoveries for Three-Point Calibration Standards: Retrofit OC/EC Analyzer, July 1, 2003, through December 31, 2003.

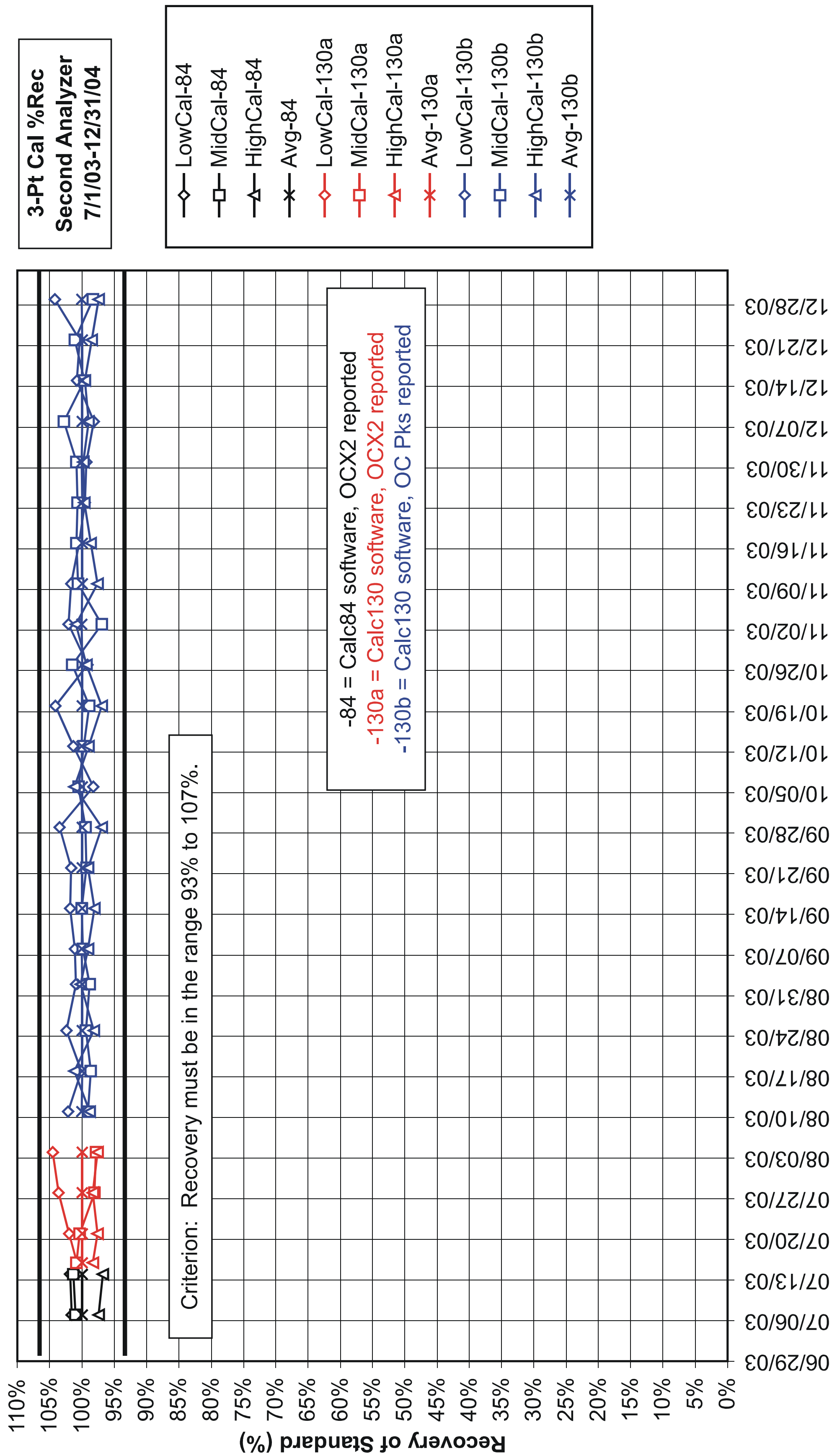


Figure 9. Percent Recoveries for Three-Point Calibration Standards: Second OC/EC Analyzer, July 1, 2003, through December 31, 2003.

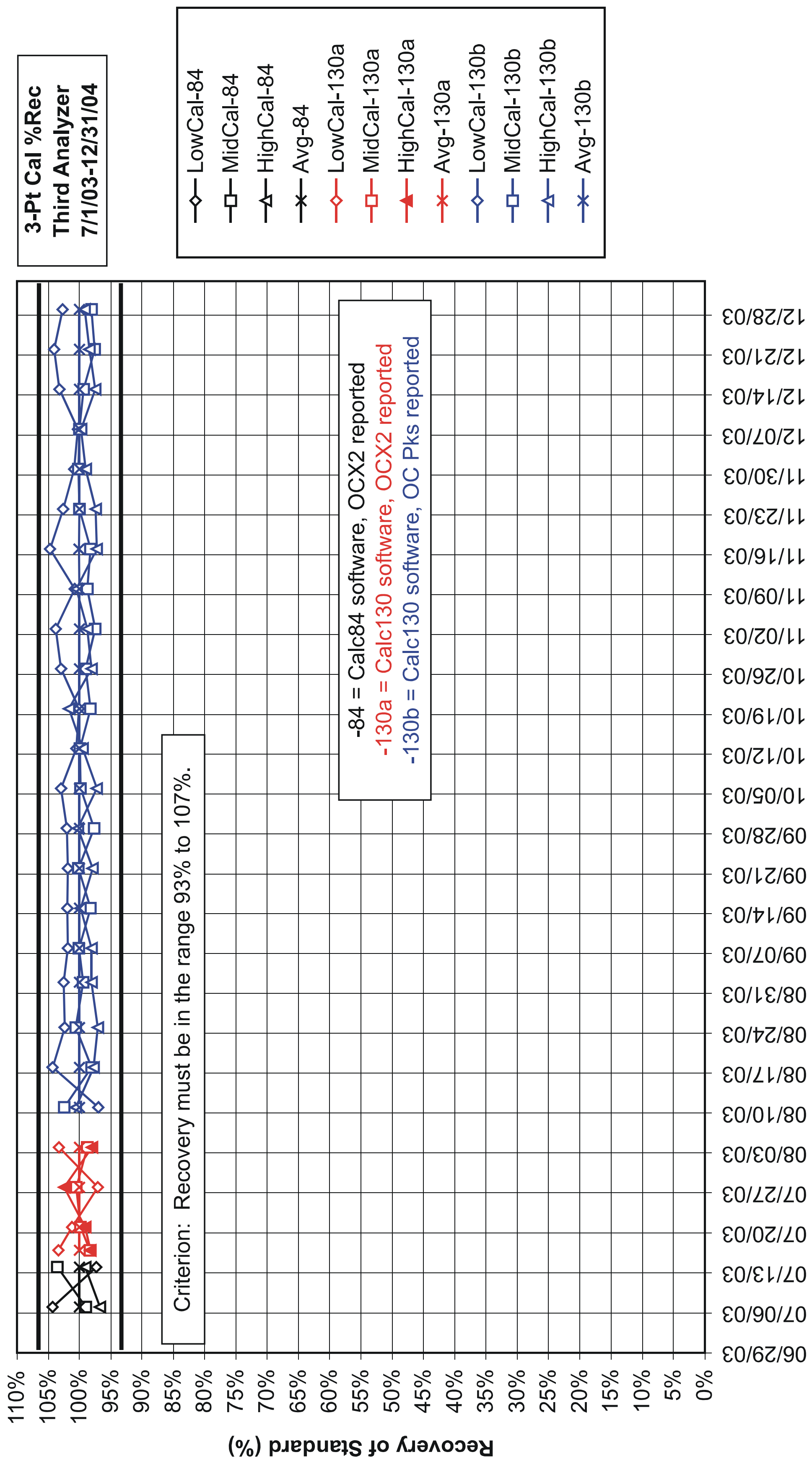


Figure 10. Percent Recoveries for Three-Point Calibration Standards: Third OC/EC Analyzer, July 1, 2003, through December 31, 2003.

Response factors for the flame ionization detector (FID) are used to monitor FID performance. **Figures 11, 12, and 13** 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. Results for three-point calibrations run using the different combinations of software versions and contracts are color-coded in the figure. 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 2.3.1. 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 14 shows the slopes of three-point calibration plots with force-fit through the origin for all three OC/EC analyzers during the reporting period. Results for three-point calibrations run using the different combinations of software versions and contracts are color-coded in the figure.

Figure 15 shows percent recovery for all daily calibration checks run on all three instruments during the reporting period. Results for daily calibration checks run using the different combinations of software versions and contracts are color-coded in the figure. All daily calibration checks met the acceptance criterion of 93% to 107% 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 in Section 2.3.1 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 16, 17, and 18** 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. Filters results that failed to meet the appropriate duplicate acceptance criterion were flagged as having a nonuniform filter deposit (LFU). None of the duplicate punches (66 on the Retrofit analyzer, 91 on the Second analyzer, and 84 on the Third analyzer) from filters collected under the old contract failed the appropriate duplicate criterion. Seven of the 363 duplicate analyses of filters samples collected under the new contract and run on the Retrofit OC/EC analyzer failed the appropriate duplicate criterion. Similar results were obtained for the other two OC/EC analyzers: 7 of 370 duplicates run on the Second analyzer and 5 of the 366 duplicates run on the Third analyzer failed the appropriate duplicate criterion.

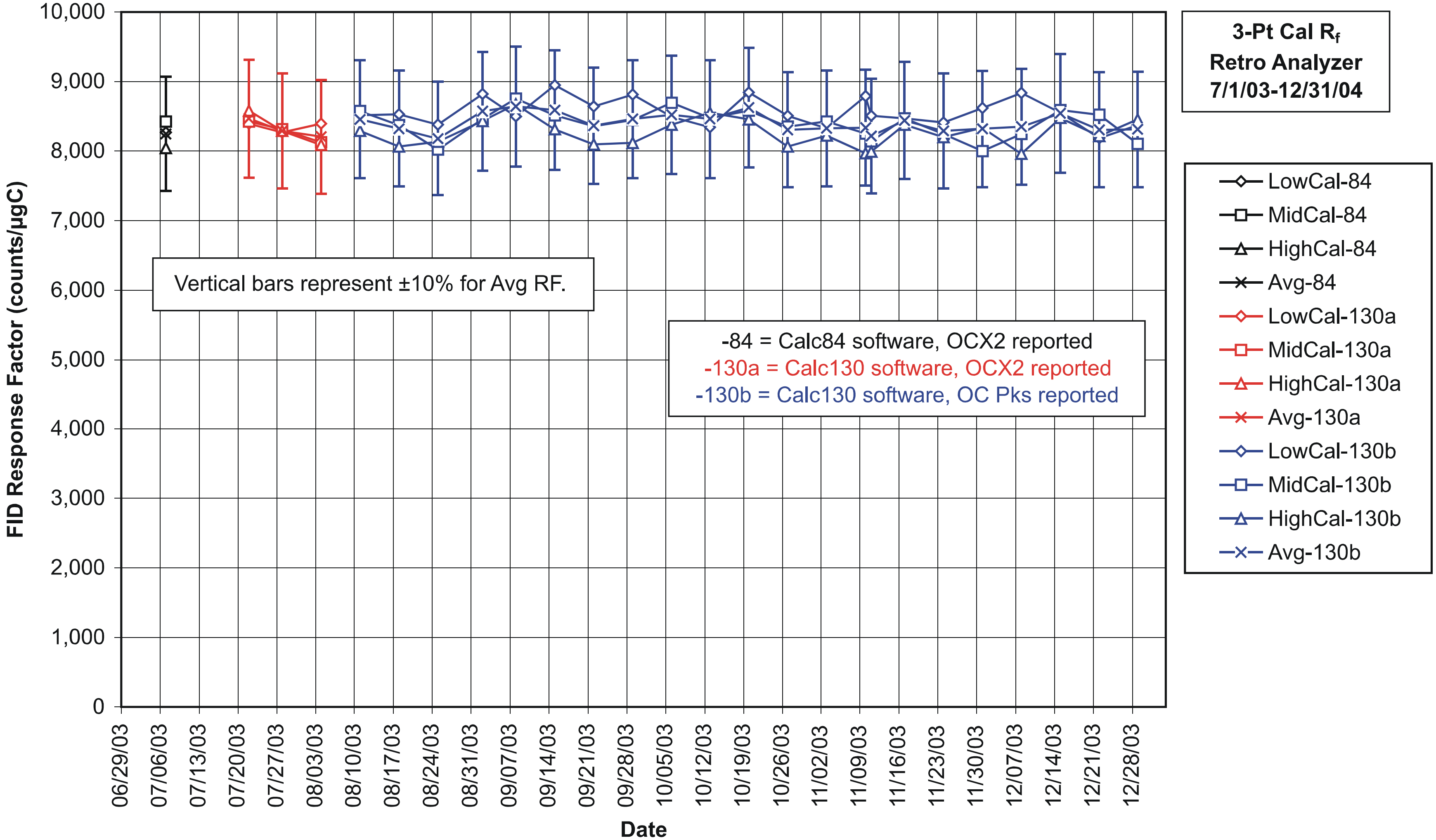


Figure 11. FID Response Factors for Three-Point Calibration Standards: Retrofit OC/EC Analyzer, July 1, 2003, through December 31, 2003.

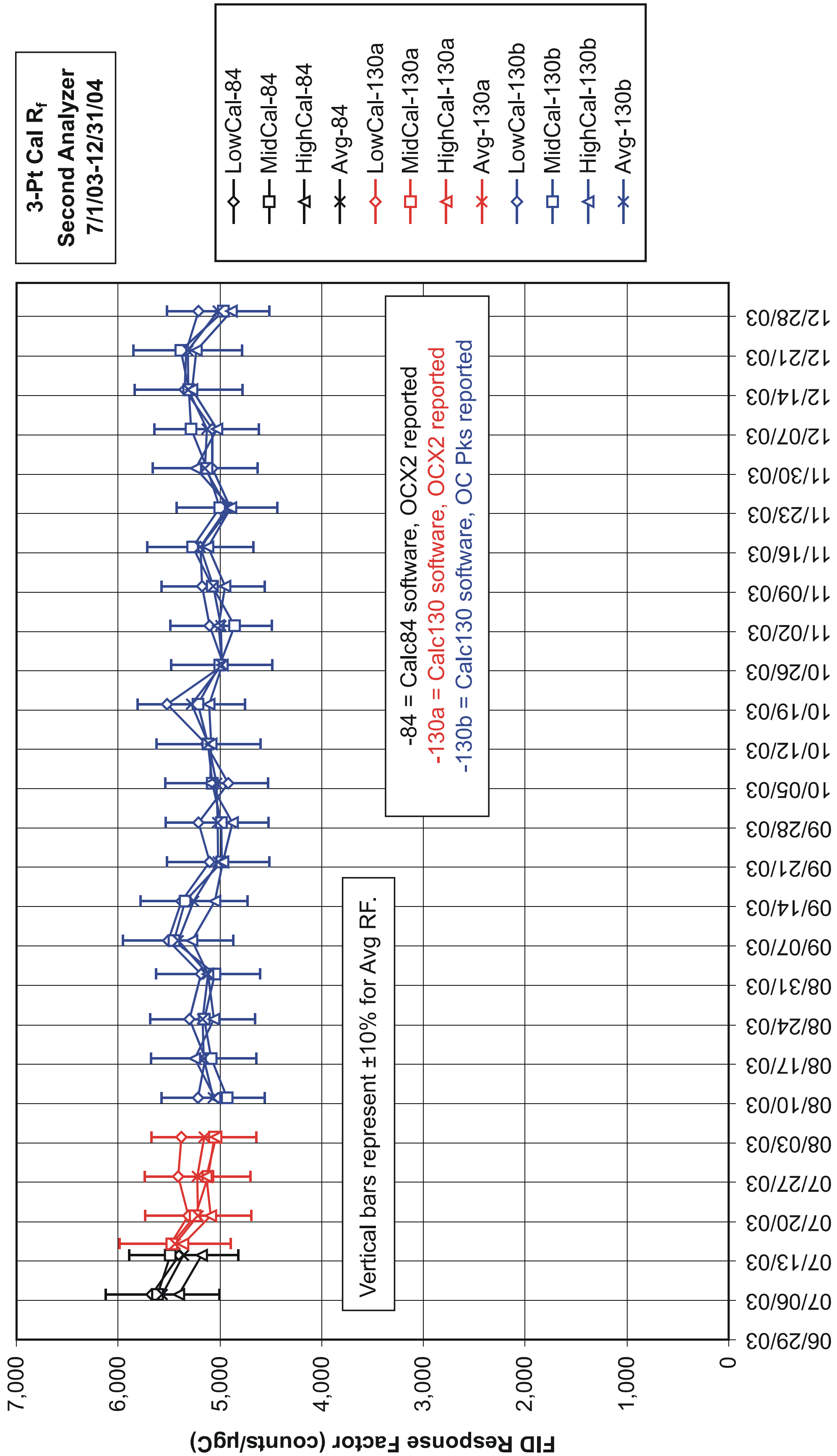


Figure 12. FID Response Factors for Three-Point Calibration Standards: Second OC/EC Analyzer, July 1, 2003, through December 31, 2003.

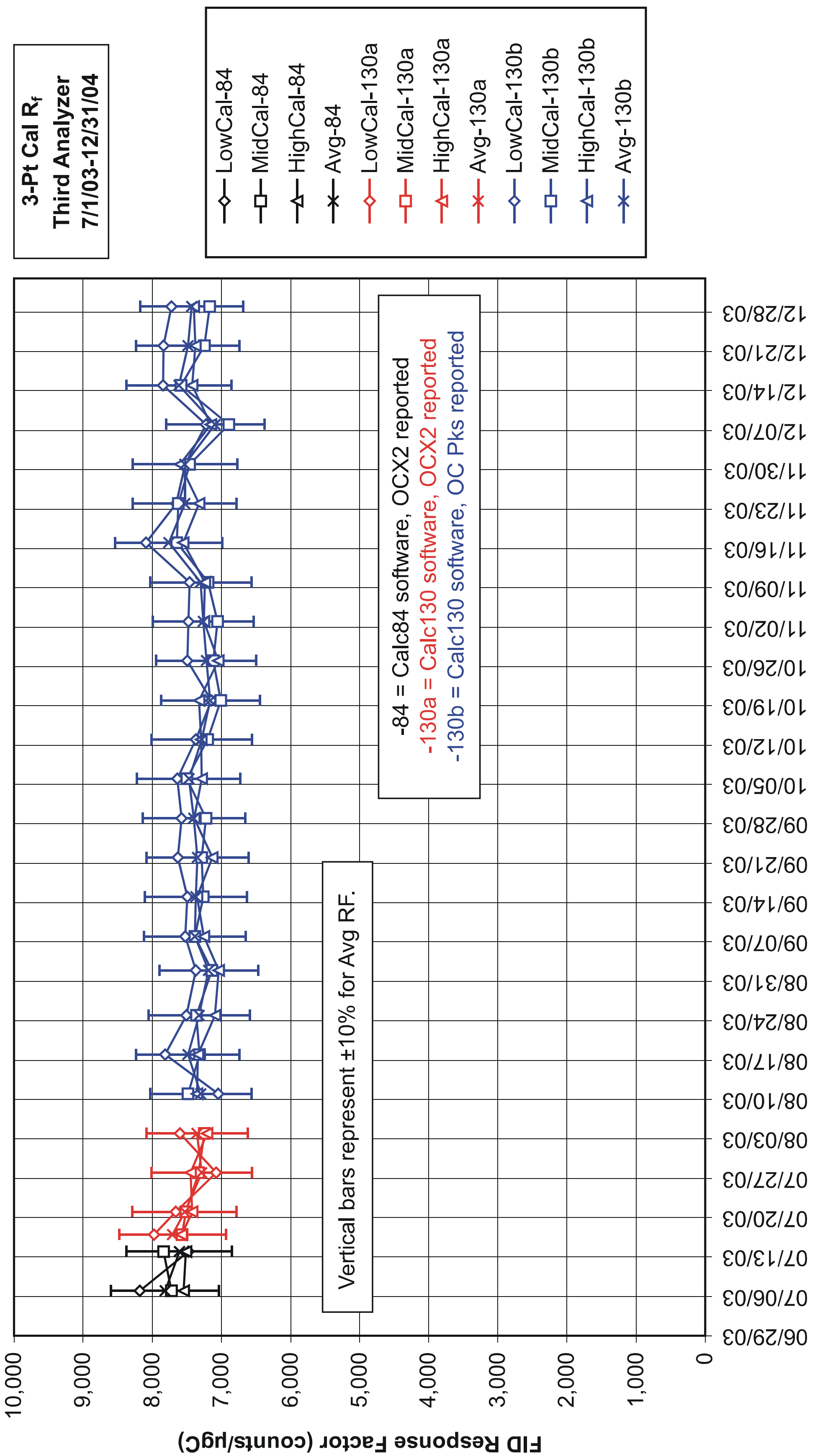


Figure 13. FID Response Factors for Three-Point Calibration Standards: Third OC/EC Analyzer, July 1, 2003, through December 31, 2003.

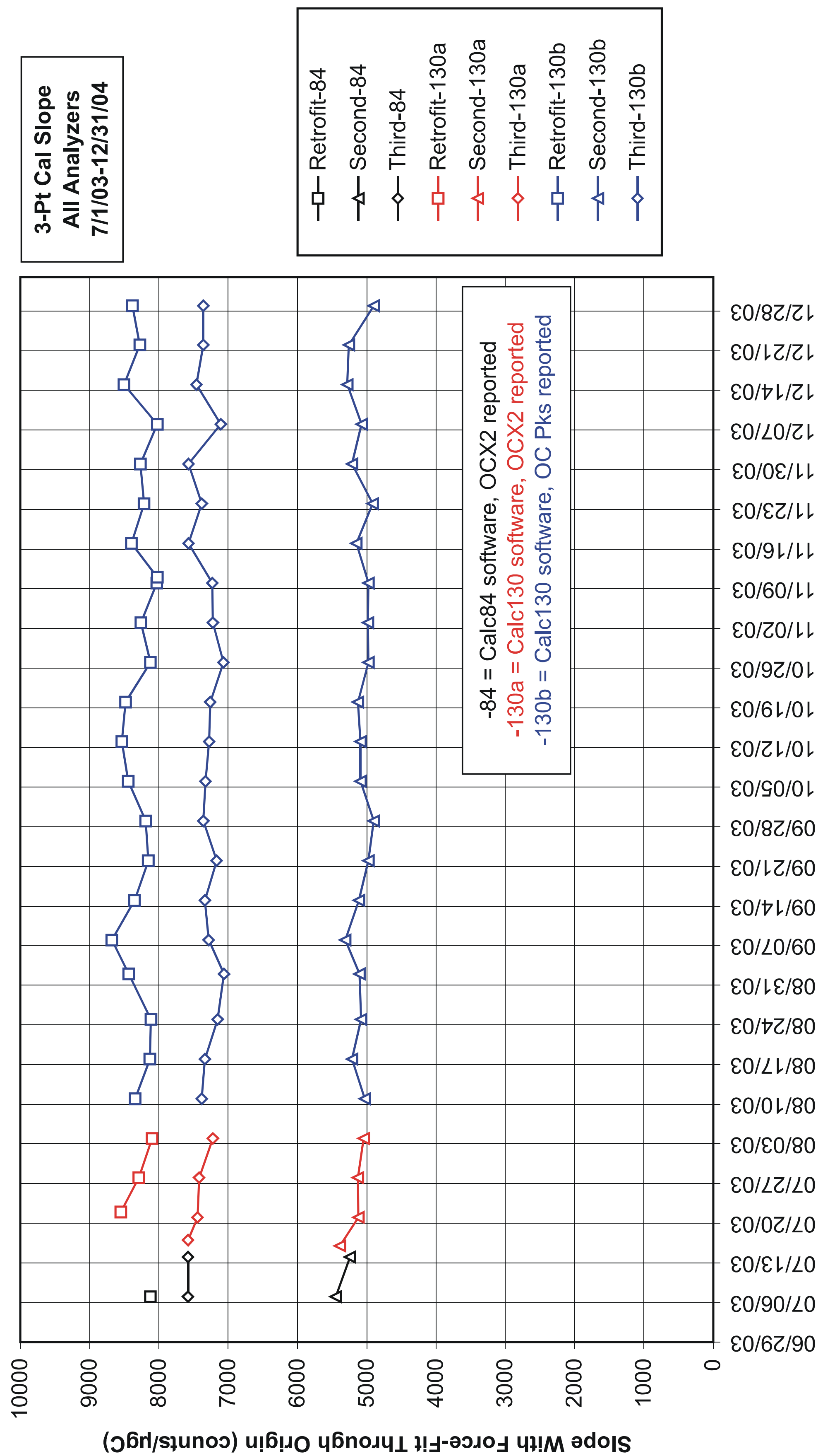


Figure 14. Slopes of Three-Point Calibration Plots With Force-Fit Through Origin (0,0): All STN OC/EC Analyzers, July 1, 2003, through December 31, 2003.

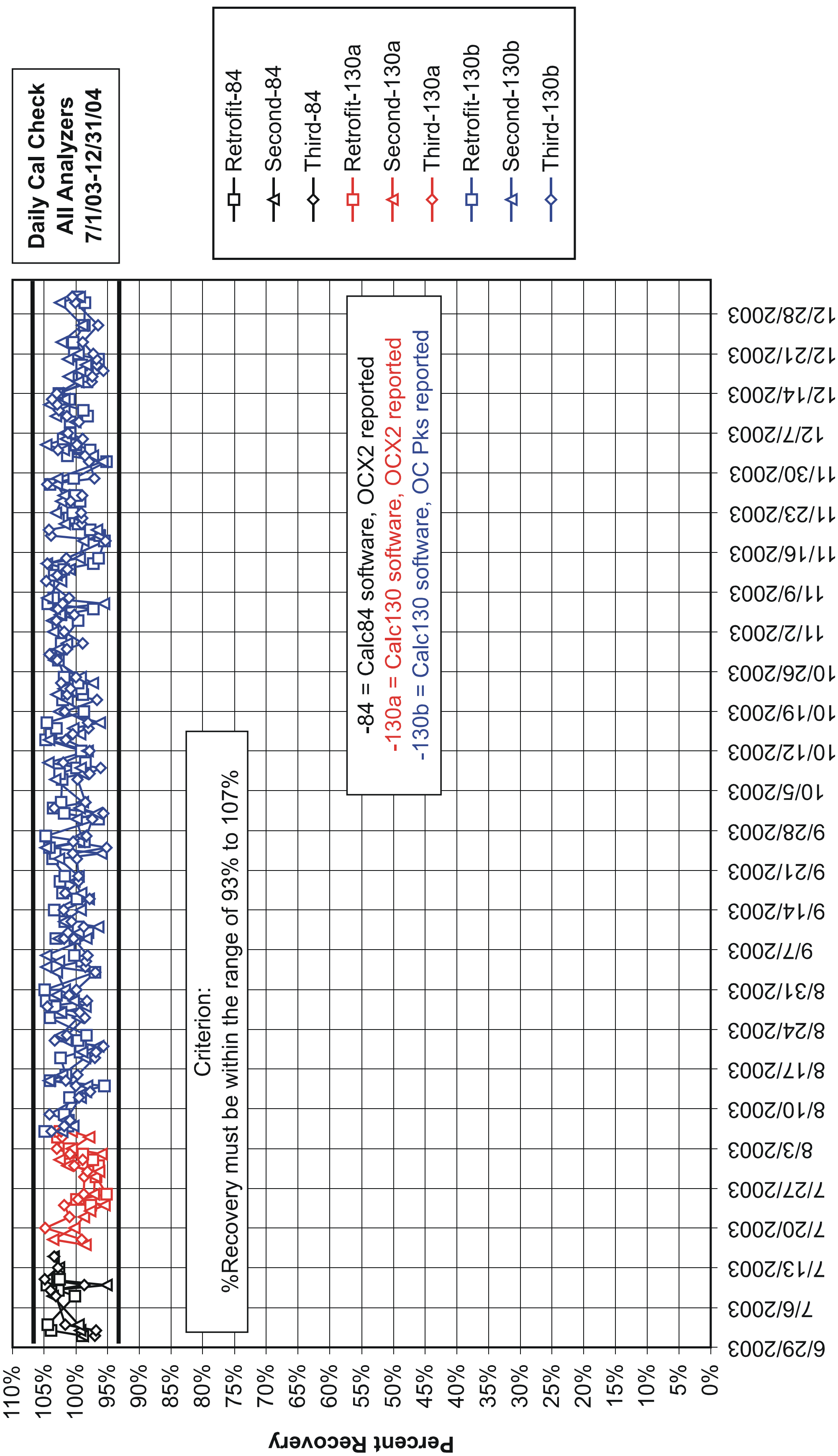


Figure 15. Daily Calibration Checks: All STN OC/EC Analyzers, July 1, 2003, through December 31, 2003.

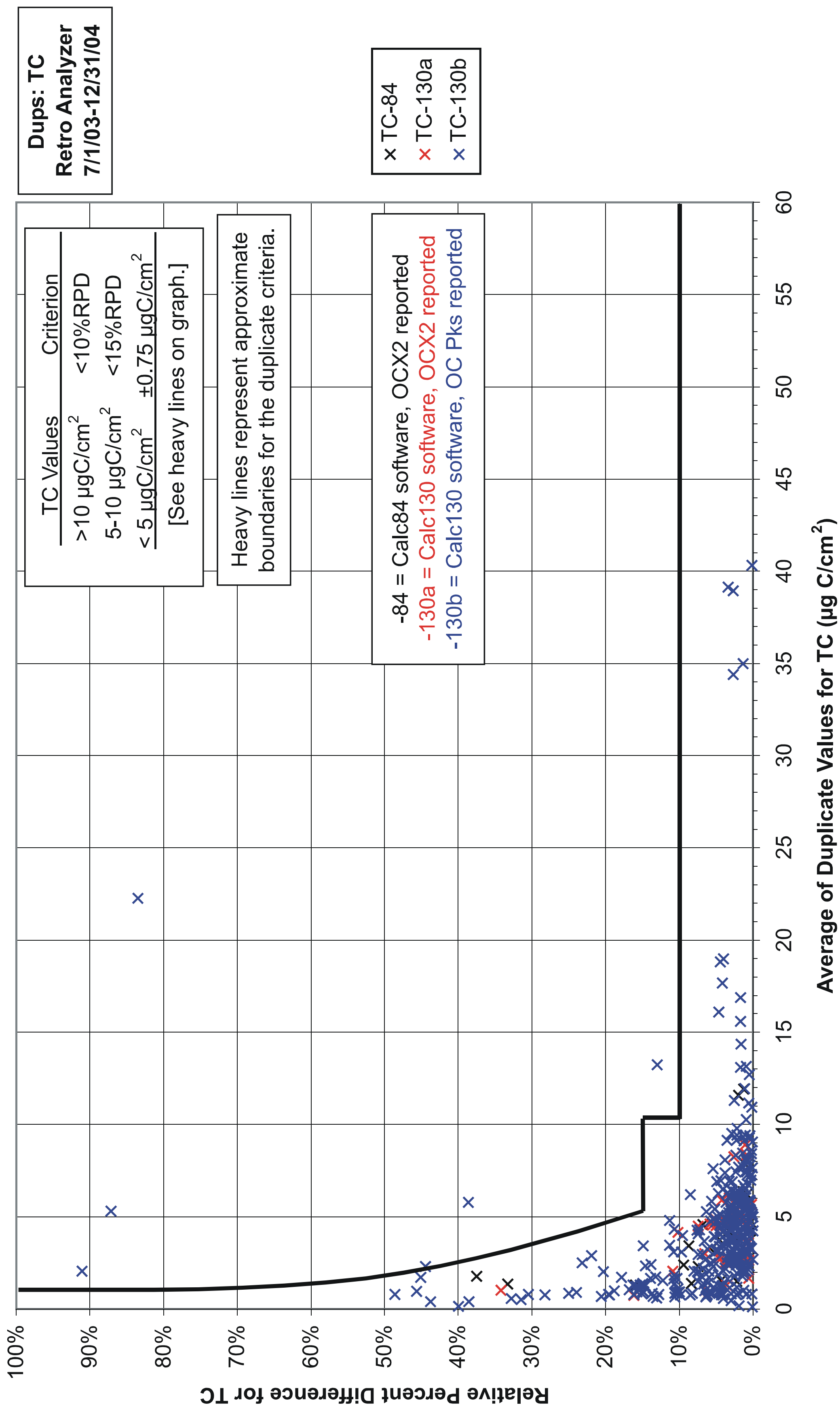


Figure 16: Relative Percent Difference of Duplicates vs. Average Value for TC: Retrofit OC/EC Analyzer, July 1, 2003, through December 31, 2003.

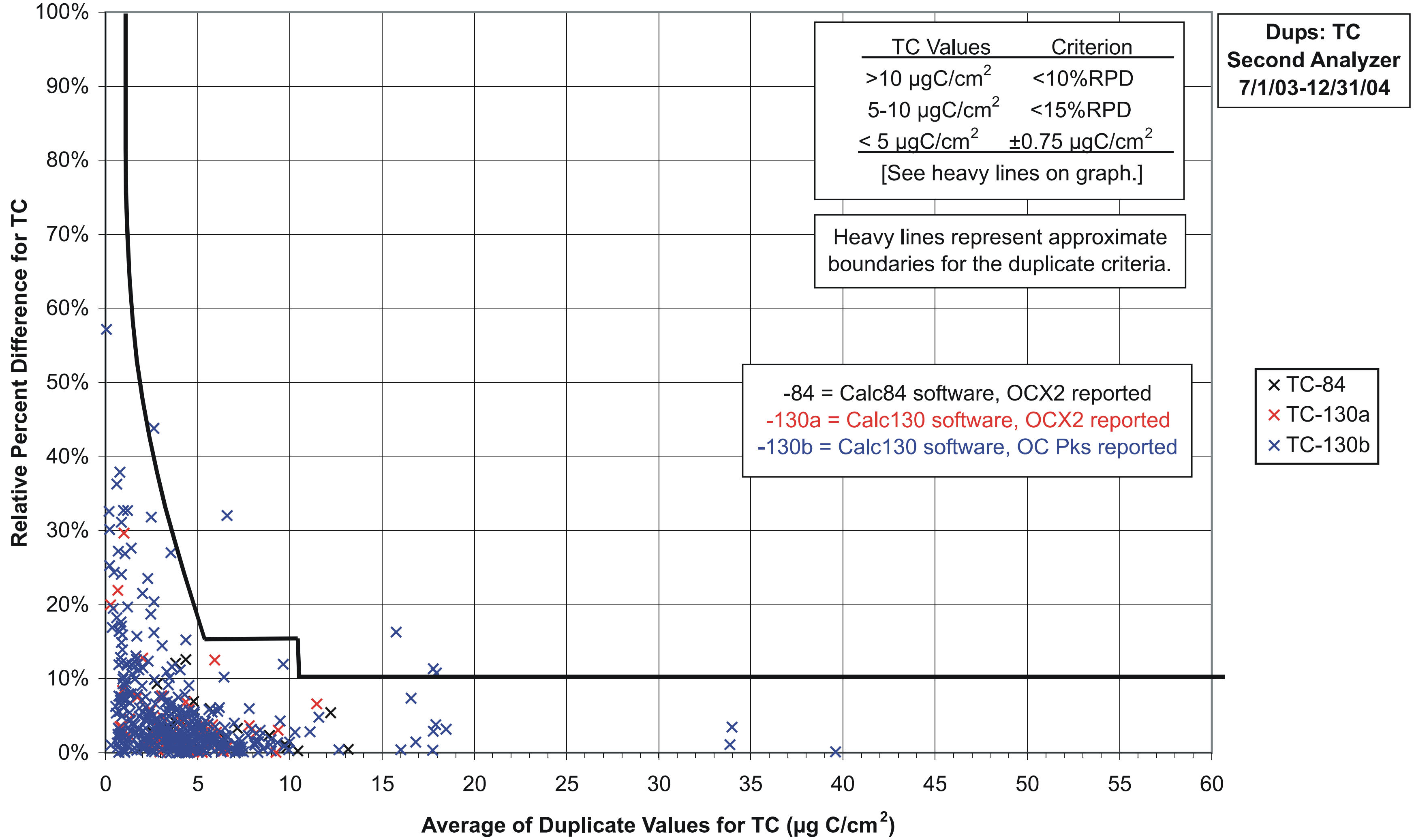


Figure 17. Relative Percent Difference of Duplicates vs. Average Value for TC: Second OC/EC Analyzer, July 1, 2003, through December 31, 2003.

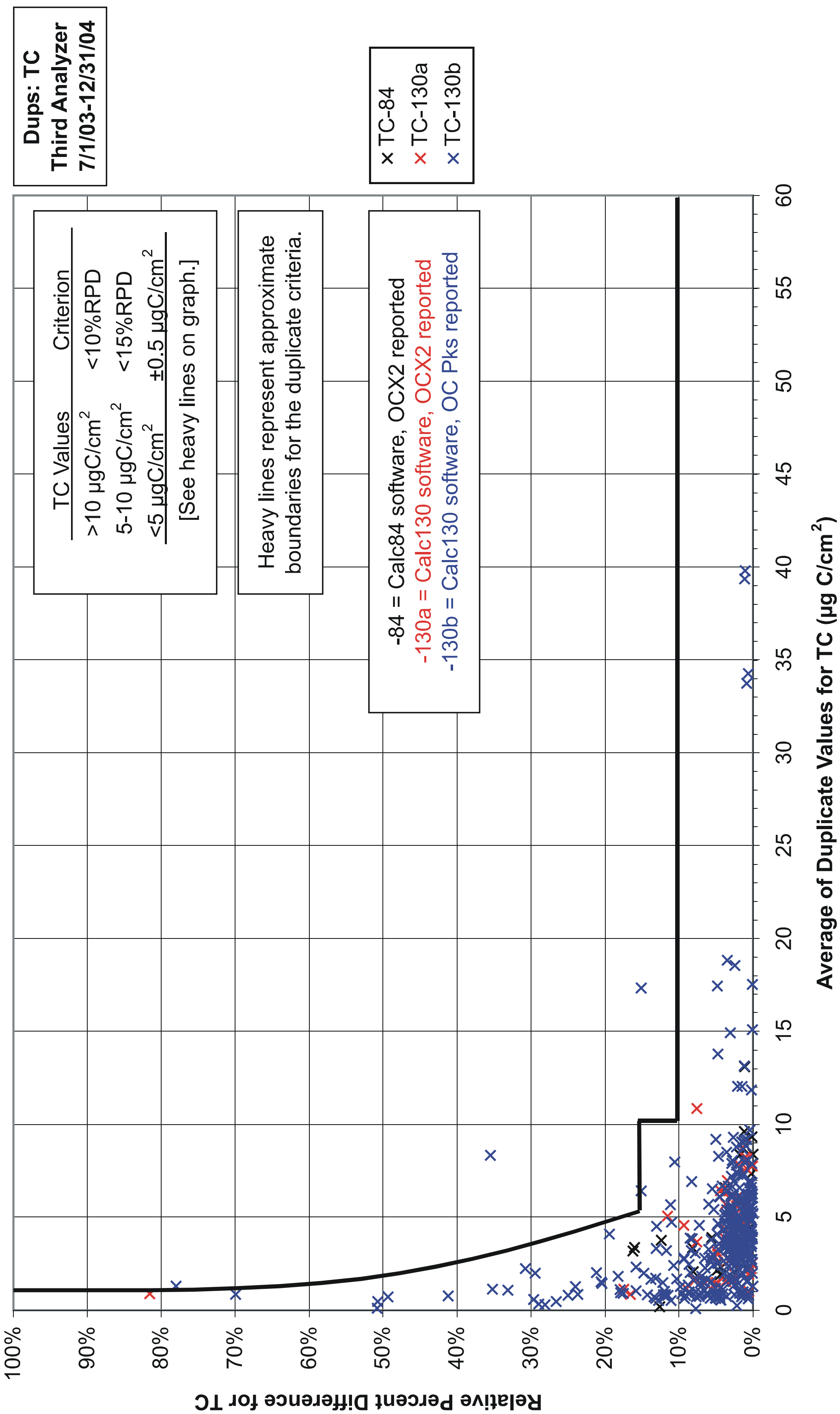


Figure 18. Relative Percent Difference of Duplicates vs. Average Value for TC: Third OC/EC Analyzer, July 1, 2003, through December 31, 2003.

In addition to OC, EC, and TC, the new speciation laboratory contract requires the reporting of fractions of OC (usually referred to as OC Peaks). The five new values reported include carbon evolved during each of the four temperature ramps (Pk1C, Pk2C, Pk3C, and Pk4C) under non-oxidizing conditions plus pyrolyzed carbon (PyrolC), which is used to correct OC for organic carbon that forms char (or light-absorbing carbon) under non-oxidizing conditions. Reporting of these additional fractions without the option of changing the heating profile presents additional challenges. The remainder of the figures in this section provide at least some insight into within-analyzer variability for OC, EC, and TC and for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC. The data points in each plot are color-coded, and the trend line equation (linear least-squares fit) is given along with the correlation coefficient (R^2) for each variable plotted. The data in the figures are all from samples collected under the new contract and analyzed at RTI between August 6, 2003, and December 31, 2003. In order to obtain reasonable data for within-instrument variability, results for duplicates that failed the appropriate duplicate criterion were not included in these plots; all of the data points shown are from duplicates that passed the appropriate duplicate criterion.

Figures 19, 20, and 21 show plots of sample vs. duplicate measurements for OC, EC, and TC on the Retrofit, Second, and Third analyzers, respectively. Correlation coefficients for all three fractions from all three analyzers were 0.98 or better.

Figures 22, 23, and 24 show plots of sample vs. duplicate measurements for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC on the Retrofit, Second, and Third analyzers, respectively. PyrolC on the Third analyzer plots (**Figure 24**) had a correlation coefficient of 0.919. Correlation coefficients for all remaining fractions from all three analyzers were 0.96 or better.

Figures 25, 26, 27, 28, and 29 show plots of sample vs. duplicate measurements on the Retrofit, Second, and Third analyzers for Pk1C, Pk2C, Pk3C, Pk4C, and PyrolC, respectively. Correlation coefficients for the Pk1C plots were 0.98 or better; correlation coefficients for the Pk2C plots were 0.97 or better; correlation coefficients for the Pk3C plots were 0.96 or better; correlation coefficients for the Pk4C plots were 0.98 or better; and correlation coefficients for the PyrolC plots were 0.97 or better. The correlation coefficient for PyrolC for the Third analyzer was 0.919, while PyrolC plots for the Retrofit and Second analyzers were 0.97 or better.

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.

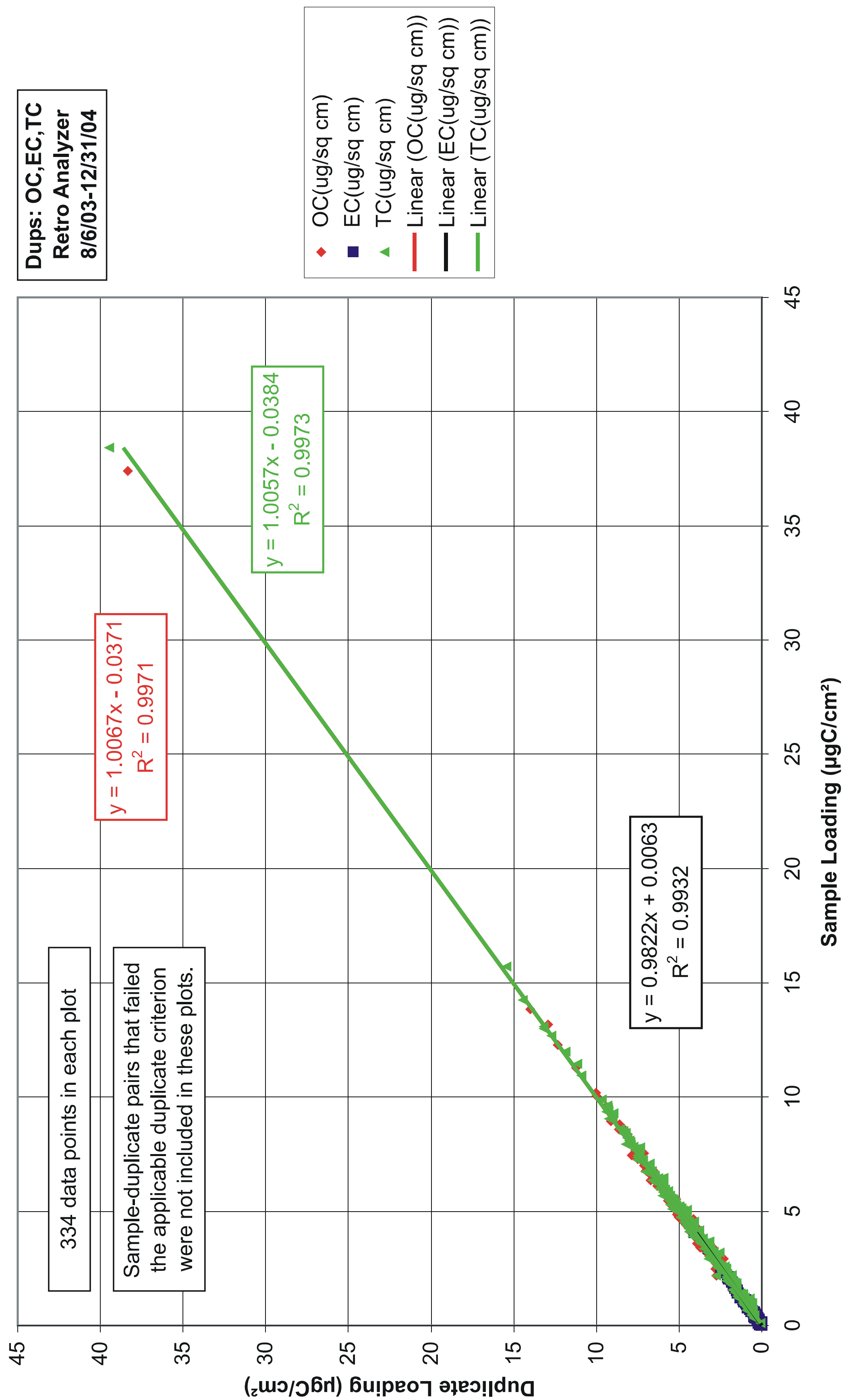


Figure 19. OC, EC, and TC: Duplicate vs. Sample, Retrofit Analyzer, August 6, 2003, through December 31, 2003.

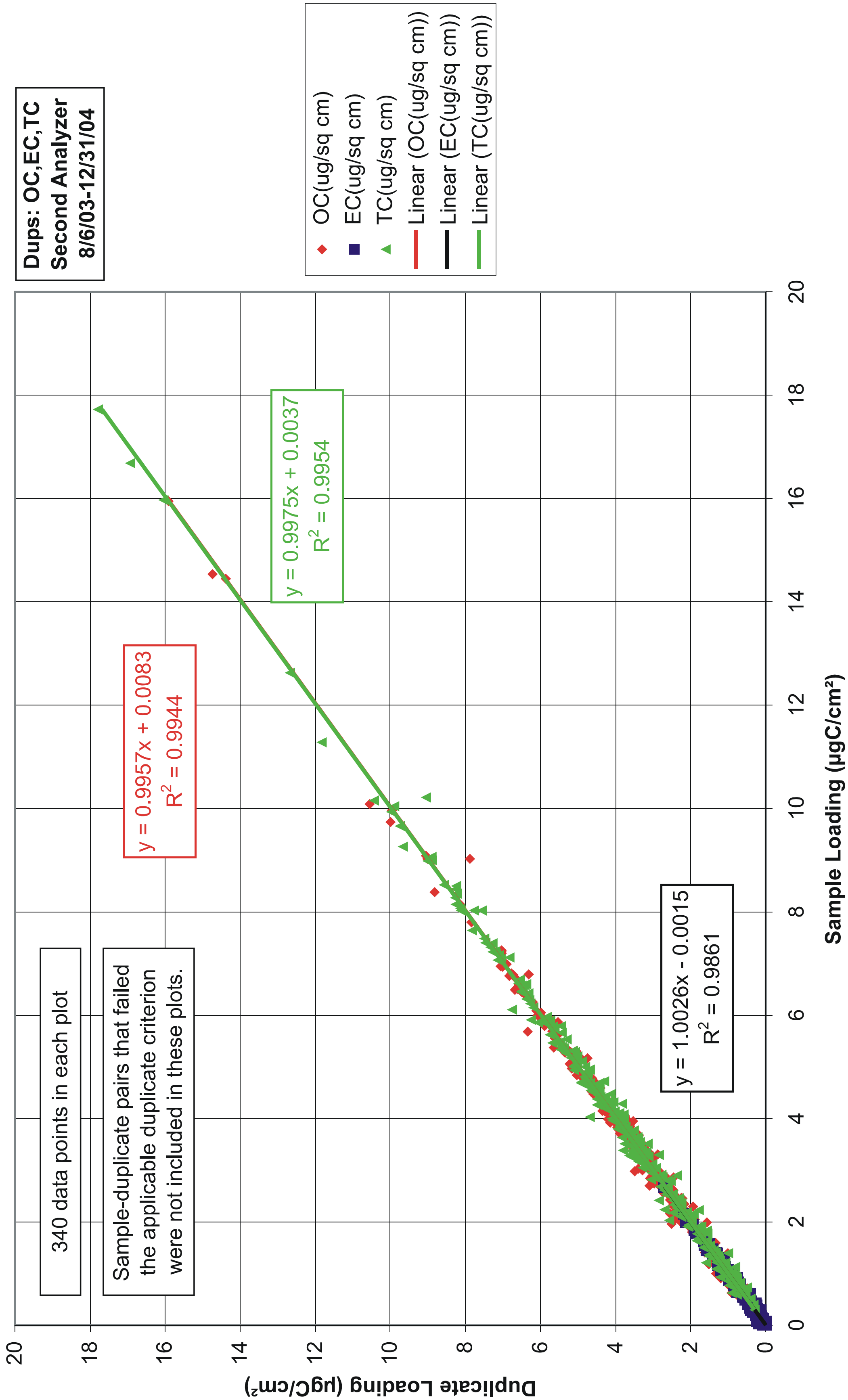


Figure 20. OC, EC, and TC: Duplicate vs. Sample, Second Analyzer, August 6, 2003, through December 31, 2003.

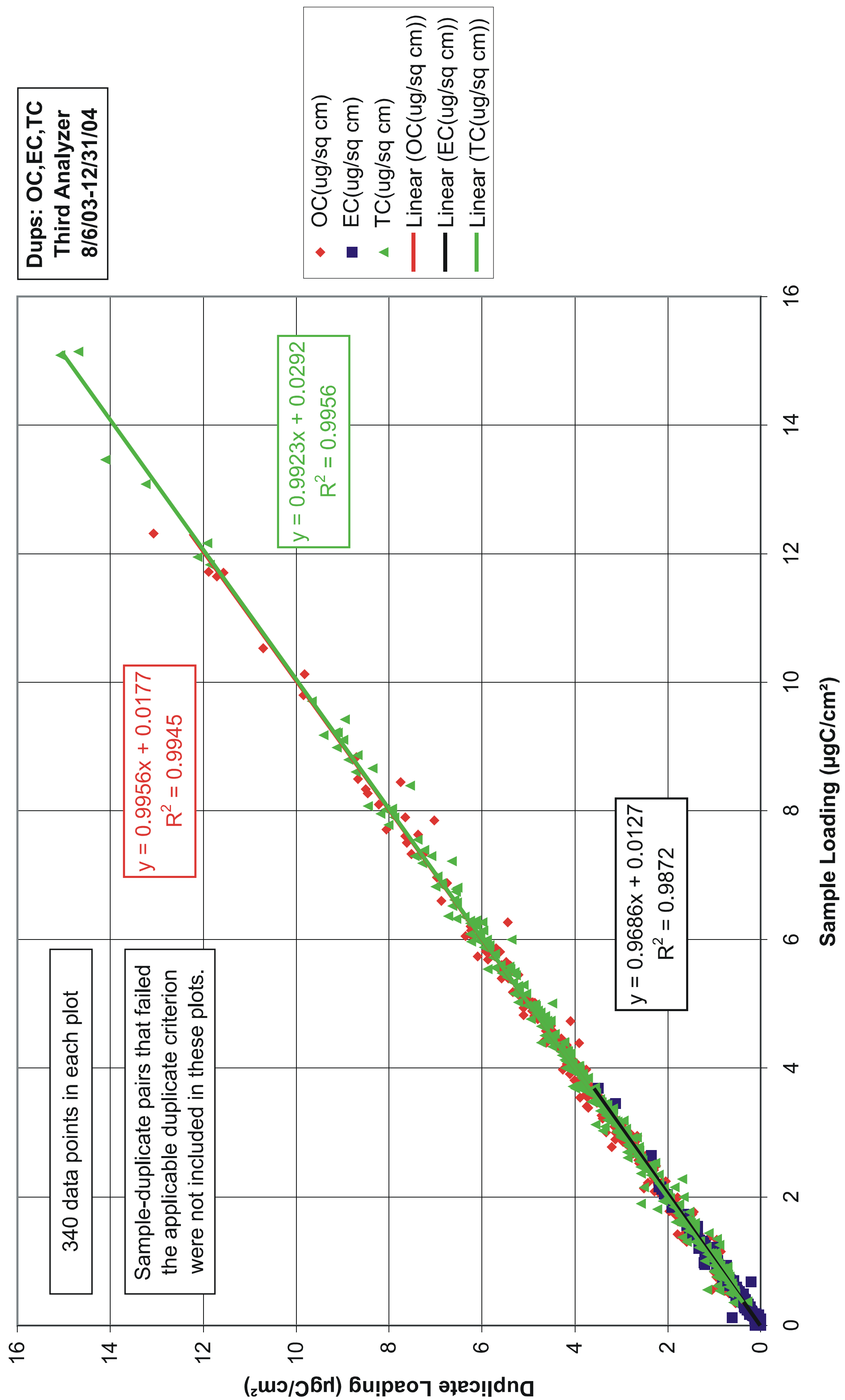


Figure 21. OC, EC, and TC: Duplicate vs. Sample, Third Analyzer, August 6, 2003, through December 31, 2003.

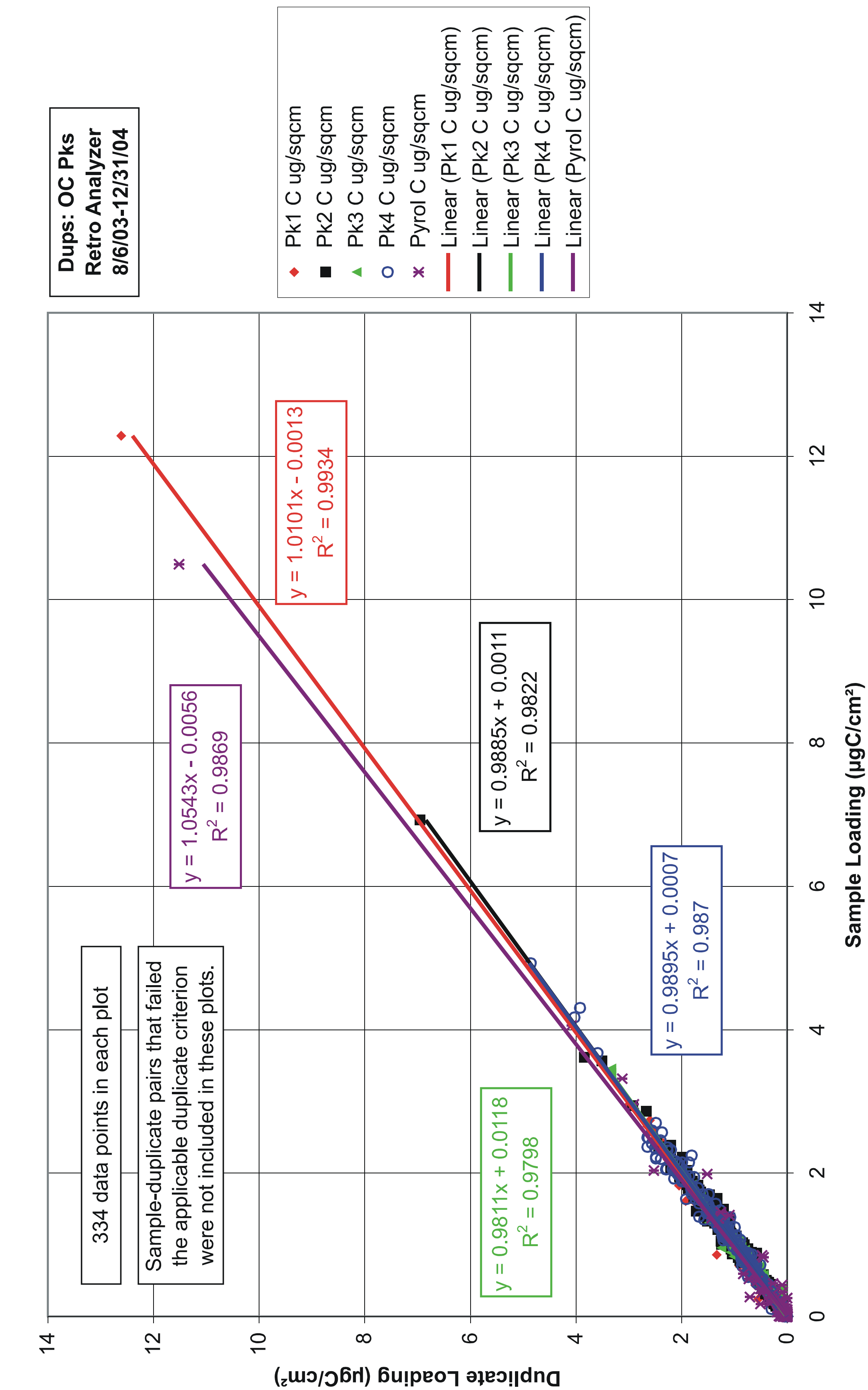


Figure 22. OC Peaks: Duplicate vs. Sample, Retrofit Analyzer, August 6, 2003, through December 31, 2003.

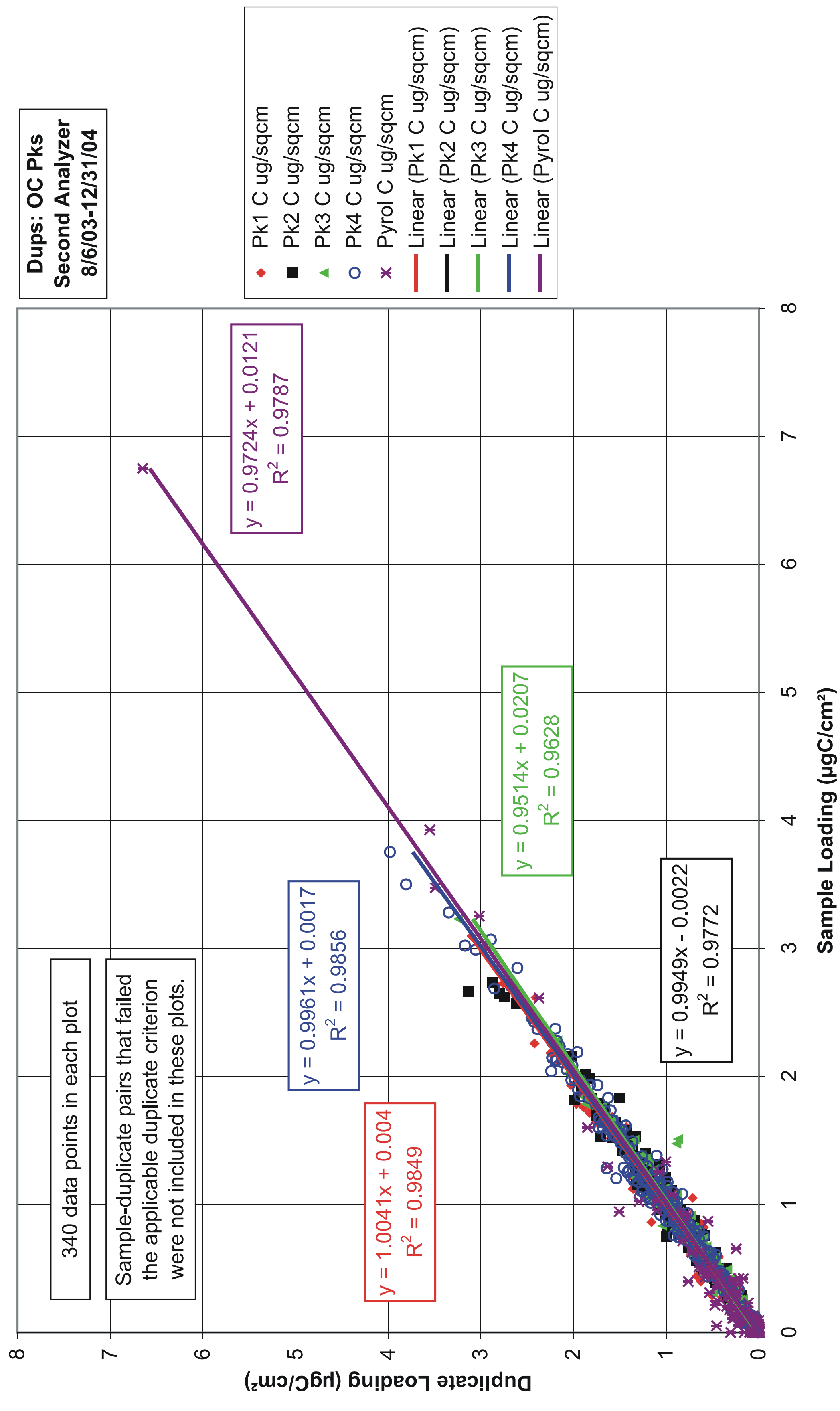


Figure 23. OC Peaks: Duplicate vs. Sample, Second Analyzer, August 6, 2003, through December 31, 2003.

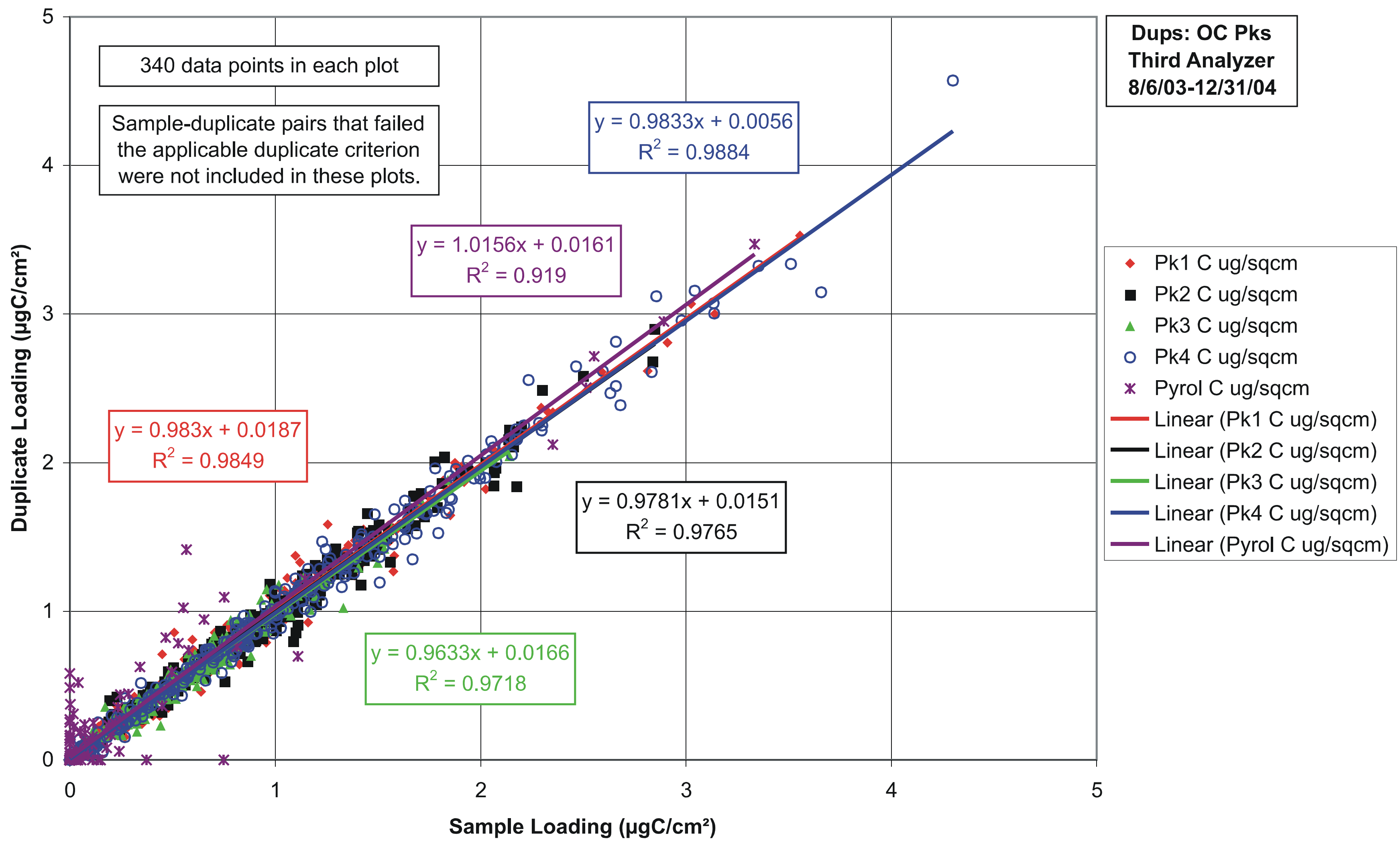


Figure 24. OC Peaks: Duplicate vs. Sample, Third Analyzer, August 6, 2003, through December 31, 2003.

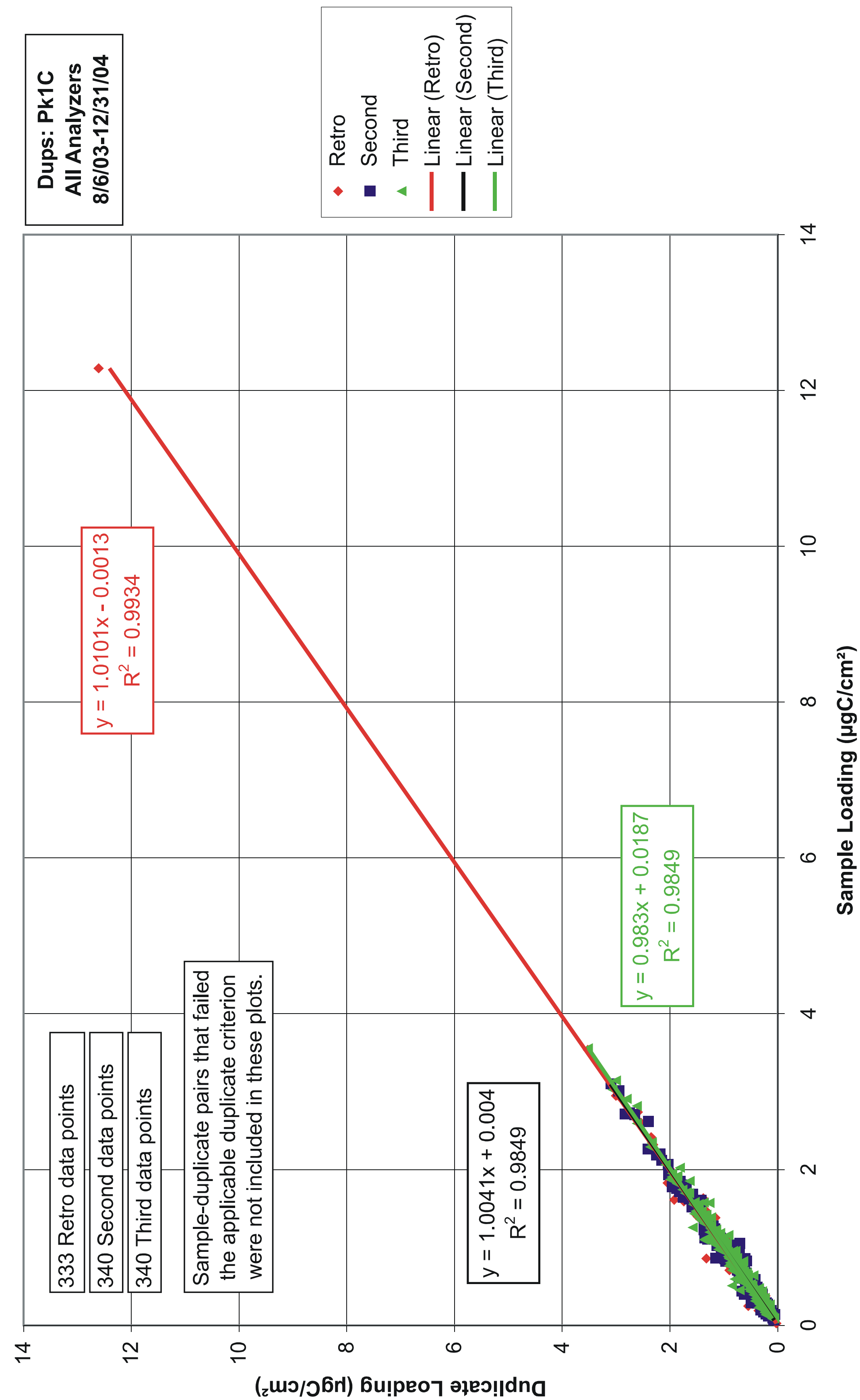


Figure 25. Pk1C Plots: Duplicate vs. Sample, All STN OC/EC Analyzers, August 6, 2003, through December 31, 2003.

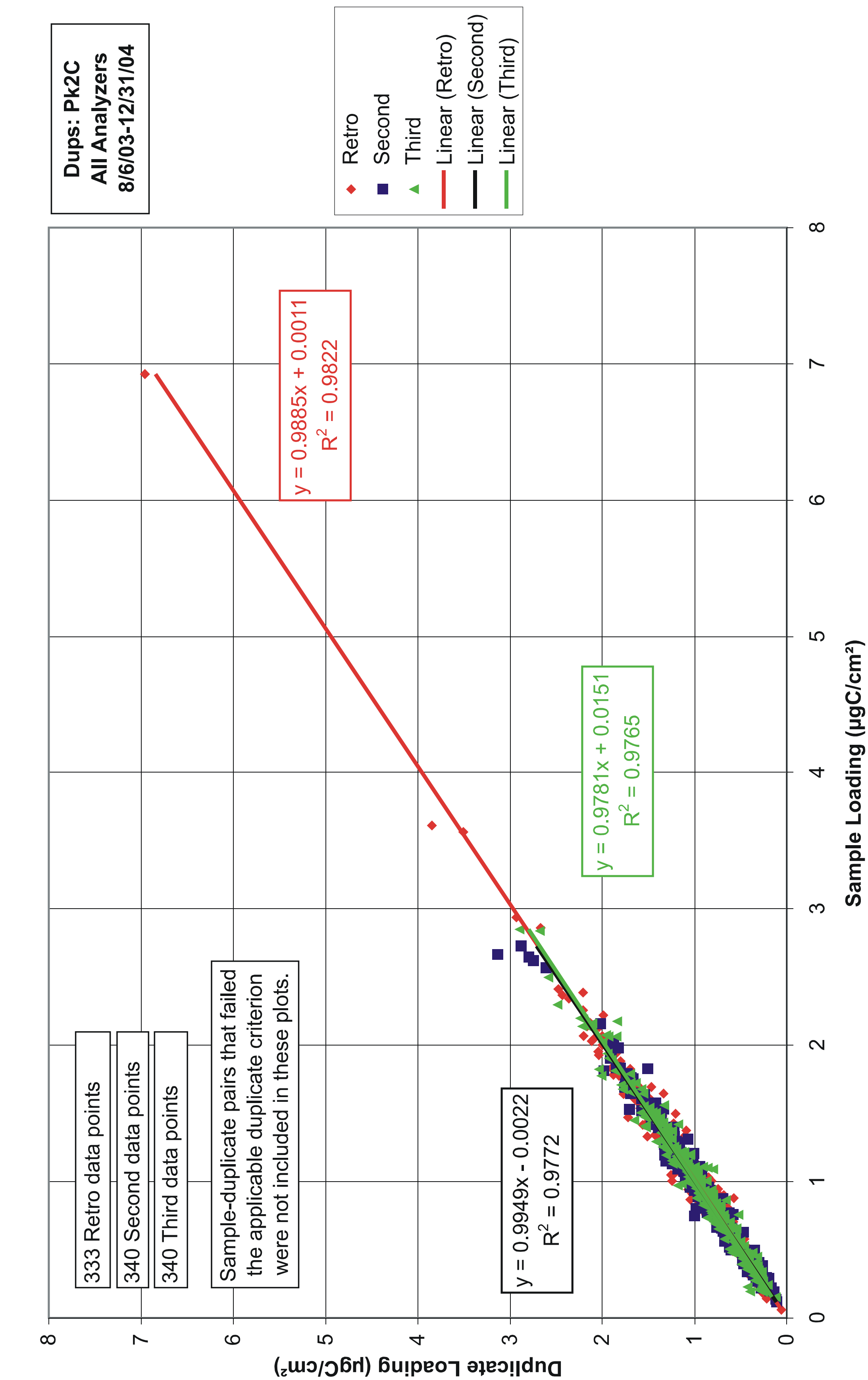


Figure 26. Pk2C Plots: Duplicate vs. Sample, All STN OC/EC Analyzers, August 6, 2003, through December 31, 2003.

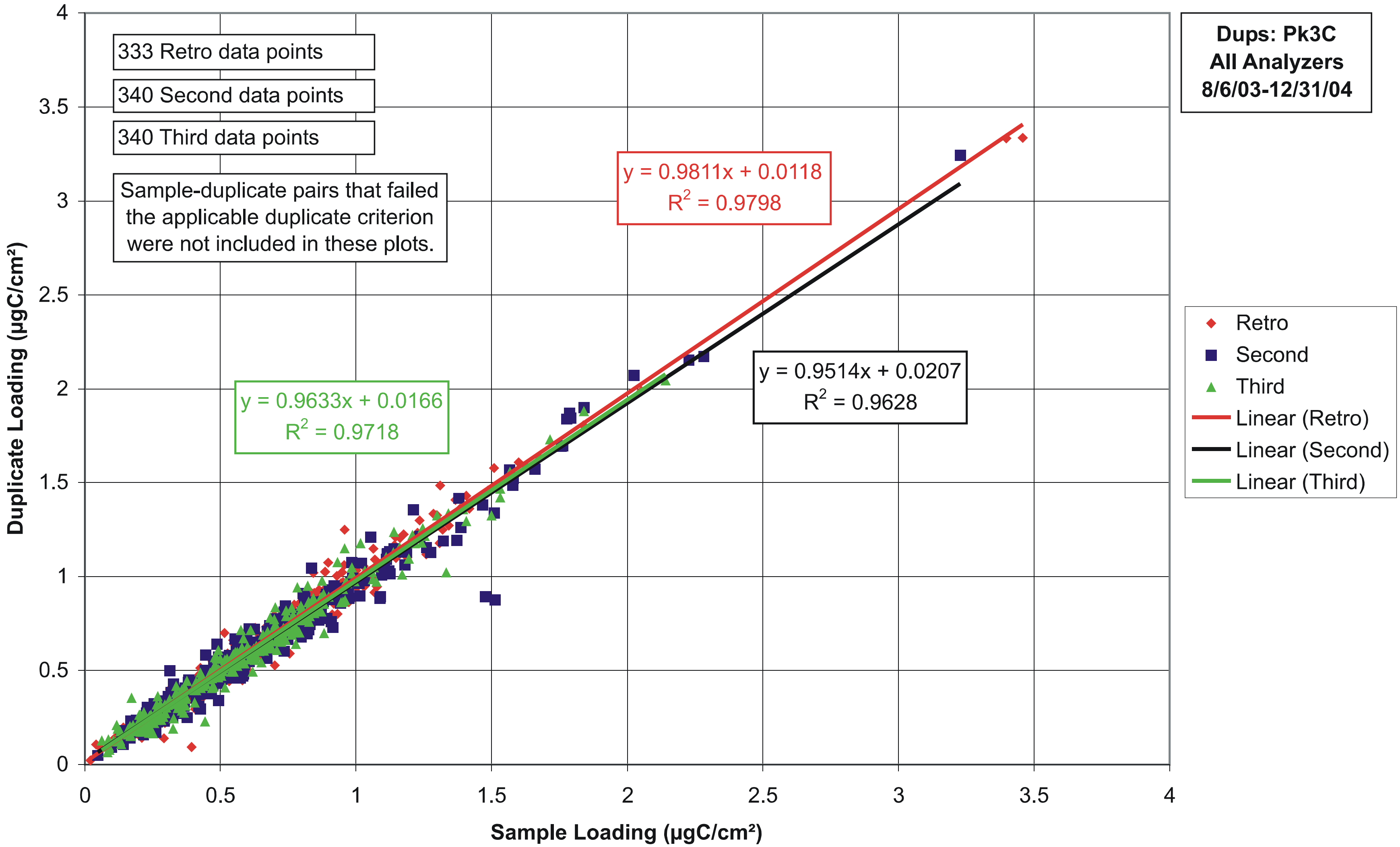


Figure 27. Pk3C Plots: Duplicate vs. Sample, All STN OC/EC Analyzers, August 6, 2003, through December 31, 2003.

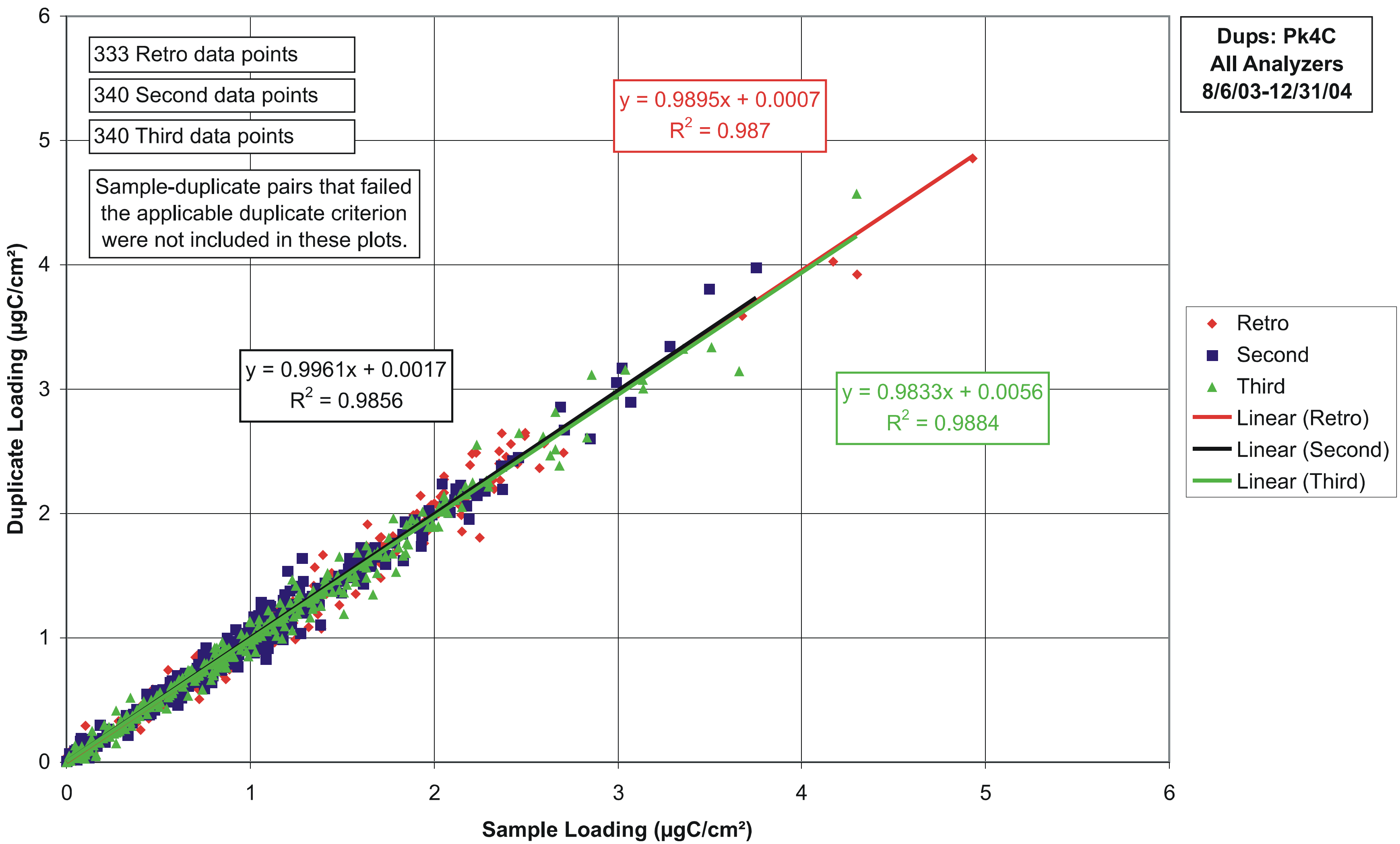


Figure 28. Pk4C Plots: Duplicate vs. Sample, All STN OC/EC Analyzers, August 6, 2003, through December 31, 2003.

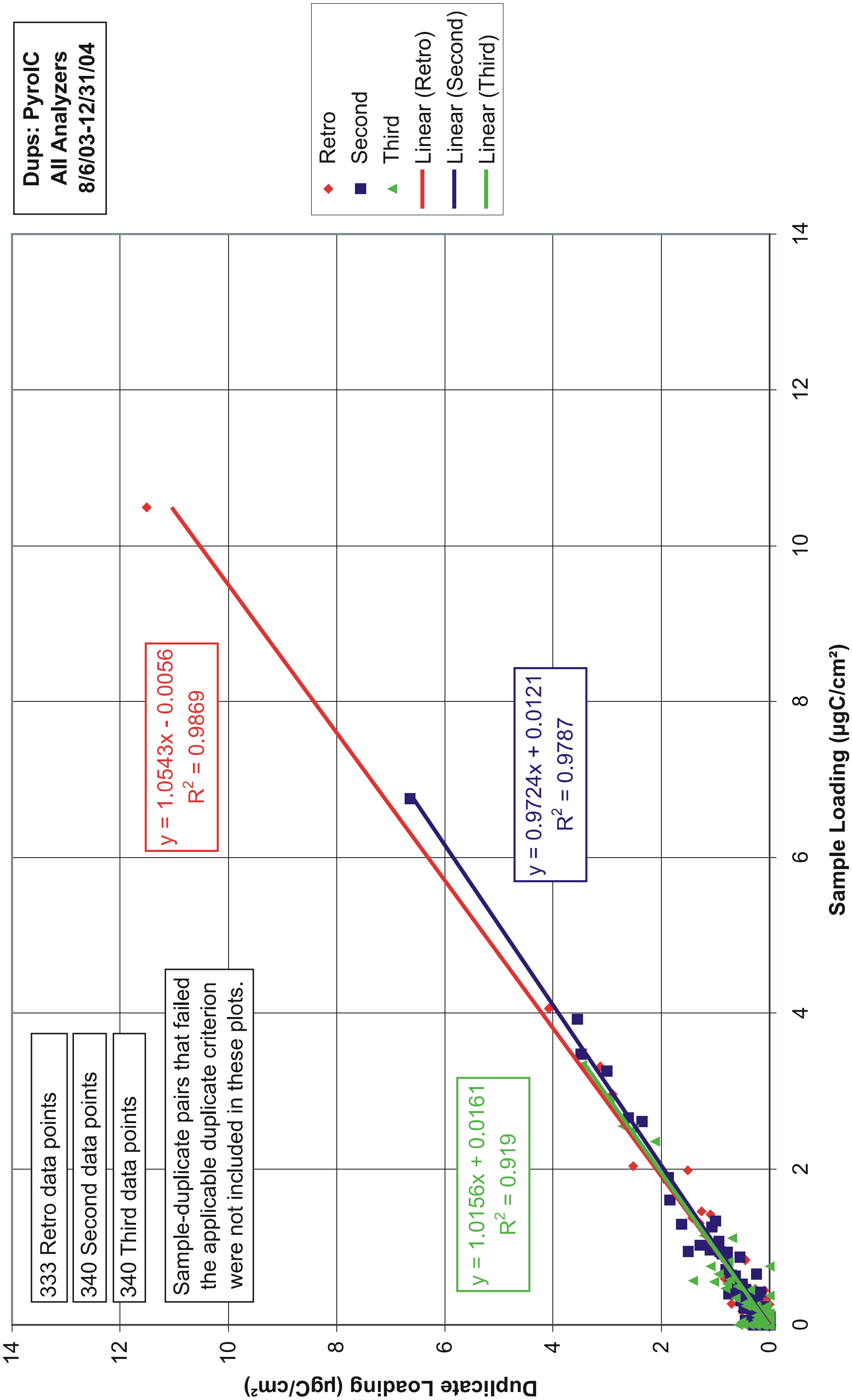


Figure 29. PyrolC Plots: Duplicate vs. Sample, All STN OC/EC Analyzers, August 6, 2003, through December 31, 2003.

On even rarer occasions, an OC/EC Laboratory analyst has dropped a filter. Any filter dropped prior to removing a punch for analysis is not analyzed, and a Laboratory Error flag is assigned to that filter ID.

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

There were no problems identified during the annual audit of the RTI OC/EC Laboratory.

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 two at RTI, and two at Chester LabNet. Each has 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 and RTI.

2.4.1 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions are shown in **Table 15**.

Table 15. QC Procedures Performed in Support of EDXRF Elemental Analysis

QC Activities	Frequency	Control Limits	Corrective Action
Calibration	as needed	--	--
Calibration verification	weekly	within NIST uncertainties	recalibrate
Instrument precision	once per batch of $\leq$ 15	90–110% recovery	batch reanalysis
Excitation condition check	every sample	within analysis uncertainty	sample reanalysis
Sample replicate precision	5%	± 50 RPD	batch reanalysis

The two-sigma (95 percent confidence level) detection limits in units of µg/cm^2 were 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.

Note that all detection limits are now being reported as 3-sigma limits to AQS. The detection limit in the equation above is multiplied by a factor of 1.5 for reporting to AQS.

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 –

<u>Precision</u>

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 30 through 42**. **Tables 16a and 16b** 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.

Table 16a. Summary of Chester QC Precision Recovery Data, Kevex 770, 7/1/03 through 12/31/03.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(0)	99.1	4.57	4.61	106.8	88.0	0.62484	0.05656	-4.05
Si(1)	98.4	3.06	3.11	105.6	90.1	-0.18423	-0.01119	-6.94
Ti(2)	99.8	2.73	2.74	108.5	91.5	-0.00677	-0.00037	-9.28
Fe(3)	98.4	2.66	2.71	107.9	90.3	0.26914	0.01424	-2.91
Se(4)	100.1	2.86	2.86	106.6	90.3	0.31333	0.01780	-3.61
Pb(4)	101.3	3.05	3.01	108.5	92.9	0.49070	0.02976	-3.35
Cd(5)	98.5	3.61	3.66	106.3	91.0	0.69772	0.05003	-7.96

N=185 for all elements.

Table 16b. Summary of Chester QC Precision Recovery Data, Kevex 771, 7/1/03 through 12/31/03.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope
							Current
Si(1)	95.1	2.06	2.17	101.4	88.0	-0.21261	-0.0087
Ti(2)	100.0	2.85	2.85	106.0	90.7	-0.41183	-0.0232
Fe(3)	99.7	2.07	2.08	103.6	92.9	-0.56874	-0.0233
Se(4)	99.4	2.34	2.36	105.8	93.1	-0.21360	-0.0099
Pb(4)	98.6	2.44	2.48	104.4	91.4	0.11937	0.0058
Cd(5)	99.0	2.69	2.72	104.9	89.9	-0.16785	-0.0089

N=185 for all elements.

Figure 30. Recovery Precision for Chester Kevex 770 XRF
Si(0) - Rh L/7.5kV/0.1mA

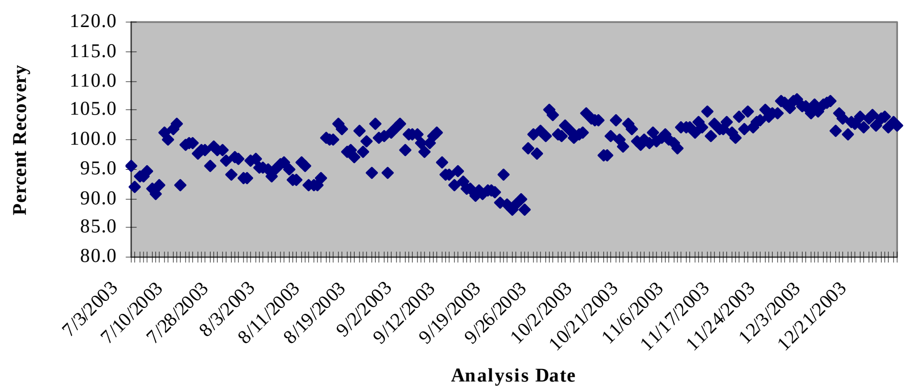


Figure 31. Recovery Precision for Chester Kevex 770 XRF
Si(1) - Ti target/25kV/1.0mA

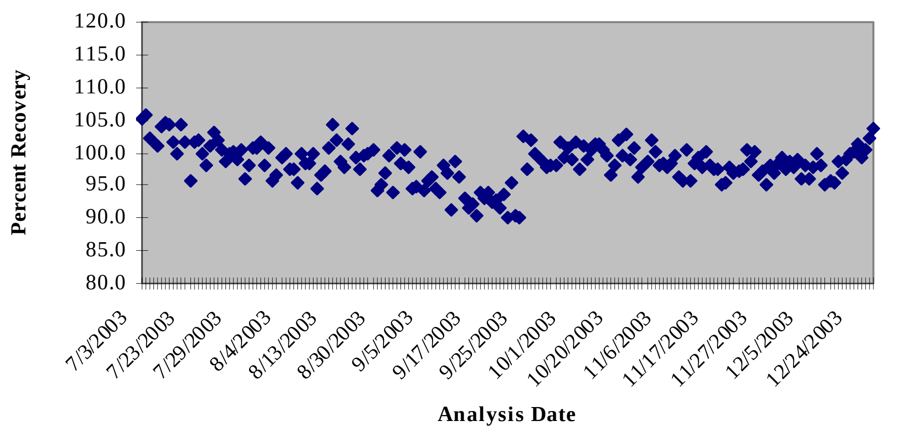


Figure 32. Recovery Precision for Chester Kevex 770 XRF
Ti(2) - Fe target/35kV/0.5mA

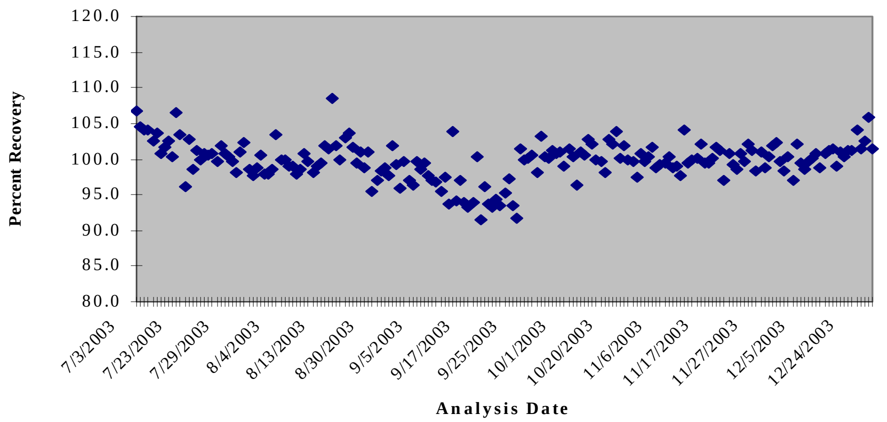


Figure 33. Recovery Precision for Chester Kevex 770 XRF
Fe(3) - Ge target/35kV/0.5mA

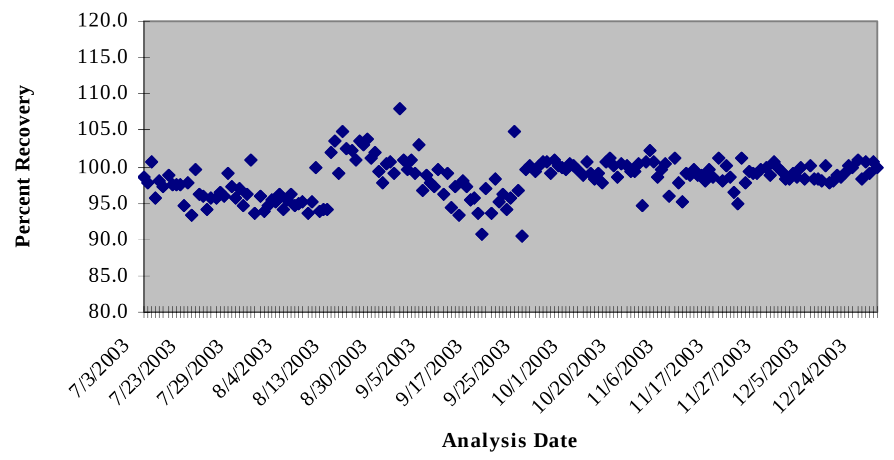


Figure 34. Recovery Precision for Chester Kevex 770 XRF
Se(4) - Rh K/35kV/0.25mA

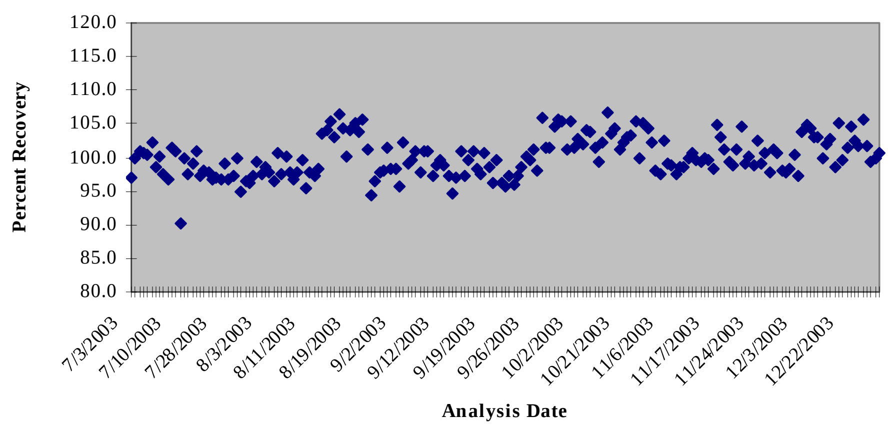


Figure 35. Recovery Precision for Chester Kevex 770 XRF
Pb(4) - Rh K/35kV/0.25mA

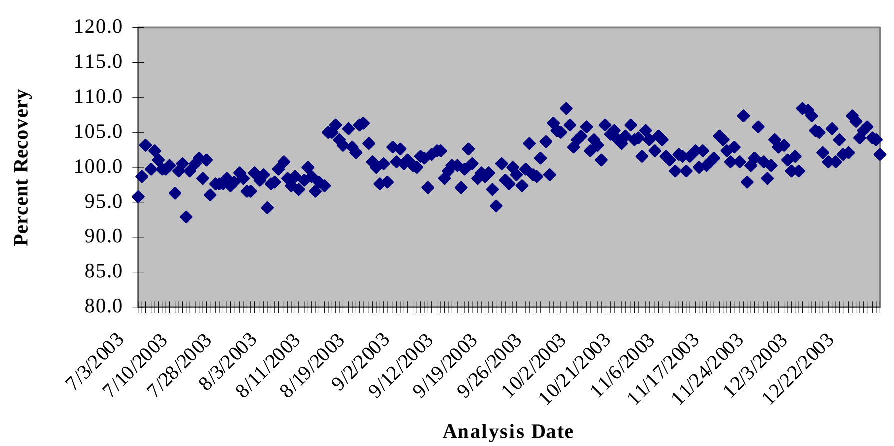


Figure 36. Recovery Precision for Chester Kevex 770 XRF
Cd(5) - Rh K/W filter/55kV/0.25mA

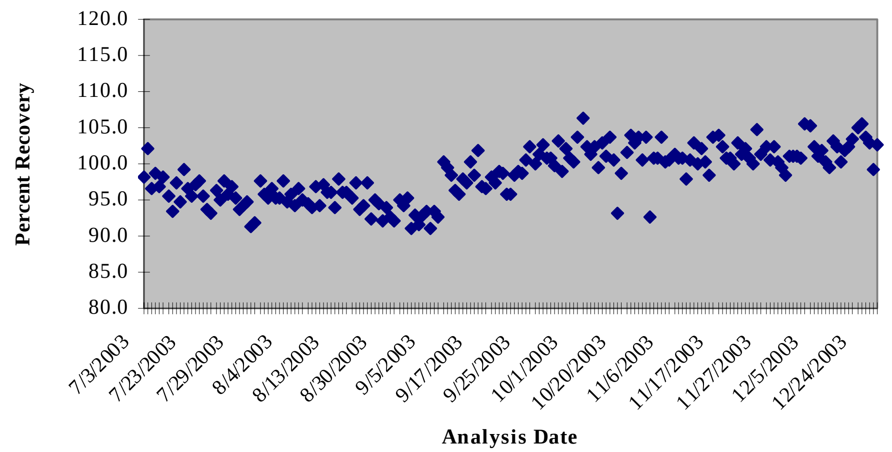


Figure 37. Recovery Precision for Chester Kevex 771 XRF
Si(1) - Rh L-alpha 6.0kV

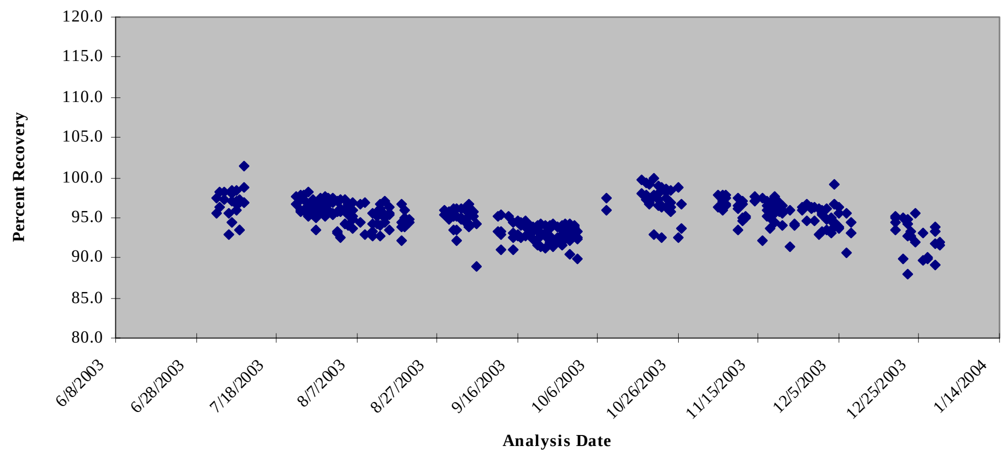
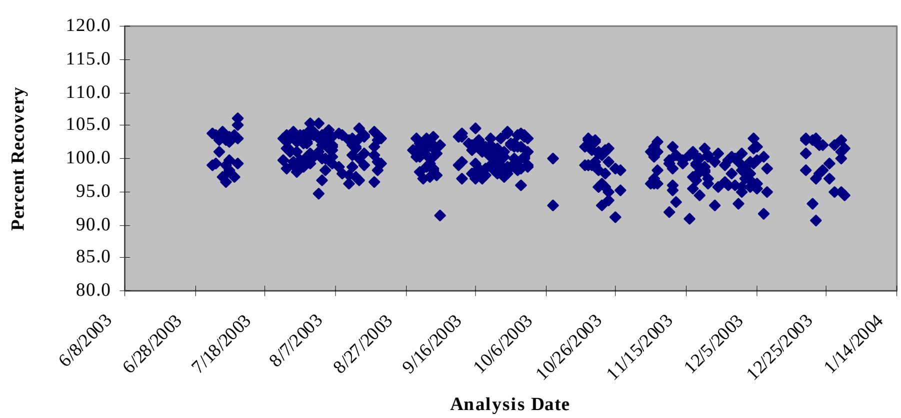


Figure 38. Recovery Precision for Chester Kevex 771 XRF
Ti(2) - Fe target 35kV



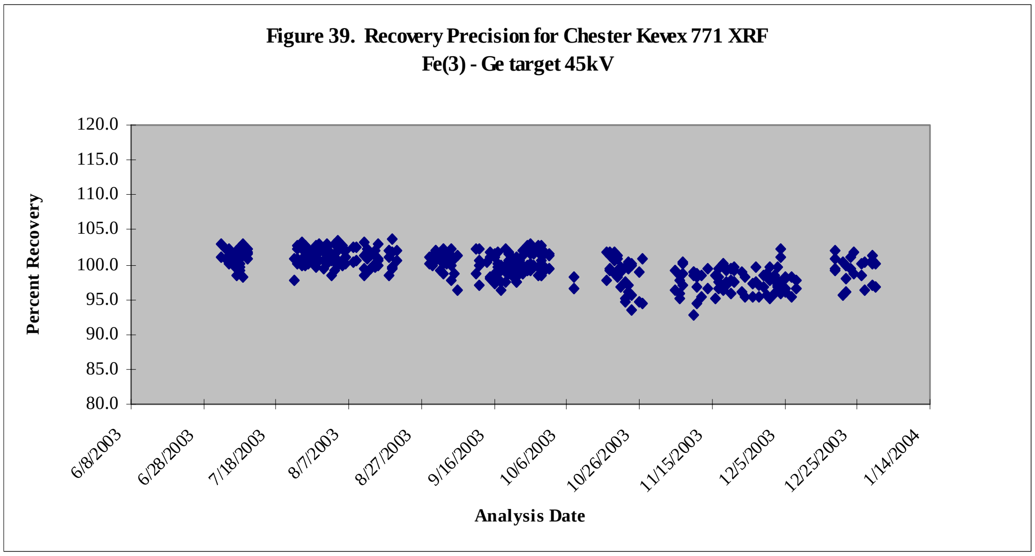


Figure 39. Recovery Precision for Chester Kevex 771 XRF
Fe(3) - Ge target 45kV
Percent Recovery
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
6/8/2003
6/28/2003
7/18/2003
8/7/2003
8/27/2003
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10/6/2003
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11/15/2003
12/5/2003
12/25/2003
1/14/2004
Analysis Date

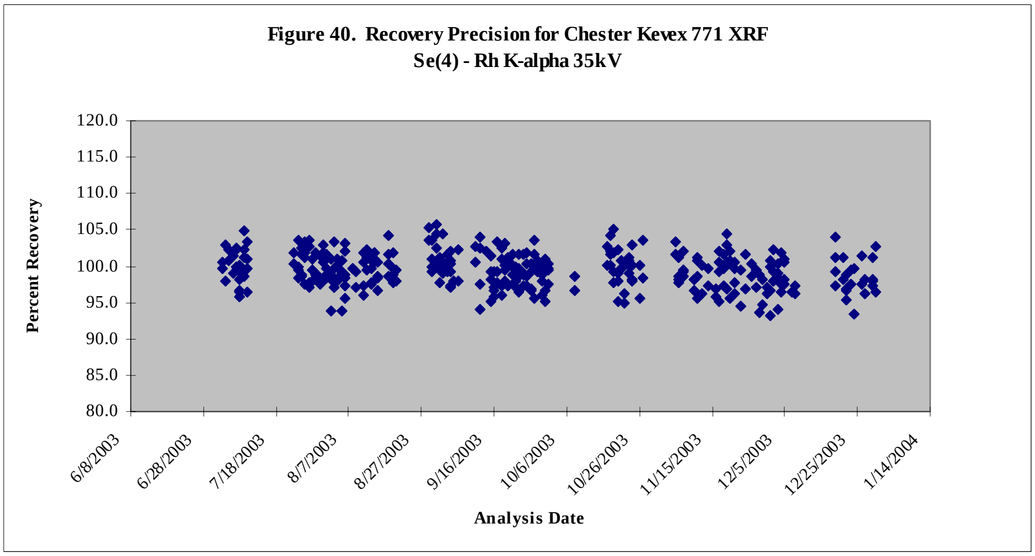


Figure 40. Recovery Precision for Chester Kevex 771 XRF
Se(4) - Rh K-alpha 35kV
Percent Recovery
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
6/8/2003
6/28/2003
7/18/2003
8/7/2003
8/27/2003
9/16/2003
10/6/2003
10/26/2003
11/15/2003
12/5/2003
12/25/2003
1/14/2004
Analysis Date

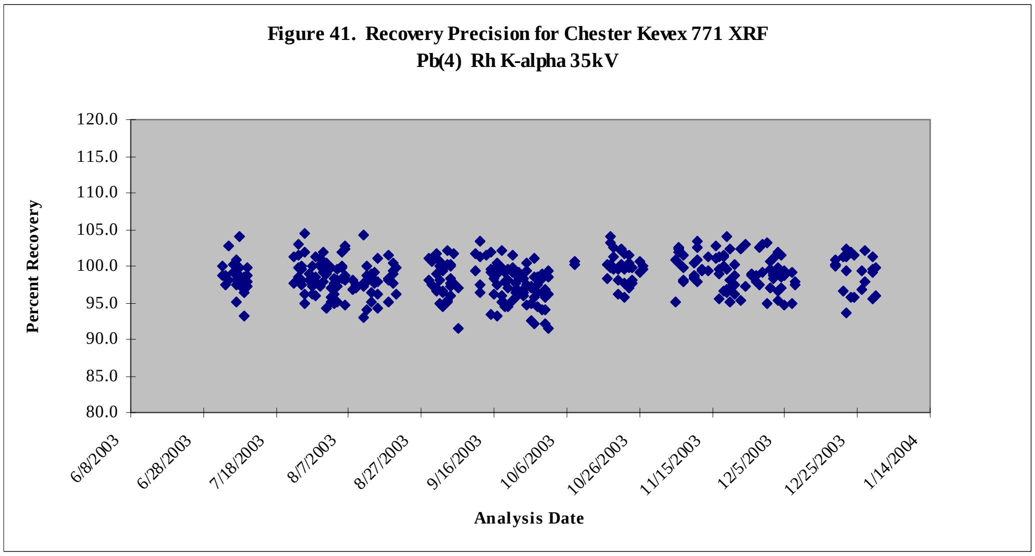
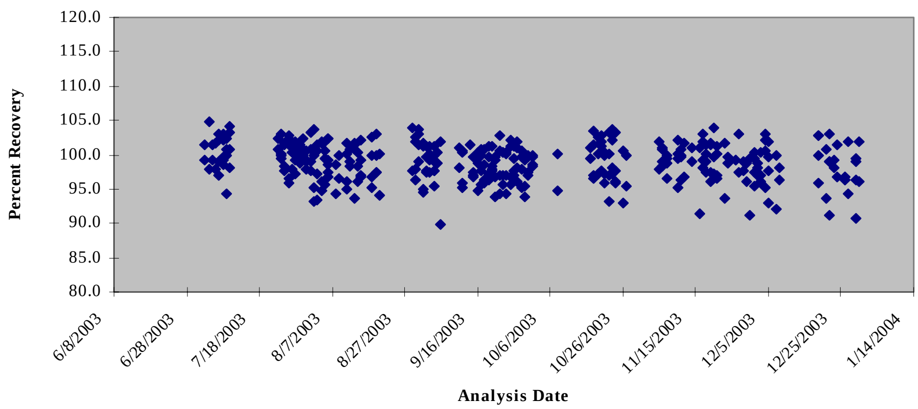


Figure 41. Recovery Precision for Chester Kevex 771 XRF
Pb(4) Rh K-alpha 35kV
Percent Recovery
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
6/8/2003
6/28/2003
7/18/2003
8/7/2003
8/27/2003
9/16/2003
10/6/2003
10/26/2003
11/15/2003
12/5/2003
12/25/2003
1/14/2004
Analysis Date

Figure 42. Recovery Precision for Chester Kevex 771 XRF Cd(5) W filter 55kV



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 43 through 68** show recovery for 12 select elements spanning the range of the 48 elements normally measured. The recovery values for all elements ranged between 91 and 107 percent for the 770 and between 91 and 113 percent for the 771, as shown in **Table 17**. For the 771 instrument, the high value of 113% was for sulfur, which had several points above the 110% limit. All other elements were in control (> 90%, < 110%) at all times.

Table 17. Recovery Determined from Analysis of NIST Standard Reference Material Filters, Kevex 770 and 771, 7/1/03 through 12/31/03.

Element	Kevex 770	Kevex 771
	Range % Recovery	Range % Recovery
Al	93 - 105	94 - 101
Si*	95 - 107	94 - 101
Si**	91 - 102	91 - 97
S	93 105	95 113
K	94 - 103	98 - 105
Ca	94 - 103	100 - 107
Ti	96 - 101	92 - 98
V	95 - 103	96 - 105
Mn	95 - 103	94 - 103
Fe	94 - 103	96 - 102
Cu	95 - 103	96 - 102
Zn	92 - 101	96 - 104
Pb	98 - 106	97 - 105

*SRM 1832. **SRM 1833.

Figure 43. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester Kevex 770

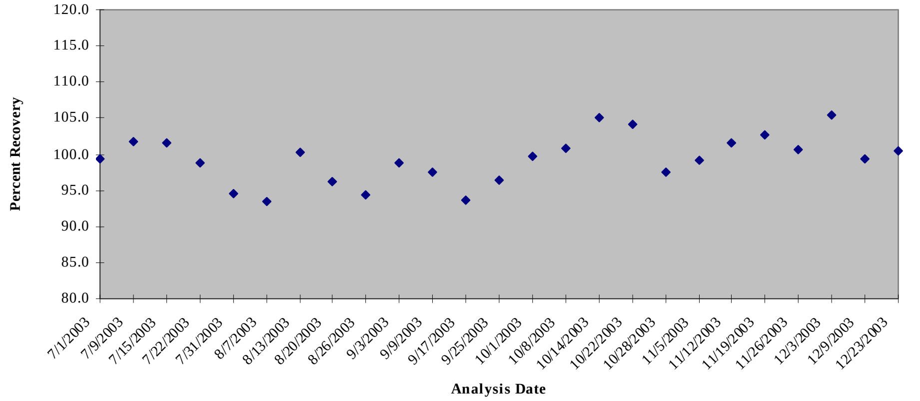


Figure 44. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 770

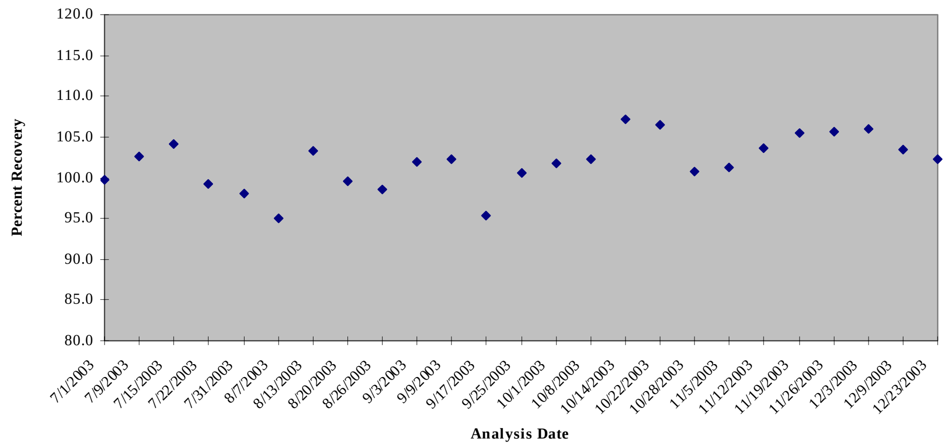


Figure 45. Recovery of Silicon (Si) in NIST SRM 1833 with Chester Kevex 770

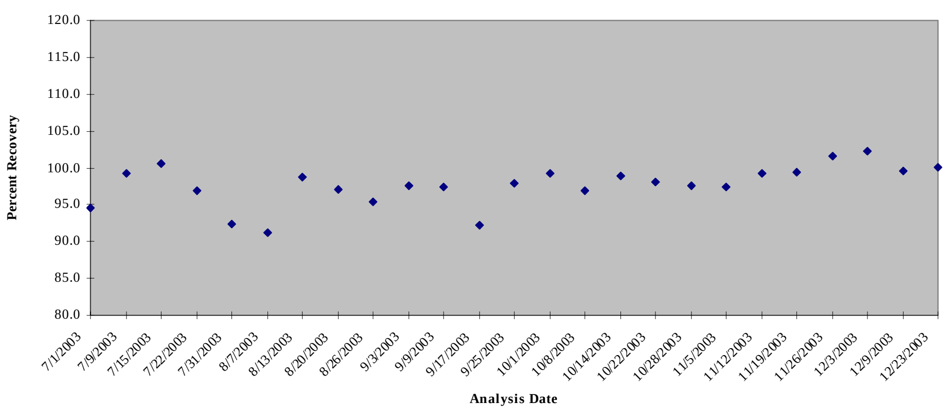


Figure 46. Recovery of Sulfur (S) in NIST SRM 2708 with Chester Kevex 770

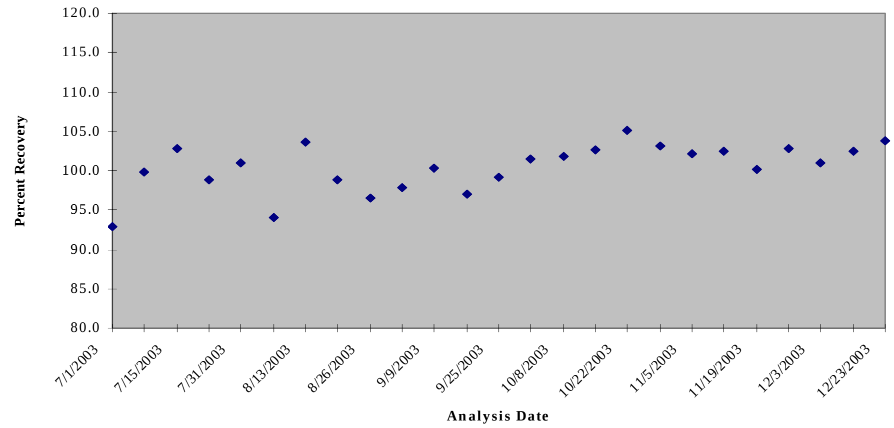


Figure 47. Recovery of Potassium (K) in NIST SRM 1833 with Chester Kevex 770

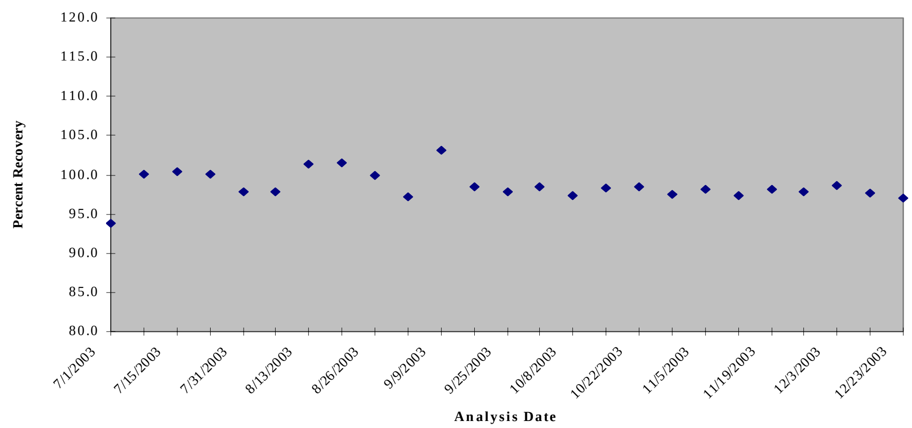


Figure 48. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester Kevex 770

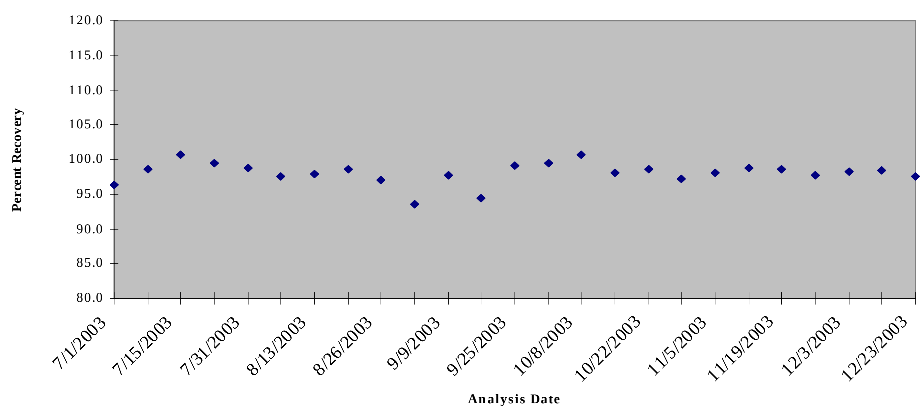


Figure 49. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester Kevex 770

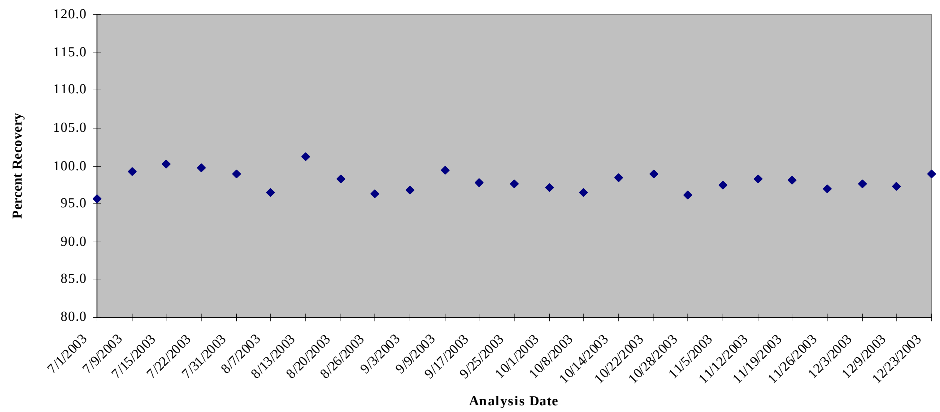


Figure 50. Recovery of Vanadium (V) in NIST SRM 1832 with Chester Kevex 770

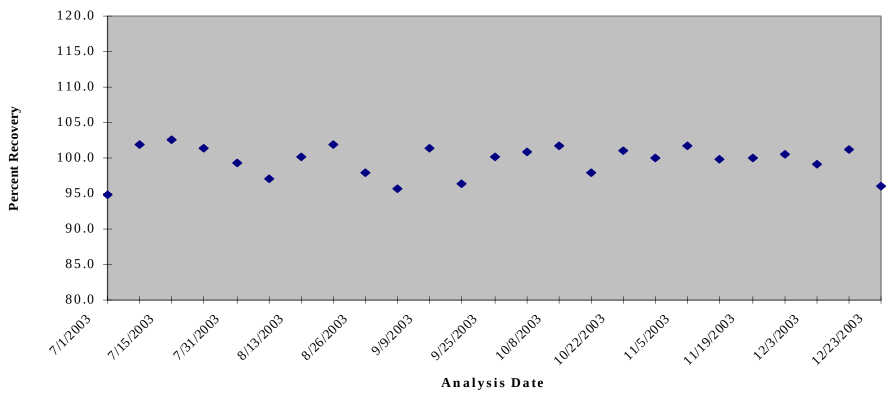


Figure 51. Recovery of Manganese (Mn) in NIST SRM 1832 with Chester Kevex 770

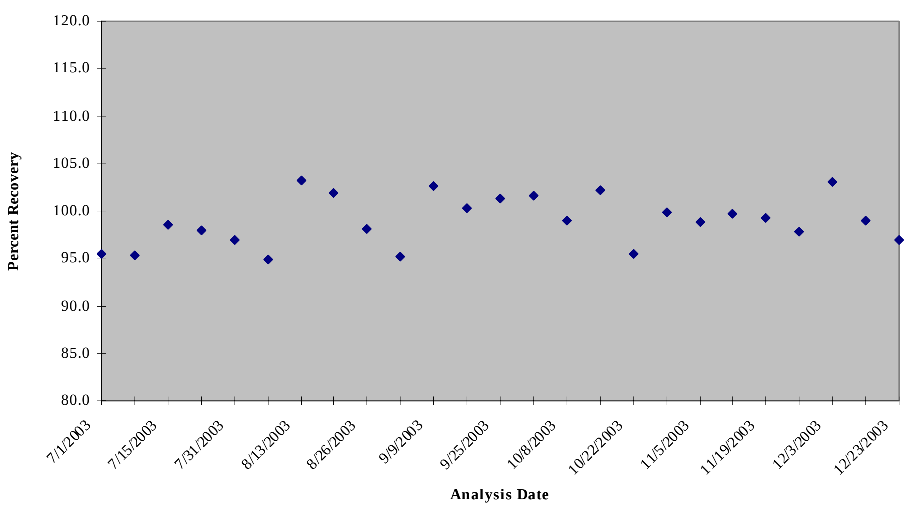


Figure 52. Recovery of Iron (Fe) in NIST SRM 1833 with Chester Kevex 770

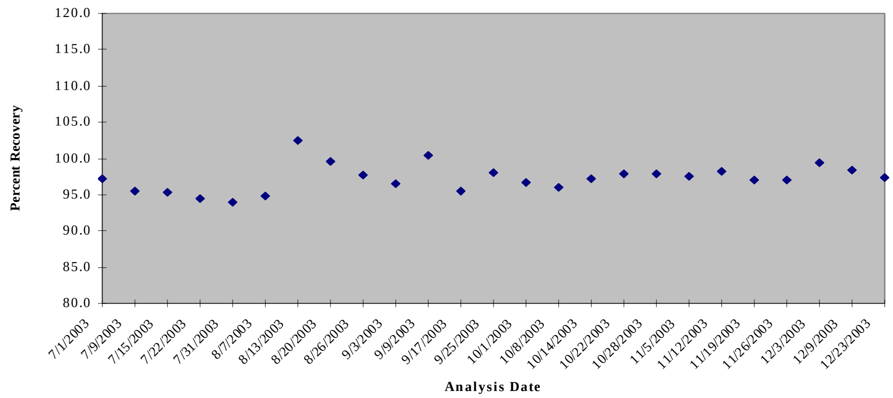


Figure 53. Recovery of Copper (Cu) in NIST SRM 1833 with Chester Kevex 770

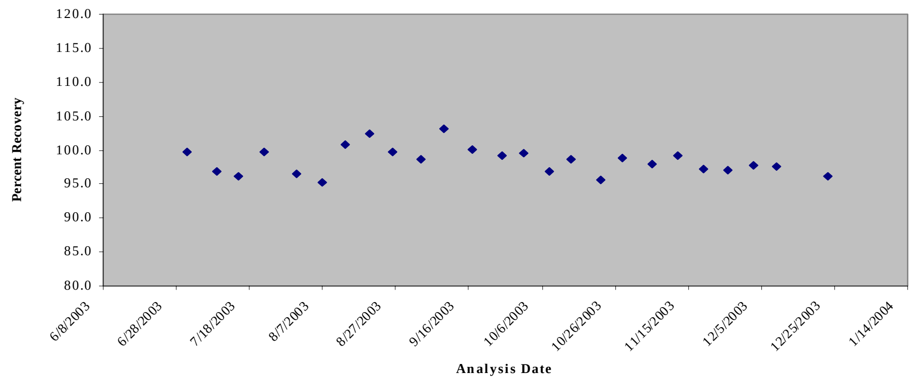


Figure 54. Recovery of Zinc (Zn) in NIST SRM 1833 with Chester Kevex 770

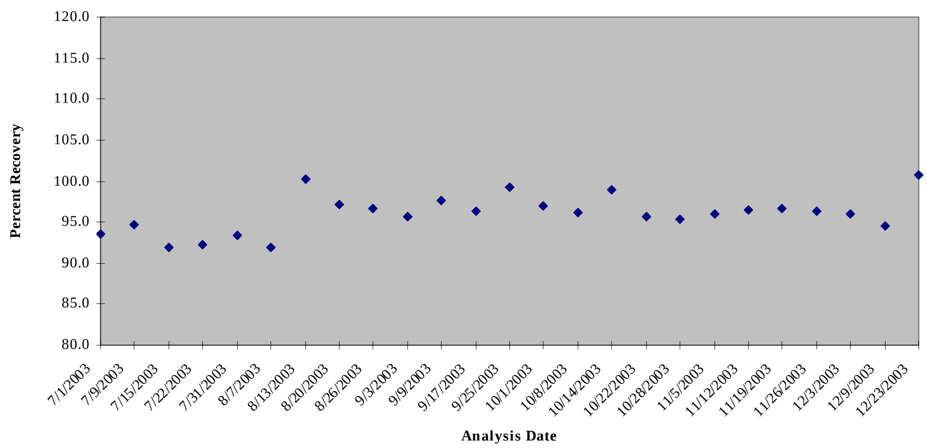


Figure 55. Recovery of Lead (Pb) in NIST SRM 1833 with Chester Kevex 770

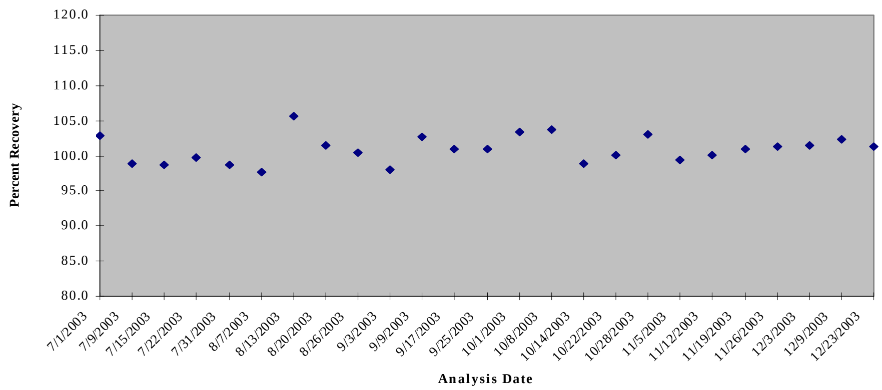


Figure 56. Recovery of Aluminum (Al) in NIST SRM 1832 with Chester Kevex 771

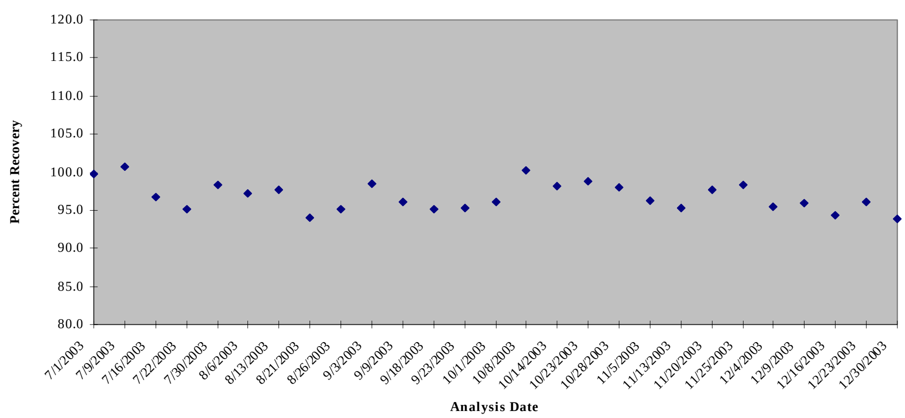


Figure 57. Recovery of Silicon (Si) in NIST SRM 1832 with Chester Kevex 771

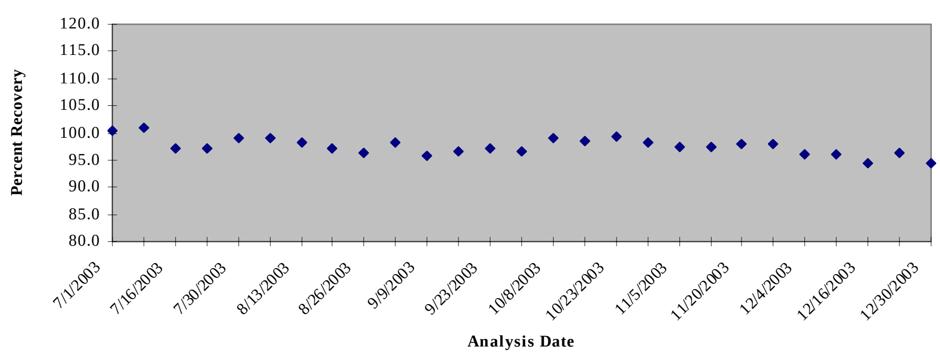


Figure 58. Recovery of Silicon (Si) in NIST SRM 1833 with Chester Kevex 771

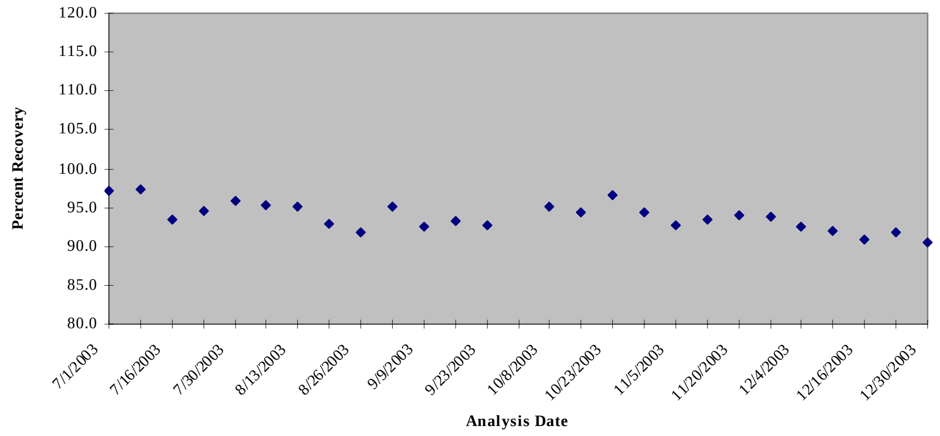


Figure 59. Recovery of Sulfur (S) in NIST SRM 2708 with Chester Kevex 771

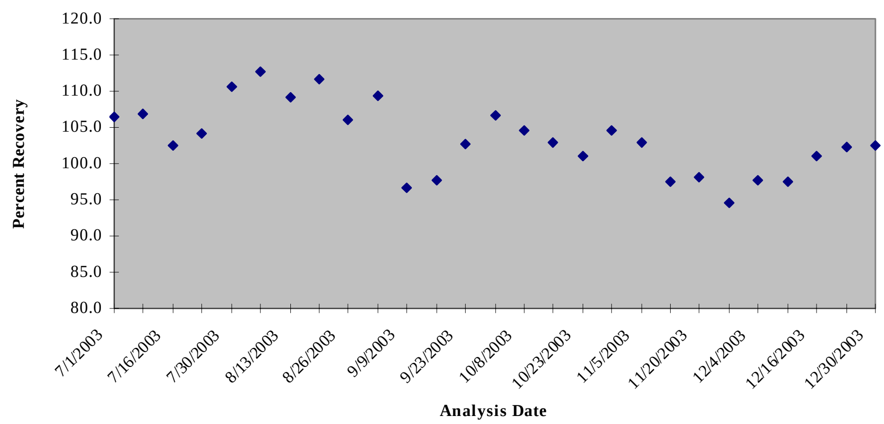


Figure 60. Recovery of Potassium (K) in NIST SRM 1833 with Chester Kevex 771

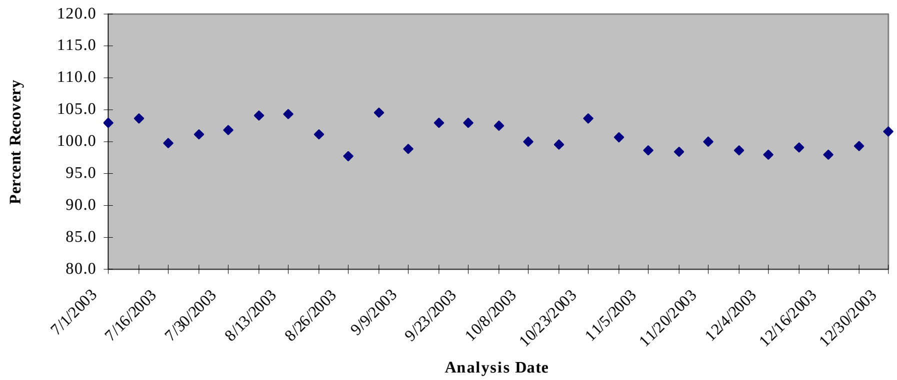


Figure 61. Recovery of Calcium (Ca) in NIST SRM 1832 with Chester Kevex 771

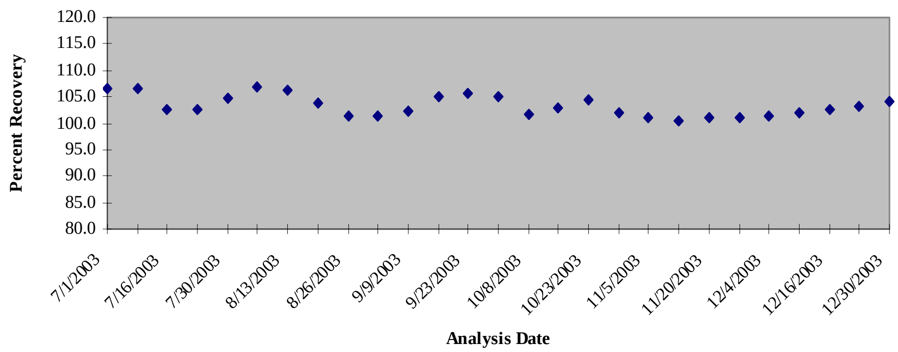


Figure 62. Recovery of Titanium (Ti) in NIST SRM 1833 with Chester Kevex 771

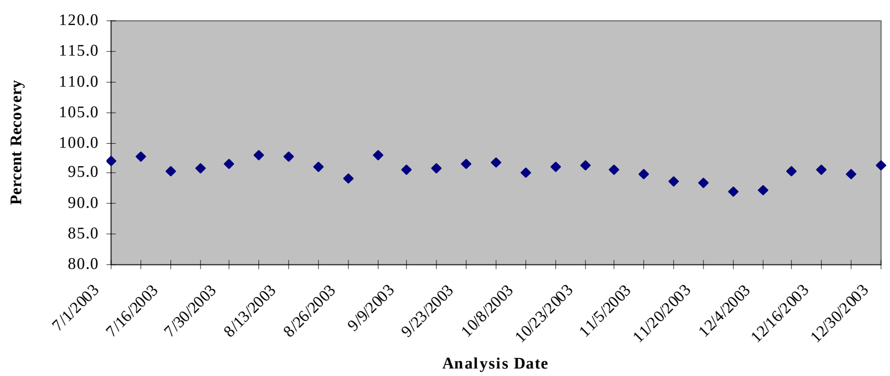


Figure 63. Recovery of Vanadium (V) in NIST SRM 1832 with Chester Kevex 771

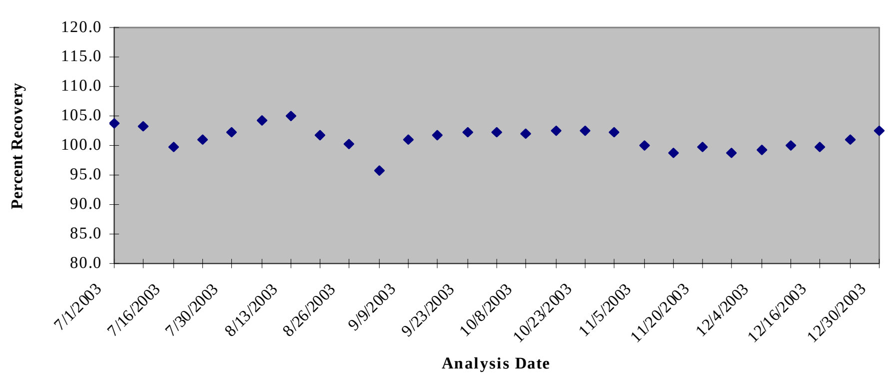


Figure 64. Recovery of Manganese (Mn) in NIST SRM 1832 with Chester Kevex 771

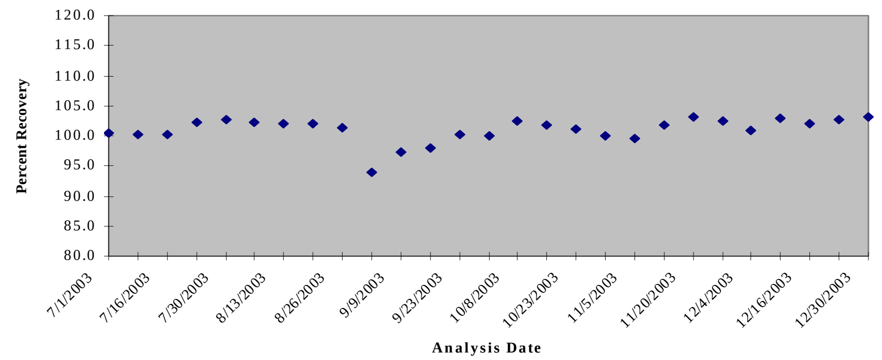


Figure 65. Recovery of Iron (Fe) in NIST SRM 1833 with Chester Kevex 771

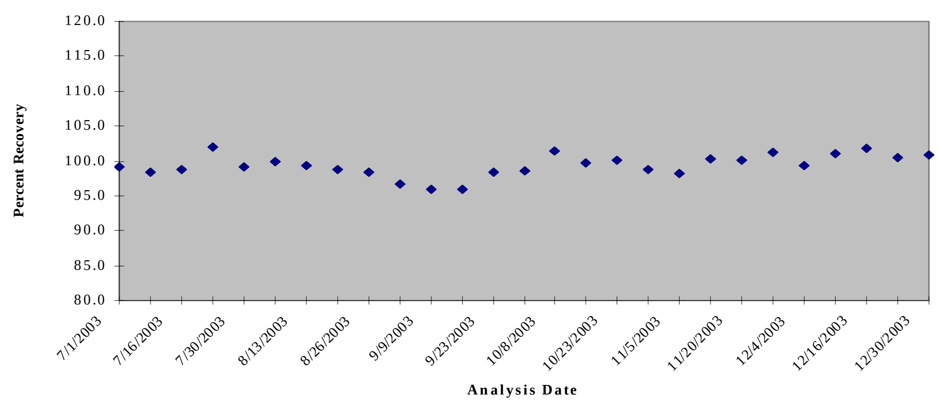


Figure 66. Recovery of Copper (Cu) in NIST SRM 1832 with Chester Kevex 771

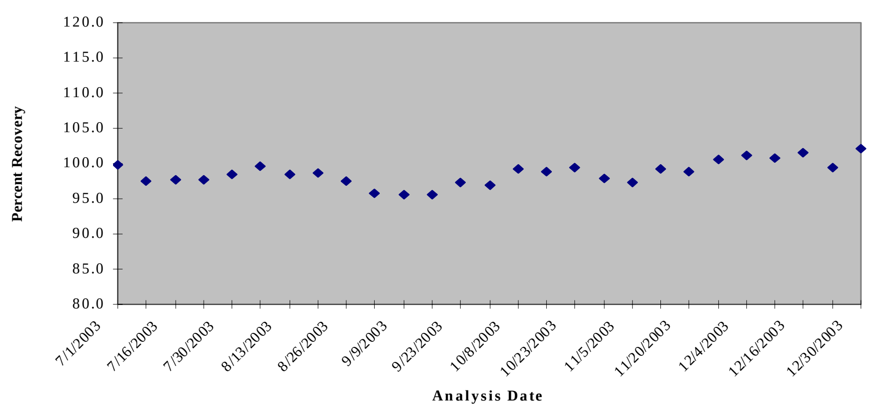


Figure 67. Recovery of Zinc (Zn) in NIST SRM 1832 with Chester Kevex 771

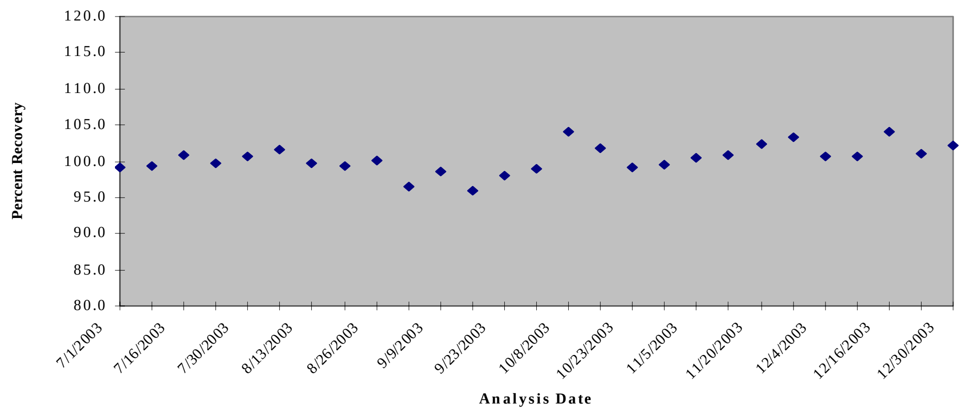
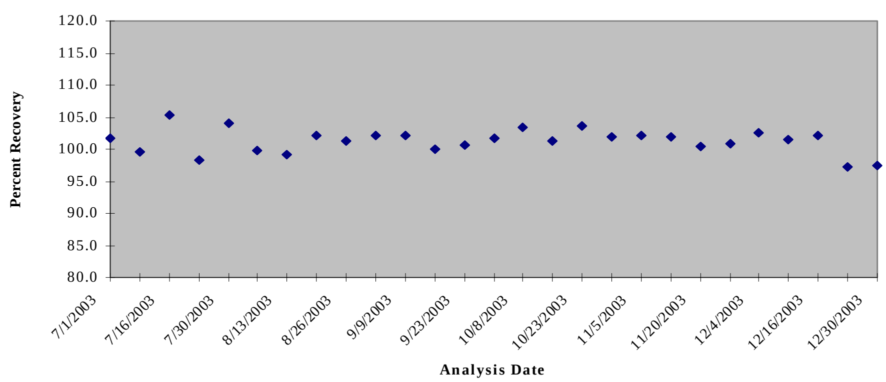


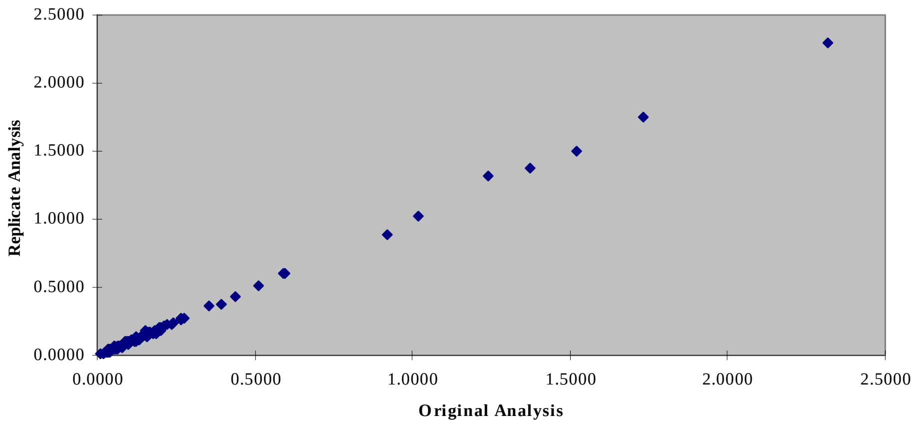
Figure 68. Recovery of Lead (Pb) in NIST SRM 1833 with Chester Kevex 771



Replicates

Five percent of the filters are re-analyzed and the results for select elements are compared. **Figures 69 through 80** compare replicate values for elements through regression analysis.

Figure 69. Results of Replicate Silicon (Si) Analysis with Chester 770 XRF



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.

2.4.3 RTI XRF Laboratory

2.4.3.1 Statistical Summary of QC Results –

Precision

The precision was monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for a select element were 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 (**Tables 18 and 19**). The data used to monitor precision are presented in **Figures 81 through 92**.

Table 18. Summary of RTI XRF 1 Laboratory QC Precision Recovery Data, ug/cm^2, 7/1/03 through 12/31/03

Element	n	Min	Max	Average	Std Dev	%CV
Si	431	9.90	10.8	10.3	0.20	1.95
Ti	431	9.00	9.50	9.20	0.11	1.22
Fe	431	10.3	10.9	10.7	0.13	1.24
Cd	431	5.43	5.91	5.69	0.08	1.43
Se	431	4.30	4.40	4.35	0.03	0.64
Pb	431	10.0	10.8	10.4	0.19	1.83

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 19. Summary of RTI XRF 2 Laboratory QC Precision Recovery Data, ug/cm^2, 7/1/03 through 12/31/03

Element	n	Min	Max	Average	Std Dev	%CV
Si	454	4.91	5.20	5.08	0.06	1.24
Ti	454	7.00	7.30	7.13	0.08	1.08
Fe	454	6.17	6.60	6.44	0.09	1.35
Cd	454	5.34	5.75	5.58	0.05	0.95
Se	454	4.00	4.99	4.14	0.07	1.63
Pb	454	8.03	8.69	8.35	0.16	1.87

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

Figure 70. Results of Replicate Sulfur (S) Analysis with Chester 770 XRF

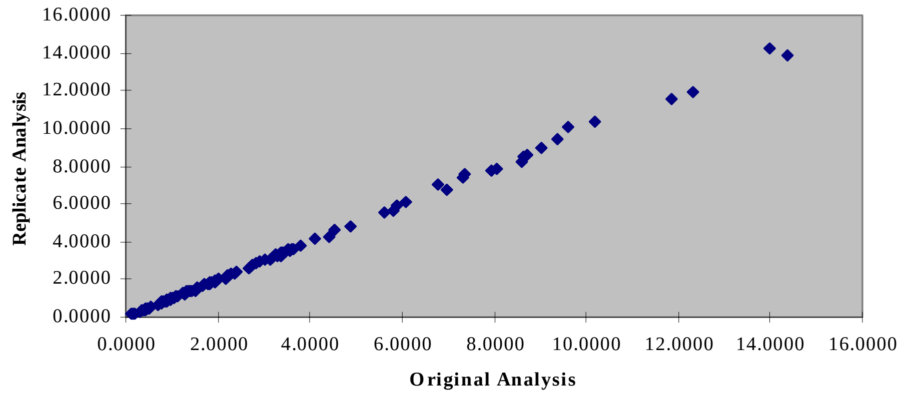


Figure 71. Results of Replicate Potassium (K) Analysis with Chester 770 XRF

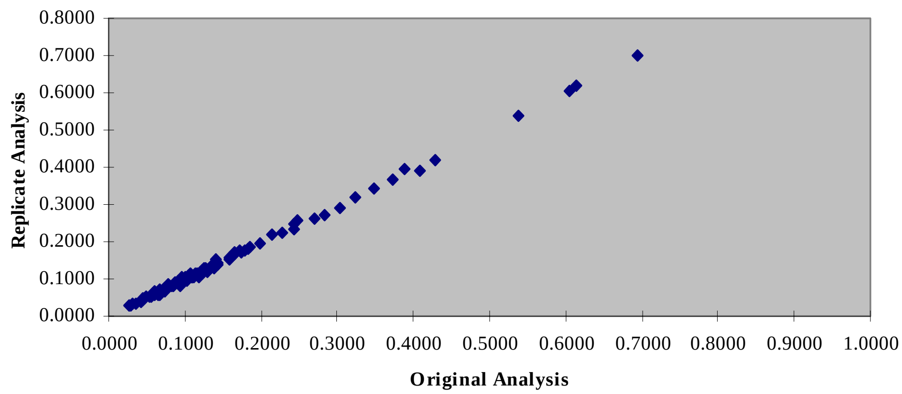


Figure 72. Results of Replicate Calcium (Ca) Analysis with Chester 770 XRF

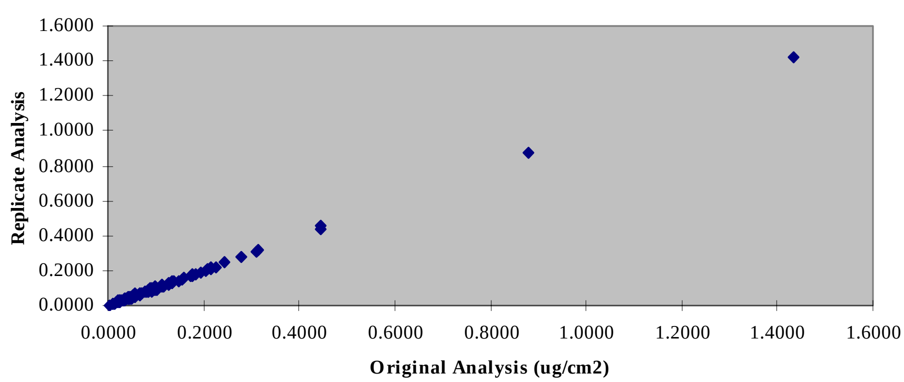


Figure 73. Results of Replicate Iron (Fe) Analysis with Chester 770 XRF

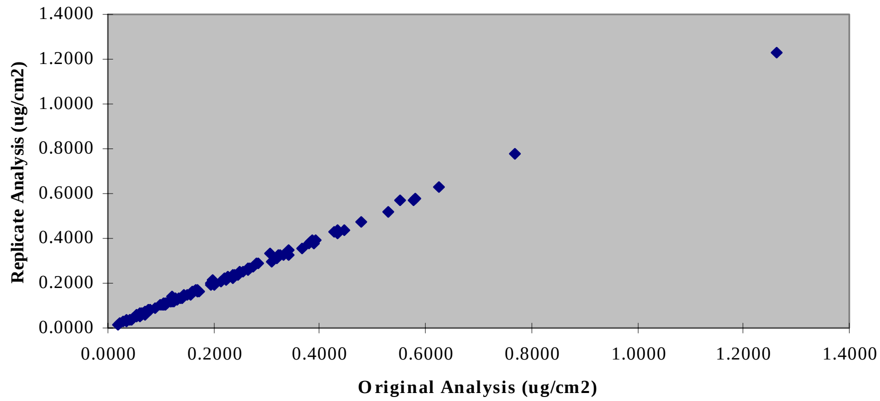


Figure 74. Results of Replicate Zinc (Zn) Analysis with Chester 770 XRF

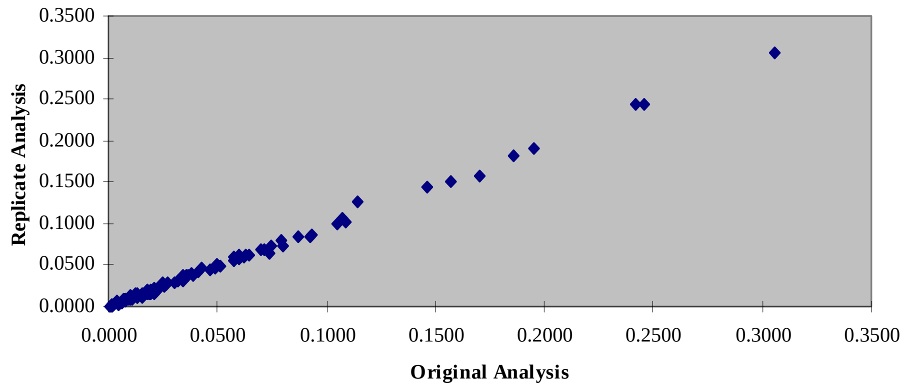


Figure 75. Results of Replicate Silicon (Si) Analysis with Chester 771 XRF

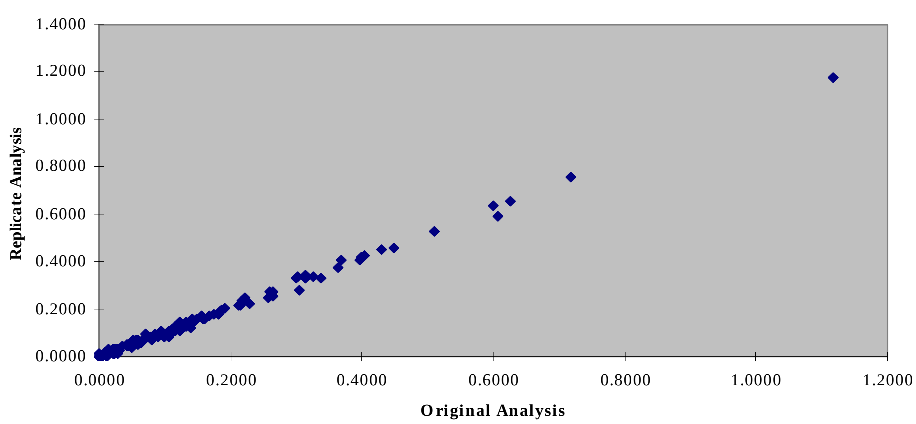


Figure 76. Results of Replicate Sulfur (S) Analysis with Chester 771 XRF

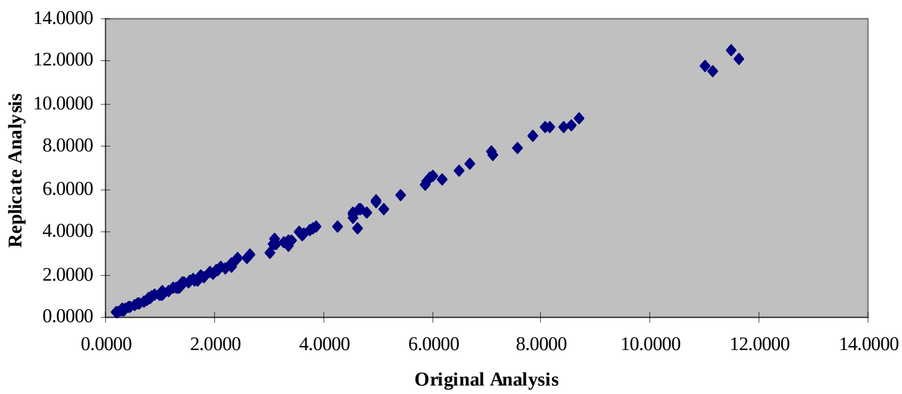


Figure 77. Results of Replicate Potassium (K) Analysis with Chester 771 XRF

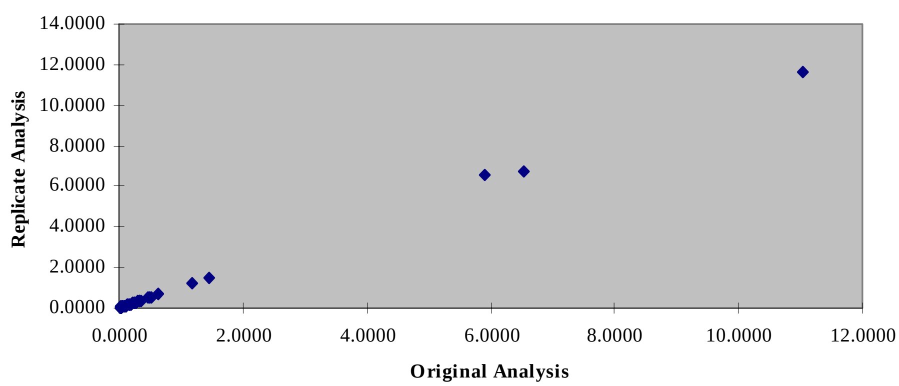


Figure 78. Results of Replicate Calcium (Ca) Analysis with Chester 771 XRF

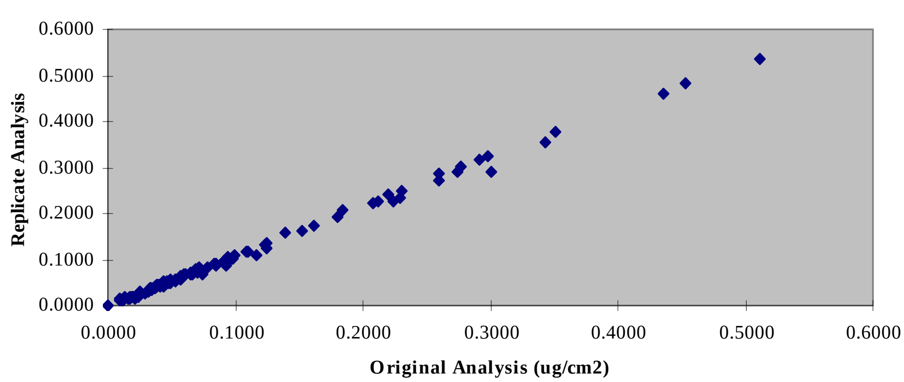


Figure 79. Results of Replicate Iron (Fe) Analysis with Chester 771 XRF

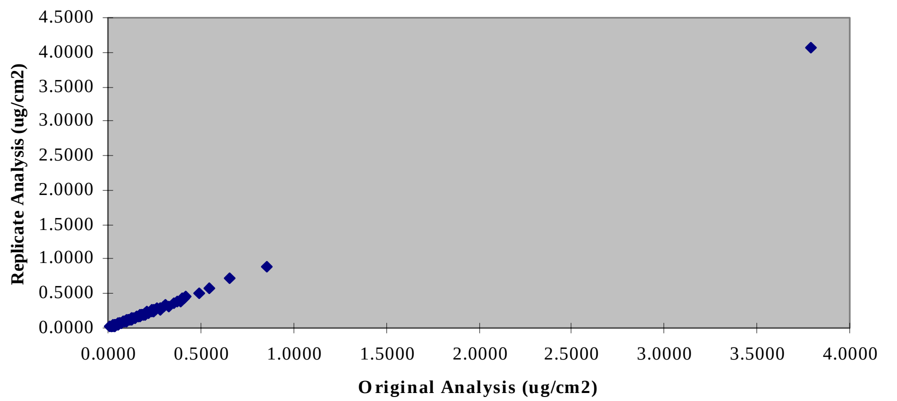


Figure 80. Results of Replicate Zinc (ZN) Analysis with Chester 771 XRF

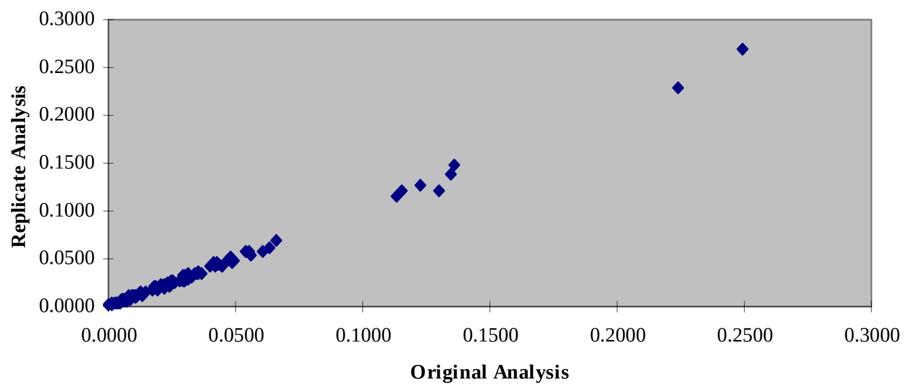


Figure 81. Recovery Precision for RTI XRF 1 with Silicon (Si)

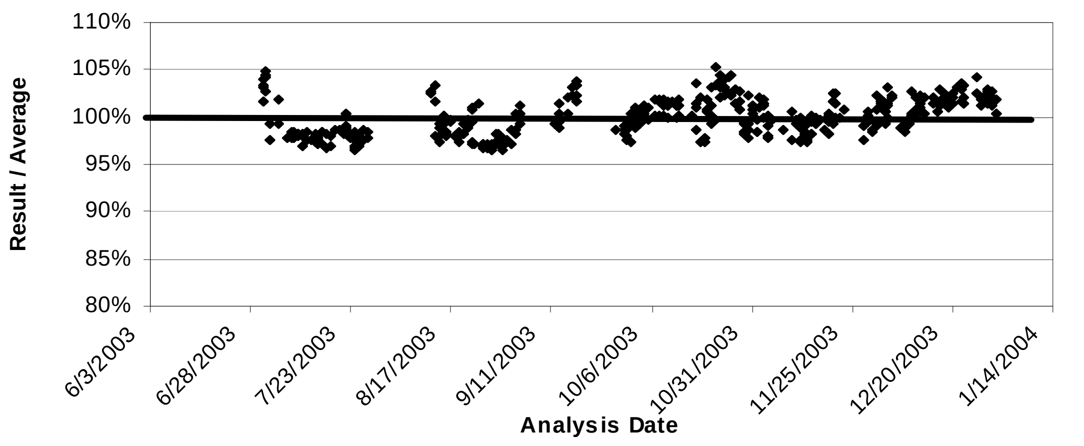


Figure 82. Recovery Precision for RTI XRF 1 with Iron (Fe)

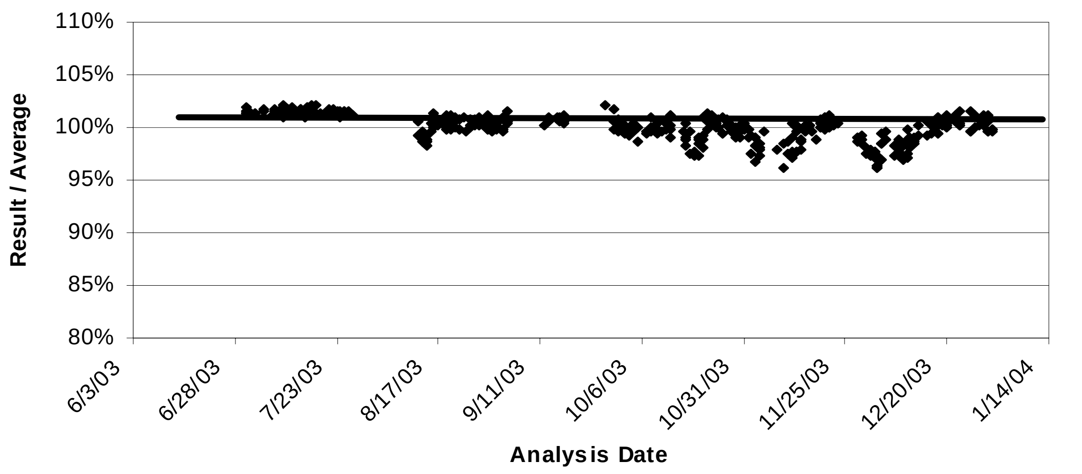


Figure 83. Recovery Precision for RTI XRF 1 with Selenium (Se)

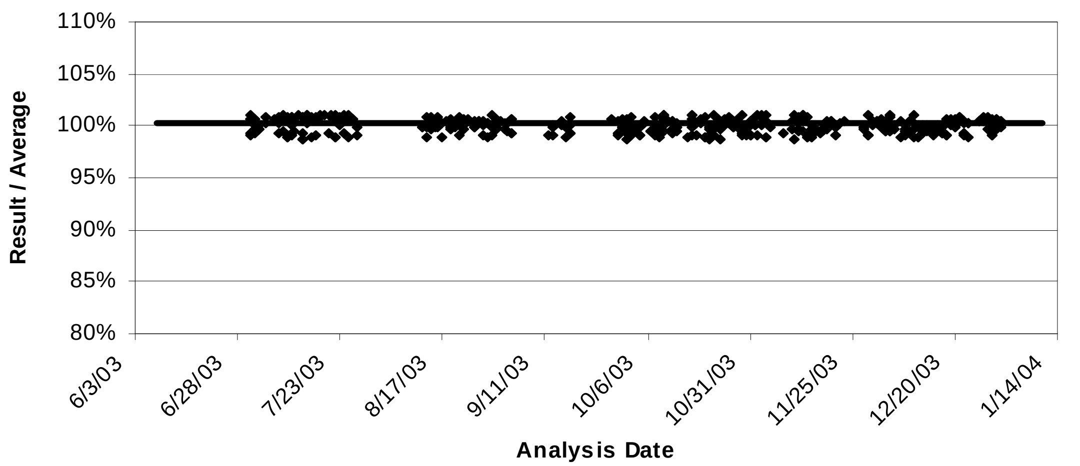


Figure 84. Recovery Precision for RTI XRF 1 with Titanium (Ti)

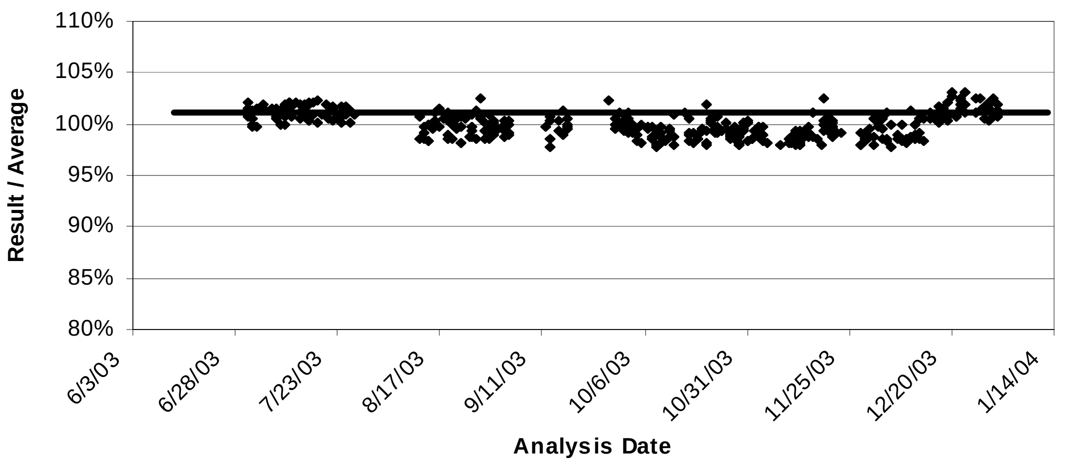


Figure 84. Recovery Precision for RTI XRF 1 with Cadmium (Cd)

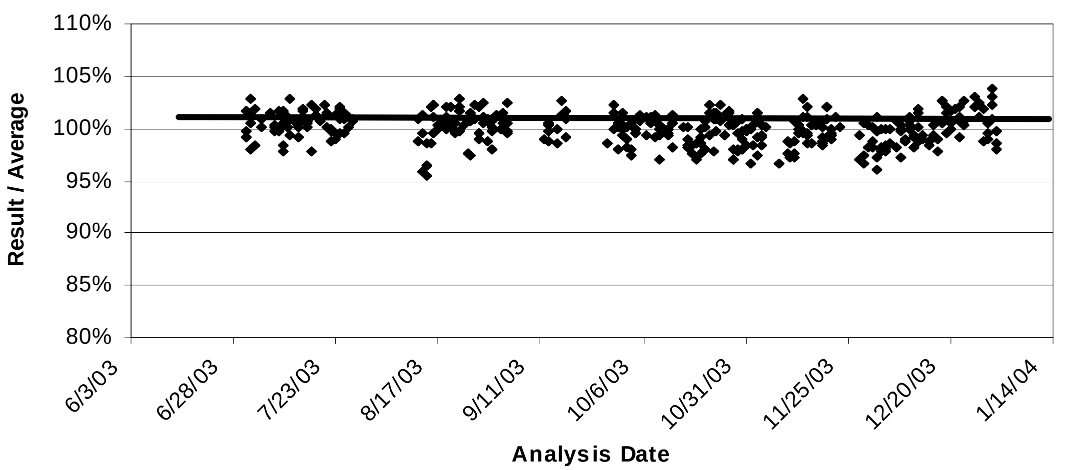


Figure 86. Recovery Precision for RTI XRF 1 with Lead (Pb)

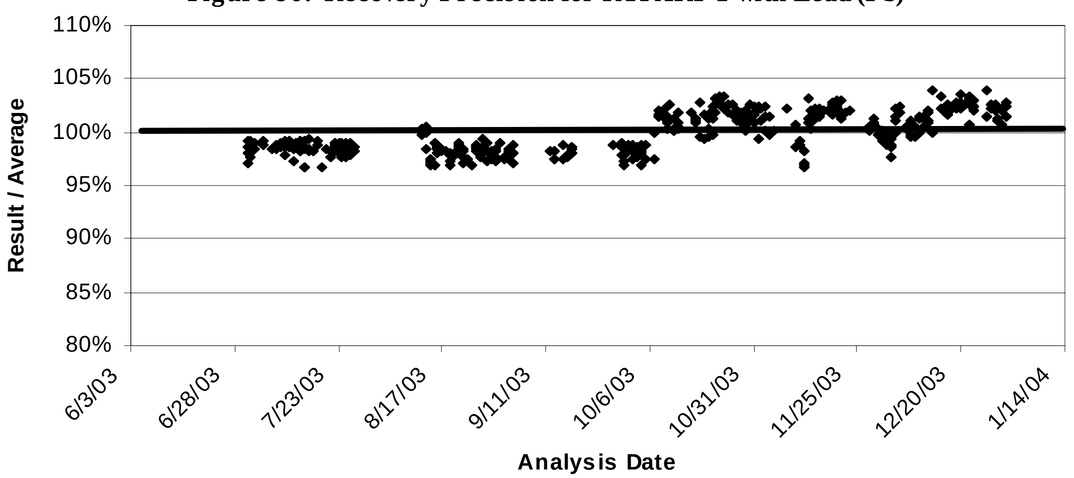


Figure 87. Recovery Precision for RTI XRF 2 with Silicon (Si)

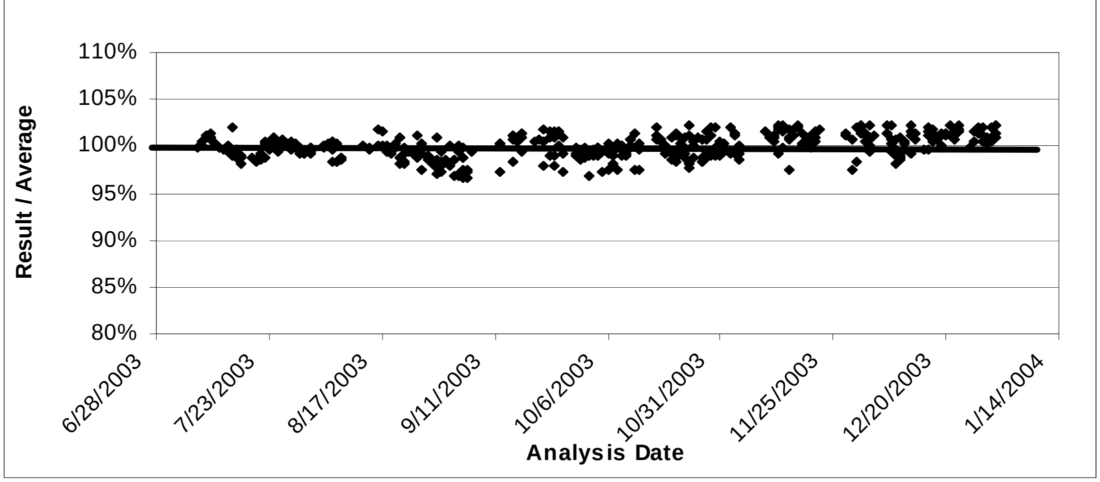


Figure 88. Recovery Precision for RTI XRF 2 with Iron (Fe)

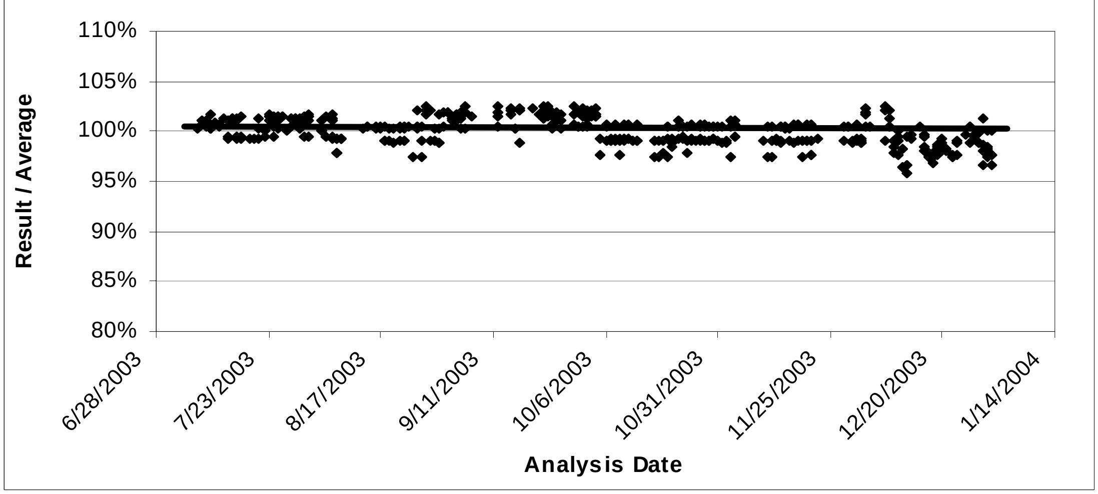


Figure 89. Recovery Precision for RTI XRF 2 with Selenium (Se)

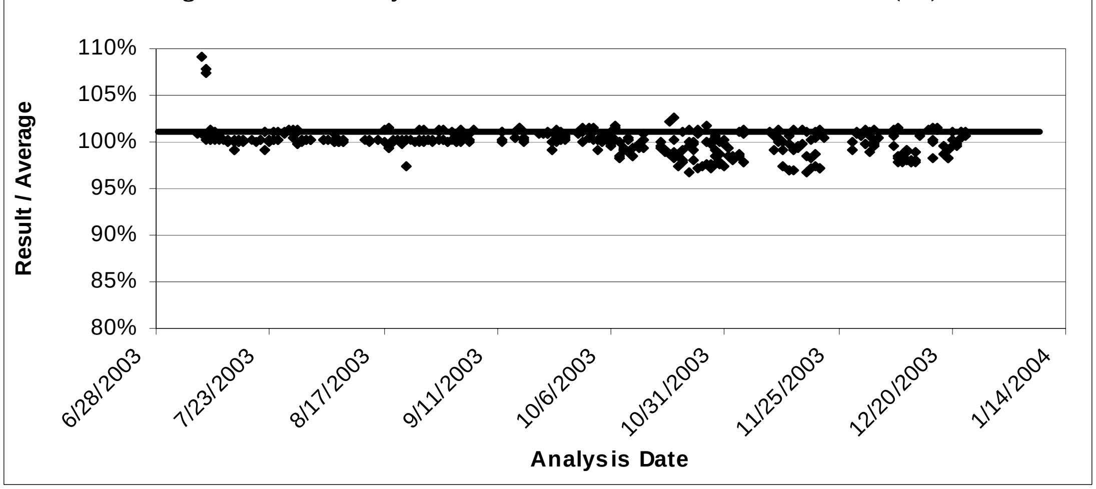


Figure 90. Recovery Precision for RTI XRF 2 with Titanium (Ti)

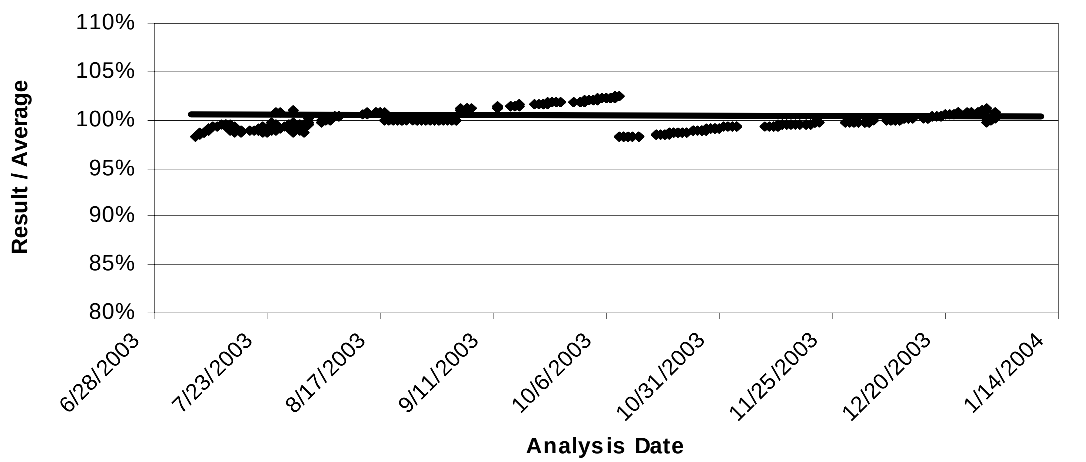


Figure 91. Recovery Precision for RTI XRF 2 with Cadmium (Cd)

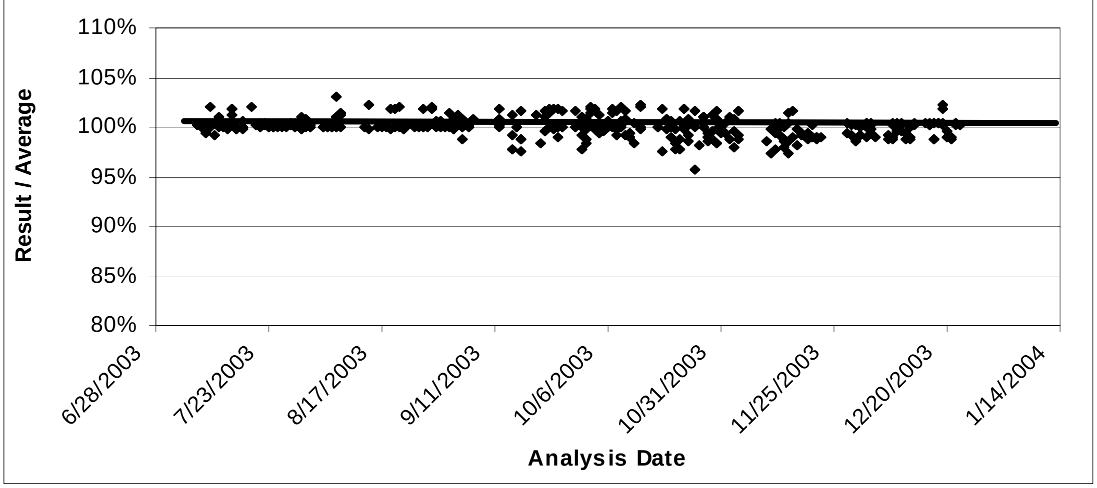
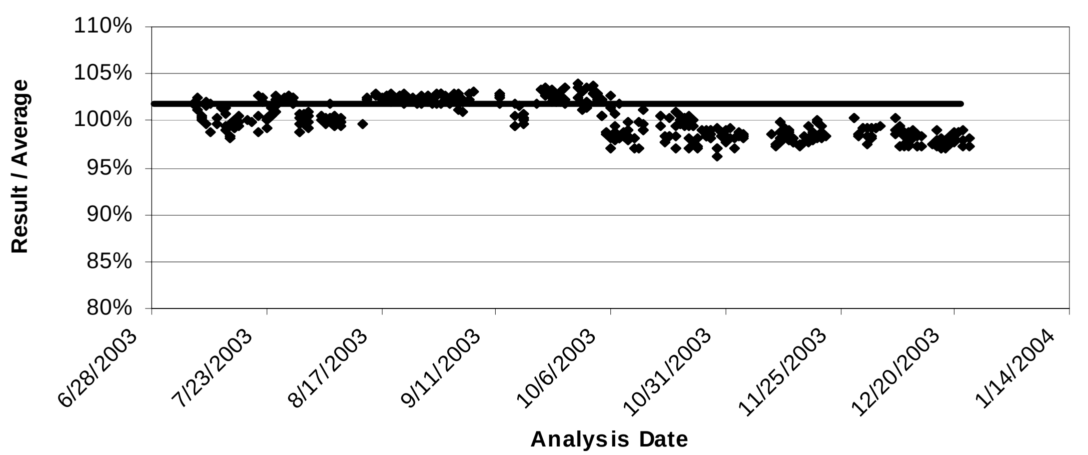


Figure 92. Recovery Precision for RTI XRF 2 with Lead (Pb)



Recovery

Recovery or system accuracy was determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of measured and expected values. **Figures 93 through 118** show recovery for 12 select elements spanning the range of the 48 elements normally measured. The recovery values for all elements ranged between 89 and 102 percent for XRF 1 and between 90 and 101 percent for XRF 2, as shown in **Table 20.**

Table 20. Recovery Determined from Analysis of NIST Standard Reference Material Filters 1832 and 1833, XRF 1 and 2, 7/1/03 through 12/31/03

Element	XRF 1	XRF 2
	Range % Recovery	Range % Recovery
Al	93 - 102	93 - 101
Si*	90 - 93	90 - 92
Si**	90 - 99	91 - 96
K	91 - 97	91 - 98
Ca	95 - 101	95 - 100
Ti	89 - 96	90 - 96
V	96 - 101	95 - 100
Mn	93 - 100	96 - 100
Fe	92 - 96	91 - 96
Co	95 - 99	95 - 101
Cu	89 - 95	90 - 96
Zn	90 - 97	90 - 94
Pb	92 - 100	90 - 101

*SRM 1832
**SRM 1833

Figure 93. Recovery Precision of Aluminum (Al) in NIST SRM 1832 with RTI XRF 1

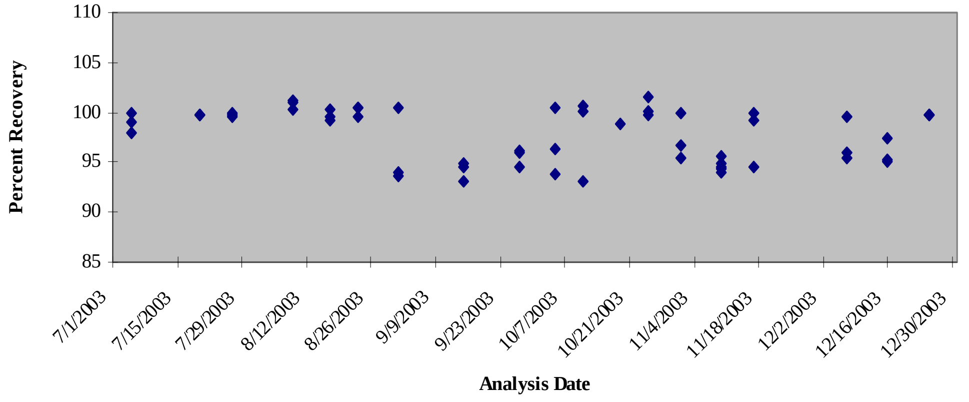


Figure 94. Recovery Precision of Silicon (Si) in NIST SRM 1832 with RTI XRF 1

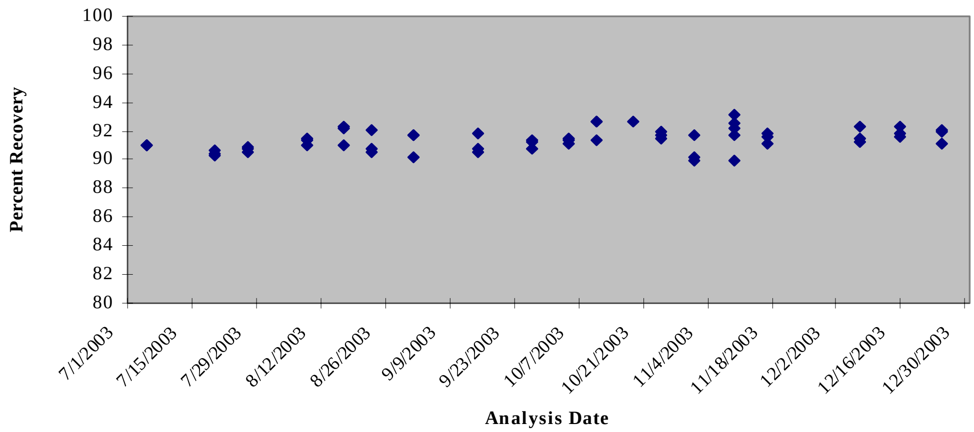


Figure 95. Recovery Precision of Silicon (Si) in NIST SRM 1833 with RTI XRF 1

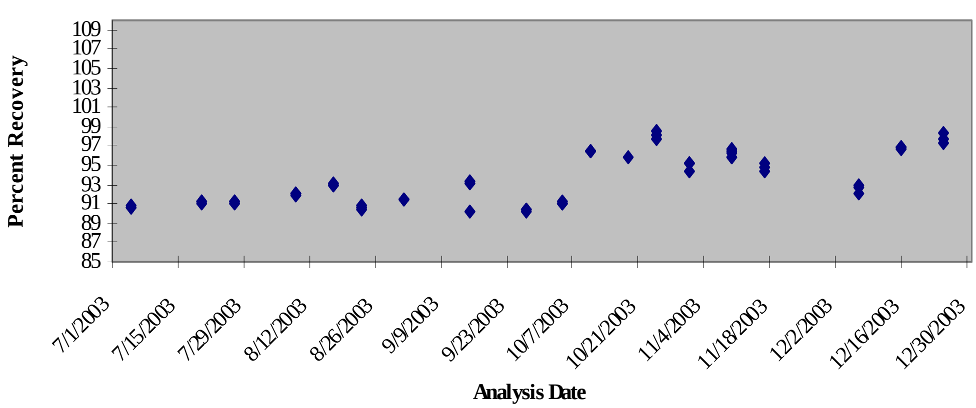


Figure 96. Recovery Precision of Potassium (K) in NIST SRM 1833 with RTI XRF 1

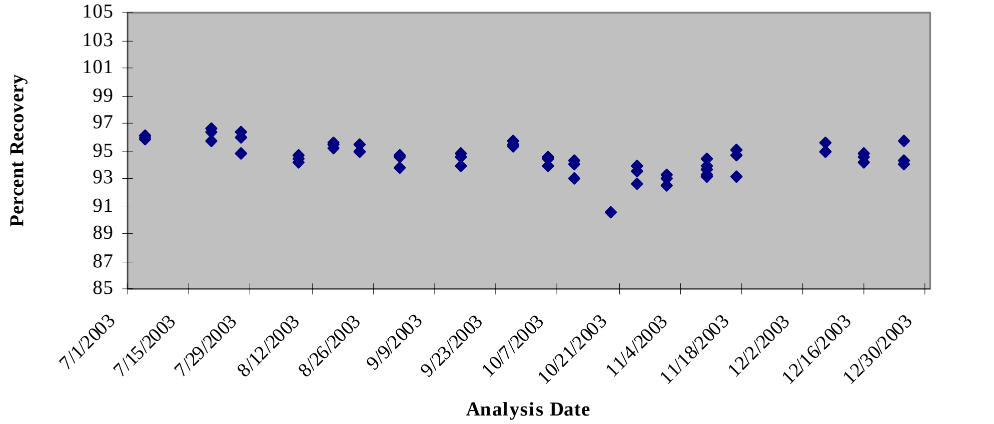


Figure 97. Recovery Precision of Calcium (Ca) in NIST SRM 1832 with RTI XRF 1

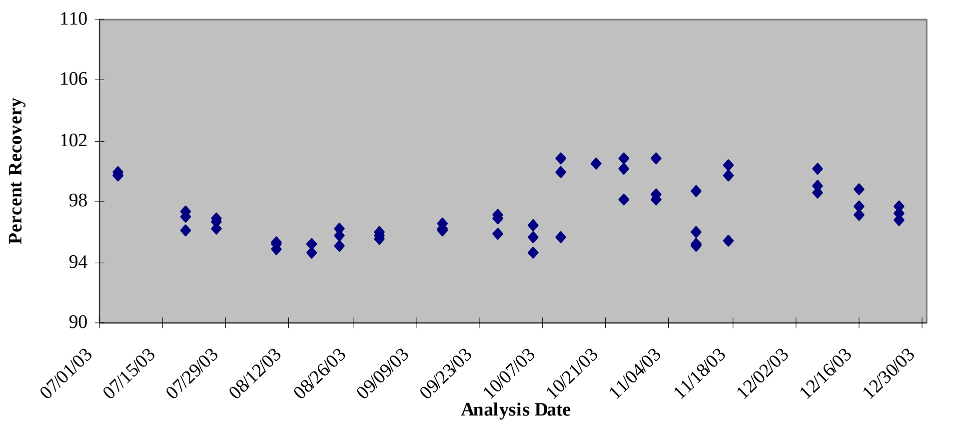


Figure 98. Recovery Precision of Titanium (Ti) in NIST SRM 1833 with RTI XRF 1

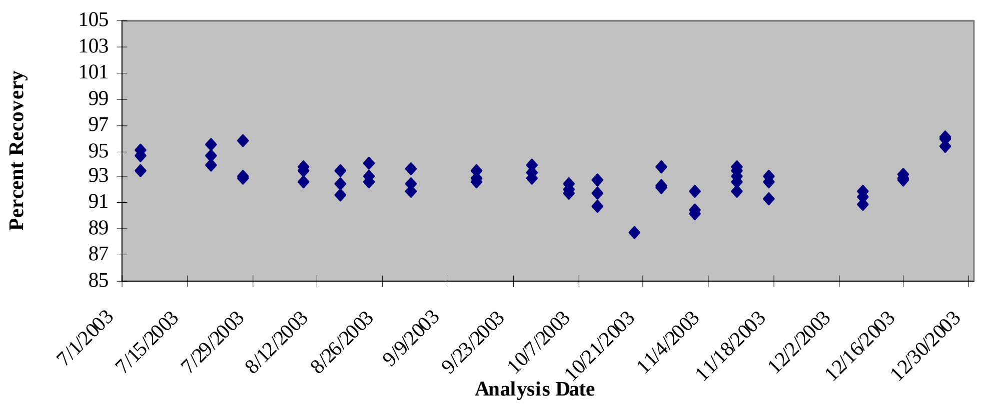


Figure 99. Recovery Precision of Vanadium (V) in NIST SRM 1832 with RTI XRF 1

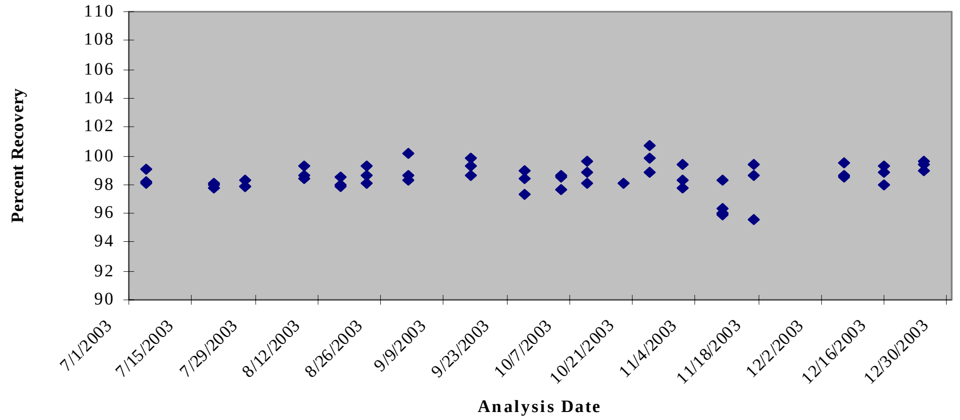


Figure 100. Recovery Precision of Manganese (Mn) in NIST SRM 1832 with RTI XRF 1

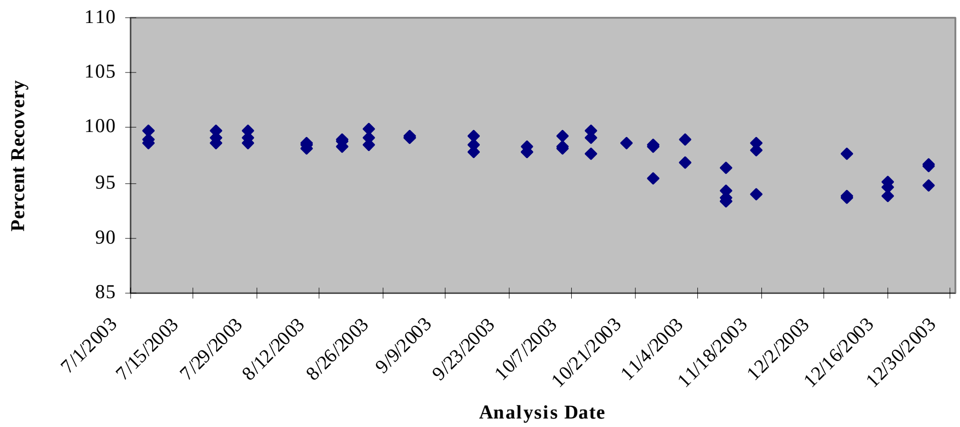
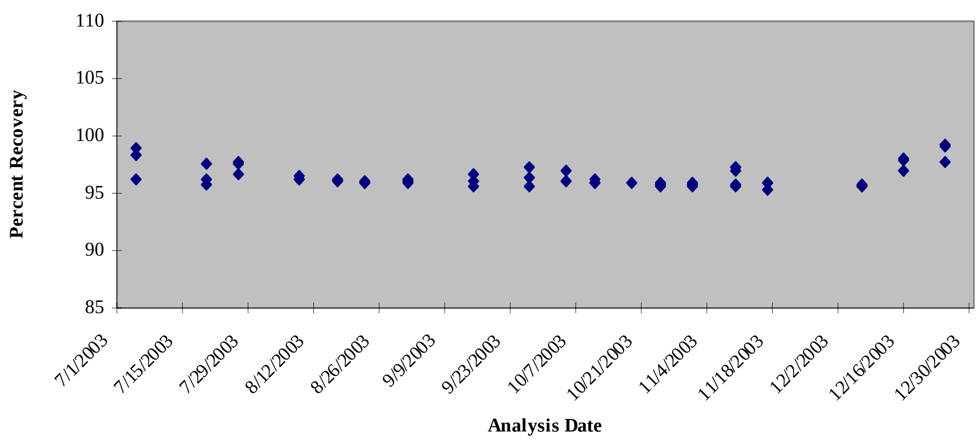


Figure 101. Recovery Precision of Cobalt (Co) in NIST SRM 1832 with RTI XRF 1



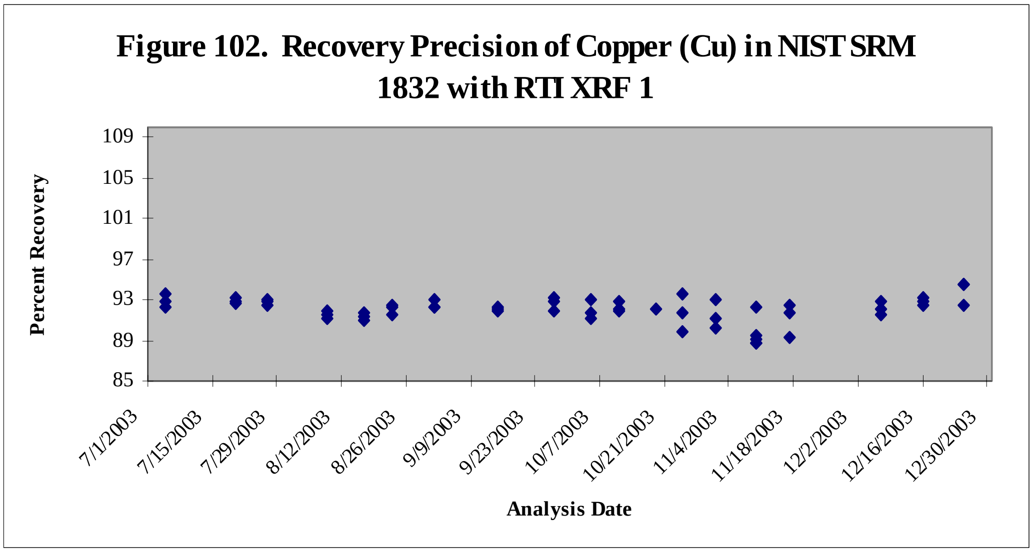


Figure 102. Recovery Precision of Copper (Cu) in NIST SRM 1832 with RTI XRF 1
Percent Recovery
109
105
101
97
93
89
85
7/1/2003
7/15/2003
7/29/2003
8/12/2003
8/26/2003
9/9/2003
9/23/2003
10/7/2003
10/21/2003
11/4/2003
11/18/2003
12/2/2003
12/16/2003
12/30/2003
Analysis Date

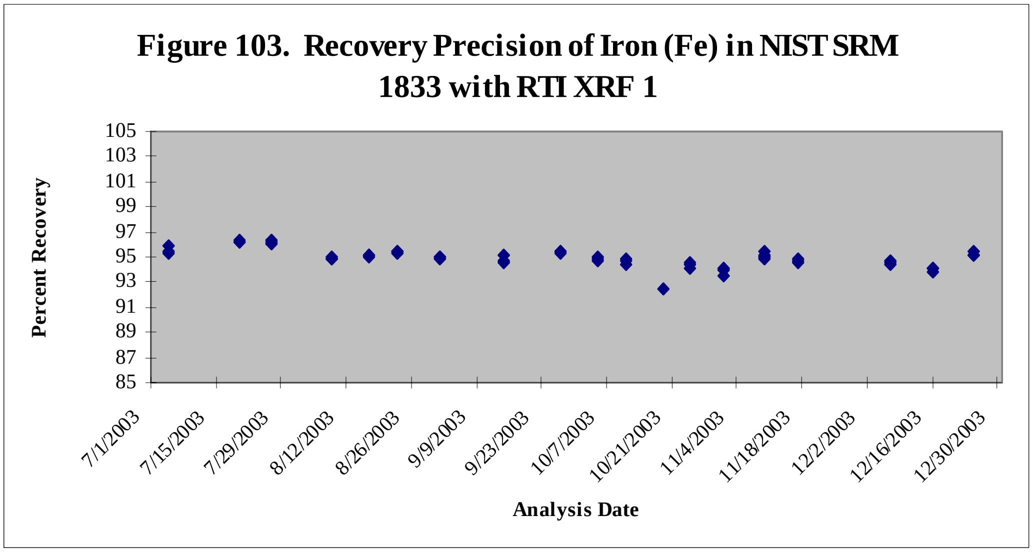


Figure 103. Recovery Precision of Iron (Fe) in NIST SRM 1833 with RTI XRF 1
Percent Recovery
105
103
101
99
97
95
93
91
89
87
85
7/1/2003
7/15/2003
7/29/2003
8/12/2003
8/26/2003
9/9/2003
9/23/2003
10/7/2003
10/21/2003
11/4/2003
11/18/2003
12/2/2003
12/16/2003
12/30/2003
Analysis Date

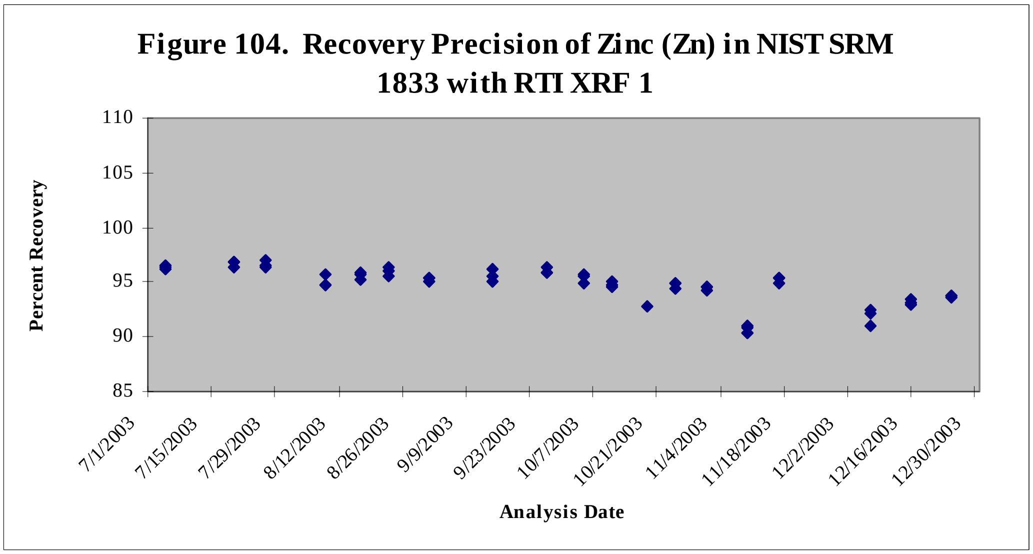


Figure 104. Recovery Precision of Zinc (Zn) in NIST SRM 1833 with RTI XRF 1
Percent Recovery
110
105
100
95
90
85
7/1/2003
7/15/2003
7/29/2003
8/12/2003
8/26/2003
9/9/2003
9/23/2003
10/7/2003
10/21/2003
11/4/2003
11/18/2003
12/2/2003
12/16/2003
12/30/2003
Analysis Date

Figure 105. Recovery Precision of Lead (Pb) in NIST SRM 1833 with RTI XRF 1

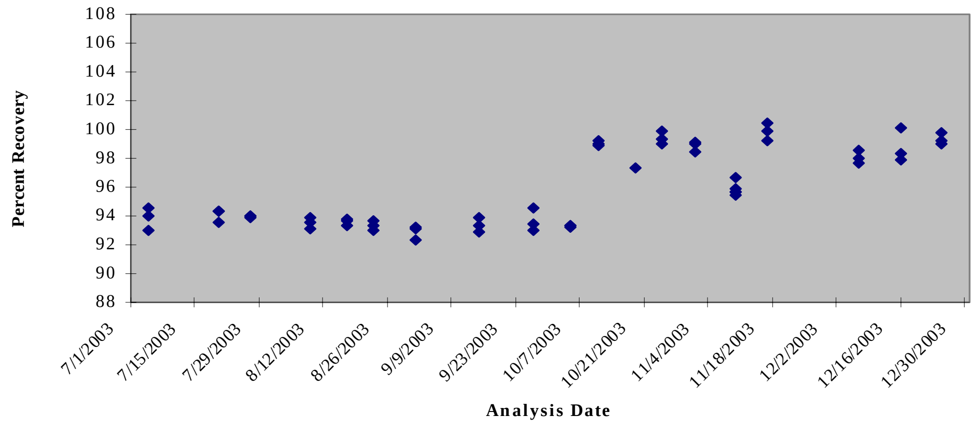


Figure 106. Recovery Precision of Aluminum (Al) in NIST SRM 1832 with RTI XRF 2

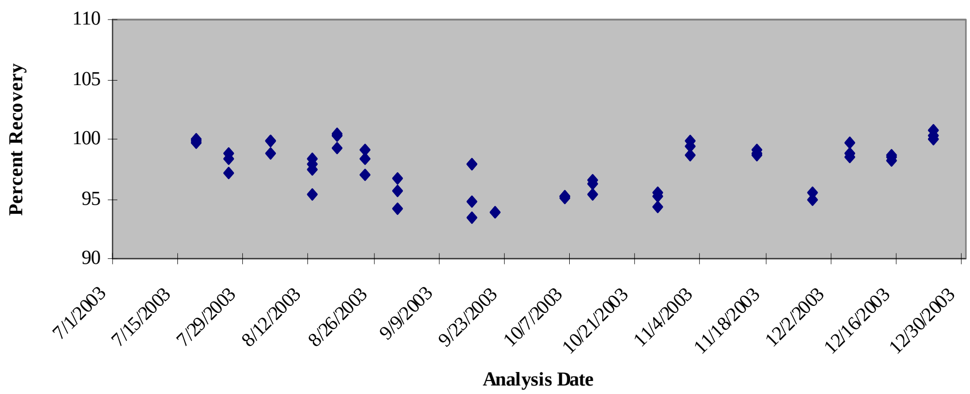


Figure 107. Recovery Precision of Silicon (Si) in NIST SRM 1832 with RTI XRF 2

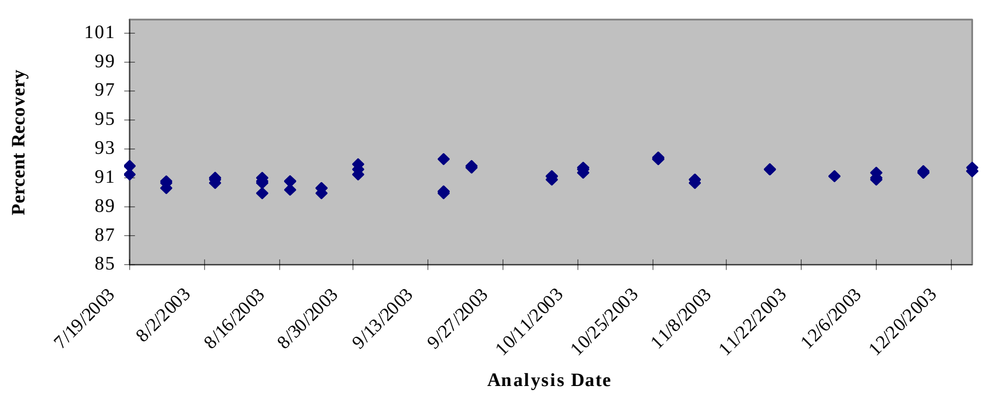


Figure 108. Recovery Precision of Silicon (Si) in NIST SRM 1833 with RTI XRF 2

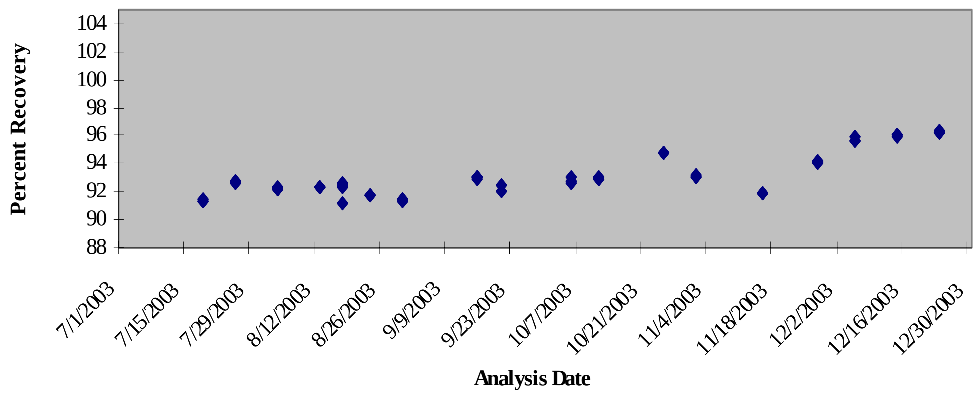


Figure 109. Recovery Precision of Potassium (K) in NIST SRM 1833 with RTI XRF 2

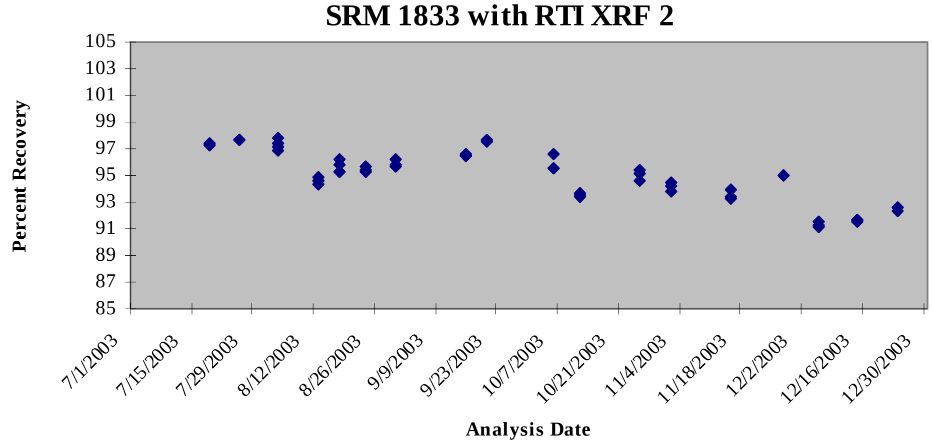


Figure 110. Recovery Precision of Calcium (Ca) in NIST SRM 1832 with RTI XRF 2

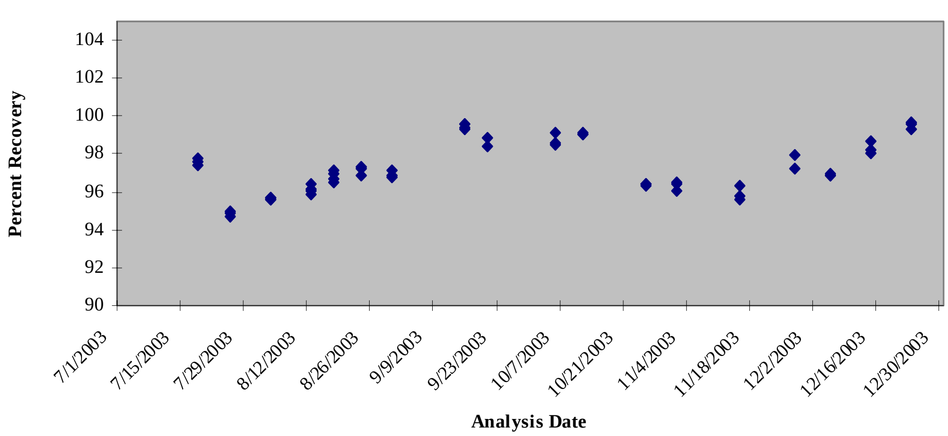


Figure 111. Recovery Precision of Titanium (Ti) in NIST SRM 1833 with RTI XRF 2

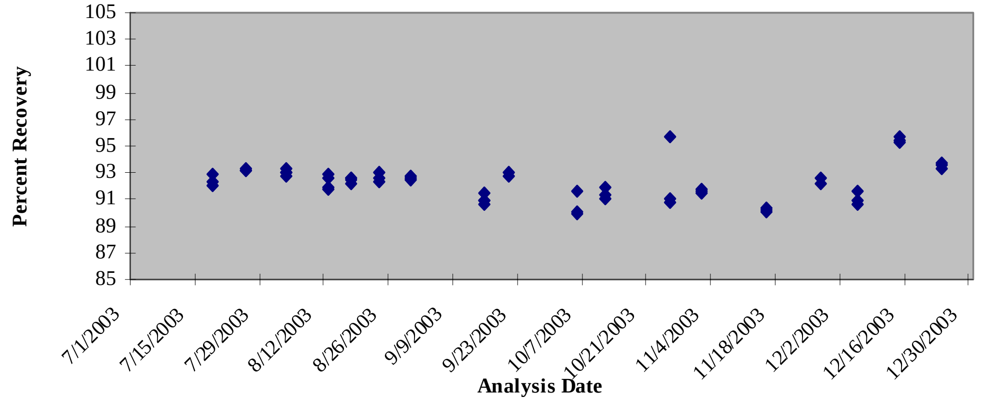


Figure 112. Recovery Precision of Vanadium (V) in NIST SRM 1832 with RTI XRF 2

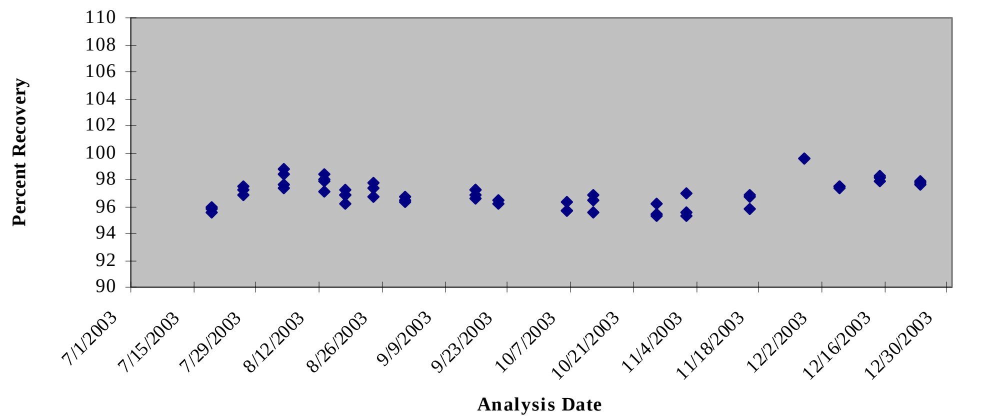


Figure 113. Recovery Precision of Manganese (Mn) in NIST SRM 1832 with RTI XRF 2

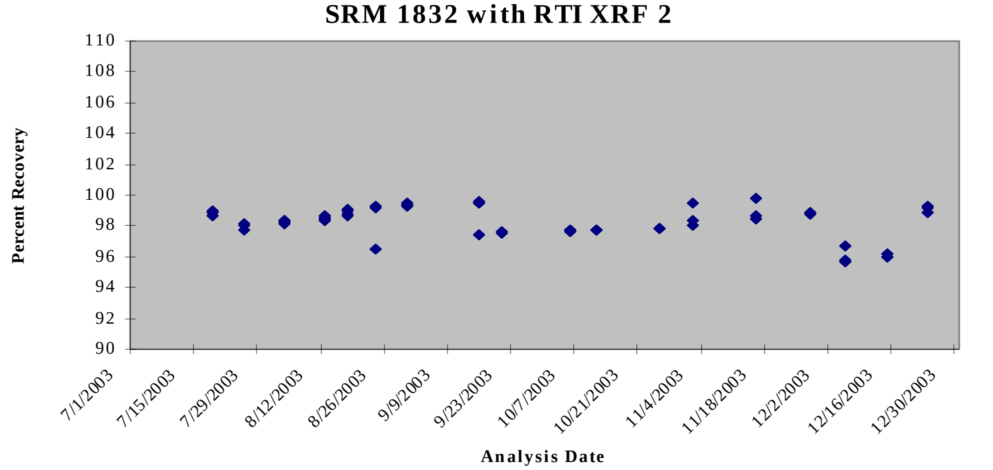


Figure 114. Recovery Precision of Cobalt (Co) in NIST SRM 1832 with RTI XRF 2

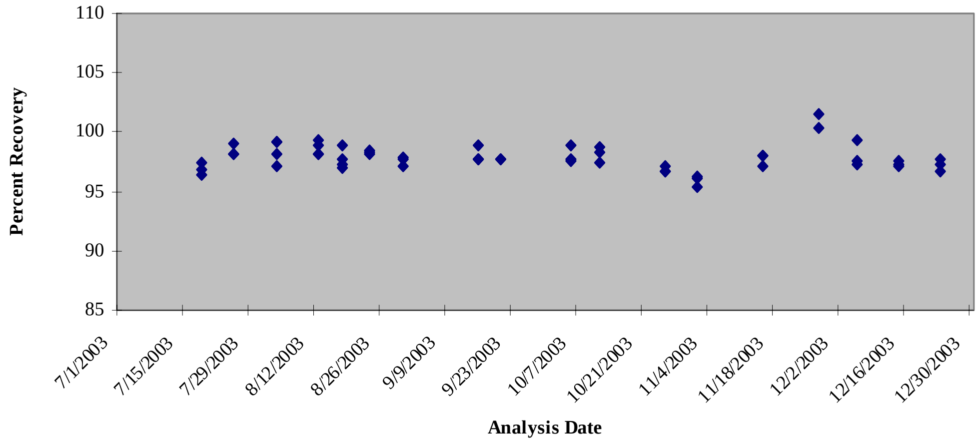


Figure 115. Recovery Precision of Iron (Fe) in NIST SRM 1833 with RTI XRF 2

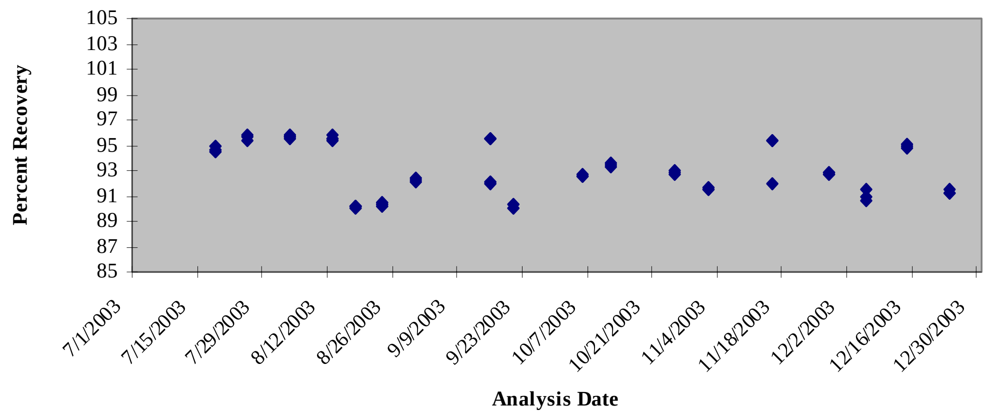


Figure 116. Recovery Precision of Copper (Cu) in NIST SRM 1832 with RTI XRF 2

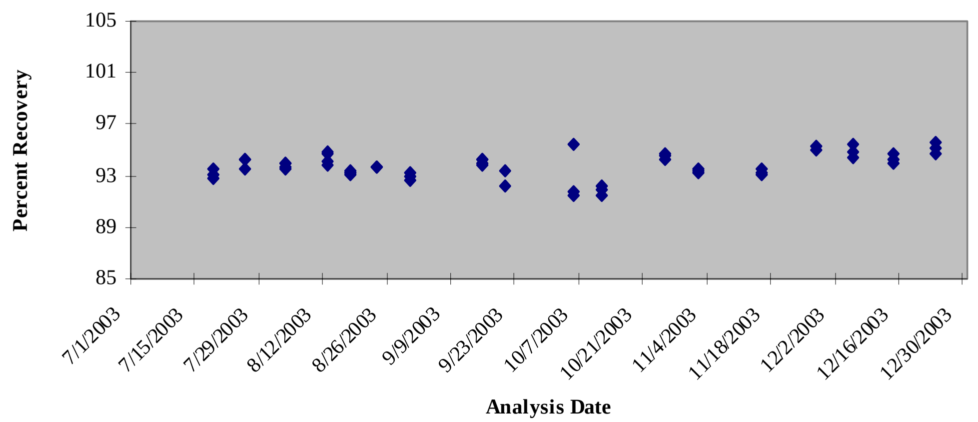


Figure 117. Recovery Precision of Zinc (Zn) in NIST SRM 1833 with RTI XRF 2

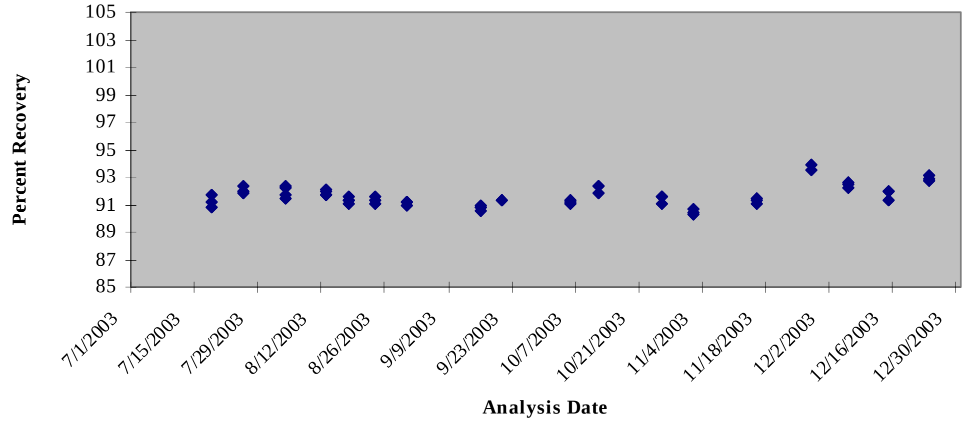
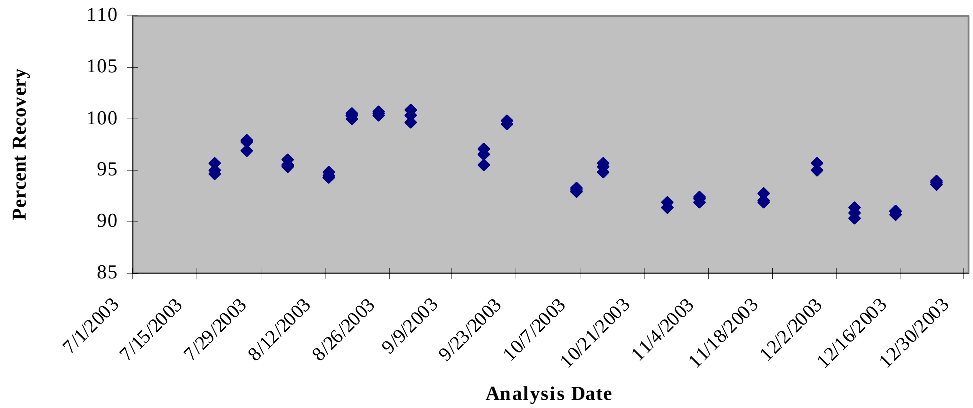


Figure 118. Recovery Precision of Lead (Pb) in NIST SRM 1833 with RTI XRF 2



Replicates

Ten percent of the filters were re-analyzed and the results for select elements compared. **Figures 119 through 130** compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.9920, except for potassium on XRF 1. The RPD values for potassium on XRF 1 did not exceed 20 RPD, which indicates good correlation and were within QC acceptance limits. The values and correlation coefficients for XRF 1 range from 0.9818 to 1.0003, and the values and correlation coefficients for XRF 2 range from 0.9957 to 1.0003, indicating acceptable replication on both instruments.

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 and a problem with the cellulose filter on the second excitation condition for both instruments in September 2003.

2.4.3.3 Corrective Actions – Both RTI XRF's experienced a problem with the second excitation condition, in which the cellulose filter used in this condition became damaged due to high run tine and exposure to the high powered x-ray tubes. In October 2003, the cellulose filter in both instruments was replaced, 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 failed to meet the QC requirements and each element is shown to be stable. The cellulose filter is replaced on a monthly basis and calibration is verified. To correct the breakdown of the cellulose filter, ThermoNoran has designed a graphite filter for the second condition. The graphite filter will be more durable, and through testing, showed no change in recovery for those elements in the second condition.

In September 2003, concern was expressed that there is a bias or difference between results for the different XRF's near to, but above the detection limits, that is, in the range of the MDL and MQL. It was revealed that RTI's XRF results have a slight positive bias relative to Chester Labnet for several elements and that the biases arise from the differences in the ways the laboratory blank filter backgrounds are treated by both laboratories. In order to reduce the bias between the two laboratories, we determined median values for selected elements from analysis of ten laboratory blank filters, and subtracted these values from those of the routine field samples. The median value was used rather than the average because the XRF does not report values less than zero; consequently, the average of this "censored" data is biased high relative to the true average. Use of the median value also protects against outliers in the laboratory blank data caused by trace contamination. Only elements for which the average laboratory blank value is above three (3) times the uncertainty calculated by the ThermoNoran software were subject to this correction, but, as noted above, it is the median value that is subtracted to make the correction. Examples of elements that are currently subject to correction on both instruments are Al, Ba, Cu, and Fe. It should be noted that the application of the bias (laboratory background) corrections affects the recovery values for the NIST SRM's and Micromatter standards less than 1%. This correction has shown to eliminate any significant bias between the two laboratories at the lowest concentration levels.

Figure 119. Results of Replicate Silicon (Si) Analysis with RTI XRF 1

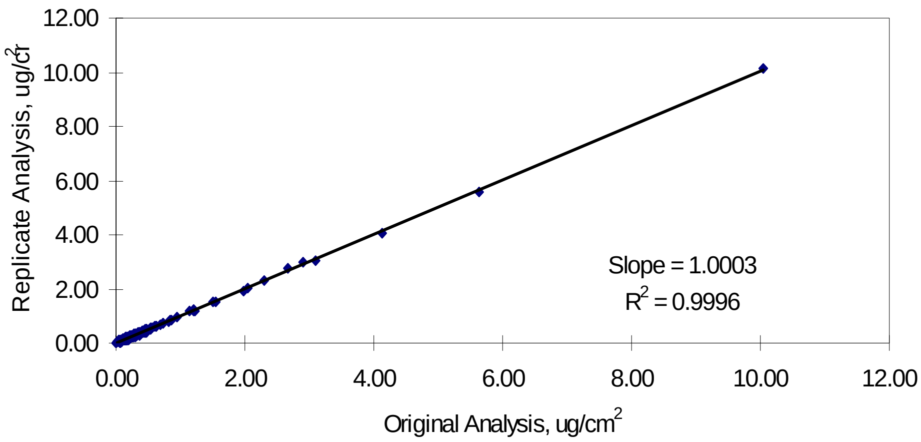


Figure 120. Results of Replicate Sulfur (S) Analysis with RTI XRF 1

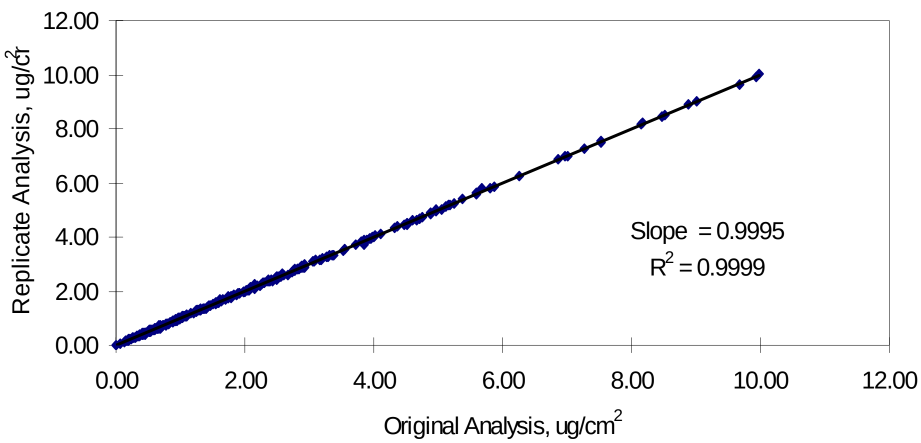


Figure 121. Results of Replicate Potassium (K) Analysis with RTI XRF 1

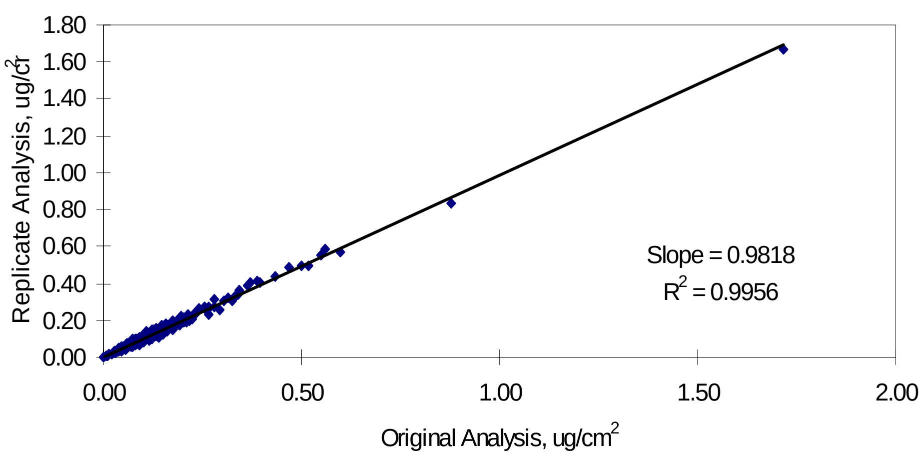


Figure 122. Results of Calcium (Ca) Analysis with RTI XRF 1

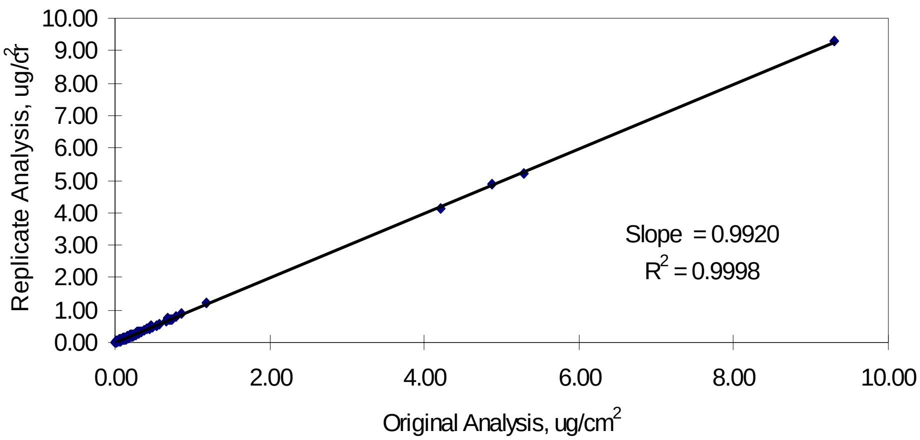


Figure 123. Results of Replicate Iron (Fe) Analysis with RTI XRF 1

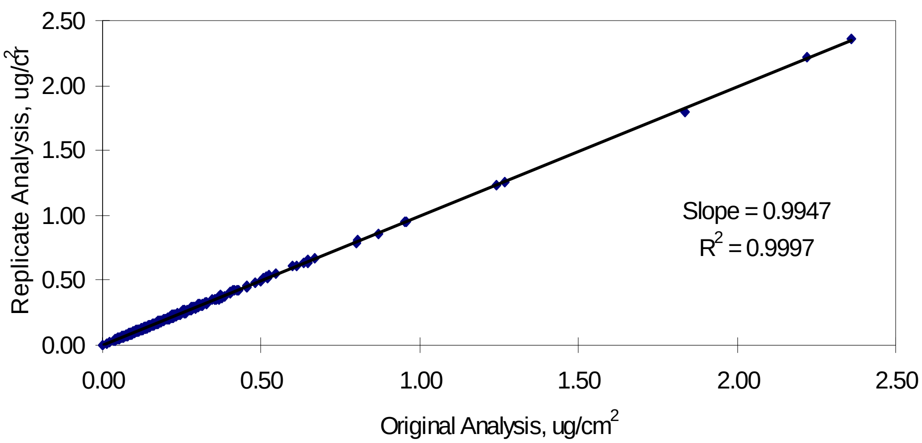


Figure 124. Results of Replicate Zinc (Zn) Analysis with RTI XRF 1

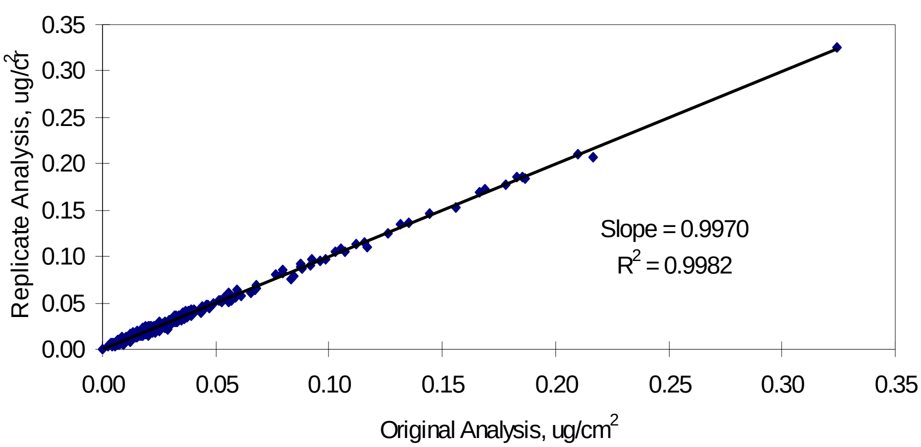


Figure 125. Results of Replicate Silicon (Si) Analysis with RTI XRF 2

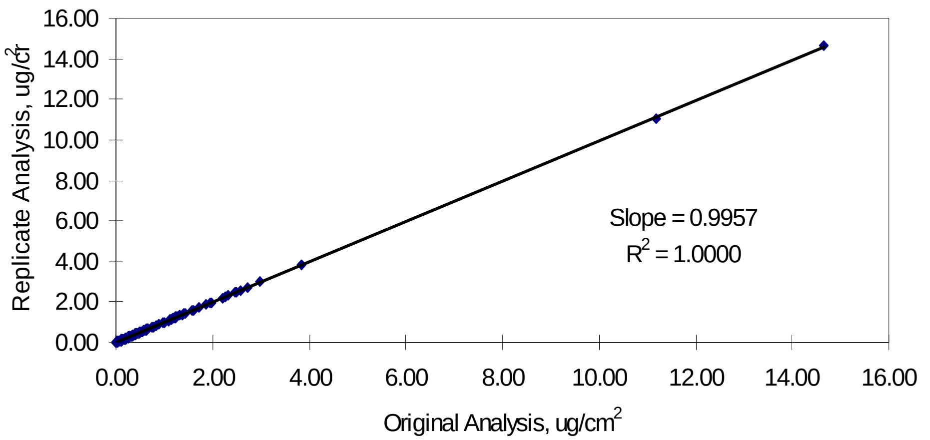


Figure 126. Results of Replicate Sulfur (S) Analysis with RTI XRF 2

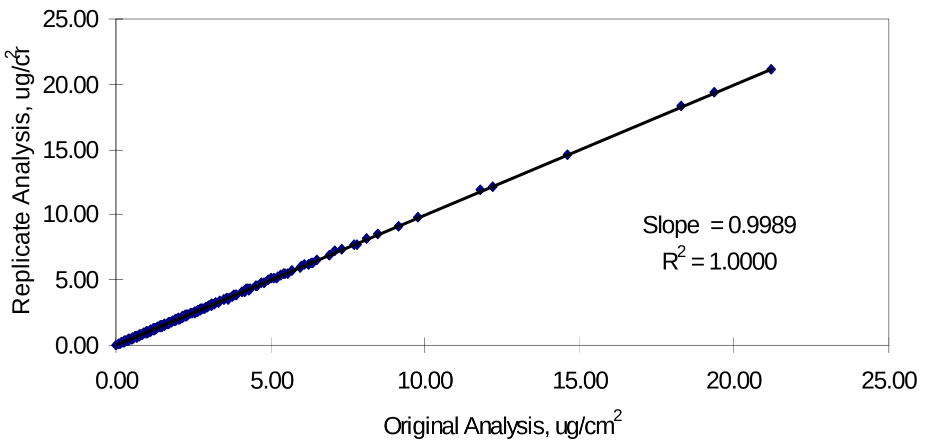


Figure 127. Results of Replicate Potassium (K) Analysis with RTI XRF 2

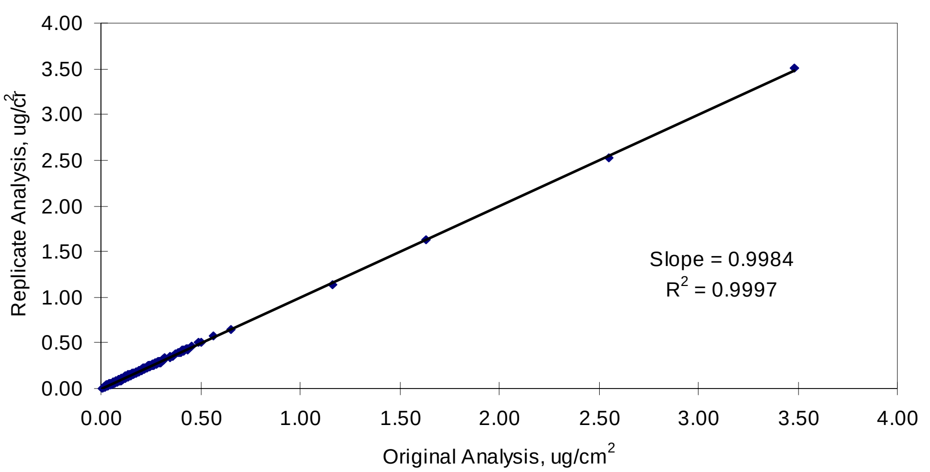


Figure 128. Results of Replicate Calcium (Ca) Analysis with RTI XRF 2

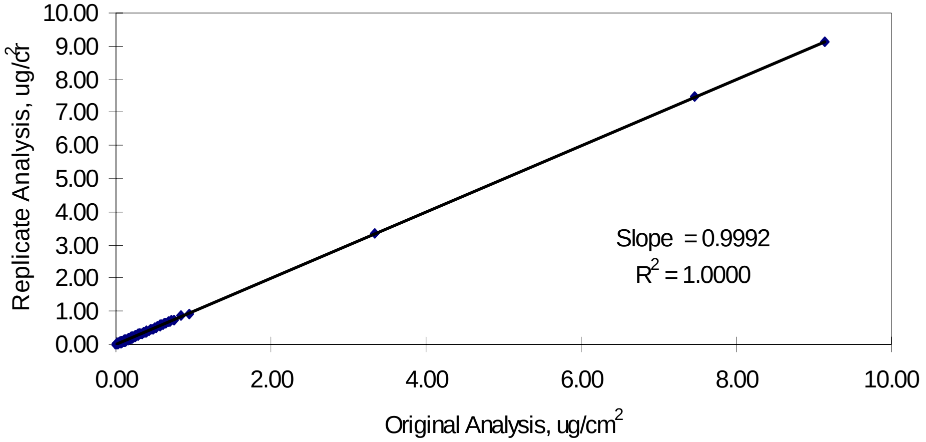


Figure 129. Results of Replicate Iron (Fe) Analysis with RTI XRF 2

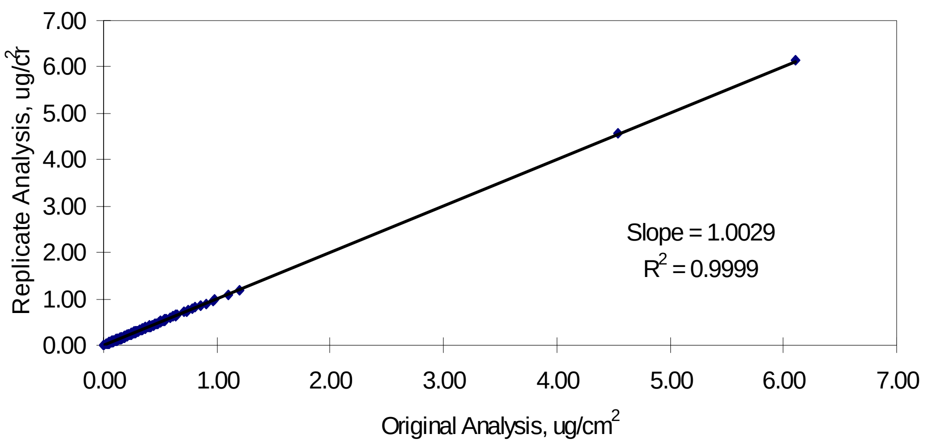
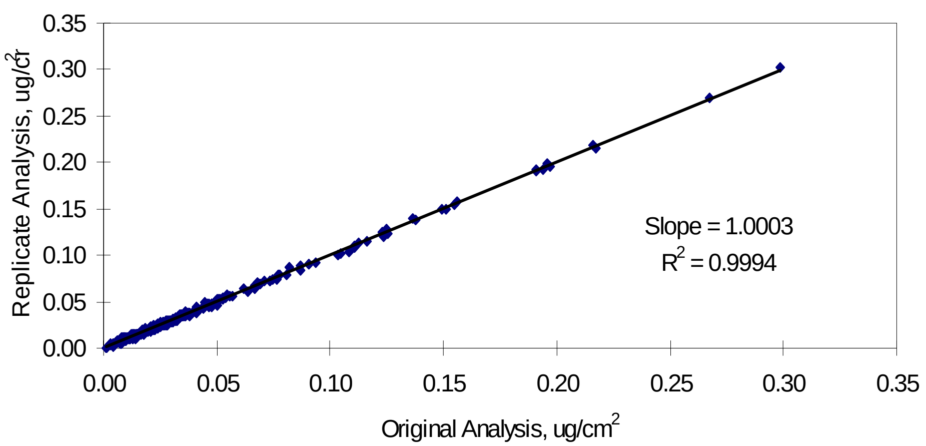


Figure 130. Results of Replicate Zinc (Zn) Analysis with RTI XRF 2

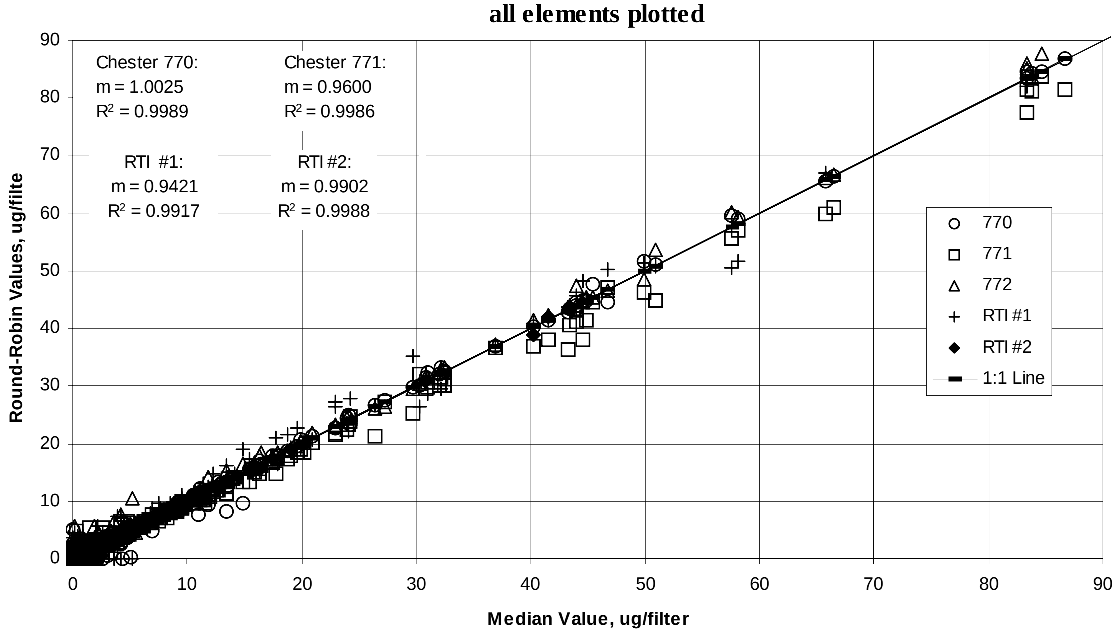


2.4.4 Round-Robin Intercomparison Results

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. A total of one hundred and twenty-five (125) round-robin filters have been used during the Speciation program. The uncertainty value for each analyte was not considered in the overall evaluation of the round robin data.

Figure 131 shows the round-robin analyses vs. the median of all observations. That is, the measured values the 48 elements for each filter/element combination on the four instruments plotted against the median value (median value is calculated from the results for each of the four instruments).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, along with correlation coefficients (R-square). All four instruments have a slope greater than 0.94, which indicates good agreement between the instruments.

Figure 131. Round Robin Results vs Median of all Reported Values all elements plotted



2.4.5 Summary of Audit Findings and Recommendations

There were no problems identified during the annual audit of RTI's XRF Laboratory.

2.5 Sample Handling and Archiving Laboratory (SHAL)

2.5.1 Facilities

RTI has leased a 10,000 square foot facility located at 1000 Parliament Court in Durham, NC and dedicated the facility to the PM2.5 speciation SHAL laboratory. The space is approximately 3.5 miles from the main RTI campus and allows easy transfer of filters between the SHAL and the analytical laboratories. The area is a secured facility with access limited to those personnel working directly on the speciation project.

The sample handling area within the SHAL is a 4,000 square foot space equipped with fourteen workstations for the assembly and disassembly of the various filter modules. Each workstation contains a PC connected to a dedicated server and a barcode reader for inputting data into the database. As a set of speciation filters is processed, the worker immediately enters the information for the sampling event into the speciation database. This allows the information for the sampling event and tracking information for the shipment of the samples to be input directly at the time of handling. The use of barcoded labels and paperwork allows for the entry of data with minimal typographical errors.

Other features of the sample handling area include ten foot high shelving along two walls for the storage of client modules, custom built tables for the loading/unloading of the sample filters, refrigerators and freezers for storage of filters at the proper temperature, and additional space for future program needs.

The SHAL laboratory also includes a 6,000 foot warehouse area separate from the sample handling area. The warehouse area has a loading dock with pneumatic lift to accommodate different sizes of trucks. The loading dock has ample space for the unloading of incoming shipments including work areas for the measurement of the temperature of the incoming sampled filter modules. Next to the loading dock is a custom built walk-in-cooler dedicated to the speciation project. The cooler measures 16' X 10' X 7' and will hold the incoming filter modules at or below 4 degrees Centigrade. The warehouse area also has additional space if needed for future project needs and ample space for storage of packaging materials and coolers.

2.5.2 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.

- 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.

- Blank filters are taken from the SHAL refrigerator and returned unopened to the laboratories for analysis. These QC filters results are being used to improve the overall quality of the program.

- The SHAL supervisor or his designee will periodically 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. A summary of the observations for the period July - December 2003 is shown in the following table.

Module Type	Number Observed	Findings	Findings Reviewed With Worker
MET ONE	26	1	1
Andersen	2	0	0
Texas R&P FRM	2	1	1
URG	2	0	0
R&P Spec	4	0	0

2.5.3 Corrective Actions Taken

Problem: Coolers arriving late at the RTI SHAL laboratory delay the processing and analysis of filters and may even cause a missed sampling event if RTI cannot repack new filters into the modules and ship them to the site in time for the next sampling event. Late arriving coolers are typically due to late returns by the site or delays in transit by the carrier. A summary of late arriving coolers for the time frame of August 26, to December 31, 2003 NOTE: RTI began collecting these statistics on August 23, 2003 at EPA's request) is presented below as **Figure 132**.

Corrective Action: Late arriving coolers are usually caused by delays in the field or by Federal Express. Whenever a site has a backlog of missed shipments, it is impossible for RTI to ship a new set of modules on schedule. The DOPO is notified and the missed exposure is flagged as "scheduled but not collected" (AF).

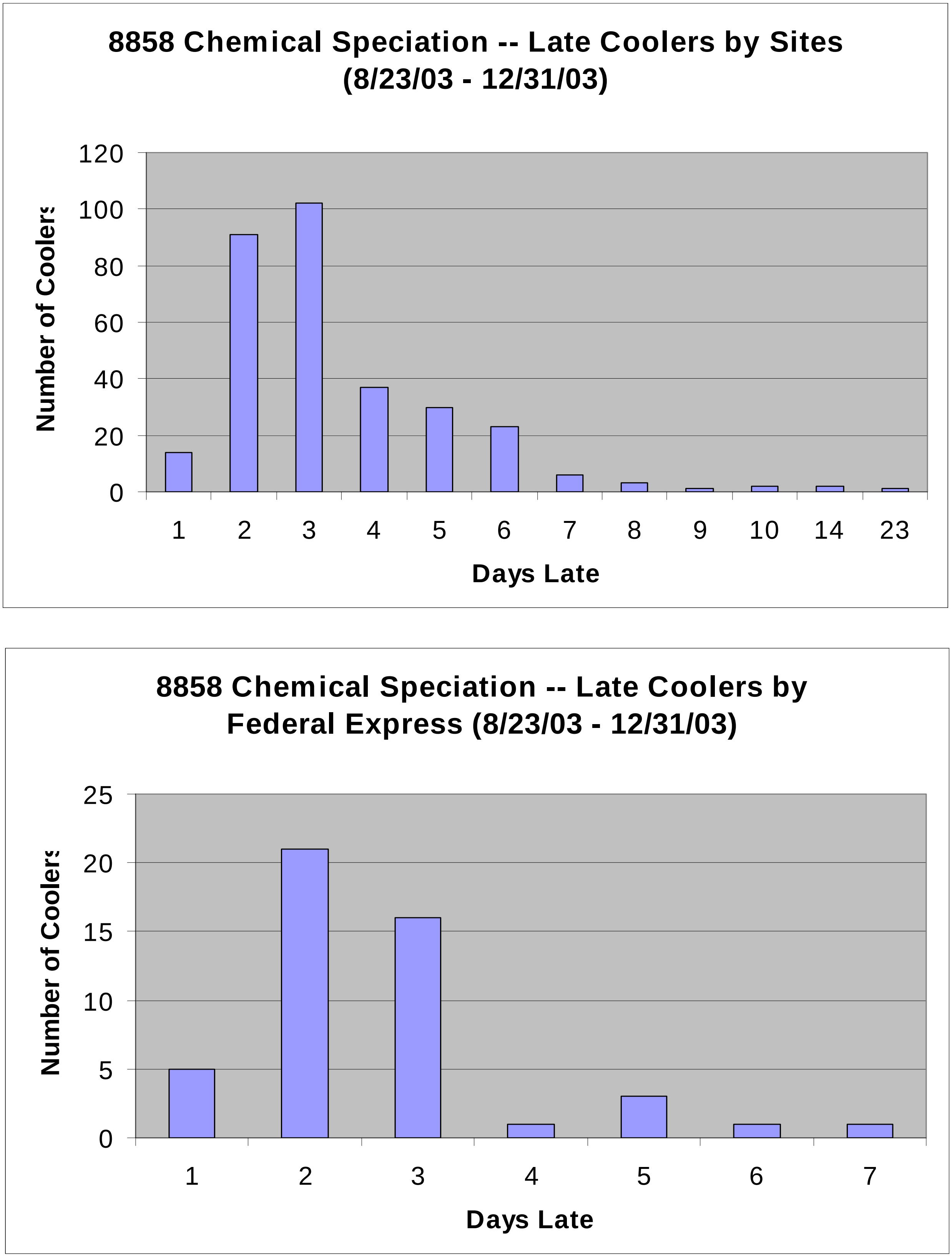


Figure 132. Graphs showing number of coolers and days late via site and Federal Express.

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 October 2003 ; the next scheduled change-out will occur in January 2004.

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. 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.

As personnel assignments changed, additional workers were trained in the techniques of denuder refurbishment. Hands-on training was conducted according to the several SOPs for denuder refurbishment.

2.7 Data Processing

2.7.1 Operational Summary

Significant changes were made to accommodate the new data reporting requirements of the new contract and to improve program efficiency and data quality. These changes included:

- Addition of measurement uncertainties and detection limits for each measured events, both in the site data reports and AQS data files.
- Updating the reporting and AQS processing routines to deal with the possibility of multiple AQS validity code flags for each event.
- Updating the AQS data file format to that used by the "new" AQS. This update was necessary to report uncertainties and detection limits to AQS.
- Revision of the module assembly and disassembly forms to more closely match the actual flow of work in the SHAL and improve error checking.
- Redesign of field data entry forms to more closely match the actual paper copy of the field and speed data entry.

These changes, as well as a number of smaller changes, are described below.

2.7.2 Operational Changes and Improvements

2.7.2.1 Addition of measurement uncertainties and detection limits - Although uncertainty values have historically been supplied from carbon and XRF analyzers, they were not supplied for other laboratories. Additional processing routines were added to calculate uncertainties for these results from absolute (intercept) and relative (slope) values supplied by the other analytical laboratories (gravimetry and ion chromatography). The analytical data import procedures were also modified to associate detection limits with each measured value. Routines were created to combine the analytical uncertainties with an estimate of flow uncertainty. A value of 5% relative uncertainty was adopted for flows based in part on use of this value by the IMPROVE program for calculating overall uncertainties.

2.7.2.2 Updating reporting for multiple AQS validity flags - The old AQS system allowed only a single validity code flag (which is used to indicate potential data issues that are not severe enough to require data invalidation). The new AQS system permits a single "exceptional" validity code and any number of QA validity codes. Our processing and reporting system was updated to incorporate the extended flagging capabilities.

2.7.2.3 Updating the AQS data file format - The AQS file generation routines were revised to use the new (vertical bar delimited) AQS data file format. Updating to the new output format was necessary to report uncertainties, detection limits, and multiple validity code flags to AQS.

2.2.2.4 Revising module assembly and disassembly forms - The module assembly and disassembly forms were rewritten to more closely match SHAL operations. These changes reduced the potential for data entry errors, improved data quality, and reduced QA review time (by reducing data entry errors).

2.2.2.5 Redesign of field data entry forms - Field data entry forms were completely rewritten to more closely match the actual paper form used by the field sites. These changes improved data entry and reduced rework resulting from data entry errors. Validation of the new forms was done by using the new forms for the first data entry and the older forms for the second data entry. The double-entry field data comparison programs (created earlier) allowed us to do a thorough (100%) test of the new forms.

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

- Summary reports to show frequencies of each flag by reporting batch. This helps to detect systematic problems that would cause invalid or flagged data.
- Reports to detect reported blank values that exceeded laboratory analytical uncertainties.
- Summary reports for review of sampling volumes and flow rates.

2.7.3 Problems and Corrective Actions

Missing blank values in Rich Text Format (RTF) data review reports - Changes made in the reporting software to report uncertainties and detection limits (described above) caused problems with the Rich Text Format (RTF) reports (used by some sites for data review). Although the values for blank samples were correctly calculated and reported in all spreadsheet-based reports and our QA review reports, their values were omitted in the RTF reports. Routine samples were not affected by this problem. The RTF report was revised to correctly display blank data values. Revised site data reports for delivery batches 44 and 45 were regenerated and placed on the external web site. RTI has changed its procedures to include a visual review of an RTF report for each batch to prevent recurrence of this or similar problems.

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 2004), 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 2004).

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.

Some additional validation checks have been added to improve tracking of changes between batches. These include summaries by batch of the number of records that contain AIRS null value codes and AIRS validity status codes. These checks allow QA review of trends and to spot sudden changes in the performance of the validation checks.

Because the EPA has recently expressed interest in reporting blank samples to AQS, RTI is making extra effort to resolve problems with the blank data such as "swaps" between exposed and unexposed filters due to handling or data entry. Whenever filter swaps cannot be resolved with high confidence, the affected filter(s) will be invalidated.

2.8.3 Corrective Actions

Issue: R&P Sampler Inlet Dirty

Inspection by an operator in the field indicated that impactor grease, which was visible through the module inlet, appeared dirty. This report raised a concern because opening any STN module in the field is strongly discouraged since it can lead to filter damage or contamination. However, when the operator was contacted, it was determined that the module had not been opened to conduct the inspection. The R&P sampler is different from all the other sampler types because a viscous silicone grease is used to coat the impactor plate. RTI's procedure for renewing the grease before each new usage does not require complete replacement of the grease; instead, only the contaminated spot in the middle of the plate is removed, additional grease is added as needed, and the surface is smoothed over with a straightedge. In this process, some visible contaminants can remain within the layer of grease; however, it is very unlikely that this visible discoloration will contaminate the filter sample.

RTI's operational response was to institute a policy that all R&P sampler modules should be checked by senior personnel before they are sealed.

Issue: Teflon Filter Numbering Discrepancies

In September 2003 approximately nine Teflon filters were found to be in the incorrect petri slide according to the number printed on the filter itself. The label on the petri slide did not agree with the imprinted printed number. These errors were tracked down by SHAL and gravimetric laboratory personnel and fixed on an ad hoc basis. Affected data for exposed filters (filters used as blanks or routine samples) were carefully evaluated to be sure that they had been assigned to the correct event.

Because of persistent problems of this type, RTI has just instituted new procedures designed to intercept discrepancies of this type before the filters are used for sampling. This will involve manual checks of both the labels and the filters as they enter the gravimetric lab or the SHAL, respectively. This corrective action was taken in January 2004, and the corrective action will be described more fully in the next Data Summary Report.

Prior Issue: MetOne Date/Clock Problem March 2003

In the previous Data Summary Report RTI described a serious problem with the internal date for the MetOne SASS units that sampled in early March 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. A software bug in the sampler was found to be the problem. RTI is not aware of any reoccurrence of the problem, which was most likely related to a leap year correction. RTI will be on the alert for a similar problem in 2004.

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 43 through 47. **Table 21** 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 21. Delivery Batches by Delivery Date

Delivery Batch ID	Report Date	Earliest Sample	Latest Sample	Number of Samples
43	8/14/2003	6/14/2003	7/14/2003	2006
44	9/12/2003	7/14/2003	8/13/2003	1886
45	10/13/2003	8/13/2003	9/12/2003	1884
46	11/14/2003	9/12/2003	10/12/2003	1952
47	12/16/2003	10/12/2003	11/14/2003	2073

Turnaround times from sample receipt remained steady during the reporting period, as shown in **Table 22**. 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 22. Data Turnaround Times

Delivery Batch	Date	Turnaround Time (days)	Number of Events
43	8/14/2003	43	1972
44	9/12/2003	40	1860
45	10/13/2003	41	1864
46	11/14/2003	41	1952
47	12/16/2003	42	2073

3.2 Trip, Field, and SHAL Blanks

The number of blanks run during this period are summarized in **Table 23**. Blank data are not currently submitted to AIRS, but are reported to the state monitoring agencies and to EPA for statistical analysis. RTI will report blank data to AIRS whenever a format for reporting is finalized by EPA. As required by the QAPP, trip blanks are being scheduled at a frequency of

Table 23. Number of Blanks Reported in Batches 35 through 42

Delivery Batch ID	Sample Type	Number of Samples
43	FIELD BLANK	277
43	ROUTINE	1641
43	TRIP BLANK	21
43	UNSAMPLED_BLANK	33
44	FIELD BLANK	154
44	ROUTINE	1550
44	TRIP BLANK	121
44	UNSAMPLED_BLANK	35
45	FIELD BLANK	297
45	ROUTINE	1475
45	TRIP BLANK	42
45	UNSAMPLED_BLANK	50
46	FIELD BLANK	358
46	ROUTINE	1532
46	TRIP BLANK	33
46	UNSAMPLED_BLANK	29
47	FIELD BLANK	164
47	ROUTINE	1639
47	TRIP BLANK	266
47	UNSAMPLED_BLANK	4

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 24 summarizes the Trip and Field Blank results for the reporting period. 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 24 also includes averages for SHAL blanks, which are blank filters that are simply sent to the SHAL and returned to the laboratory, but are not mounted in modules or sent to the sites. Because of the low number of total samples, the SHAL blanks are not broken out by delivery batch. Compared with the Field and Trip Blanks, the SHAL blanks have lower background values for most analytes, particularly gravimetric mass and organic carbon, which

Table 24. Trip and Field Blanks Average for the Reporting Period (µg/filter)

Trip Blanks

Analysis	Analyte	43	44	45	46	47
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.00	0.02	0.10	0.04	0.02
Cations - PM2.5 (NH4, Na, K)	Potassium	0.00	0.00	0.00	0.04	0.00
Cations - PM2.5 (NH4, Na, K)	Sodium	0.15	0.36	0.19	0.20	0.23
Mass - PM2.5	Particulate matter 2.5u	4.62	2.95	6.64	5.15	3.74
Nitrate - PM2.5	Nitrate	0.29	0.43	0.60	0.22	0.27
Nitrate - PM2.5 (MASS/nylon)	Nitrate (volatile)	0.90	0.55	0.52	0.55	0.58
Nitrate - PM2.5 (MASS/teflon)	Nitrate (non-volatile)	0.54	1.16	3.66	0.63	1.10
Sulfate - PM2.5	Sulfate	0.39	0.54	1.05	0.46	0.26
OC/EC	Elemental carbon	0.51	0.34	0.08	0.11	0.28
OC/EC	Organic carbon	8.37	12.71	9.85	8.94	12.59

Field Blanks

Analysis	Analyte	43	44	45	46	47
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.08	0.03	0.00	0.03	0.00
Cations - PM2.5 (NH4, Na, K)	Potassium	0.01	0.00	0.01	0.01	0.00
Cations - PM2.5 (NH4, Na, K)	Sodium	0.25	0.50	0.19	0.27	0.18
Mass - PM2.5	Particulate matter 2.5u	8.71	4.62	4.83	7.59	5.74
Nitrate - PM2.5	Nitrate	0.57	0.49	0.31	0.35	0.49
Nitrate - PM2.5 (MASS/nylon)	Nitrate (volatile)	0.60	0.10	0.35	0.31	0.53
Nitrate - PM2.5 (MASS/teflon)	Nitrate (non-volatile)	0.35	0.82	1.17	0.92	0.82
Sulfate - PM2.5	Sulfate	0.39	0.71	0.70	0.51	0.27
OC/EC	Elemental carbon	0.27	0.27	0.15	0.20	0.32
OC/EC	Organic carbon	14.06	13.59	14.09	12.32	12.13

SHAL Blanks for 7/1/2003 through 12/31/2003

ANALYSIS	ANALYTE	Filter Type	Average	Std Dev	N
Cations - PM2.5 (NH4, Na, K)	Ammonium	Nylon	0.008	0.060	53
Cations - PM2.5 (NH4, Na, K)	Potassium	Nylon	0.000	0.000	53
Cations - PM2.5 (NH4, Na, K)	Sodium	Nylon	0.113	0.600	53
Nitrate - PM2.5	Nitrate	Nylon	0.140	0.221	53
Sulfate - PM2.5	Sulfate	Nylon	0.208	0.295	53
Cations - PM2.5 (NH4, Na, K)	Ammonium	Teflon	0.000	0.000	53
Cations - PM2.5 (NH4, Na, K)	Potassium	Teflon	0.000	0.000	53
Cations - PM2.5 (NH4, Na, K)	Sodium	Teflon	0.072	0.0173	53
Nitrate - PM2.5	Nitrate	Teflon	0.805	0.888	53
Sulfate - PM2.5	Sulfate	Teflon	0.189	0.336	53
OC/EC	Elemental carbon	Quartz	0.072	0.124	52
OC/EC	Organic carbon	Quartz	3.560	1.326	52
Mass - PM2.5	Particulate matter 2.5u	Teflon	1.686	3.734	51

may reflect real differences in the opportunity for filter contamination between the Trip/Field blanks and the SHAL blanks. The SHAL blanks also have a relatively high average level of nitrate on teflon filters, but this is comparable to the nonvolatile nitrate seen on the Trip and Field blanks.

3.3 Data Completeness by Site

Table 25 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) relative to the number of records for scheduled events for that batch. Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval. Percentages less than 80 are usually the result of a sample being out of service or one or more exposures being missed because of problems at the site or problems with the shipping.

Table 25. Summary of Percent Valid AIRS Data by Delivery Batch

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	**42**	**43**	**44**	**45**
20th St. Fire Station	120861016	5	81	90	100	93	99
5 Points	391530023	5	100	100	87	100	100
Air Monitoring, VA DEQ	517600020	5	100	87	100	100	88
Aldine	482010024	5	91	81	100	80	74
Allen Park	261630001	5	100	100	100	100	100
Alpine	480430002	5	100	100	100	84	98
Alton	171192009	5	65	100	100	100	100
APCD (Barret)	211110048	5	100	100	100	100	100
Arendtsville	420010001	5	100	99	100	80	100
Army Reserve Center	191130037	5	100	80	83	60	80
Arnold	290990012	5	100	100	100	100	100
Ashland Health Department	210190017	5	100	80	100	100	100
Athens	130590001	5	100	100	100	100	84
Augusta	132450091	5	100	100	100	40	80
Bakersfield-California Ave	060290014	5	60	89	61	90	67
Bakersfield-California Ave (Collocated)	060290014	6	82	90	70	100	70
Bates House (USC)	450790019	5	100	100	100	80	100
Bayland Park	482010055	5	92	100	92	100	91
Beacon Hill	530330080	6	100	100	100	100	100
Bethune School	040138006	5	81	100	100	100	80
Big Bend National Park	480430101	5	76	100	80	72	100
Bismarck Residential	380150003	5	100	100	100	100	100
Blair Street	295100085	6	100	100	100	100	100
Bonne Terre	291860006	5	71	82	100	100	93
Bountiful (before 6/25/2003)	490110001	5	100	100	100		
Bountiful (after 6/25/2003)	490110004	5			100	100	100
Bowling Green-Kereiakes Park	212270007	5	100	80	100	100	100
Bristol	515200006	5	100	100	100	80	100
Buffalo	360290005	6	80	80	100	100	80

Table 25. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	42	43	44	45
Buncombe County Board of Education	370210034	5	97	80	100	100	100
Burlington	500070012	5	100	90	99	93	100
Camden	340070003	5	100	100	100	100	100
Canal St. Post Office	360610062	5	74	100	70	100	100
Canton Health Dept.	391510020	5	100	100	100	100	100
Capitol	220330009	5	59	80	89	90	36
Chamizal	481410044	5	91	80	90	91	100
Channelview	482010026	5	100	92	100	100	100
Cherry Grove	370330001	5	100	100	100	100	100
Chester	340273001	5	99	83	95	98	88
Chester (PA)	420450002	5	100	82	67	100	100
Chesterfield	450250001	5	97	97	98	97	97
Chickasaw	010970003	5	100	100	100	100	100
Children's Park	040191028	5	100	60	100	100	100
Chiwaukee Prairie Site	550590019	5	100	100	100	80	100
Columbus	132150011	5	80	100	64	100	100
Com ED	170310076	5	89	88	100	100	88
Commerce City	080010006	5	100	100	89	100	100
Conroe Airport	483390078	5	99	83	99	80	90
Courthouse Annex-Libby	300530018	5	100	100	100	40	59
Covington - University College	211170007	5	100	100	100	100	100
CPW	450190049	5	100	100	100	91	80
Crossett	050030005	5		98	100	100	100
Dallas Convention Center	481130050	5	82	99	88	93	95
Dearborn	261630033	5	100	60	100	100	100
Decatur	011030011	5	100	100	100	100	100
Deer Park	482011039	6	100	100	100	100	99
Deer Park (Collocated)	482011039	7	90	100	100	99	98
Dona Park	483550034	5	100	81	100	100	84
Douglas	130690002	5	100	60	100	100	100
Dover	100010003	5	100	100	100	100	100
Durango - Park School	080670008	5	100	100	100	100	75
Duwamish	530330057	6	100	100	100	100	98
East Charleston	320030560	5	100	80	100	99	80
El Cajon	060730003	5	100	88	100	89	100
Elizabeth Lab	340390004	5	89	100	100	100	100
Ellis County WMA	400450890	5	80	100	100	100	100
Ellyson	120330004	6	100	100	100	100	100
Elmwood	421010136	5	100	100	85	100	100
Erie	420490003	5	100	100	99	98	80
Essex	240053001	5	100	100	100	100	100
Evansville - Mill Road	181630012	5	100	98	100	100	100
Fargo NW	380171004	5	100	92	100	100	100

Table 25. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	42	43	44	45
Florence	421255001	5	100	100	83	100	100
Fort Meade	240030019	5	100	100	100	100	100
Fort Wayne CAAP	180030004	5	58	100	100	100	55
Francis Elementary School	440071010	5	100	100	99	100	98
Freemansburg	420950025	5	100	100	100	100	100
Fresno - First Street	060190008	5	100	80	88	100	100
G.T. Craig	390350060	5	89	90	100	90	89
G.T. Craig - Collocated	390350060	6	82	80	100	81	89
Galveston Airport	481670014	5	90	100	82	90	80
Garden St.	020200018	5	100	100	100	91	100
Garinger High School	371190041	5	90	100	100	100	100
Gary litri	180890022	5	80	100	100	40	100
General Hospital	390870010	5	100	100	100	100	100
Georgetown (Andersen)	530330032	6	100	100	83	100	100
Grand Rapids	260810020	5	100	100	100	80	100
Greensburg	421290008	5	80	100	100	100	100
Grenada	280430001	5	100	100	100	100	75
Guaynabo	720610005	5	100	92	92	74	90
Guiding Hands School	390530003	5	100	100	100	100	100
Gulfport	280470008	5	100	88	100	100	88
Guthrie	471570047	5	80	100	99	100	100
Hamshire	482450022	5	100	92	100	100	100
Harrisburg	420430401	5	100	100	100	100	100
Hattie Avenue	370670022	5	80	100	100	100	100
Hattiesburg	280350004	5	100	80	100	100	100
Hawthorne	490353006	5	100	100	89	100	100
Hazard - Perry County Horse Park	211930003	5	80	69	67	100	100
Hazelwood	420030021	5	100	100	83	79	80
Head Start	390990014	5	100	100	67	100	100
Hendersonville	471650007	5	100	100	100	100	100
Hickory	370350004	5	100	100	100	99	100
Hinton	481130069	5	80	90	100	91	100
Holland	260050003	5	83	100	100	100	100
Houghton Lake	261130001	5	100	100	100	100	90
Huntsville Old Airport	010890014	5	100	100	87	100	100
IL - Decatur	171150013	5	100	100	100	100	100
IS 52	360050110	5	100	92	100	90	100
Jackson Hinds Co.	280490018	5	100	100	100	50	100
Jefferson Elementary (10th and Vine)	191630015	5	91	100	99	91	100
JFK Center	202090021	5	100	100	100	56	100
Kalamazoo	260770008	5	100	100	100	100	85
Karnack	482030002	5	100	100	100	100	91
Kaufman	482570005	5	100	100	100	100	80

Table 25. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	42	43	44	45
Kelo	460990006	5	100	100	100	80	100
Kingsport	471631007	5	80	100	99	100	100
Lake Forest Park	530330024	6	100	100	100	100	100
Lancaster	420710007	5	100	100	100	100	100
Laurel	280670002	5	100	100	83	100	100
Lawrence County	470990002	5	100	100	100	100	80
Lawrenceville	420030008	6	82	89	80	91	80
Lenoir Community College	371070004	5	100	100	100	100	99
Lewis	120571075	5	91	90	100	100	100
Lexington Health Department	210670012	5	100	100	83	100	100
Liberty	290470005	5	91	100	100	100	100
Lindon	490494001	5	100	100	100	100	100
Lockeland School	470370023	5	100	100	100	100	100
London-Laurel County	211250004	5	100	100	83	100	100
Lorain	390933002	5	100	100	100	100	60
LPH	390610042	5	100	100	100	85	98
Lubbock	483030001	5	100	100	100	100	100
Luna Pier	261150005	5	100	100	100	100	100
Macon	130210007	5	100	100	87	100	100
Mae Drive	482011034	5	100	100	100	100	100
Manchester	330110020	5	94	80	100	100	100
Manitowoc, Woodland Dunes site	550710007	5	100	100	100	80	100
Maple Canyon	390490081	6	100	100	100	100	100
Mauriceville	483611100	5	99	76	100	100	92
Mayville Hubbard Township site	550270007	5	99	100	100	82	100
McDonald Observatory	482430004	5	100	100	80	100	100
McMillan Reservoir	110010043	5	100	88	99	100	100
Mendenhall	370810013	5	100	100	100	100	100
Mesa County Health Department	080770003	5	100	83	40	98	100
Middletown	390171004	5	100	100	100	100	100
Midlothian Tower	481390015	5	100	100	100	100	60
Millbrook	371830014	5	100	100	100	100	100
Mille Lacs	270953051	5	80	90	90	100	90
Mingo	292070001	5	100	80	100	100	80
Missoula County Health Dept.	300630031	5	73	100	100	100	100
MLK	100032004	5	100	100	100	100	100
MN - Rochester	271095008	5	100	100	100	100	100
MOMS	011011002	5	100	100	100	100	100
Nampa NNC	160270004	5	100	100	100	91	80
New Brunswick	340230006	5	100	100	100	100	100
New Brunswick (Collocated)	340230006	6	100	100	100	100	100
New Garden	420290100	5	100	100	100	100	80
NLR Parr	051190007	5	100	100	100	65	100

Table 25. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	42	43	44	45
North Birmingham	010730023	5	100	100	100	100	100
North Los Angeles	060371103	5	100	100	100	100	100
Northbrook	170314201	5	80	100	100	100	100
NY Botanical Gardens	360050083	6	100	82	100	100	100
OCUSA Campus	401091037	5	80	100	100	100	100
Olive Street	530330048	6	100	100	87	100	100
Owensboro - KY Wesleyan College	210590014	5	69	80	67		40
Padre Island National Seashore	482730314	5	99	80	100	100	80
Paducah Middle School	211451004	5	100	100	100	100	100
Pearl City	150032004	5	80	60	100	100	80
Peoria Site 1127	401431127	5	100	100	100	100	100
PerkinstownCASNET	551198001	5	99	100	100	100	100
Perry County	420990301	5	82	100	98	100	99
PHILA - AMS Laboratory	421010004	7	100	92	100	100	100
Philips	270530963	5	100	100	90	89	100
Phoenix Supersite	040139997	7	91	90	100	100	70
Pinnacle State Park	361010003	5	100	90	100	99	100
Platteville	081230008	5	85	100	100	100	100
Pleasant Green (Central MO)	290530001	5	100	62	100	80	80
Portland N. Roselawn	410510246	6	100	100	100	100	99
Portsmouth	330150014	5	100	100	80	91	100
Providence	010731009	5	100	97	99	100	100
Public Health Building	191530030	5	100	100	83	80	100
Queens College	360810124	6	90	100	90	91	88
RBD	080410011	5	100	100	100	100	100
Reno	320310016	5	99	100	100	100	100
Riverside-Rubidoux	060658001	5	100	90	100	91	90
Riverside-Rubidoux (Collocated)	060658001	6	100	90	100	91	90
Roanoke	517700014	5	100	100	100	100	100
Rochester Fire Headquarters	360556001	5	100	100	100	100	99
Rome	131150005	5	100	83	60	100	100
Roxbury (Boston)	250250042	5	93	100	100	100	80
Roxbury (Boston) - collocated	250250042	6	100	90	91	100	100
Sacramento - Del Paso Manor	060670006	5	91	100	100	91	100
San Jose - Jackson Street	060850005	5	100	100	89	100	100
Sault Ste Marie	260330901	5	91	100	100	100	90
Savannah	130510017	5	100	80	100	100	100
Scranton	420692006	5	100	100	100	98	100
Searcy	051450001	5	100		33	11	
SER-DNR Headquarters	550790026	5	100	100	90	100	100
Shenandoah High School	180650003	5	100	100	86	95	100
Sherwood Is. St. Pk.	090019003	5	100	88	90	100	99
Shreveport Airport	220150008	5	100	100	100	100	100

Table 25. (Continued)

Location	AIRS Code	POC	Percent by Delivery Batch				
			41	42	43	44	45
Simi Valley	061112002	5	100	100	100	100	100
South DeKalb	130890002	5	100	100	100	91	100
Southwick Community Center	211110043	5	100	100	100	100	100
Spring Hill Elementary School	470931020	5	100	100	100	100	100
Springfield Pumping Station	170310057	5	100	60	83	100	100
St Theo	390350038	6	100	66	85	100	100
St. Croix - USVI	780010012	5		86	61	82	16
St. Paul Harding	271230871	5	100	100	100	100	100
State College	420270100	5	100	100	100	80	100
Sun Metro	481410053	5	100	100	40	60	100
Tallahassee Community College	120730012	5	100	80	100	80	100
Taylors Fire Station	450450009	5	100	100	100	100	100
Toledo Airport	390950026	5	99	100	87	100	100
TRNP - NU	380530002	5	100	100	100	100	100
Urban League	440070022	5	100	100	100	100	100
UTC	470654002	5	100	85	100	100	100
Washington Park	180970078	5	100	78	80	91	90
Waukesha, Cleveland Ave. Site	551330027	5	100	100	100	100	100
West 43rd Ave	040134009	5	100	100	100	100	100
Whiteface	360310003	5	89	80	100	91	90
Wichita Dept. of Environmental Health	201730010	5					11
Wilbur Wright Middle School	391130031	5	60	100	100	98	80
William Owen Elem. School	370510009	5	80	100	100	100	100
Woolworth St	310550019	5	87	85	97	97	97
Wylam	010732003	5	82	100	87	100	100
York	421330008	5	46	80	100	100	100
Ypsilanti	261610008	5			100	100	100