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

October 1, 2001 through March 31, 2002

Prepared for:
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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). Establishment of a 1500-site mass measurements network and a 250-site chemical speciation monitoring network is now under way.

The ambient air data from the 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) will consist of a core set of 54 trends analysis sites and some 200 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 March 31, 2002, RTI is providing support for 205 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 will not be performed initially; however, these analyses may be included later in the full STN program.

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 are now coming on line. As of March 31, 2002, we were providing support to 205 sites which include the 54 STN sites. This QA report covers the collection and analysis of samples from October 1, 2001 through March 31, 2002.

1.4 Major Laboratory Operational Areas

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

1.5 Significant Corrective Actions Taken

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

- Gravimetric Mass – No significant corrective actions have been taken.

- Elemental Analysis – No significant corrective actions have been taken, however, the three new XRF instruments have been included for the elemental analysis. These instruments include: one Keevex 771 from Chester LabNet, one ThermoNoran from CES, and one ThermoNoran from RTI. Intercomparison studies have been performed between the three instruments, and approved by EPA prior to using them for analysis.

- Ion Analysis – Beginning in September 2001, it was observed that the relative percent difference for replicate analyses were higher than usual for sodium and sulfate. A contamination problem was suspected and subsequently corrected by replacing all tubing in the ion chromatographs and established a more rigorous cleaning procedure for auto sampler vials and injection vials.

  During the same time period, it was observed during the nylon filter extraction procedure, that material (apparently nylon) was being removed from some of the filters, leaving bare (transparent) areas on filter substrate. It was concluded after several experiments in the laboratory that the nylon filters in that particular lot were defective and subsequently the manufacturer (Whatman) replaced these filters with a new batch.

- OE/EC Analysis – No significant corrective actions have been taken.

- Sample Handling and Archiving Laboratory (SHAL) – Initially, there were many anomalous data points for R&P samplers. The staff were retrained in the processing of the R&P modules. Similarly RTI has identified the major cause of the higher masses for Teflon filters as the white Delrin rings in the Met One samplers. RTI has subsequently replaced all the white Delrin rings with the blue poly rings for the cassettes holding the Teflon filters in the Met One modules.

- Data Processing – No significant correction actions have been taken.

1.6 Delrin Ring Study

In early 2001, routine data screening revealed trends for high field blank levels. It was determined that the MetOne SASS samplers were associated with most of the high field blanks. RTI staff looked into the sources for high blank levels and finally concluded that the contamination could be coming from the cassette filter holder rings. RTI also learned from the sampler manufacturer that these rings are made of Delrin, a plastic based on polyformaldehyde, which may be out-gassing from the rings. In an effort to find a solution to this significant problem, a series of experiments was performed to determine the extent of transfer of material from the Delrin cassettes to the Teflon filter and at the same time, to devise a method (based on either heating and/or washing the cassette) to minimize such transfer. The heating experiments performed indicated that the Delrin rings sets lose more than 15,000 µg of weight with heating. They also showed that heating filters in new, untreated rings for 20 hours at about 40°C resulted in a mass contamination of the filters of 10 to 25 µg. A report summarizing the experiments performed and the results obtained was reported to EPA in July 2001.

This work continued at EPA/Montgomery laboratories and confirmed RTI's preliminary findings. The Delrin rings were subsequently replaced with blue poly rings in all the Teflon filter holders in the MetOne Samplers for this project. RTI continues to monitor blank levels from each of the different analyzer types, but no further problems of this type have been seen.

2.0 Laboratory Quality Control Summaries

2.1 Gravimetric Laboratory

2.1.1 Personnel and Facilities

The Earth and Mineral Sciences Department (EMSD), previously part of the Center for Environmental Measurements and Quality Assurance (CEMQA), is now in the Center for Environmental Measurements (CEM) since the formation of RTI's Engineering Group (EG). Departmental responsibility for the gravimetric analysis of Teflon® filters for the PM2.5 Chemical Speciation Trends Network has not changed since the previous QA report. No changes in personnel have occurred in the CEM PM2.5 Gravimetry Laboratory since the submission of the previous QA report in October 2001. Three full-time analysts continue to perform the PM2.5 gravimetric analyses for Chemical Speciation, FRM clients, and others. The analysts' experience and competence result in reliable and timely gravimetric analyses.

In February 2002, the laboratory expanded into a second weigh chamber maintained by RTI's Center for Environmental Technology (CET). Use of the CET Weigh Chamber in addition to the CEM Weigh Chamber is necessary to accommodate the increasing volume of tared Teflon® filters needed for the PM2.5 Chemical Speciation Trends Network. Like the CEM chamber, the CET Weigh Chamber is equipped with a Dickson temperature and relative humidity data logger. The CET Weigh Chamber was used for the analysis of 200 of the 7021 Teflon® filters tared for Chemical Speciation between August 2001 and February 2002. Weigh Chamber malfunctions since the previous QA report have occasionally resulted in excessive laboratory holding times; however, neither filters nor analytical equipment have been affected by the malfunctions. One Dickson RH and temperature data logger was removed from service in February 2002 because it failed its RH calibration, and could not be adjusted by the manufacturer. **Tables 1 and 2** summarize the facility problems and corrective actions for the CEM and CET Weigh Chambers, respectively.

2.1.2 Statistical Summary of QC Results

The types and frequency of QC checks applied to the gravimetric analysis of filters for the PM2.5 Chemical Speciation Trends Network have not changed since the previous QA report. QC data for the laboratory are summarized in **Tables 3 and 4**.

2.1.3 Data Validity Discussion

Filters were assigned the appropriate Chemical Speciation Validity Flags due to problems arising in the PM2.5 Gravimetry Laboratory. Problems consisted of excessive laboratory holding times, laboratory blank replicate weighings exceeding the 15-µg criterion, and the use of a 100-mg standard reference weight belonging to the CET Weigh Chamber which had not recently been calibrated. Each of the problems is discussed below.

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

Duration of Problem	Nature of Problem	Corrective Action
08/13/01	RH spikes over the weekend	RTI HVAC personnel confirmed that Building 11 Bay 6 air handler had been shut down over the weekend for repairs.
08/13/01	Laboratory staff reported gasoline-like odor in chamber	Laboratory Supervisor determined that RTI Facilities & Maintenance personnel had sprayed a hornet's nest near the fresh air intake – odor dissipated within an hour.
09/26/01	High temperature Dialout temperature alarm	RTI HVAC personnel confirmed that they had received an alarm from the system and had already responded before laboratory staff noticed temperature increase and telephoned HVAC department. Temperature increase was due to failure of the smaller of the two chillers that provide chilled water to Building 11. Time delay in larger chiller coming online was designed into unit by manufacturer. HVAC personnel contacted manufacturer's service rep - trying to determine whether this can be adjusted.
11/01/01	High temperature Dialout temperature alarm	Laboratory staff noticed that the fans sounded louder, checked temperature and noted that temperature was climbing, and telephoned John Berkley to report it before it even reached the alarm point. Laboratory staff then telephoned Laboratory Supervisor to inform her of the situation. RTI HVAC personnel determined that the water chiller circuit breaker had tripped because of power glitches, and as a result, temperature spiked. They said that something was happening in the power lines because breakers were tripping across RTI's campus. Because Duke Power Company was not expected to be working on the power lines at that time, RTI HVAC personnel didn't know what was causing the electrical problems. RTI HVAC personnel showed laboratory personnel the two reset switches for the chamber system so that they could reset them if needed. Waited until chamber conditions stabilized before resuming work. Downtime of several hours.
11/08/01 - 11/09/01	High RH (Spiked evening of 11/08/01, discovered morning of 11/09/01)	RTI HVAC personnel determined that defective damper operator on the chamber's dehumidifier caused rise in RH. They replaced part with a spare actuator from a different manufacturer and promised to locate a replacement. Note: RTI HVAC Department did not receive an alarm because the chamber's humidity and temperature alarm setpoints had been changed by persons unknown. Downtime of several hours while weighing environment stabilized.

Table 1 (Continued).

Duration of Problem	Nature of Problem	Corrective Action
11/26/01	High temperature Dialout temperature alarm	RTI HVAC personnel determined that temperature alarm was caused by a loss of chilled water flow due to a high bus voltage fault at the pump drive. The pump failed at 12:56:59, the chamber alarm triggered the HVAC department's system at 01:19:25 and callouts began at about 1:30:23.
12/11/01	High-pitched whine associated with fans	Laboratory staff reported that they had contacted RTI HVAC Department concerning fan noise, but had received no response. Laboratory Supervisor followed up with an email requesting check of system. Follow-up with RTI HVAC Supervisor – determined that bearings in evaporator motor are wearing. The motor was not designed to operate at the relatively low speed at which it is operating. Bearings are only producing nuisance noise at this time, but will eventually fail.
02/13/02	High-pitched whine associated with fans	Laboratory staff reported that they had contacted RTI HVAC Department at approximately 06:30 concerning fan noise. RTI HVAC personnel responded at approximately 09:00 to make minor adjustment to motor...again indicated that problem would recur.
02/25/02	High RH; High temperature Dialout temperature alarm	RTI HVAC personnel determined that chilled water pump variable speed drive (VSD) serving A and B buildings, Bldg 11 Bay 6, and the environmental chambers in Bay 6 failed at approximately 06:04 on a High Line Voltage fault, resulting in a high temperature alarm from chamber 1 (CET) at 06:29 and a dialout alarm from Datatalk (chamber 2 - CEM) to the on-call HVAC technician at 06:44. RTI HVAC personnel spoke with the factory service representative, who indicated that this type of fault is typically caused by the utility (Duke Power Company) switching capacitors, and recommended the use of a line reactor to avoid future failures. RTI HVAC personnel also determined that the part had a 2 to 3 week lead time and that the pump would need to be shut down during the installation. Monday, 03/11/02 - RTI HVAC personnel received and mounted the line reactor for the chilled water pump VSD, and coordinated with laboratory staff to complete installation during laboratory's downtime. Saturday, 03/16/02 - RTI HVAC personnel shut down the chilled water system and installed the line reactor.

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

NOTE: Began to routinely utilize CET chamber for Chemical Speciation project in February 2002; CET chamber does not have a dialout alarm, has only standard audible alarm.

Duration of Problem	Nature of Problem	Corrective Action
02/25/02	High RH; High temperature Dialout temperature alarm from CEM chamber	RTI HVAC personnel determined that chilled water pump variable speed drive (VSD) serving A and B buildings, Bldg 11 Bay 6, and the environmental chambers in Bay 6 failed at approximately 06:04 on a High Line Voltage fault, resulting in a high temperature alarm from Chamber 1 (CET) at 06:29 and a dialout alarm from Datatalk (Chamber 2 - CEM) to the on-call HVAC technician at 06:44. RTI HVAC personnel spoke with the factory service representative, who indicated that this type of fault is typically caused by the utility (Duke Power Company) switching capacitors, and recommended the use of a line reactor to avoid future failures. RTI HVAC personnel also determined that the part had a 2 to 3 week lead time and that the pump would need to be shut down during the installation. Monday, 03/11/02 - RTI HVAC personnel received and mounted the line reactor for the chilled water pump VSD, and coordinated with laboratory staff to complete installation during laboratory's downtime. Saturday, 03/16/02 - RTI HVAC personnel shut down the chilled water system and installed the line reactor.
03/25/02	High Temperature	RTI HVAC personnel determined that three of the six supply air fan motors had failed on internal overload, which seemed to be caused by damaged run capacitors. Within the three motors, they were able to find two capacitors that were working in order to bring one motor back on line. The four fans worked well enough to clear the alarm, and replacement capacitors have been ordered from Charlotte, NC. RTI HVAC personnel promised to contact laboratory staff when repairs are completed.
04/02/02	High Temperature	Laboratory staff reported that they had contacted RTI HVAC personnel about high temperature, but had received no response. Laboratory Supervisor followed up with a telephone call requesting that HVAC personnel be paged to check the system. HVAC personnel investigated and confirmed that temperature alarm had been triggered, but did not isolate cause. Since Chamber 2 was unaffected, chilled water system was deemed functional.

Table 2 (Continued).

Duration of Problem	Nature of Problem	Corrective Action
04/03/04	High Temperature	RTI HVAC personnel determined that the actuator had been damaged, contacted the manufacturer, and found that the valve assembly is now obsolete. Also determined that the recommended replacement valve and actuator had a 2 week lead time. Noted that an alternative would be to retrofit the existing valve with the new style actuator which is in stock in Florida. RTI HVAC personnel noted, " Both units would require the addition of an isolation transformer and signal conditioner.... As this actuator would work with both chamber chilled water valves, and given the time involved in getting replacements, I would strongly suggest that you consider keeping a spare actuator in stock." When contacted by Lisa Greene, HVAC Department confirmed that the modification they were recommending is identical to the modification made to the CEM chamber (Chamber 2) in July and August 2001.

Table 3. Sample Throughput for the Gravimetry Laboratory

Number of Filters	Previous QA Report	This QA Report
Tared	5502 (2/23/01-8/10/01)	7021 (8/13/01-3/11/02)
Tared in CET Weigh Chamber	0	200
Retained by Grav Lab for use as Lab Blanks	26 (.47%)	35 (.50%)
Not Transferred to SHAL; does not include lab blanks	0	45 filters not picked up by SHAL
Initially Transferred to SHAL to be Loaded into Sampler Modules	5476	6941
Not used by SHAL due to filter ID no.s being incompatible with project database	0	132
Used for Background Monitoring of new SHAL Facilities	6	0
Used for Met One Cassette Experiment to monitor possible Delrin® contamination	20	0
Used for check for Delrin® or impactor oil contamination	0	1
Total Transferred to and Retained by SHAL for Sampler Modules	5450	6808
Returned to Grav Lab by SHAL for Final Weighing	5223 (95.8% return rate) (3/29/01-10/2/01)	6634 (97.4% return rate) (9/27/01-4/4/02)
Voided by SHAL and Grav Lab	4 (0.08%)	4 (0.06%)
Flagged by Grav Lab for Exceeding 10-day Holding Time in Lab	63 (1.2%)	489 (7.4%)

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

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Working standard reference weights (mass reference standards)	Verified value ± 3 µg (CEM weights verified by North Carolina Department of Agriculture (NCDA) Standards Laboratory)	100-mg (Property of CEM) Verified Value = 99.957 mg (NCDA 8/01)	99.956 mg ± 0.001 for 1317 weighings	Lab mean falls within range.
		200-mg (Property of CEM) Verified Value = 199.978 mg (NCDA 8/01)	199.977 mg ± 0.002 for 1228 weighings	Lab mean falls within range.
		20-mg (Property of CEM) Verified Value = 19.993 mg (NCDA 11/01)	19.990 mg ± 0.001 for 16 weighings	Lab mean falls within range.
		100-mg (Property of CET) Certified Weight Range = 99.990 - 100.010 mg (Original Purchase Certification 6/9/95)	99.993 mg ± 0.001 for 62 weighings	Lab mean falls within range.
Laboratory (Filter) Blanks	Initial weight ± 15 µg	292 total replicate weighings of 35 lab blanks	Mean difference between final and initial weight: 6 µg ± 4.8 µg	2 (0.7%) of the 292 replicate weighings exceeded the 15 µg criterion, both by 8 µg.
Lot Blanks (Lot Stability Filters)	24-hour weight change < ± 5 µg	Whatman Lot 1169016 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -4 µg 48 hours = -2 µg 72 hours = 1 µg 96 hours = 1 µg	Fall well within required range.
		Whatman Lot 1169017 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -3 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 3 µg	
		Whatman Lot 1169018 - 9 filters weighed (3 randomly selected from each of 3 randomly selected boxes)	24 hours = -1 µg 48 hours = 0 µg 72 hours = -1 µg	
		Whatman Lot 1169019 - 9 filters weighed (3 randomly selected from each of 3 randomly selected boxes)	24 hours = -2 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	
		Whatman Lot 1045023 - 9 filters weighed (3 randomly selected from each of 3 randomly selected boxes)	24 hours = -1 µg 48 hours = -2 µg 72 hours = 2 µg 96 hours = 0 µg	

Table 4 (Continued).

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Lot Blank (Lot Stability Filters) (continued)	24-hr weight change < ± 5 µg	Whatman Lot 1331005 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = 1 µg 48 hours = -2 µg 72 hours = 2 µg	Fall well within required range.
		Whatman Lot 201704 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -1 µg 48 hours = 1 µg 72 hours = 0 µg	
		Whatman Lot 1152001 - 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	
Replicates	Initial weight ± 15 µg	683 Presampled Replicates (8/13/01 - 2/11/01)	0 µg	Max = 3 µg; within required range
		704 Postsampled Replicates (9/25/01 - 4/4/02)	0 µg	Max = 5 µg; within required range
Calibrations • Working Mass Reference Standards (CEM)	Annually	Last calibrated by NCDA on November 21, 2001	N/A	
• Working Mass Reference Standards (CET)		Weight certified by manufacturer upon purchase in June, 1995	N/A	
• Balances (CEM Balance B-serial no. 1118311244 and CET Balance - serial no. 1118252777)	Auto (internal) calibration daily External calibration annually or as needed	Daily Last inspected and calibrated by Mettler Toledo on July 18, 2001 using NIST-traceable weights	N/A N/A	

Table 4 (Continued).

QC Check	Requirements	QC Checks Applied to RTI Laboratory	Lab Mean	Comments
Calibrations (continued) • RH/T Data Logger	Annually	Calibration of Dickson D200 Data Logger (serial no. 98122054) by Dickson Calibration Services in January 2002 Purchased and placed in service third Dickson data logger (serial no. 00102174) in April 2001 Placed Dickson data logger (serial no. 01042219) in CET Weigh Chamber in February 2002	N/A	Data logger (serial no. 98122054 purchased in 1998) removed from service due to RH being "out of spec" in January 2002 calibration. Both chambers currently equipped with calibrated Dickson data loggers (CEM chamber - serial no. 00102174 and CET chamber - serial no. 01042219).
Audits • Balance (B - serial no. 1118311244) (internal)	Annually	Last performed by RTI QA May 10, 2001 using Class S-1 NIST-traceable weights	N/A	Included environmental evaluation, level test, scale-clarity test, zero-adjustment test, off-center (corner load error) test, precision test, and accuracy test; balance performed adequately.
• Technical Systems (external)		EPA - NAREL and EPA - OAQPS, February 5, 2002	N/A	Found no deficiencies.

2.1.3.1 Laboratory Holding Times Exceeding 10 Days

The analyses of 489 (7.4%) of the filters were flagged due to laboratory holding times exceeding the 10-day limit. Excessive laboratory holding times resulted from many factors, including: the closure of RTI due to a major winter storm; weigh chamber malfunction; and laboratory error. Although factors such as chamber malfunction are inevitable, the PM2.5 Gravimetry Laboratory has taken measures to avoid excessive laboratory holding times due to laboratory error. These measures include the use of the CET Weigh Chamber in addition to the CEM Weigh Chamber for the equilibration and analysis of Chemical Speciation filters. The use of the CET chamber allows two analysts to concurrently weigh Speciation filters, greatly increasing productivity. The gravimetry analysts have also worked on an overtime schedule in order to meet the schedule for tared filter pickups and to avoid excessive laboratory holding times. Additional personnel from the Earth and Mineral Sciences Department have been trained in the equilibration of unsampled and sampled Chemical Speciation filters, and are actively employed in the PM2.5 Gravimetry Laboratory. This additional help allows the gravimetry analysts to continue weighing, instead of spending time on the nontechnical aspects of the analysis. Measures taken to avoid laboratory error which results in excessive laboratory holding times include clearly labeling equilibration dates and the expiration dates on each shelf containing sampled filters in the PM2.5 Gravimetry Laboratory. As of this writing, the addition of a laboratory-specific Chemical Speciation Chain of Custody Logbook allows for tracking each batch of sampled filters, and notification of the analysts two days before the 5-day turnaround date has arrived. The measures taken currently have allowed the sample turnaround times in the PM2.5 Gravimetry Laboratory to decrease greatly.

The laboratory has also enlisted the assistance of the project's database managers to develop and implement database routines to streamline sample handling and data acquisition. These routines will expedite the weighing and data transfer procedures, while adding more opportunities for quality control measures. The direct connection from the PM2.5 Gravimetry Laboratory to the Chemical Speciation database will result in an increase in the number of samples analyzed with a decrease in the opportunity for laboratory error.

2.1.3.2 Laboratory Blank Replicate Weighings

One of the 35 laboratory blanks exhibited two replicate weight differences exceeding the 15-µg criterion. The laboratory blank contained visible droplets of contamination which may have been Staticide®, a solution used to clean and reduce static electricity on the weigh table and surrounding surfaces. Because the laboratory blank was visibly contaminated, the Chemical Speciation QA officer recommended using a laboratory blank from a previous batch of filters for the remaining replicate weighings for the affected batch of filters. As a corrective action, the gravimetry analysts were advised to not spray Staticide® directly onto the weigh table and surrounding areas, but to wipe the areas with a lint-free cloth containing the cleaning solution. Also, the staff were reminded to make sure that all filters were removed from the weigh table prior to cleaning the table.

2.1.3.3 Standard Reference Weight

When the gravimetric analysis of Chemical Speciation filters began in the CET Weigh Chamber, the 100-mg standard reference weight from the CET chamber was used for replicate weighings, instead of one of the recently calibrated standard reference weights from the CEM Weigh Chamber. Upon discovery of this problem, the CEM laboratory supervisor advised the gravimetry analysts to discontinue using the CET 100-mg standard reference weight, and to transfer a standard reference weight from the CEM Weigh Chamber for future use. The original purchase certification information for the 100-mg CET standard reference weight was obtained from the CET laboratory supervisor. A Chemical Speciation Trends Network Corrective Action Request (CAR) was completed in response to the problem. A copy of this form is included in Appendix A.

2.1.3.4 Invalidated Data

Four (0.06%) of the filters analyzed were invalidated. One filter was invalidated by SHAL, and the remaining three filters were invalidated by the PM2.5 Gravimetry Laboratory due to anomalous net mass loadings. These filters were flagged appropriately.

2.1.4 Audit and Performance Evaluation

Since October 2001, the PM2.5 Gravimetry Laboratory has had one formal audit and one performance evaluation (PE) by EPA-NAREL and EPA-OAQPS. The lab also participated in a PE sample exercise with Desert Research Institute (DRI). Audit and performance evaluation findings are summarized in **Table 5**.

Table 5. Audit and Performance Evaluation

Responsible Agency	Date/Activity	Recommendation	RTI Response
EPA-NAREL and EPA-OAQPS	November and December, 2001 - Performance Evaluation Sample Analysis	No deficiencies noted - good agreement for the 10 air filter mass measurements performed at RTI and NAREL	N/A
EPA-NAREL and EPA-OAQPS	February 5, 2002 - Technical Systems Audit for Speciation Network Laboratory	No deficiencies noted	N/A
Desert Research Institute	November 2001	Have not yet received results	

2.2 Ion Analysis Laboratory

2.2.1 Facilities

Ion chromatographic analyses are performed by personnel from RTI's Environmental Industrial Chemistry Department (EICD). Five ion chromatographic systems were used for performance of the measurements. These are described in **Table 6**. The use of these five systems was determined by the workload.

Table 6. Description of Ion Chromatographic Systems used for Analysis of PM2.5 Filter Samples

System No.	Dionex IC Model	Ions Measured
1	Model 500 (SA)	SO_4, NO_3
2	Model 500 (S2A)	SO_4, NO_3
3	DX-600 (D6A)	SO_4, NO_3
4	Model 500 (D5C)	Na, NH4, K
5	DX-600 (D6C)	Na, NH4, K

2.2.2 Description of QC Checks Applied

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

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

Table 7. 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 measures 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 8 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 98.4% to 101.8% over the six month period; average recoveries for the two QA samples ranged from 99.4% to 102.6%.

Table 9 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 99.1% to 101.7% over the six month period; average recoveries for the two QA samples ranged from 98.7% to 102.1%.

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 10 shows percent recovery for nitrate and sulfate spikes by filter type for the six month period. There was no significant difference in the spike recoveries of nitrate or sulfate for the three different filter types. The average recoveries of nitrate for all types of filters ranged from 93.5% to 103.9%, while the average recoveries for sulfate ranged from 97.0% to 101.5%.

Table 11 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 0.0309 ppm (25 mL extract) for nitrate and 0.0322 ppm for sulfate; the highest average reagent blank was 0.0029 ppm for nitrate and 0.0178 ppm for sulfate.

Table 8. Average Percent Recovery for Nitrate QA and QC Samples.

Inst	QC Sample	Count	Conc.,ug/mL	Av NO3 Rec, %	SD NO3, %	Min NO3 Rec, %	Max NO3 Rec, %
D6A	QC-HIGH	32	6.0	101.73%	0.97%	97.60%	104.11%
D6A	QA-MED-HI	23	3.0	102.61%	1.55%	96.33%	105.20%
D6A	QC-MED	51	1.5	98.47%	1.50%	91.54%	104.21%
D6A	QA-LOW	33	0.6	99.65%	1.81%	95.84%	105.63%
D6A	QC-LOW	41	0.6	98.41%	1.19%	93.65%	102.20%
S2A	QC-HIGH	47	6.0	101.53%	0.48%	100.61%	102.80%
S2A	QA-MED-HI	35	3.0	102.03%	0.80%	100.17%	103.59%
S2A	QC-MED	86	1.5	98.94%	0.42%	98.21%	100.51%
S2A	QA-LOW	49	0.6	99.36%	1.03%	97.34%	101.35%
S2A	QC-LOW	68	0.6	99.06%	0.68%	97.29%	101.86%
S3A	QC-HIGH	94	6.0	101.78%	0.69%	100.42%	104.38%
S3A	QA-MED-HI	70	3.0	102.57%	1.46%	100.03%	108.51%
S3A	QC-MED	163	1.5	99.55%	1.24%	97.49%	105.18%
S3A	QA-LOW	100	0.6	99.90%	1.95%	97.04%	108.13%
S3A	QC-LOW	134	0.6	99.41%	1.35%	96.56%	103.98%

Table 9. Average Percent Recovery for Sulfate QA and QC Samples.

Inst	QC Sample	Count	Conc.,ug/mL	Av SO4 Rec, %	SD SO4, %	Min SO4 Rec, %	Max SO4 Rec, %
D6A	QC-HIGH	32	12.0	101.52%	1.60%	96.20%	104.25%
D6A	QA-MED-HI	23	6.0	102.03%	1.38%	96.85%	104.43%
D6A	QC-MED	51	3.0	99.92%	1.39%	93.65%	105.31%
D6A	QA-LOW	33	1.2	98.71%	1.79%	95.81%	105.17%
D6A	QC-LOW	41	1.2	99.06%	1.21%	94.37%	103.50%
S2A	QC-HIGH	47	12.0	101.69%	0.81%	99.72%	102.81%
S2A	QA-MED-HI	35	6.0	101.51%	0.39%	100.26%	102.03%
S2A	QC-MED	86	3.0	100.07%	0.38%	99.40%	101.21%
S2A	QA-LOW	49	1.2	99.08%	0.87%	96.89%	101.07%
S2A	QC-LOW	68	1.2	99.95%	0.64%	98.19%	101.60%
S3A	QC-HIGH	94	12.0	101.71%	1.32%	98.23%	104.54%
S3A	QA-MED-HI	70	6.0	102.10%	0.89%	100.50%	107.06%
S3A	QC-MED	163	3.0	100.52%	0.94%	96.92%	103.50%
S3A	QA-LOW	100	1.2	99.06%	1.77%	95.31%	109.56%
S3A	QC-LOW	134	1.2	99.71%	1.27%	94.16%	102.91%

Figure 1

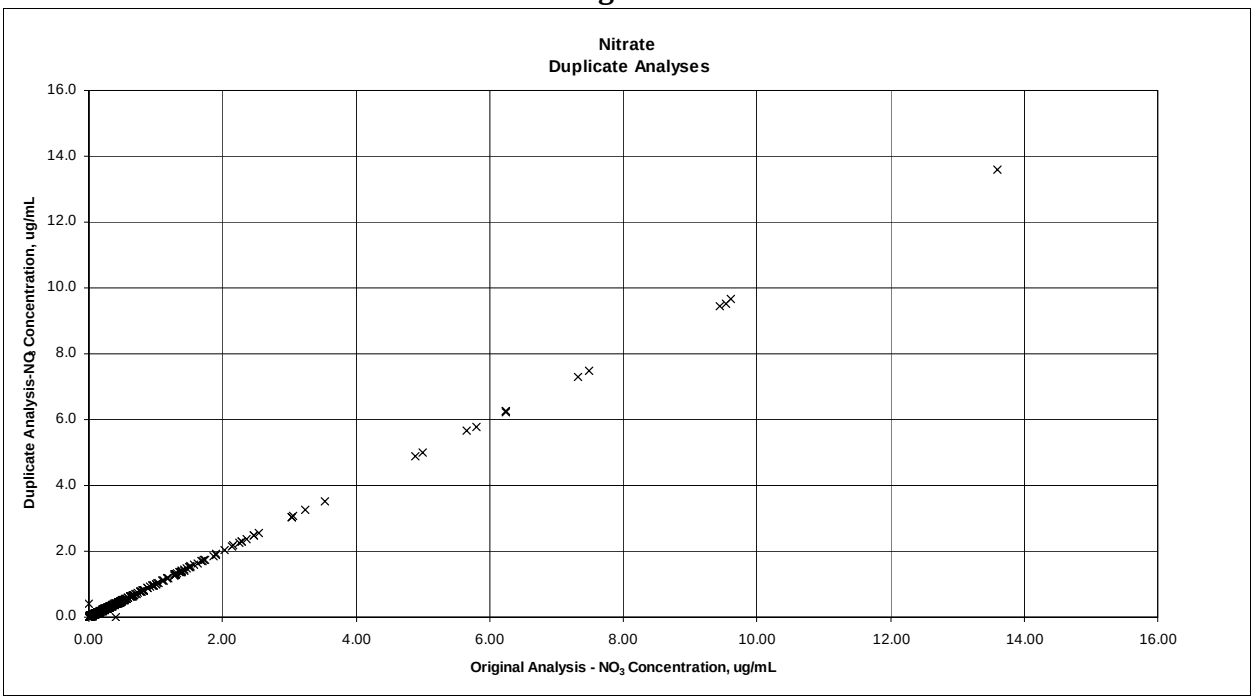


Figure 2

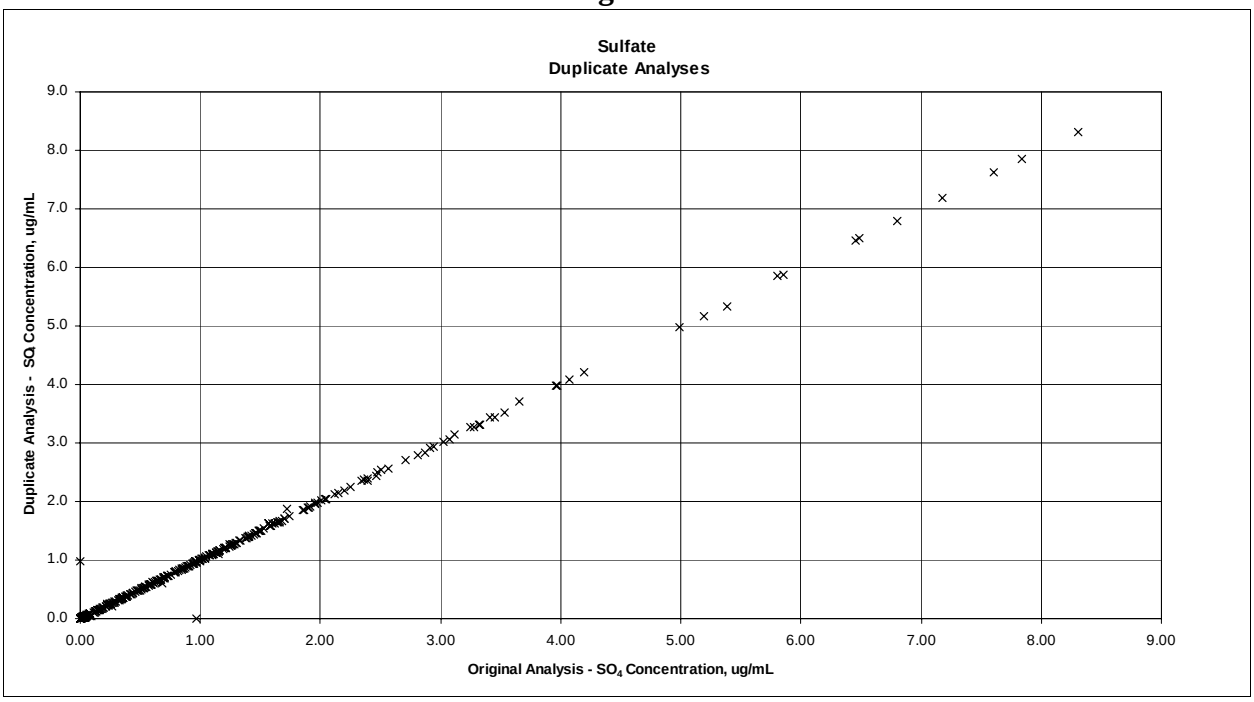


Table 10. Average Percent Recovery for Nitrate and Sulfate Spikes.

Inst:	D6A					
Filt:	Nylon filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:			102.2%	96.4%	100.0%	99.5%
St Dev:			2.0%	2.6%	1.3%	1.6%
Count:			3	4	15	33
Min:			100.6%	93.8%	97.3%	94.0%
Max			104.5%	98.7%	101.4%	101.5%

Inst:	D6A					
Filt:	Nylon filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:			101.5%	97.0%	100.1%	99.5%
St Dev:			1.4%	1.9%	0.9%	1.4%
Count:			3	4	15	34
Min:			100.2%	94.4%	97.8%	94.6%
Max			103.0%	98.8%	101.2%	101.4%

Inst:	D6A					
Filt:	Teflon Filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:			93.5%		99.4%	100.1%
St Dev:					0.2%	0.7%
Count:			1		3	3
Min:			93.5%		99.2%	99.4%
Max			93.5%		99.6%	100.8%

Inst:	D6A					
Filt:	Teflon Filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:			99.1%		99.9%	101.0%
St Dev:					0.9%	0.0%
Count:			1		3	3
Min:			99.1%		99.3%	100.9%
Max			99.1%		101.0%	101.0%

Table 10 (continued).

Inst:	S2A					
Filt:	Nylon Filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:		99.2%	100.0%	99.8%	100.0%	100.4%
St Dev:		0.8%	0.8%	0.9%	0.8%	1.5%
Count:		15	18	20	4	13
Min:		98.0%	98.8%	98.0%	98.9%	98.7%
Max		100.8%	101.6%	101.7%	100.5%	104.6%

Inst:	S2A					
Filt:	Nylon Filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:		99.6%	100.0%	100.1%	99.9%	100.2%
St Dev:		0.8%	0.7%	0.8%	0.7%	0.7%
Count:		16	19	19	4	16
Min:		97.9%	98.6%	98.4%	99.1%	99.2%
Max		101.0%	101.6%	101.8%	100.6%	101.3%

Inst:	S2A					
Filt:	Teflon Filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	99.2%	99.5%	100.2%	99.6%	99.0%	101.1%
St Dev:	0.6%	0.5%	1.1%	0.7%	0.7%	0.2%
Count:	4	7	3	4	7	3
Min:	98.7%	99.0%	99.5%	98.6%	97.5%	100.9%
Max	100.1%	100.5%	101.5%	100.3%	99.6%	101.2%

Inst:	S2A					
Filt:	Teflon Filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	99.6%	100.4%	100.6%	100.3%	100.0%	101.3%
St Dev:	1.0%	0.3%	1.2%	0.7%	0.4%	0.2%
Count:	4	7	3	4	7	3
Min:	98.1%	100.1%	99.8%	99.6%	99.3%	101.1%
Max	100.5%	101.0%	101.9%	101.3%	100.4%	101.4%

Table 10 (continued).

Inst:	S3A					
Filt:	Nylon Filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	99.7%	99.9%	100.0%	100.2%	100.5%	99.9%
St Dev:	0.7%	0.7%	0.8%	0.7%	3.0%	0.9%
Count:	20	26	20	28	22	28
Min:	98.8%	98.9%	98.3%	98.7%	97.8%	97.8%
Max	101.7%	101.4%	101.2%	101.6%	112.7%	101.5%

Inst:	S3A					
Filt:	Nylon Filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	99.8%	100.3%	100.1%	100.1%	100.0%	99.7%
St Dev:	0.9%	0.8%	0.9%	0.5%	1.5%	1.5%
Count:	23	26	20	28	23	30
Min:	98.2%	99.0%	97.5%	98.9%	97.0%	96.3%
Max	101.9%	101.8%	101.3%	101.2%	103.4%	101.7%

Inst:	S3A					
Filt:	Teflon Filter					
Analyte	Nitrate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	101.6%	102.2%	100.2%	100.6%	103.9%	102.3%
St Dev:	0.7%	1.6%	1.9%	1.2%	2.7%	0.9%
Count:	4	4	5	7	20	5
Min:	100.9%	100.6%	98.3%	99.0%	99.5%	101.3%
Max	102.6%	104.4%	103.0%	102.1%	108.9%	103.6%

Inst:	S3A					
Filt:	Teflon Filter					
Analyte	Sulfate					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	100.2%	100.6%	100.3%	100.2%	100.3%	99.9%
St Dev:	0.3%	0.5%	1.2%	1.1%	1.3%	1.4%
Count:	4	4	5	7	20	5
Min:	99.8%	100.1%	98.4%	98.5%	97.1%	98.1%
Max	100.4%	101.3%	101.3%	101.1%	102.0%	101.7%

Table 11. Filter Blank and Regent Blank Values (ppm) for Nitrate and Sulfate.

Inst	Blank Type	Count	Av NO3	STD NO3	Min NO3	Max NO3
D6A	N BLANK	18	0.0237	0.0367	0.0000	0.1466
D6A	REAGENT	64	0.0029	0.0081	0.0000	0.0389
S2A	N BLANK	14	0.0074	0.0189	0.0000	0.0534
S2A	REAGENT	83	0.0005	0.0032	0.0000	0.0243
S3A	N BLANK	76	0.0309	0.0706	0.0000	0.5906*
S3A	REAGENT	184	0.0023	0.0073	0.0000	0.0461

* 12/17/2001

Inst	Blank Type	Count	Avg SO4	STD SO4	Min SO4	Max SO4
D6A	N BLANK	18	0.0257	0.0575	0.0000	0.2414
D6A	REAGENT	64	0.0111	0.0166	0.0000	0.1129
S2A	N BLANK	14	0.0000	0.0000	0.0000	0.0000
S2A	REAGENT	83	0.0081	0.0141	0.0000	0.1069
S3A	N BLANK	76	0.0322	0.1338	0.0000	1.1701*
S3A	REAGENT	184	0.0178	0.0188	0.0000	0.0964

* 12/17/2001

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 12 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 100.7% to 105.2%. The average recovery for the QC samples ranged from 100.0% to 101.4%.

Table 13 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 99.4% to 103.5%. The average recovery for the QC samples ranged from 99.2% to 100.8%.

Table 14 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 99.2% to 103.1%. The average recovery for the QC samples ranged from 99.9% to 101.0%.

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

Inst	Sample	Count	Conc., ug/mL	Av Na rec,%	SD Na, %	Min Na Rec, %	Max Na Rec, %
D5C	GFS 0.4 PPM QA	108	0.4	105.21%	4.55%	95.82%	121.84%
D5C	GFS 4.0 PPM QA	112	4.0	100.74%	1.18%	98.43%	104.64%
D5C	RTI 2.0 PPM QC	90	2.0	100.58%	1.59%	97.42%	105.47%
D5C	RTI 5.0 PPM QC	76	5.0	100.03%	1.43%	97.11%	105.20%
D6C	GFS 0.4 PPM QA	131	0.4	104.03%	2.84%	98.30%	121.78%
D6C	GFS 4.0 PPM QA	143	4.0	101.13%	0.90%	98.91%	103.97%
D6C	RTI 2.0 PPM QC	124	2.0	101.38%	1.56%	98.92%	107.42%
D6C	RTI 5.0 PPM QC	104	5.0	100.96%	0.96%	99.04%	104.15%

Table 13. Average Percent Recovery for Ammonium QA and QC Samples.

Inst	Sample	Count	Conc., ug/mL	Av NH4 rec,%	SD NH4, %	Min NH4 Rec, %	Max NH4 Rec, %
D5C	GFS 0.4 PPM QA	108	0.4	103.46%	4.48%	95.21%	116.34%
D5C	GFS 4.0 PPM QA	112	4.0	99.72%	1.48%	96.28%	103.42%
D5C	RTI 2.0 PPM QC	90	2.0	99.15%	1.99%	95.32%	104.23%
D5C	RTI 5.0 PPM QC	76	5.0	100.25%	1.70%	96.39%	105.02%
D6C	GFS 0.4 PPM QA	131	0.4	103.33%	1.87%	97.11%	107.50%
D6C	GFS 4.0 PPM QA	143	4.0	99.44%	0.85%	95.29%	101.38%
D6C	RTI 2.0 PPM QC	124	2.0	100.81%	1.18%	97.80%	103.97%
D6C	RTI 5.0 PPM QC	104	5.0	100.63%	1.04%	97.82%	103.29%

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

Inst	Sample	Count	Conc., ug/mL	Av K rec,%	SD K, %	Min K Rec, %	Max K Rec, %
D5C	GFS 0.4 PPM QA	108	0.4	103.08%	5.32%	94.61%	127.14%
D5C	GFS 4.0 PPM QA	112	4.0	99.37%	1.14%	97.04%	103.12%
D5C	RTI 2.0 PPM QC	90	2.0	100.62%	1.91%	95.97%	109.27%
D5C	RTI 5.0 PPM QC	76	5.0	99.94%	1.36%	97.15%	103.00%
D6C	GFS 0.4 PPM QA	131	0.4	99.22%	2.03%	89.60%	105.12%
D6C	GFS 4.0 PPM QA	143	4.0	99.78%	0.82%	95.56%	101.75%
D6C	RTI 2.0 PPM QC	124	2.0	100.97%	1.15%	98.49%	103.75%
D6C	RTI 5.0 PPM QC	104	5.0	100.98%	0.90%	99.19%	103.21%

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 some scatter at the lower concentrations which may attributed to trace sodium remaining on the nylon filters after cleaning. RTI is revising the filter cleaning SOP in an effort to minimize this variability.

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

Table 15 shows average percent recovery for spikes of sodium, ammonium, and potassium by filter type over the six month period. There was no significant difference in the spike recoveries of sodium, ammonium, or potassium for the three different filter types. The average recovery values for all filter types ranged from 98.0% to 101.7% for sodium, 96.0% to 100.8% for ammonium, and 96.9% to 99.5% for potassium.

Figure 3.

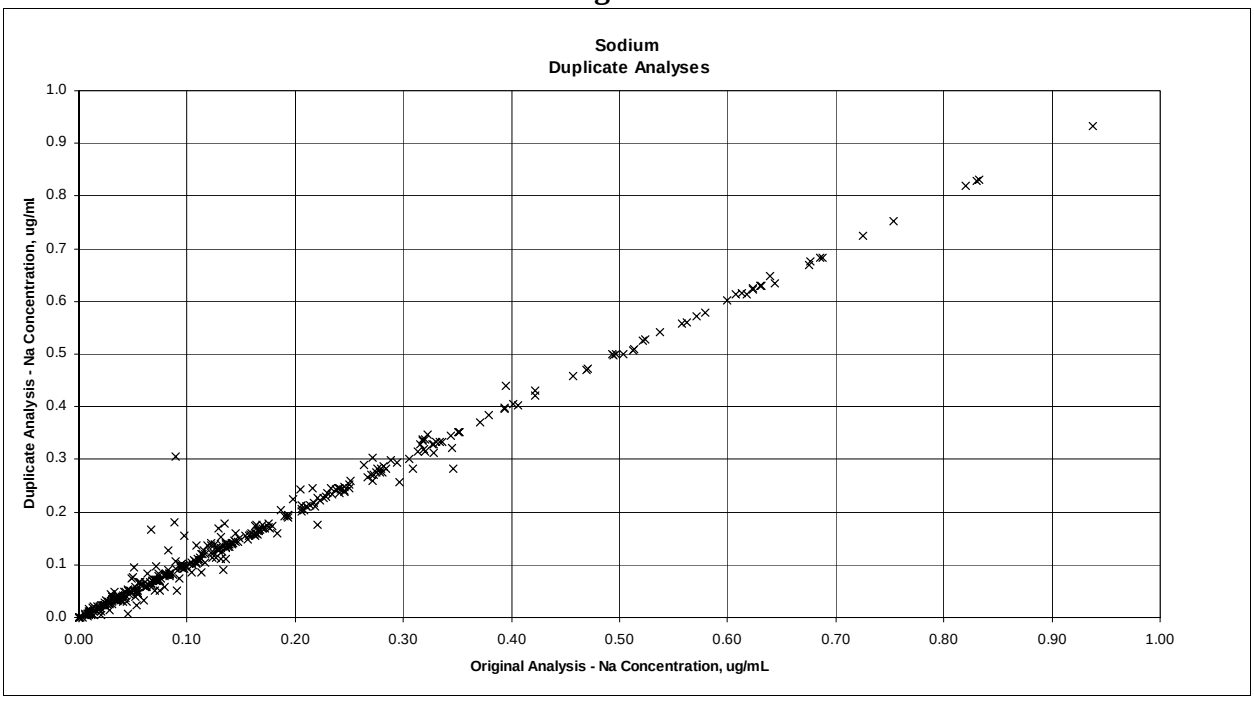


Figure 4

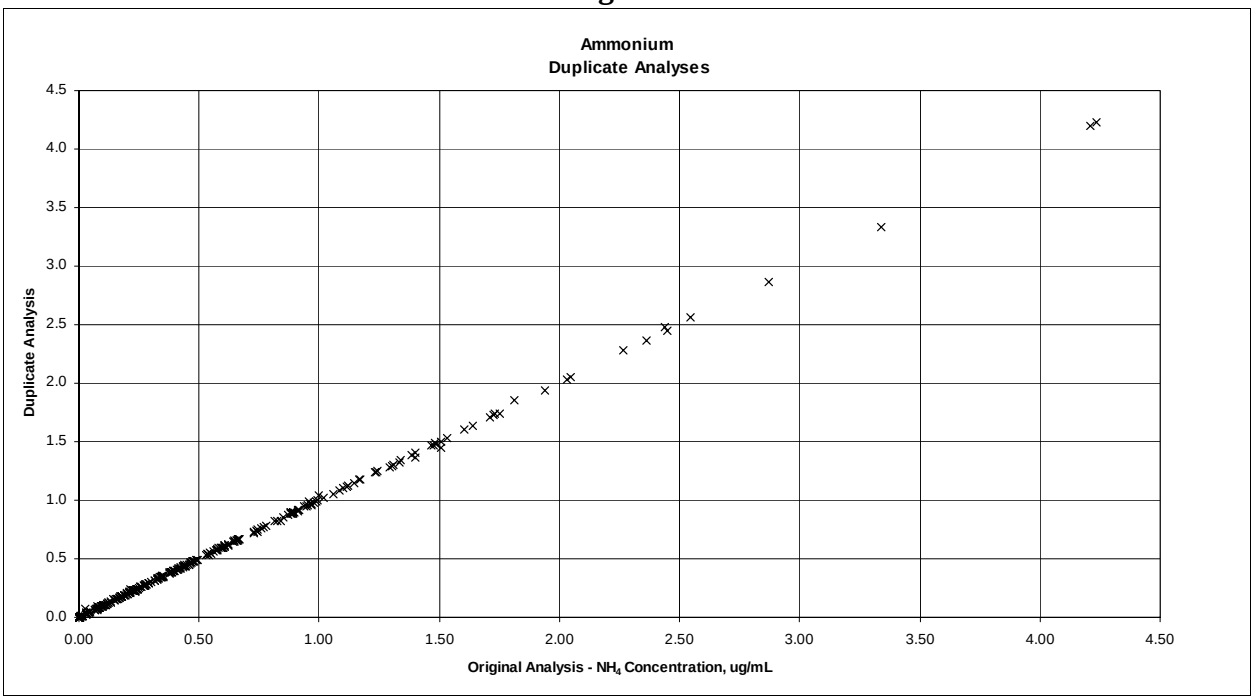


Figure 5

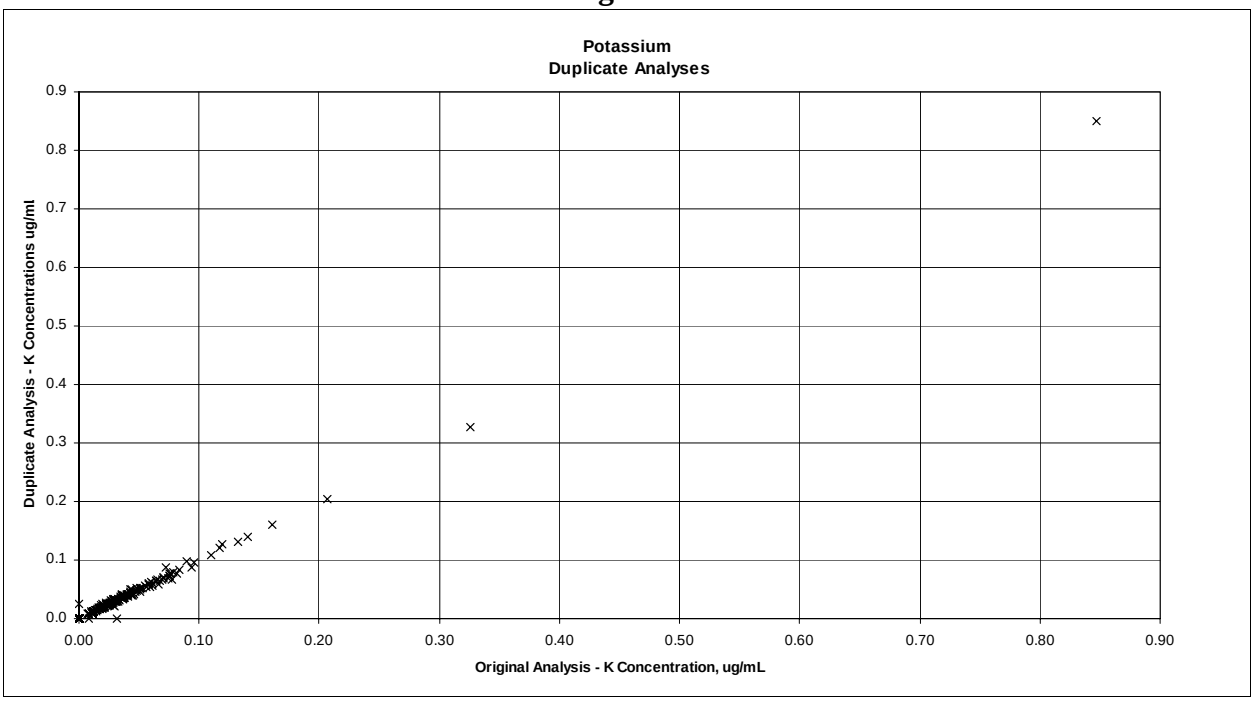


Table 15. Average Percent Recovery for Sodium, Ammonium, and Potassium Spikes.

Inst:	D5C					
Filt:	Nylon Filter					
Analyte	Sodium					
Date:	Oct-01	Nov-01	Dec-01	Jan-02	Feb-02	Mar-02
Avg:	101.7%	98.6%	98.7%	98.4%	100.3%	98.8%
St Dev:	1.5%	1.8%	1.2%	1.4%	1.5%	2.0%
Count:	3	15	15	22	22	33
Min:	100.8%	95.6%	97.3%	94.9%	97.9%	90.2%
Max	103.4%	101.7%	100.8%	100.3%	103.3%	101.8%

Inst:	D5C					
Filt:	Nylon Filter					
Analyte	Ammonium					
Date:	Oct-01	Nov-01	Dec-01	Jan-02	Feb-02	Mar-02
Avg:	96.1%	96.5%	97.0%	97.3%	99.2%	97.1%
St Dev:	0.3%	1.2%	2.1%	2.1%	2.1%	1.8%
Count:	2	15	15	22	22	34
Min:	95.9%	93.5%	93.6%	93.5%	94.7%	93.4%
Max	96.4%	98.0%	100.9%	101.8%	102.5%	101.2%

Inst:	D5C					
Filt:	Nylon Filter					
Analyte	Potassium					
Date:	Oct-01	Nov-01	Dec-01	Jan-02	Feb-02	Mar-02
Avg:	98.7%	97.6%	98.1%	97.8%	98.3%	96.9%
St Dev:	0.6%	1.1%	1.6%	2.5%	2.9%	1.3%
Count:	3	15	15	22	22	34
Min:	98.1%	94.6%	96.0%	92.7%	94.1%	94.4%
Max	99.2%	99.4%	101.1%	102.2%	103.5%	99.8%

Inst:	D5C					
Filt:	Teflon Filter					
Analyte	Sodium					
Date:	Oct-01	Nov-01	Dec-01	Jan-02	Feb-02	Mar-02
Avg:		98.6%	98.0%	99.1%	98.4%	98.9%
St Dev:		2.2%	1.1%	0.8%	1.0%	1.5%
Count:		7	4	6	9	6
Min:		96.0%	96.5%	97.4%	96.5%	97.1%
Max		103.0%	98.9%	99.6%	99.9%	101.0%

Table 15 (continued).

Inst:	D5C					
Filt:	Teflon Filter					
Analyte	Ammonium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:		96.0%	98.2%	98.2%	97.1%	96.9%
St Dev:		2.4%	4.6%	1.3%	2.0%	1.5%
Count:		7	4	6	9	6
Min:		93.3%	94.5%	96.9%	93.7%	94.9%
Max		100.7%	105.0%	100.5%	100.5%	98.8%

Inst:	D5C					
Filt:	Teflon Filter					
Analyte	Potassium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:		97.1%	97.2%	98.5%	97.1%	97.1%
St Dev:		2.2%	1.4%	0.8%	1.0%	1.3%
Count:		7	4	6	9	6
Min:		95.2%	95.0%	96.9%	95.8%	95.6%
Max		101.5%	98.1%	99.3%	98.7%	98.9%

Inst:	D6C					
Filt:	Nylon Filter					
Analyte	Sodium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	98.2%	100.1%	100.0%	100.0%	99.9%	100.8%
St Dev:	2.8%	1.5%	0.9%	0.6%	1.2%	5.4%
Count:	19	21	26	18	19	34
Min:	92.4%	96.5%	98.2%	98.8%	95.9%	97.8%
Max	103.6%	103.1%	101.5%	101.1%	101.7%	130.9%

Inst:	D6C					
Filt:	Nylon Filter					
Analyte	Ammonium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	97.8%	99.9%	99.3%	99.6%	99.4%	99.8%
St Dev:	1.8%	1.3%	1.0%	0.9%	1.4%	1.2%
Count:	18	16	25	17	19	33
Min:	94.3%	97.4%	97.4%	97.7%	94.8%	97.0%
Max	102.0%	101.9%	101.9%	101.5%	101.0%	101.8%

Table 15 (continued).

Inst:	D6C					
Filt:	Nylon Filter					
Analyte	Potassium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	98.0%	99.3%	99.5%	99.1%	98.3%	97.4%
St Dev:	1.7%	0.9%	0.9%	1.0%	1.3%	1.9%
Count:	19	21	26	18	19	34
Min:	95.9%	97.4%	97.8%	97.3%	96.2%	92.0%
Max	101.2%	101.1%	101.4%	100.8%	100.6%	101.0%

Inst:	D6C					
Filt:	Teflon Filter					
Analyte	Sodium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	98.5%	100.1%	101.1%	101.0%	99.7%	100.4%
St Dev:	1.7%	0.5%	1.5%	0.7%	0.9%	0.8%
Count:	8	3	8	5	21	7
Min:	96.6%	99.5%	99.7%	100.2%	98.1%	99.5%
Max	101.6%	100.5%	104.2%	102.0%	102.2%	101.6%

Inst:	D6C					
Filt:	Teflon Filter					
Analyte	Ammonium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	97.8%	97.3%	99.7%	100.8%	99.7%	99.8%
St Dev:	1.8%		1.7%	0.4%	0.9%	0.7%
Count:	8	1	7	4	21	7
Min:	95.4%	97.3%	96.7%	100.1%	97.3%	98.7%
Max	100.8%	97.3%	101.1%	101.1%	101.2%	100.7%

Inst:	D6C					
Filt:	Teflon Filter					
Analyte	Potassium					
Date:	**Oct-01**	**Nov-01**	**Dec-01**	**Jan-02**	**Feb-02**	**Mar-02**
Avg:	98.6%	99.1%	98.4%	99.5%	97.7%	97.9%
St Dev:	1.3%	1.1%	1.1%	0.9%	1.1%	1.2%
Count:	8	3	8	5	21	7
Min:	96.2%	97.8%	96.7%	98.3%	95.3%	96.3%
Max	99.8%	99.8%	100.2%	100.7%	99.5%	99.9%

Table 16 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 0.2074 ppm for the nylon filter blanks (25 mL extract) and 0.0072 ppm for the reagent blank. The highest average ammonium values were 0.0007 ppm (25 mL extract) for the nylon filter blanks and 0.0000 for the reagent blank. The highest average potassium values were was 0.0243 ppm for nylon filter blanks (25 mL extract) and 0.0010 ppm for the reagent blank.

Table 16. Filter Blank and Regent Blank Values (ppm) for Sodium, Ammonium, and Potassium.

Inst	TYPE	Count	Av Na	STD Na	Min Na	Max Na
D5C	N Blank	32	0.0601	0.0923	-0.0019	0.3005
D5C	Reagent Blank	102	0.0009	0.0067	-0.0188	0.0564
D6C	N Blank	79	0.2074	0.2771	-0.0024	0.8387
D6C	Reagent Blank	122	0.0072	0.0195	-0.0207	0.1295

Inst	TYPE	Count	Avg NH4	STD NH4	Min NH4	Max NH4
D5C	N Blank	32	0.0007	0.0042	-0.0031	0.0228
D5C	Reagent Blank	102	-0.0002	0.0010	-0.0071	0.0000
D6C	N Blank	79	-0.0029	0.0063	-0.0166	0.0049
D6C	Reagent Blank	122	-0.0030	0.0072	-0.0205	0.0114

Inst	TYPE	Count	Avg K	STD K	Min K	Max K
D5C	N Blank	32	0.0000	0.0000	0.0000	0.0000
D5C	Reagent Blank	102	0.0000	0.0000	0.0000	0.0000
D6C	N Blank	79	0.0243	0.0620	0.0000	0.1974
D6C	Reagent Blank	122	0.0010	0.0098	0.0000	0.1074

2.2.4 Data Validity Discussion

To date, no data have been invalidated as a result of errors in the ion chromatography laboratory. Any inconsistencies that are observed in the filter samples are flagged on the ion chromatography 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

The manufacturer of the nylon filters replaced the defective filters that were discussed in the previous QA report with new filters from a different lot. The replacement filters were carefully tested, and no erosion was observed upon sonication or shaking. However, for the extracts of some of the new filters, the sodium concentrations were higher than acceptable limits. RTI is in the process of modifying the nylon filter washing procedure to add an extra deionized water rinse to reduce the sodium content to acceptable levels. A revised SOP will be prepared when the procedure is optimized.

2.3 OC/EC Laboratory

2.3.1 Description of QC Checks Applied

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

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	annually	MDL $\leq$ 0.5 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples.
Calibration Peak Area	every analysis	Within 95% to 105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter.
Instrument Blank	daily	Blank $\leq$0.3 µg/cm^2	Determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples.
Three-Point Calibration	weekly	Correlation Coefficient (R^2) $\geq$0.99 [with force-fit through 0,0]	Determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed.
Calibration Check	daily	(1) 90% to 110% recovery, and (2) calibration peak area 90% to 110% of average for the weekly 3-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 0.5 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 OC/EC Laboratory had three carbon analyzers (designated as the Retrofit, Second, and Third analyzers) in operation during the October 1, 2001, to March 31, 2002, period. The statistical summaries in this section contain data from these three OC/EC analyzers.

The method detection limit for total carbon (TC) is determined annually. All three OC/EC carbon analyzers met the required limit of ≤0.5 µg C/cm^2 with MDLs of 0.12 µg C/cm^2 for the Retrofit analyzer on January 18 and 21, 2002; 0.19 µg C/cm^2 for the Second analyzer on February 5 and 6, 2002; and 0.18 µg C/cm^2 for the Third analyzer on June 5, 2001.

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 quality control 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 run on the New, Retrofit, Second, and Third OC/EC analyzers during the reporting period (October 1, 2001, through March 31, 2002). The instrument blank must be ≤0.3 µg C/cm^2 (bold line at the top of Figure 6). Mean and standard deviation of blank responses by instrument over the reporting period are summarized in the table below.

	OC/EC Analyzer		
	Retrofit	**Second**	**Third**
No. of Instrument Blanks	119	122	132
Mean Response (µg C/cm^2)	0.031	0.040	0.049
Standard Deviation	0.039	0.039	0.052

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

Figure 6. OC/EC Instrument Blanks

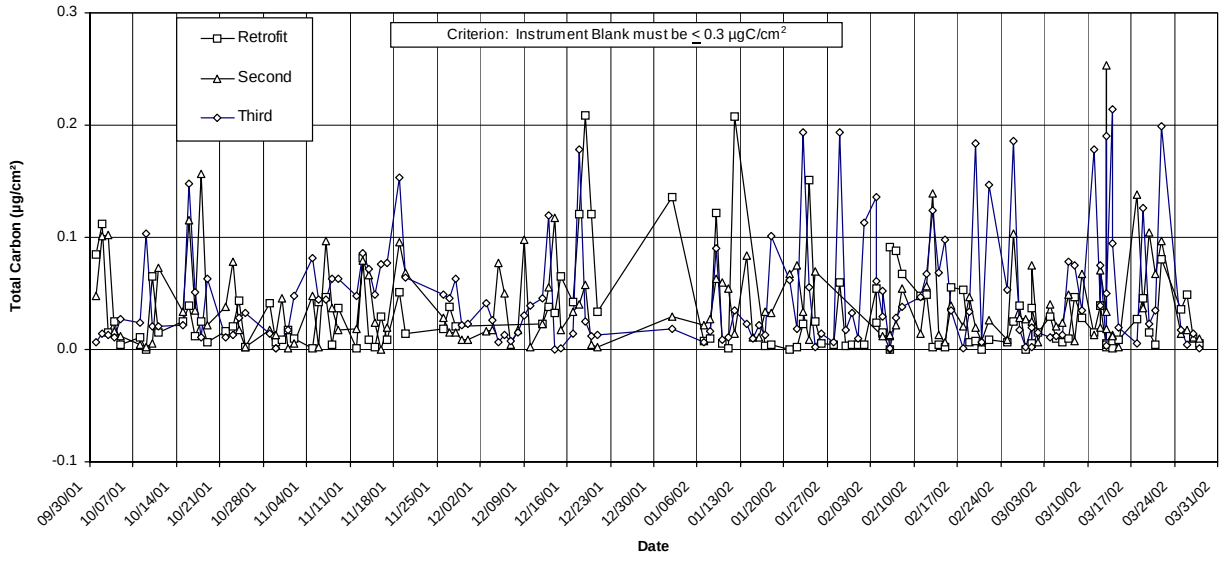
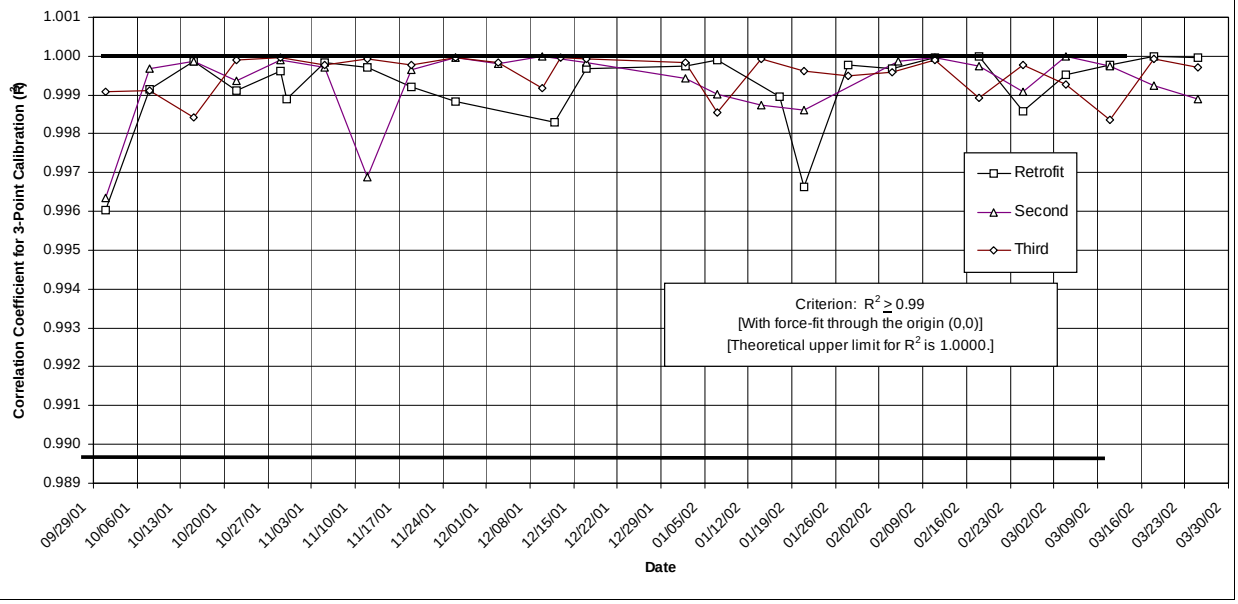


Figure 7 shows linearity (as R^2, forced-fit through the origin) for all 3-point calibrations run on all three instruments during the reporting period. All three instruments met the $R^2 \geq 0.99$ (heavy line in Figure 7) requirement for every 3-point calibration.

Figure 7. Linearity of Three-Point Calibrations



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

Response factors for the flame ionization detector (FID) are used to monitor FID performance. **Figures 9a, 9b, and 9c** show FID response factors for each of the three calibrations standards and the average FID response factor for each three-point calibration on the Retrofit, Second, and Third instruments, respectively, during the reporting period. FID response is affected by slight changes in flow rate for hydrogen and other gases, but use of the internal methane standard at the end of every analysis compensates for such changes. All 3-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.

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

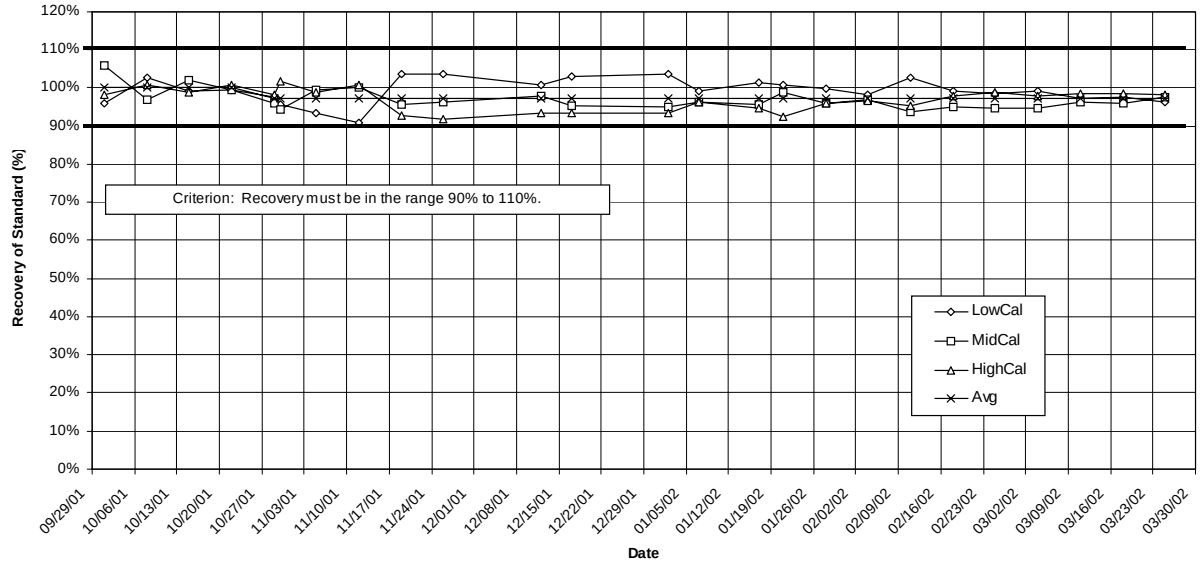


Figure 8b. Percent Recoveries for Three-Point Calibration Standards on the Second OC/EC Analyzer

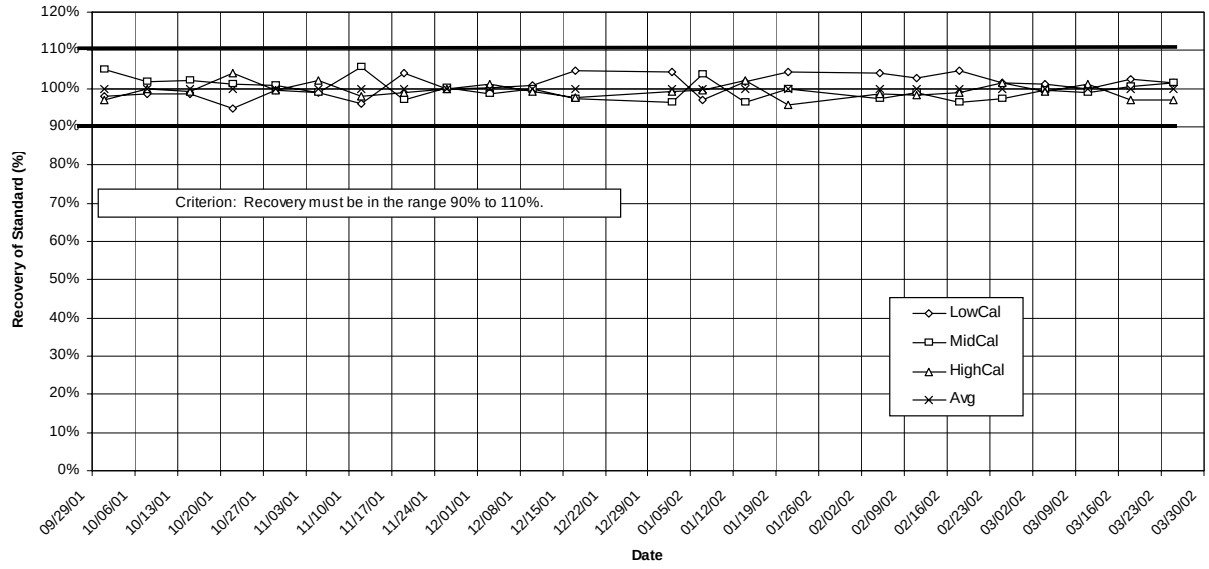


Figure 8c. Percent Recoveries for Three-Point Calibration Standards on the Third OC/EC Analyzer

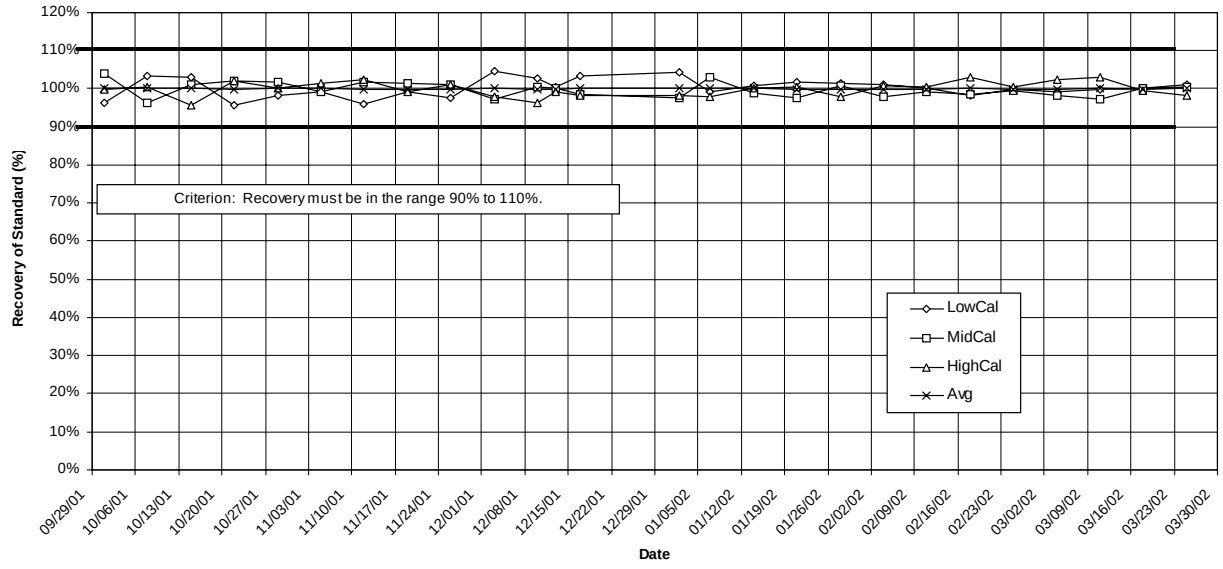


Figure 9a. FID Response Factors for Three-Point Calibration Standards on the Retrofit OC/EC Analyzer

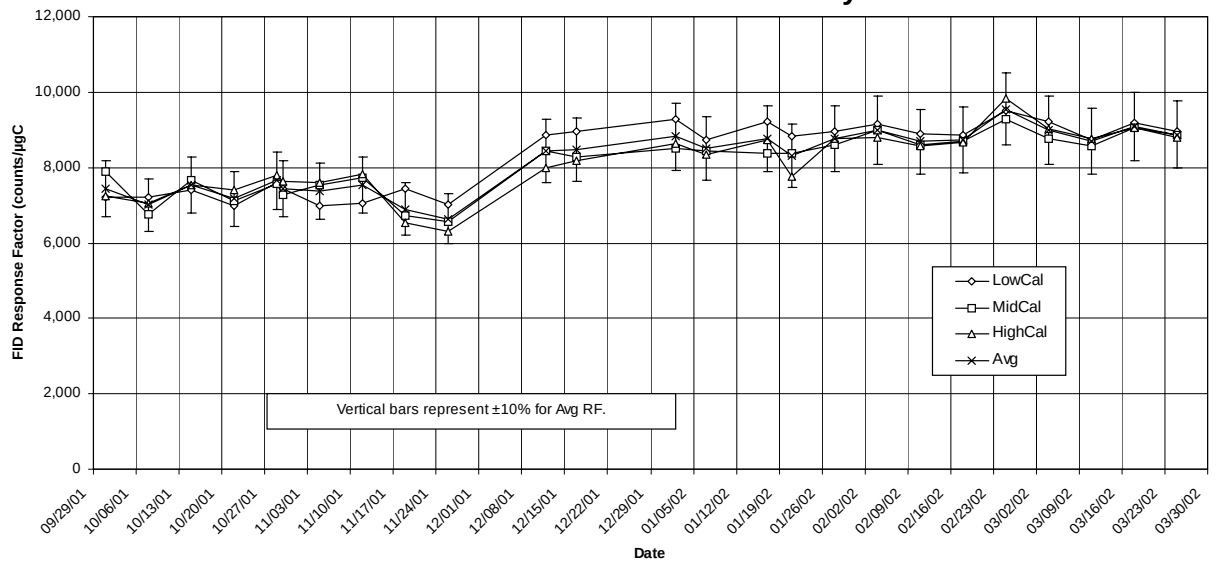


Figure 9b. FID Response Factors for Three-Point Calibration Standards on the Second OC/EC Analyzer

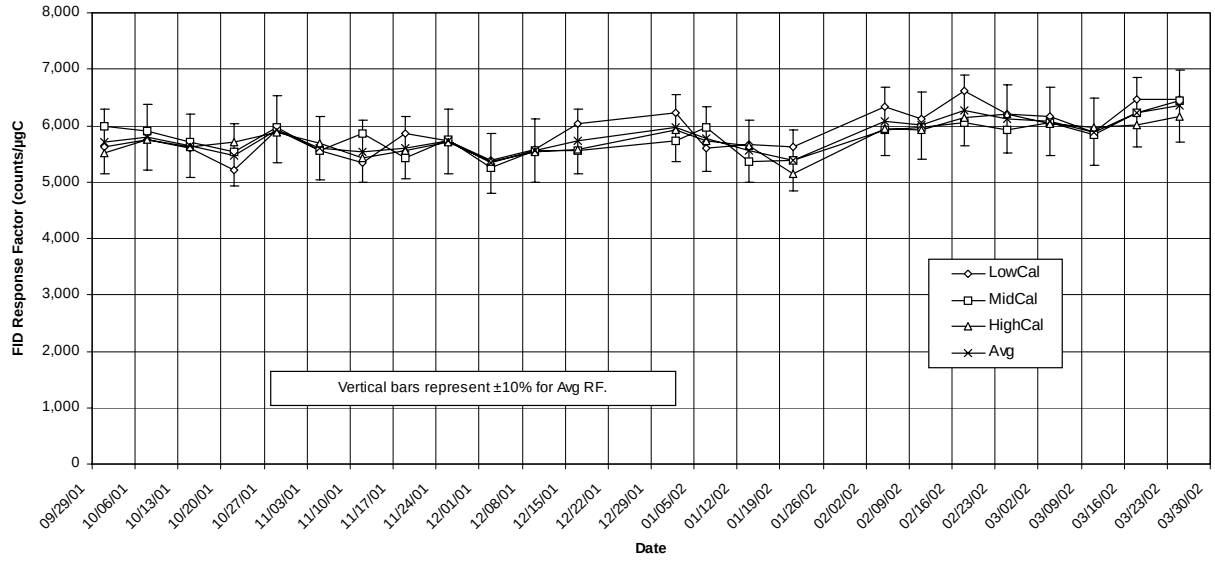
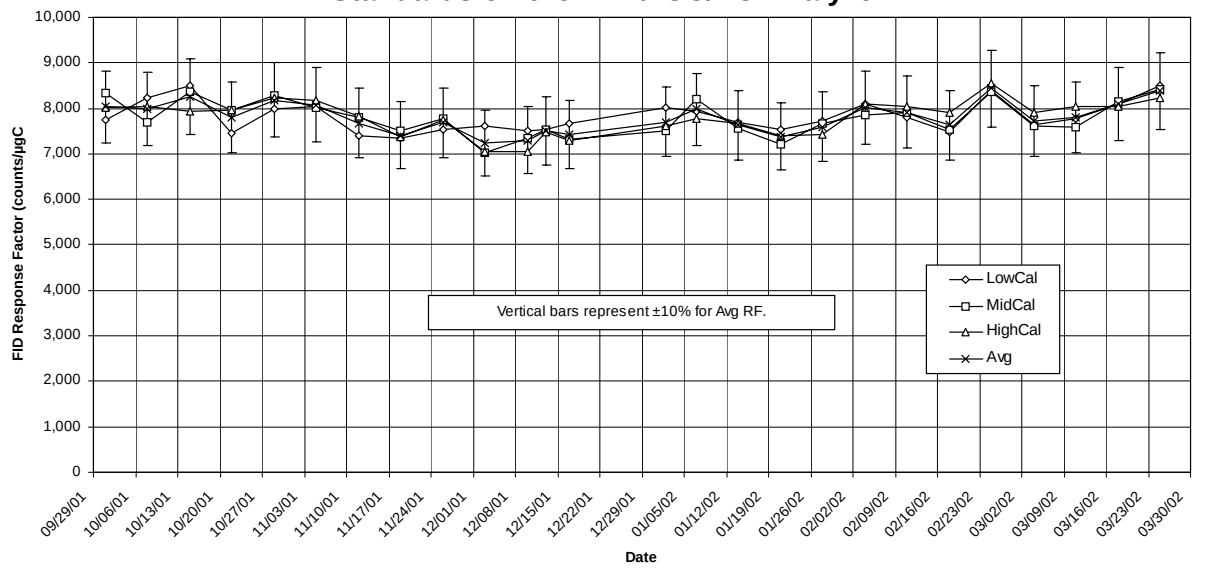


Figure 9c. FID Response Factors for Three-Point Calibration Standards on the Third OC/EC Analyzer



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

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

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

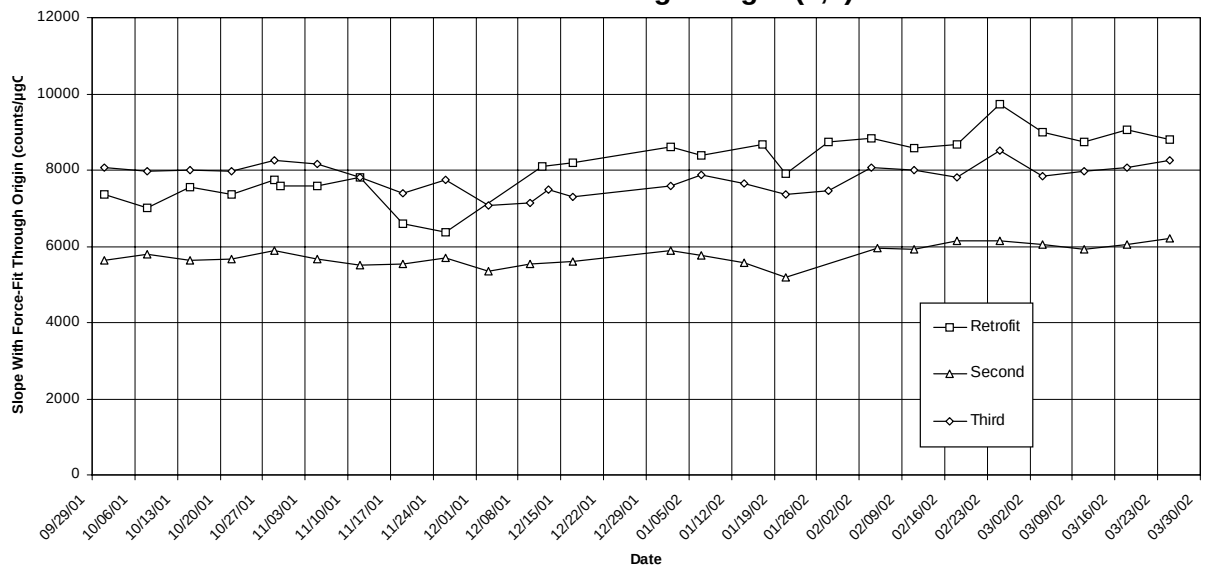


Figure 11 shows percent recovery for all daily calibration checks run on all three instruments during the reporting period. All daily calibration checks met the acceptance criterion of 90% to 110% recovery.

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

Figure 11. Daily Calibration Checks

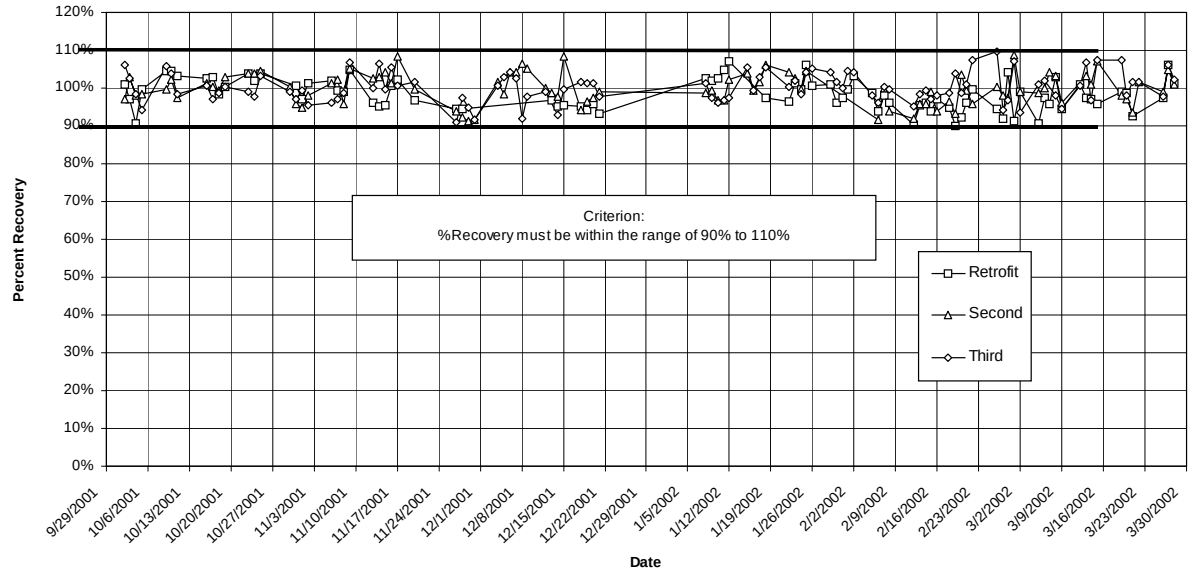


Figure 12a: Relative Percent Difference of Duplicates vs. Average Value for TC on Retrofit OC/EC Analyzer - October 1, 2001, through March 31, 2002

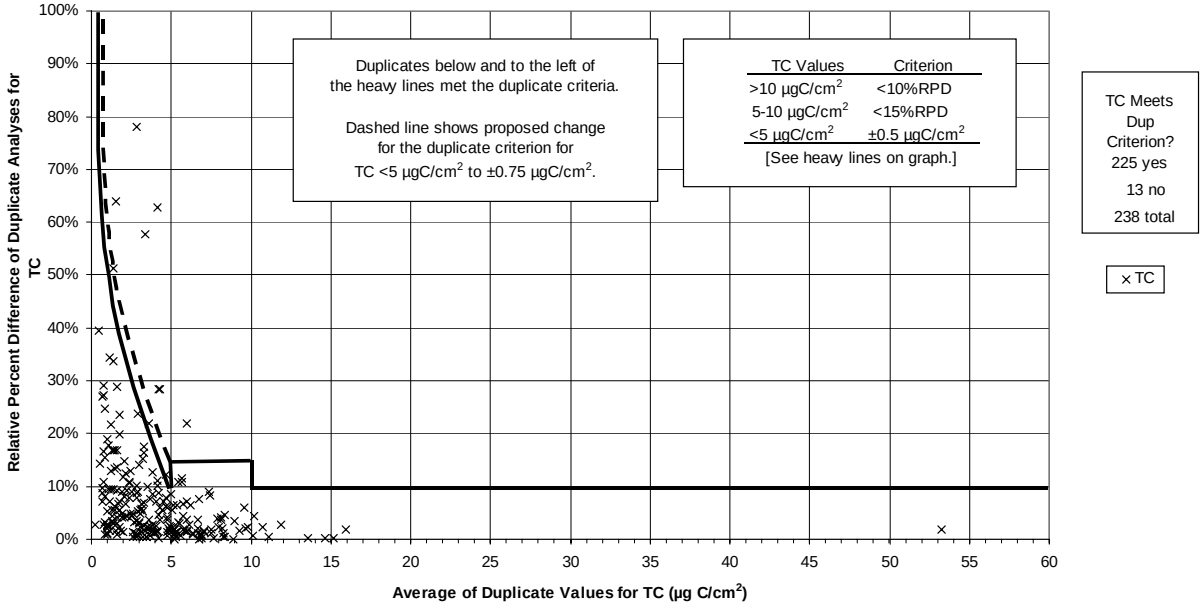


Figure 12b: Relative Percent Difference of Duplicates vs. Average Value for TC on Second OC/EC Analyzer - October 1, 2001, through March 31, 2002

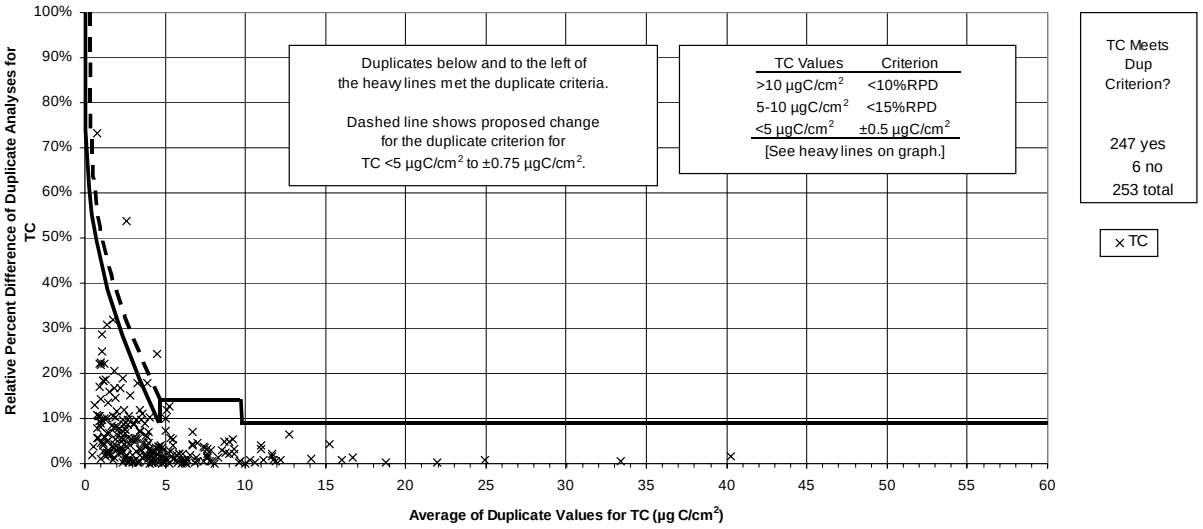
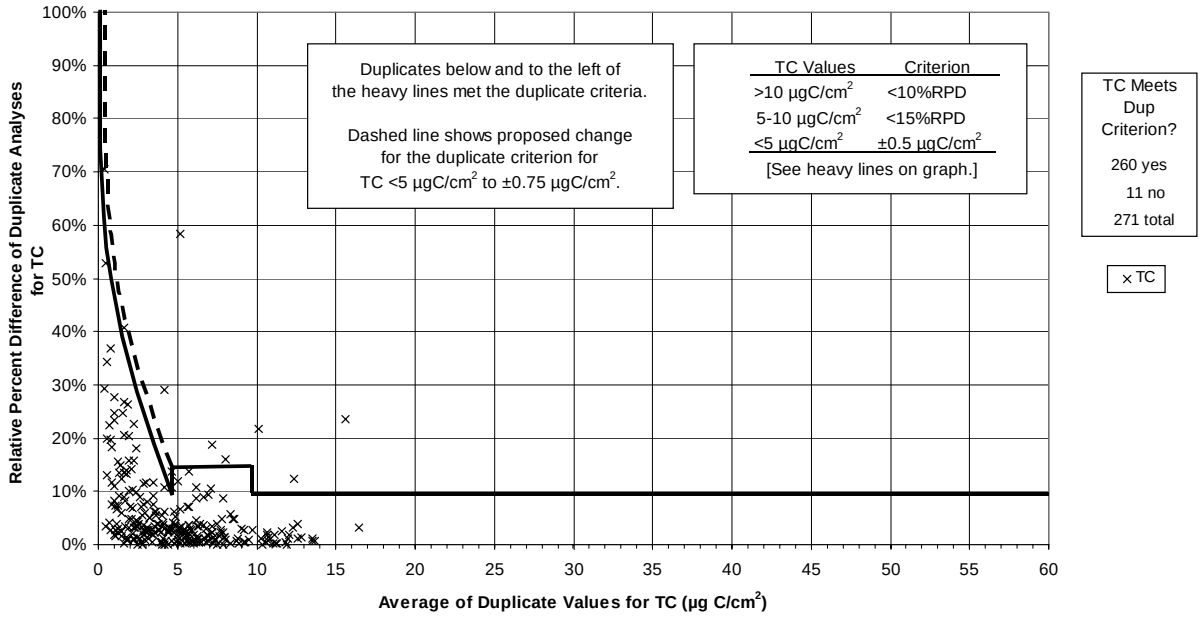


Figure 12c: Relative Percent Difference of Duplicates vs. Average Value for TC on Third OC/EC Analyzer - October 1, 2001, through March 31, 2002



2.3.3 Data Validity Discussion

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

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

2.3.4 Summary of Audit Findings and Recommendations

The February 5, 2002, audit of the OC/EC Laboratory did not result in any critical findings in the OC/EC Laboratory. A 2.10 μg/μL sucrose solution prepared and used as a standard at RTI was analyzed by NAREL chemists, and NAREL's measurement (2.14 μg/μL) differed from the RTI value by only 1.9%.

2.3.5 Corrective Actions Taken

No corrective actions were taken during the period October 1, 2001, through March 31, 2002.

2.3.6 Suggested Changes to OC/EC SOP and QAPP

The changes below are proposed for both the OC/EC SOP and the QAPP for the $PM_{2.5}$ Chemical Speciation Program.

Duplicate Criteria. The criterion for duplicates from filters with average TC loading below 5 μg C/cm^2 should be changed from "within 0.5 μg C/cm^2" to "within 0.75 μg C/cm^2." This change, which is illustrated by a heavy dashed line in Figures 12a through 12c, is necessary to be consistent with the 15% RPD criterion applied to filters with an average loading of 5 μg C/cm^2 (i.e., 15% of 5 μg C/cm^2 is 0.75 μg C/cm^2, not 0.5 μg C/cm^2).

The duplicate criterion for loadings below 5 μg C/cm^2 will be changed from "within 0.5 μg C/cm^2" to "within 0.75 μg C/cm^2" for OC/EC analyses in the May 2002 and subsequent analytical reports.

Instrument Blank. The current frequency for instrument blanks is given in Section 9.1 of the OC/EC Laboratory SOP:

> 9.1 Run an instrument blank, using a punch from a precleaned quartz fiber filter, at the beginning of each batch, at the beginning of each day, or after the analysis of approximately 30 samples, whichever comes first.

The "precleaned quartz fiber filter" punch run as the instrument blank is the punch from the previously analyzed sample; and the punch has been cleaned during the heating cycles of the previous analysis. An instrument blank is a batch blank for analyses run on a given instrument in a given day. An instrument blank is the first recorded analysis each day, and an additional instrument blank is run after the analysis of approximately 30 samples (and again after ~60 samples) in a given day on a given analyzer.

Because the instrument blank relates only to an analysis batch (i.e., about 30 samples run in sequence on an instrument in a given day) and because an analysis batch bears no relationship to the batches of quartz filter samples received from the SHAL, Section 9.1 of the OC/EC Laboratory SOP should be changed to read:

> 9.1 Run an instrument blank, using a punch from a precleaned quartz fiber filter, at the beginning of each day and after approximately every 30 samples run on the instrument on the same day.

2.4 X-ray Fluorescence Laboratories

During the reporting period, additional XRF instruments were put on-line by Chester LabNet. In addition, Cooper Environmental Services (CES) and RTI began analyzing samples by XRF. The equivalency of the new instruments was verified by a preliminary round of analyses by each new instrument or analysis laboratory.

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

2.4.1 Description of QC Checks Applied

QC elements for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions are shown in **Table 17**.

Table 17. QC Procedures Used to Analyze EDXRF Elements

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

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

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

where,

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

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

2.4.2 Chester LabNet

Chester LabNet was the original XRF subcontractor laboratory used for the STN program. To meet the high demand, Chester purchased and brought on-line a new instrument, a ThermoNoran QuanX, instrument designation 771. Quality information for both instruments is presented in this section.

2.4.2.1 Statistical Summary of QC Results

Precision

The precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for a select element are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of

reproducibility or precision. The data used to monitor precision are presented in **Figures 13 through 25**.

When plotted over time, the recoveries for several of the elements appear to exhibit a time dependence. These changes per year are all less than 10 percent and will be monitored. The recovery for these elements appear to be within the uncertainty in unknown after correction for mass absorption and spectral overlap **(Tables 18a and 18b)**.

Table 18a. Summary of Chester QC Precision Recovery Data, Kevex 770, 10/1/2001 - 3/31/2002.

Percent Recoveries

Element	Avg.	Std Dev	% RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(0)	98.07	2.26	2.30	107.27	91.38	-0.48818	-7.50	8.51
Si(1)	99.87	1.56	1.56	104.45	95.27	0.15100	1.60	0.64
Ti(2)	100.97	1.71	1.69	104.93	96.14	0.33888	3.95	-0.16
Fe(3)	99.43	1.14	1.14	102.73	96.19	-0.08157	-0.63	-1.56
Se(4)	101.02	2.36	2.34	107.13	94.48	0.23650	3.80	-5.03
Pb(4)	100.21	2.49	2.48	107.21	92.52	0.32440	5.49	1.71
Cd(5)	100.18	1.59	1.59	104.28	94.24	0.30441	3.29	-3.85

N=329 for all data.

Table 18b. Summary of Chester QC Precision Recovery Data, Kevex 771, 10/1/2001 - 3/31/2002.

Element	Avg.	Std Dev	RSD	Max	Min	R	Slope/Year	
							Current	Previous
Si(1)	101.26	1.87	1.85%	105.72	93.50	0.17874	2.77	N/A
Ti(2)	99.57	2.32	2.33%	104.49	90.71	-0.25283	-4.86	N/A
Fe(3)	99.45	2.07	2.08%	105.25	90.33	-0.33134	-5.97	N/A
Se(4)	99.53	1.79	1.80%	105.59	93.63	-0.00224	-0.03	N/A
Pb(4)	98.87	1.98	2.01%	103.83	90.91	-0.20826	-3.42	N/A
Cd(5)	99.87	2.57	2.57%	105.76	91.68	-0.02152	-0.46	N/A

Figure 13.

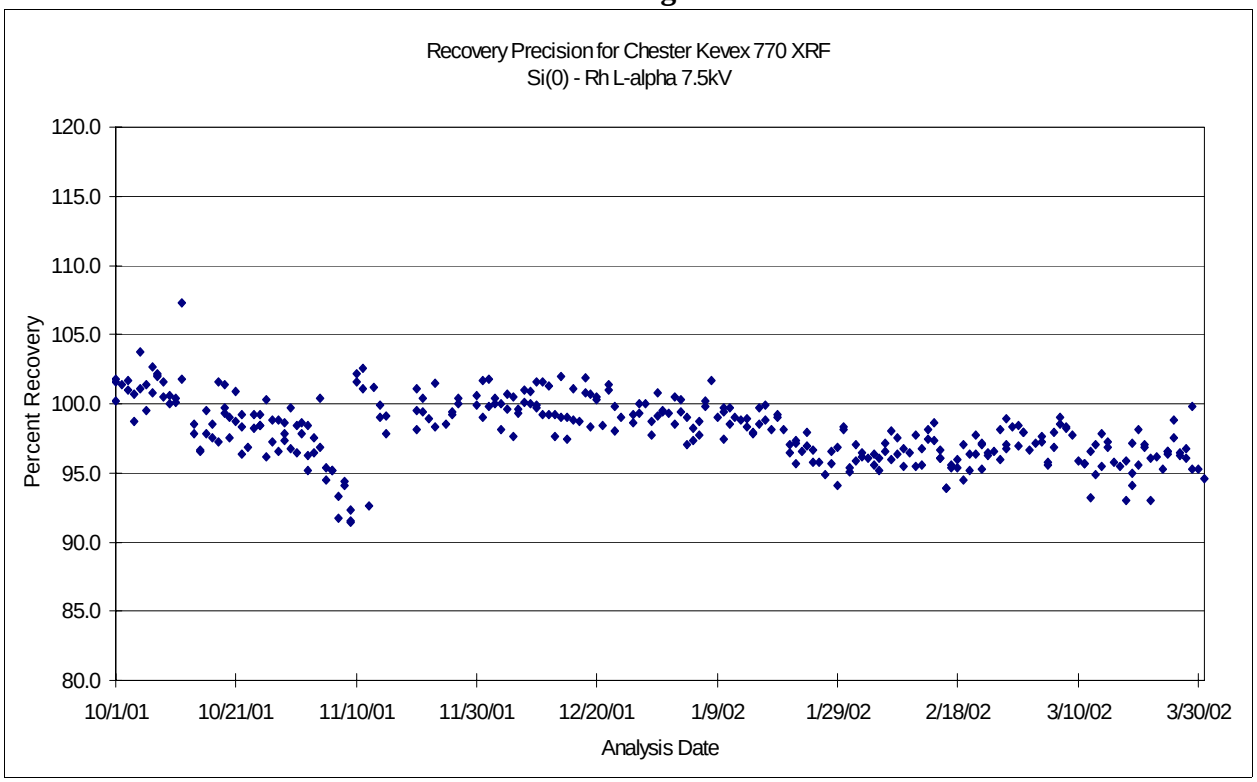


Figure 14.

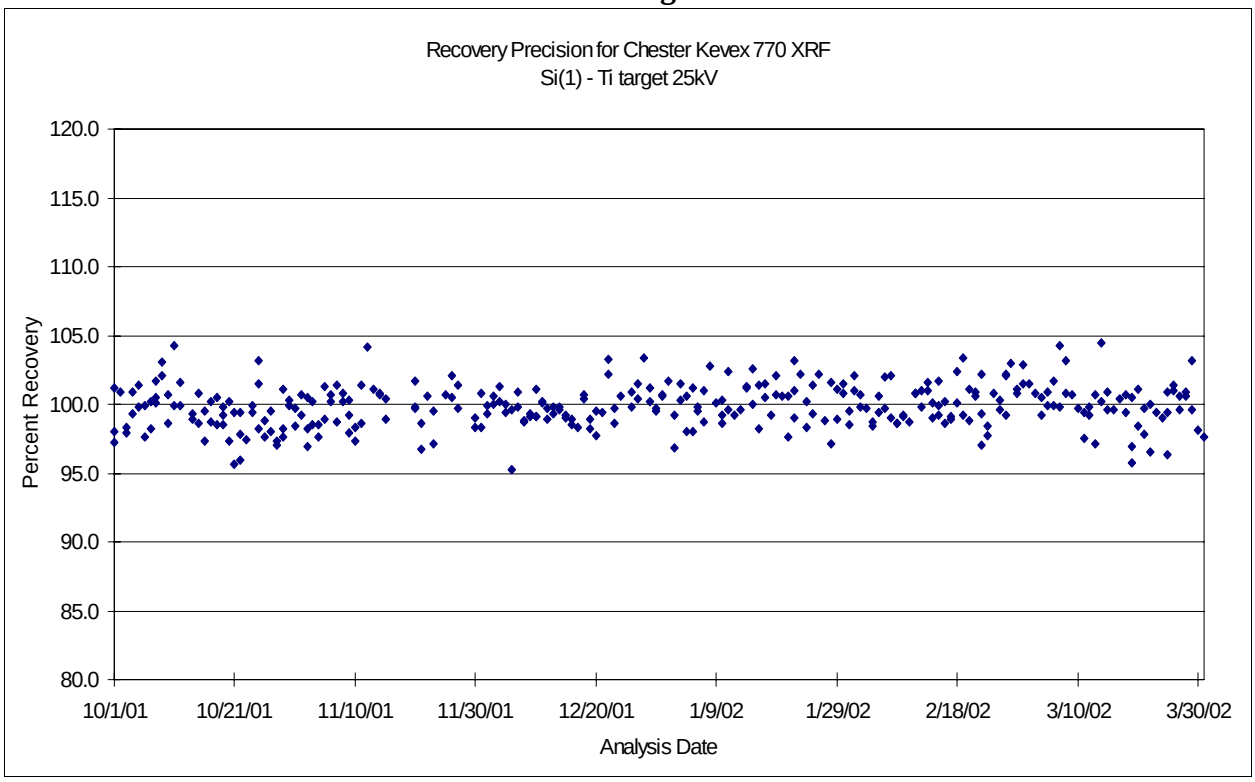


Figure 15

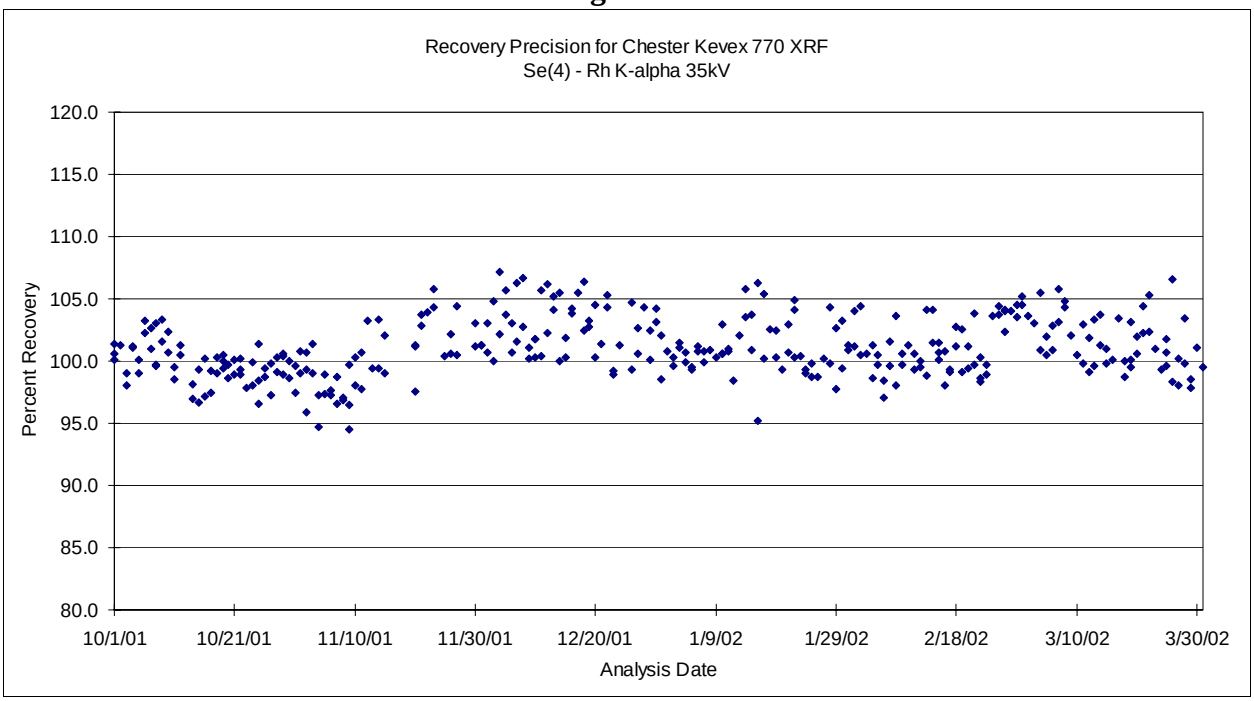


Figure 16

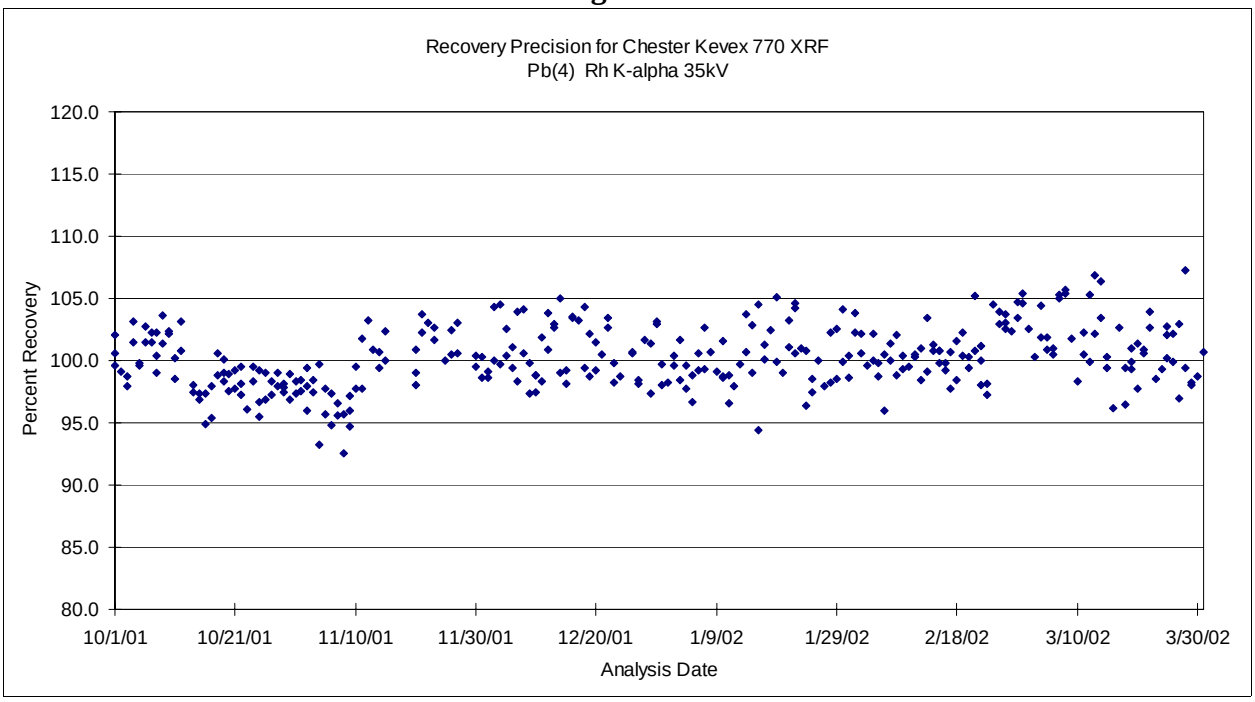


Figure 17

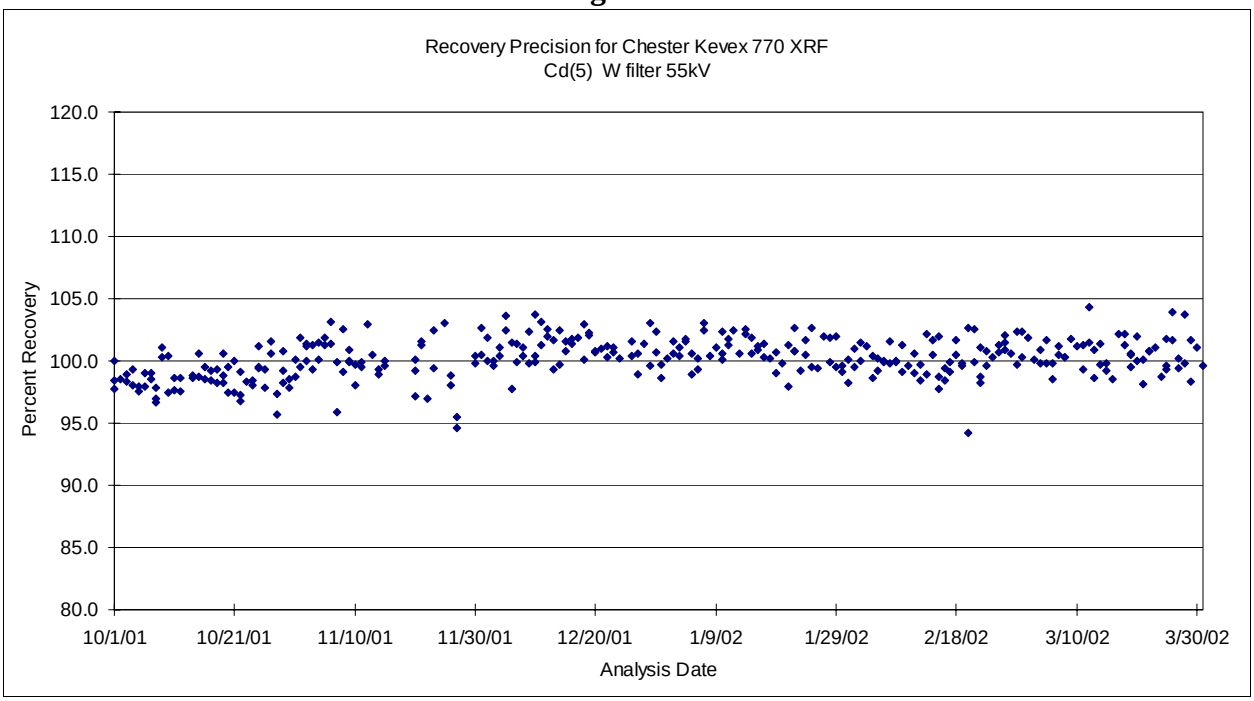


Figure 18

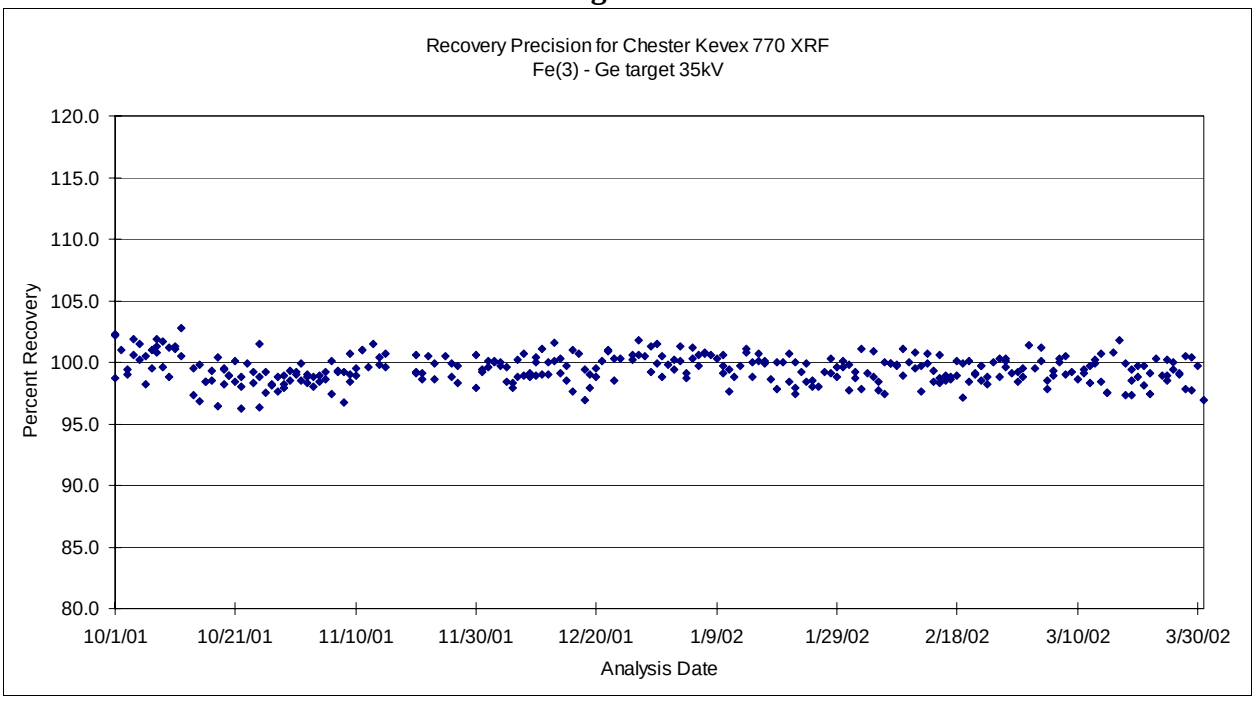


Figure 19

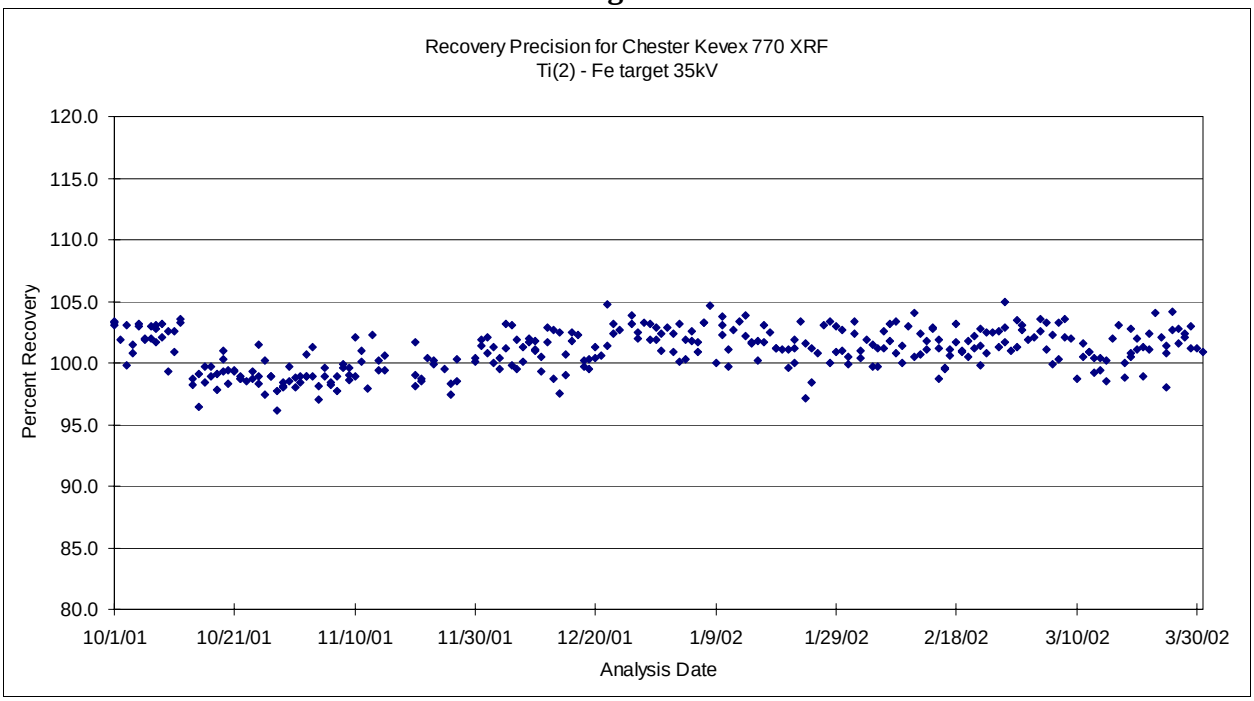


Figure 20

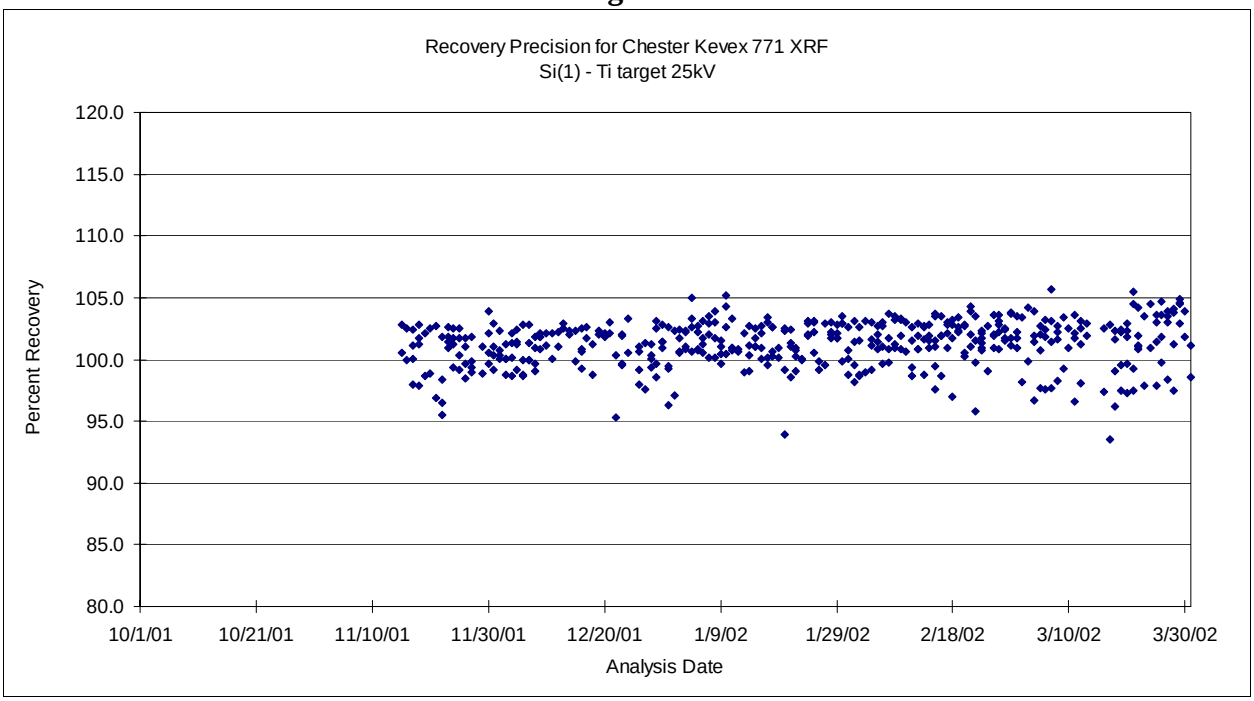
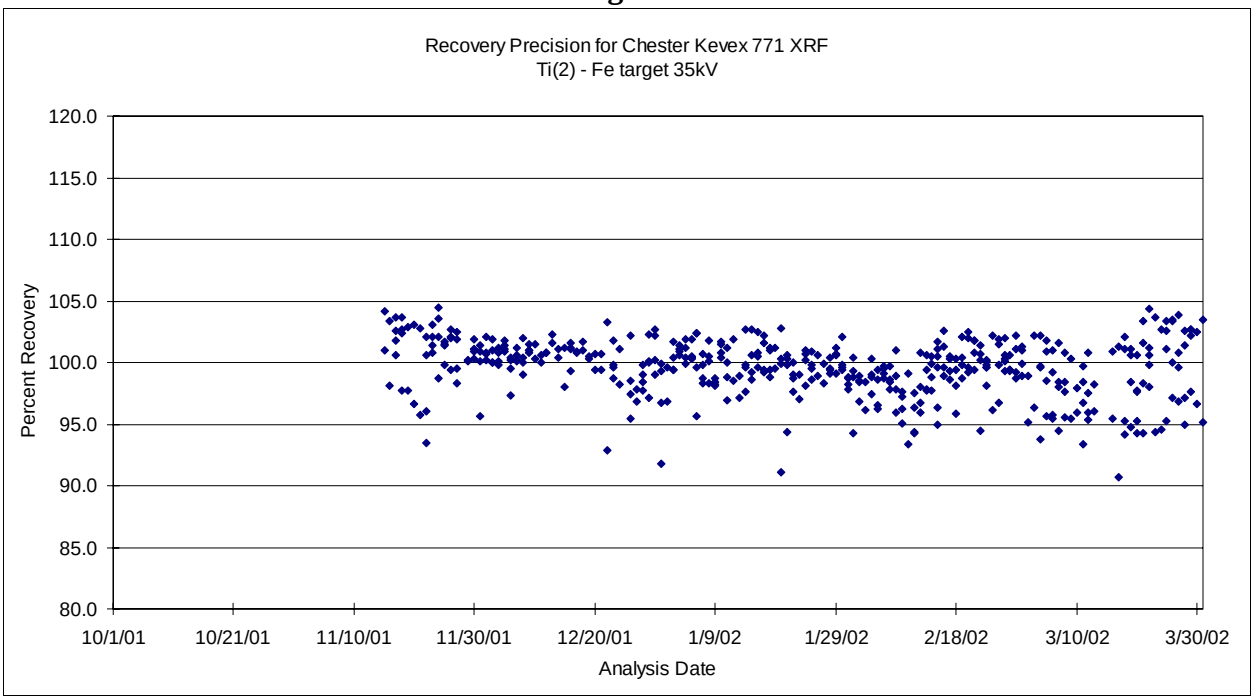


Figure 21



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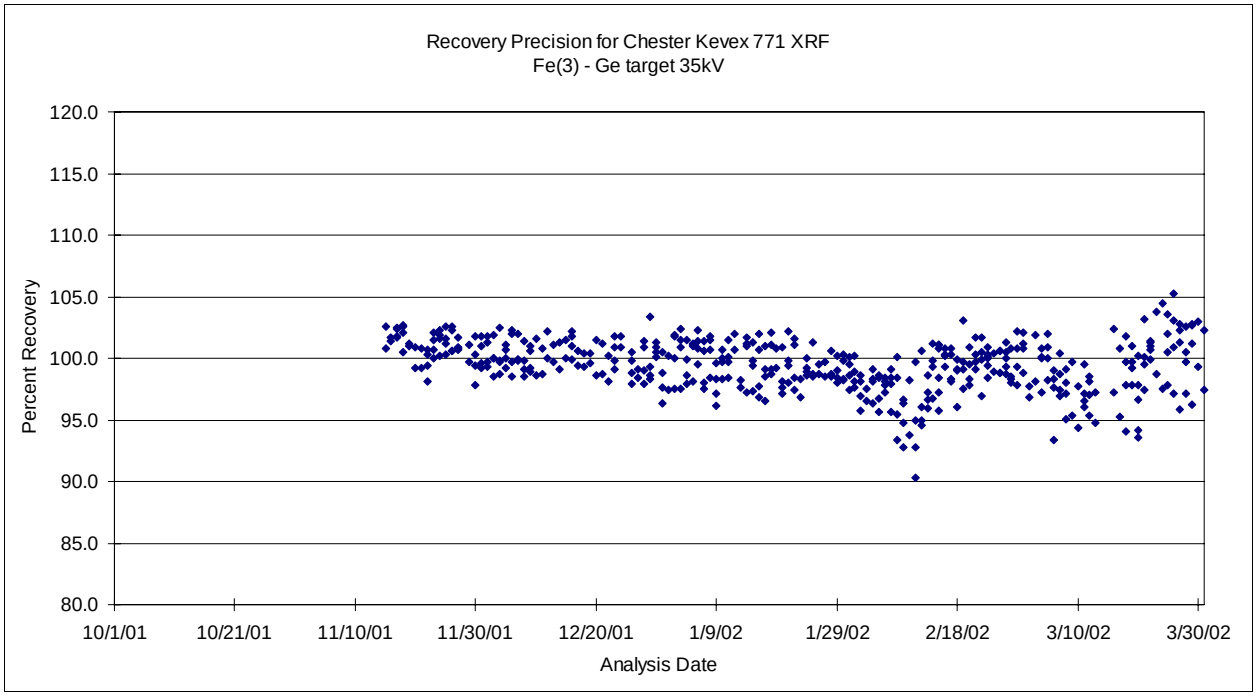


Figure 23

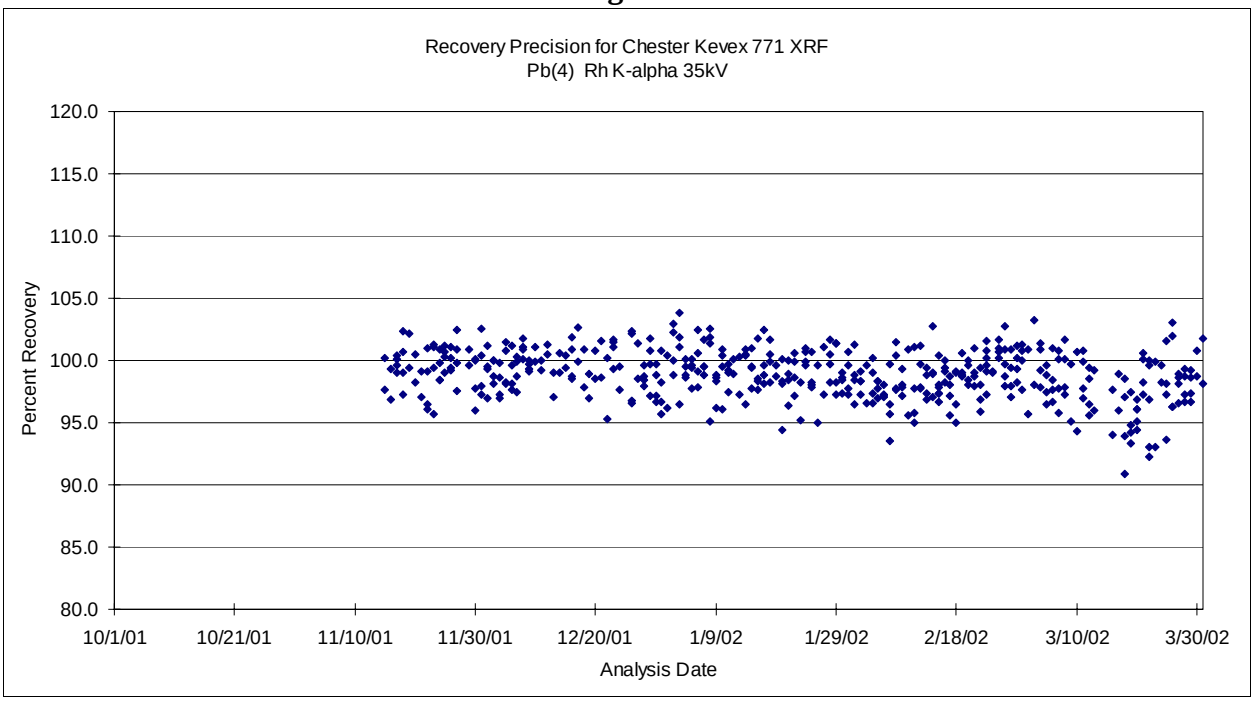


Figure 24

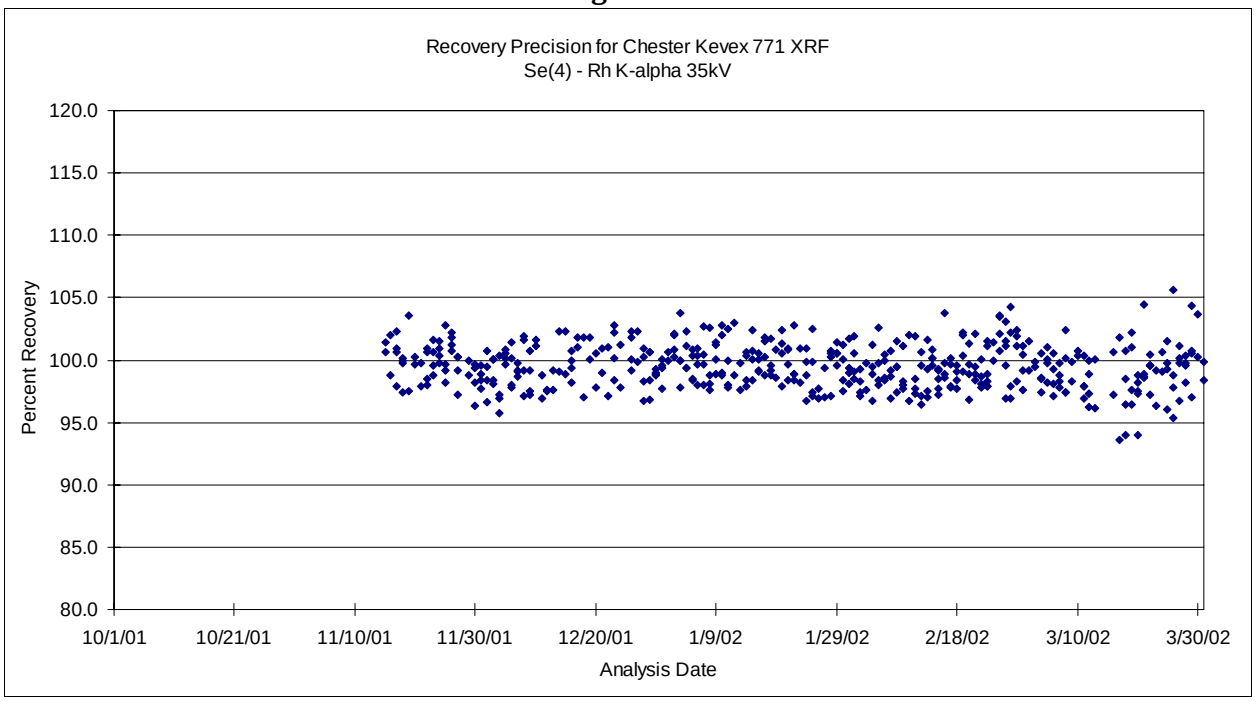
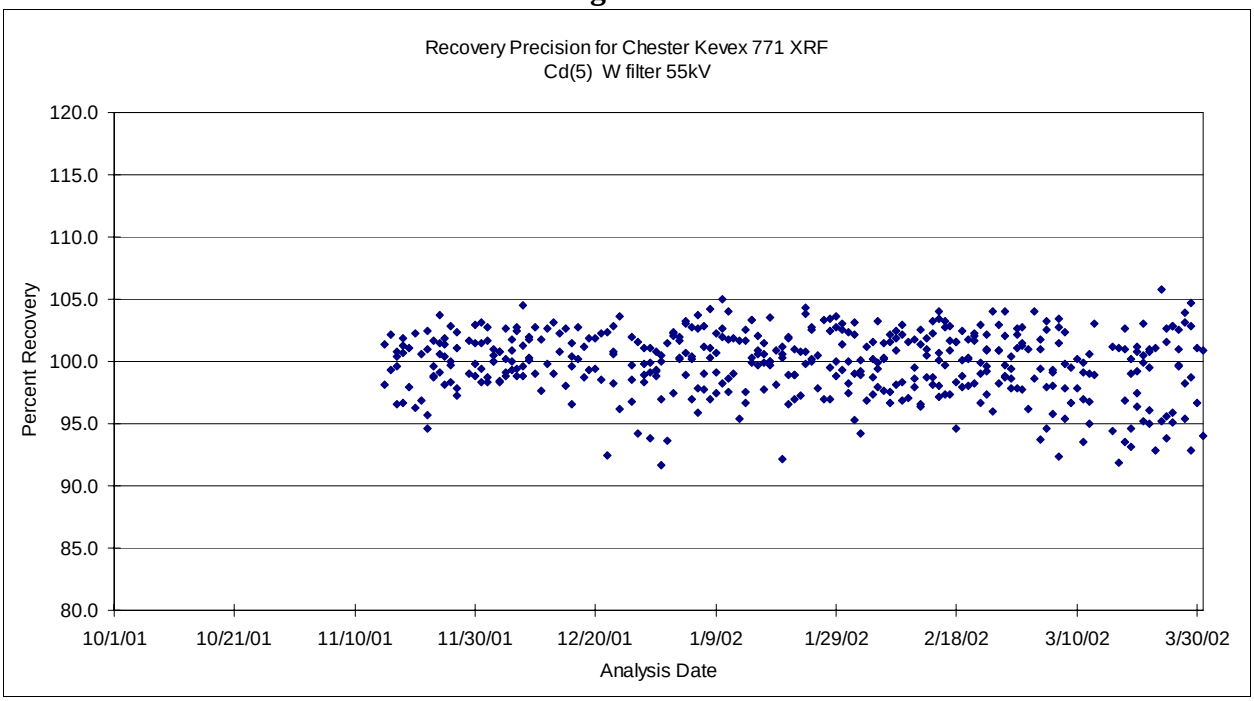


Figure 25



Recovery

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of a measured and expected values. **Figures 26 through 49** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 92.3 and 110.1 percent for the 770 and 92.0 and 112.9 percent for the 771, as shown in **Table 19**.

Table 19. Recovery Determined from Analysis of NIST Standard Reference Material Filters, Kevex 770 and 771.

Element	Kevex 770	Kevex 771
	Range % Recovery	Range % Recovery
Al	94.9 - 108.9	94.1 - 105.1
Si*	98.2 - 109.4	95.1 - 105.1
Si**	92.9 - 100.5	92.0 - 101.0
S	92.3 - 104.4	96.9 - 109.5
K	93.0 - 100.8	93.1 - 102.0
Ca	104.7 - 110.1	103.0 - 112.9
Ti	92.7 - 100.3	98.0 - 105.6
V	94.5 - 105.4	101.7 - 108.9
Mn	100.5 - 105.2	97.8 - 107.1
Fe	98.4 - 102.0	97.0 - 104.7
Cu	97.6 - 102.3	97.5 - 104.8
Zn	95.2 - 100.6	97.0 - 104.2
Pb	95.6 - 109.3	94.6 - 105.7

*SRM 1832. **SRM 1833.

Figure 26

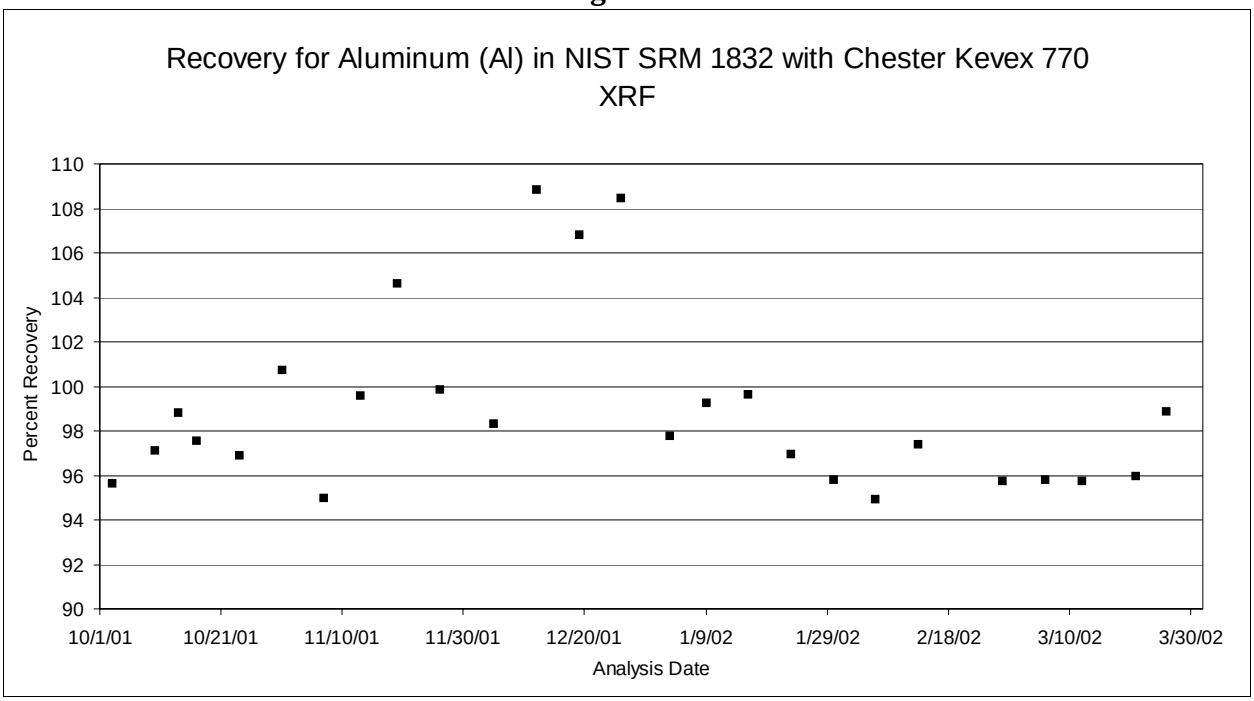


Figure 27

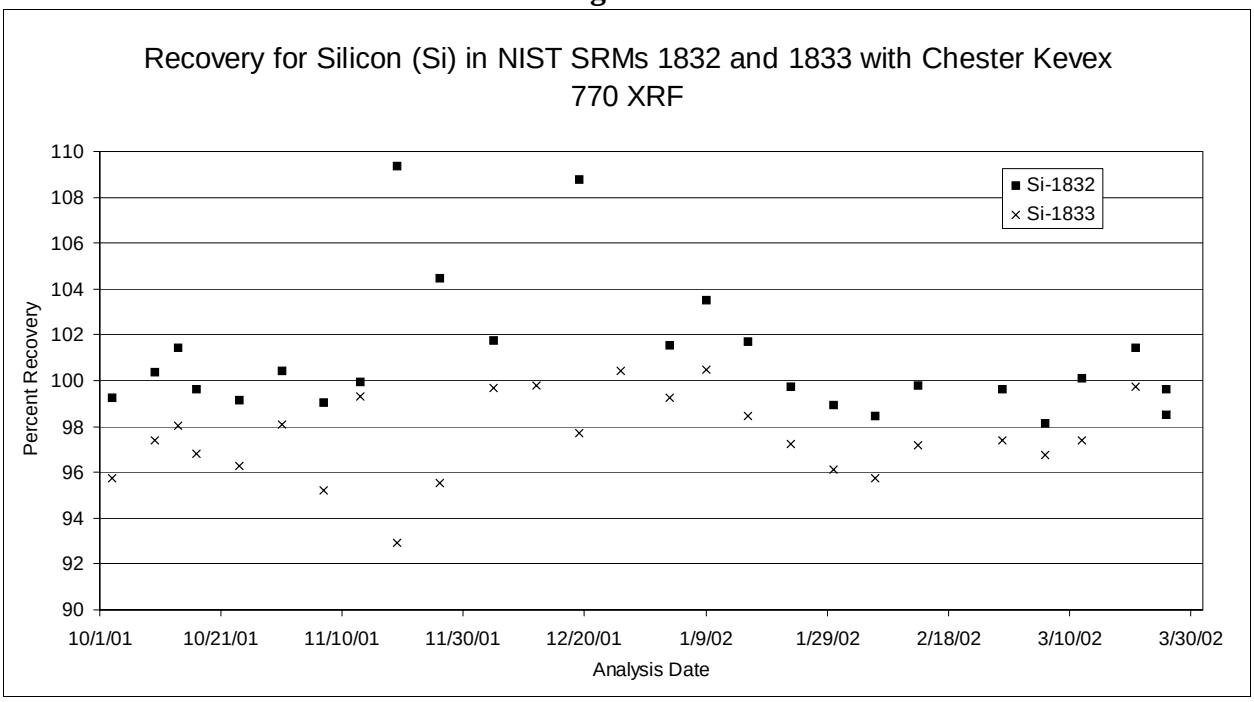


Figure 28

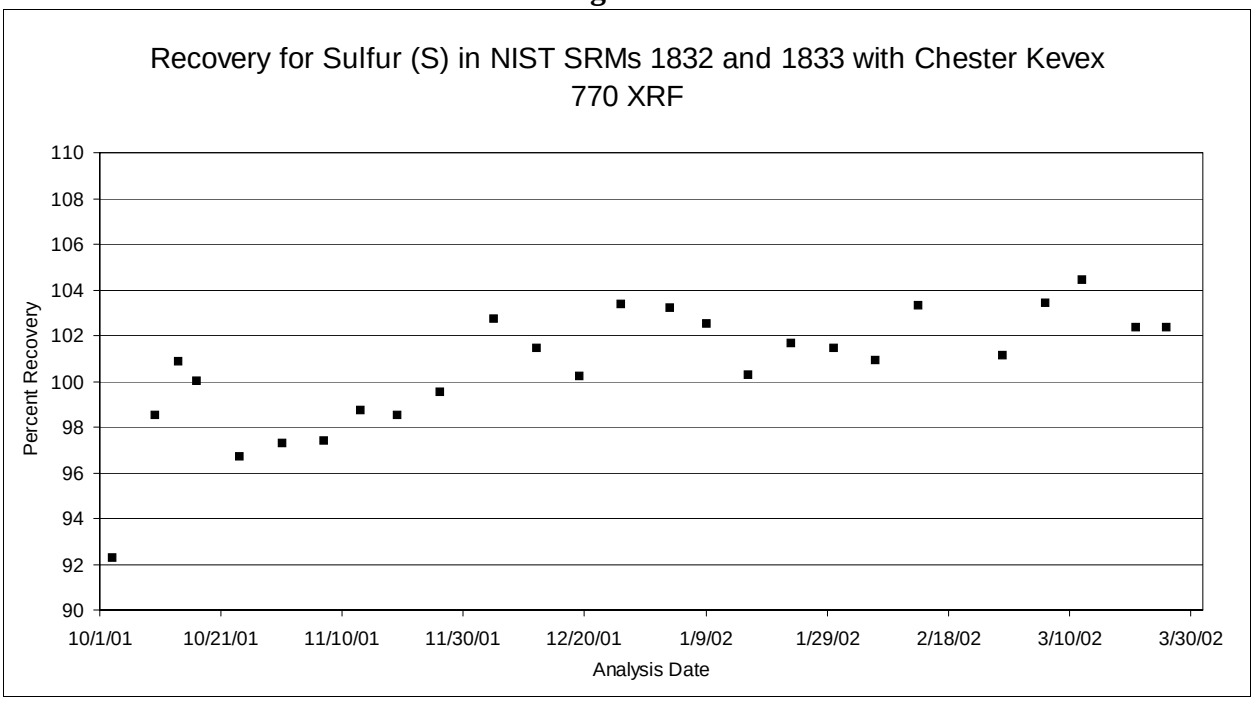
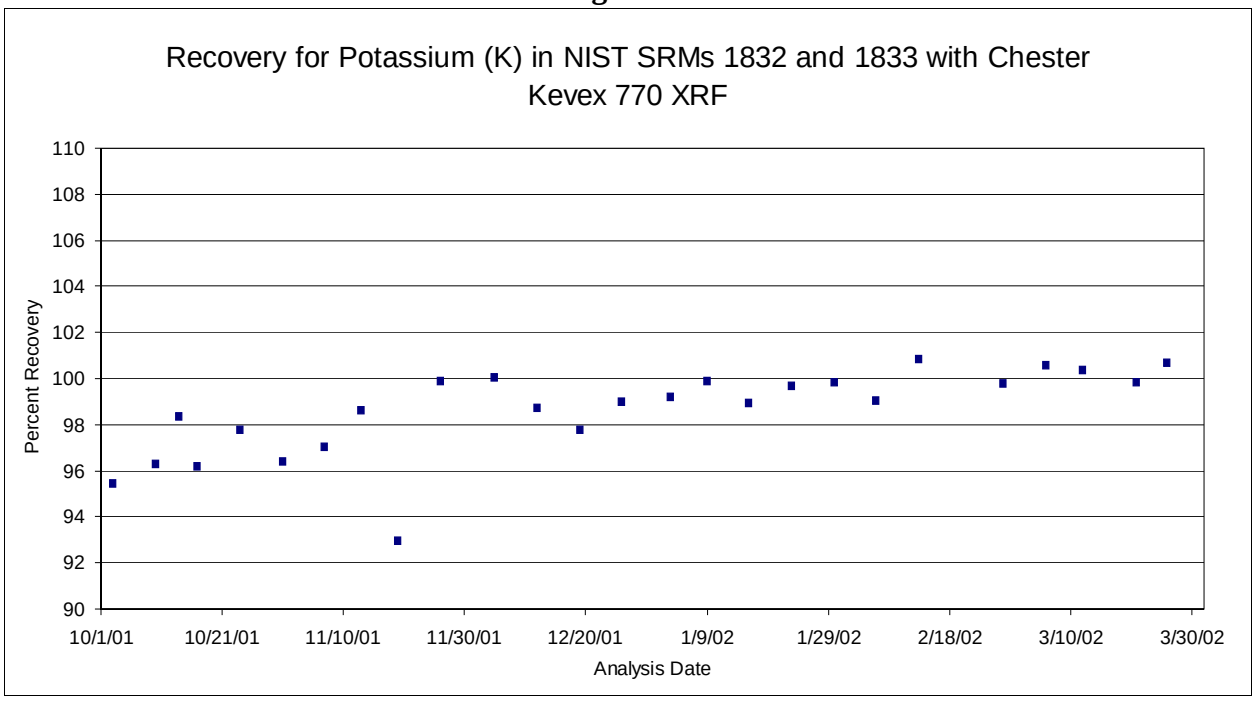


Figure 29



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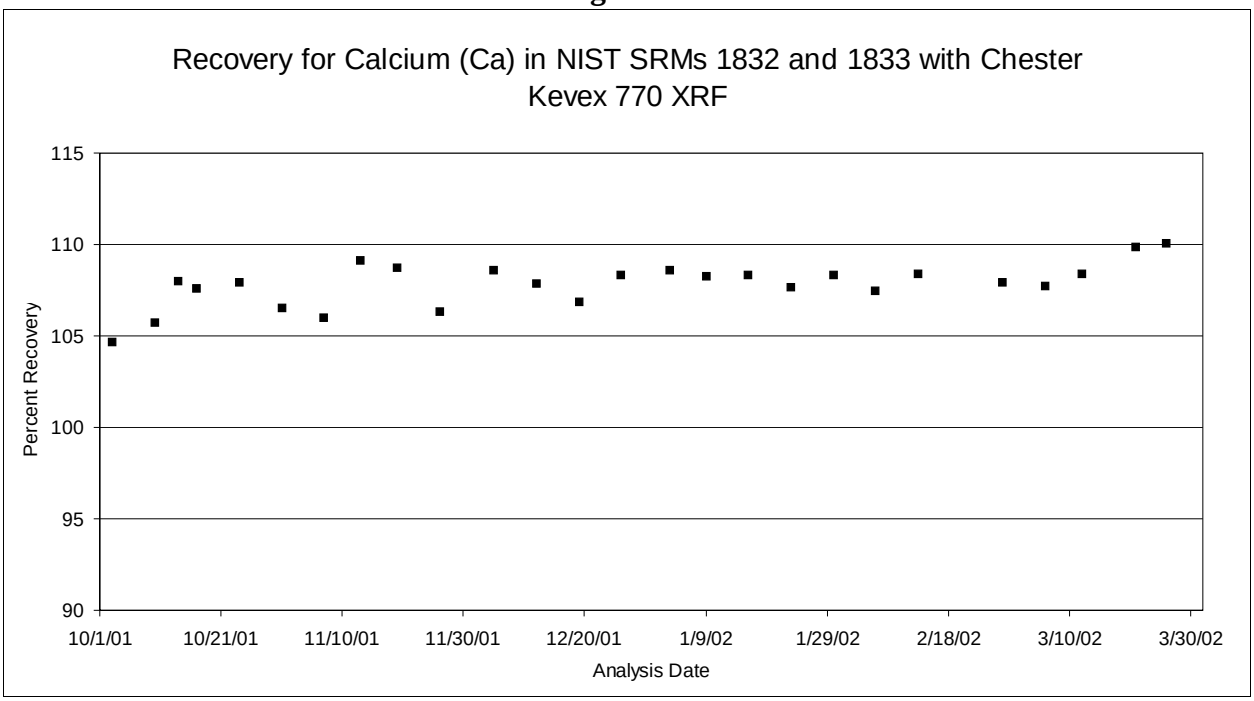


Figure 31

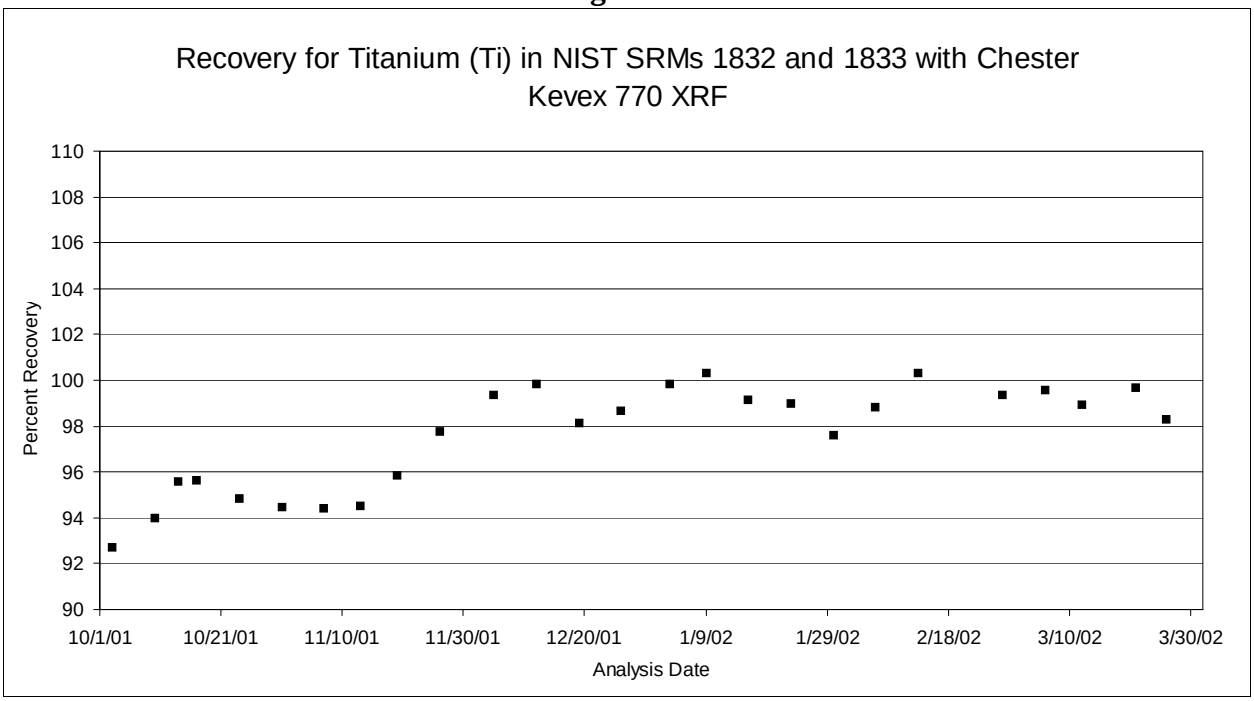


Figure 32

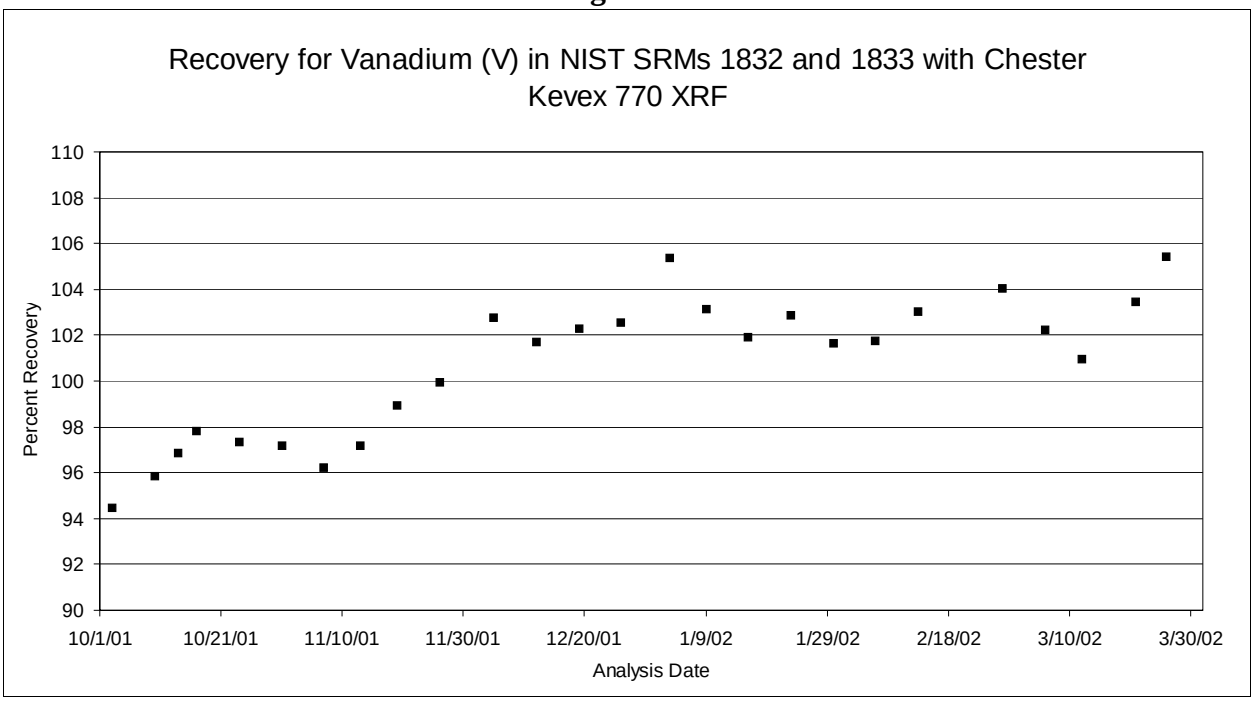


Figure 33

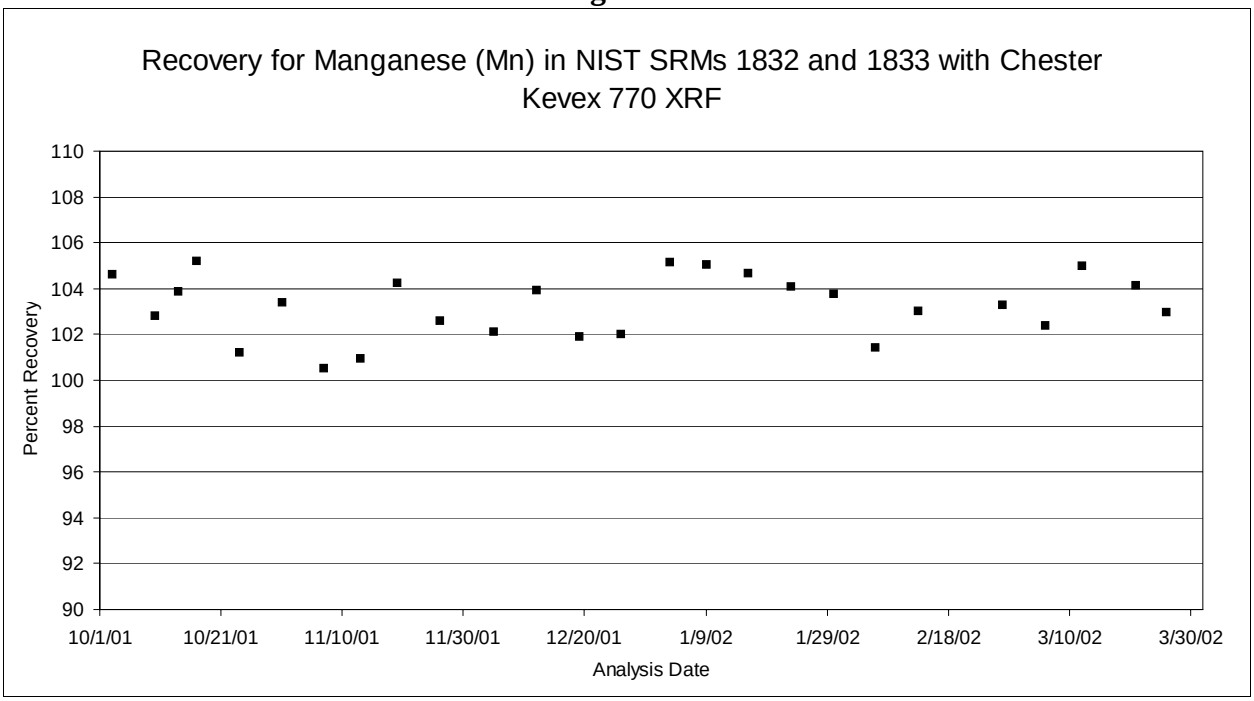


Figure 34

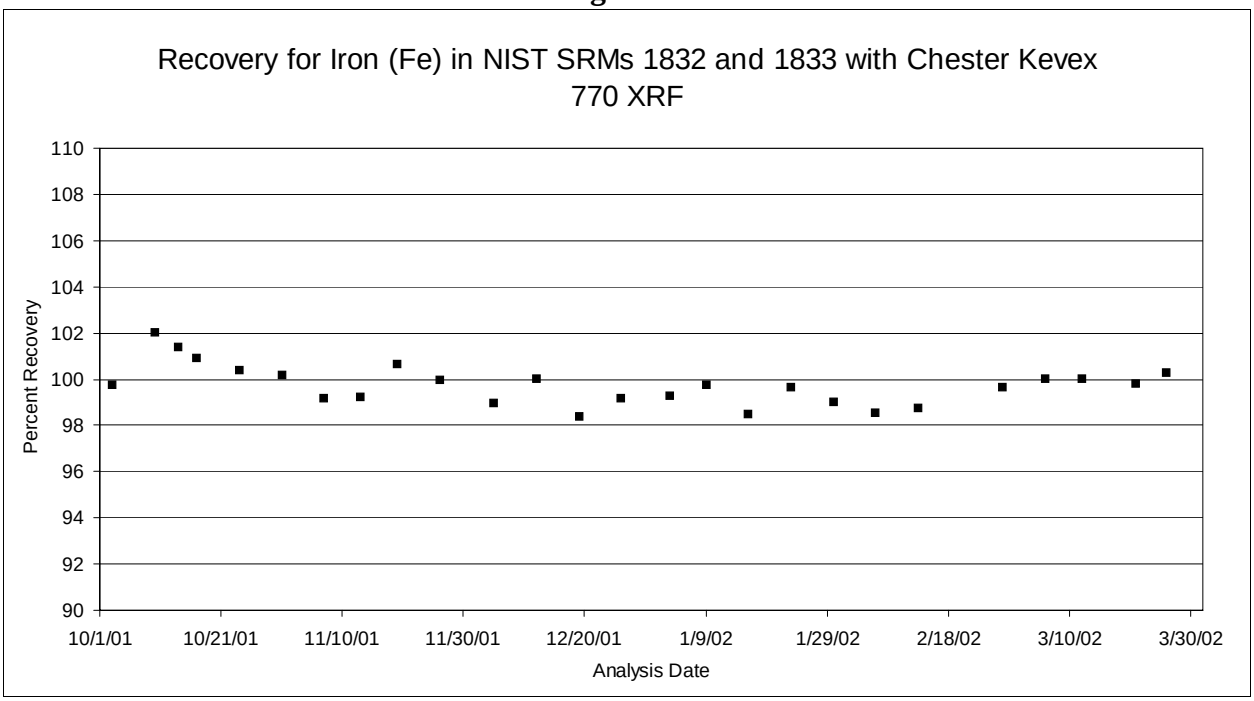


Figure 35

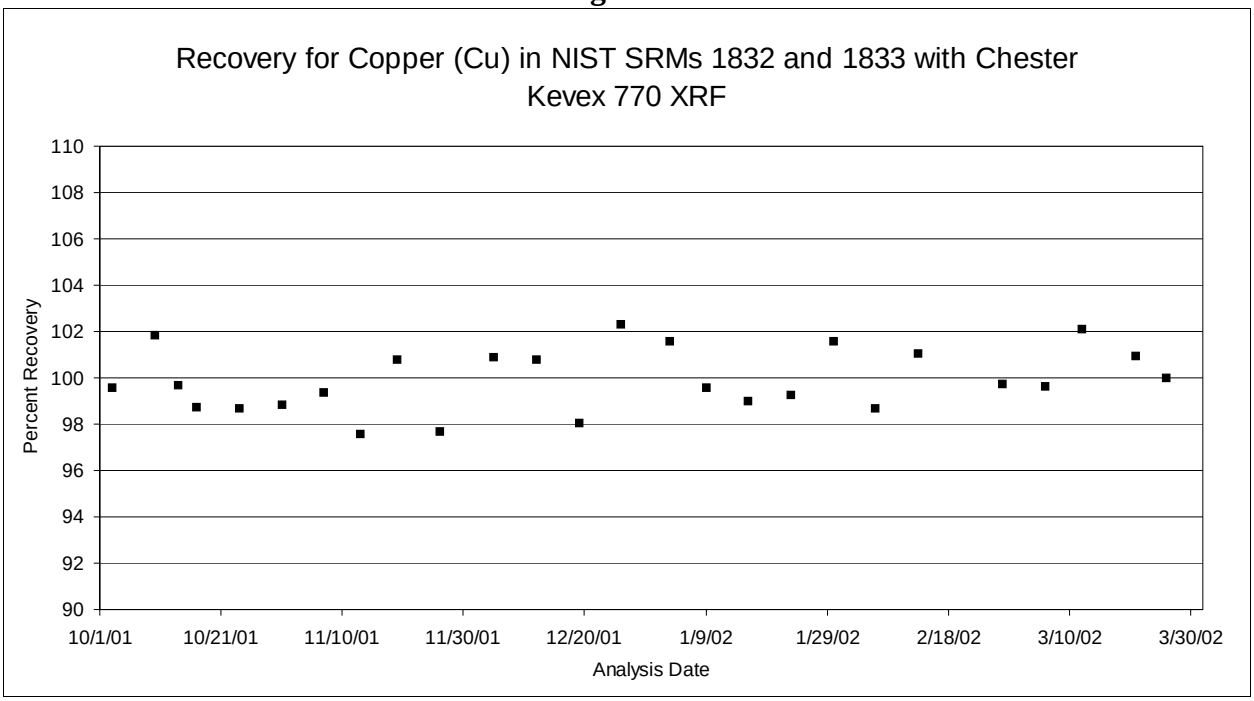
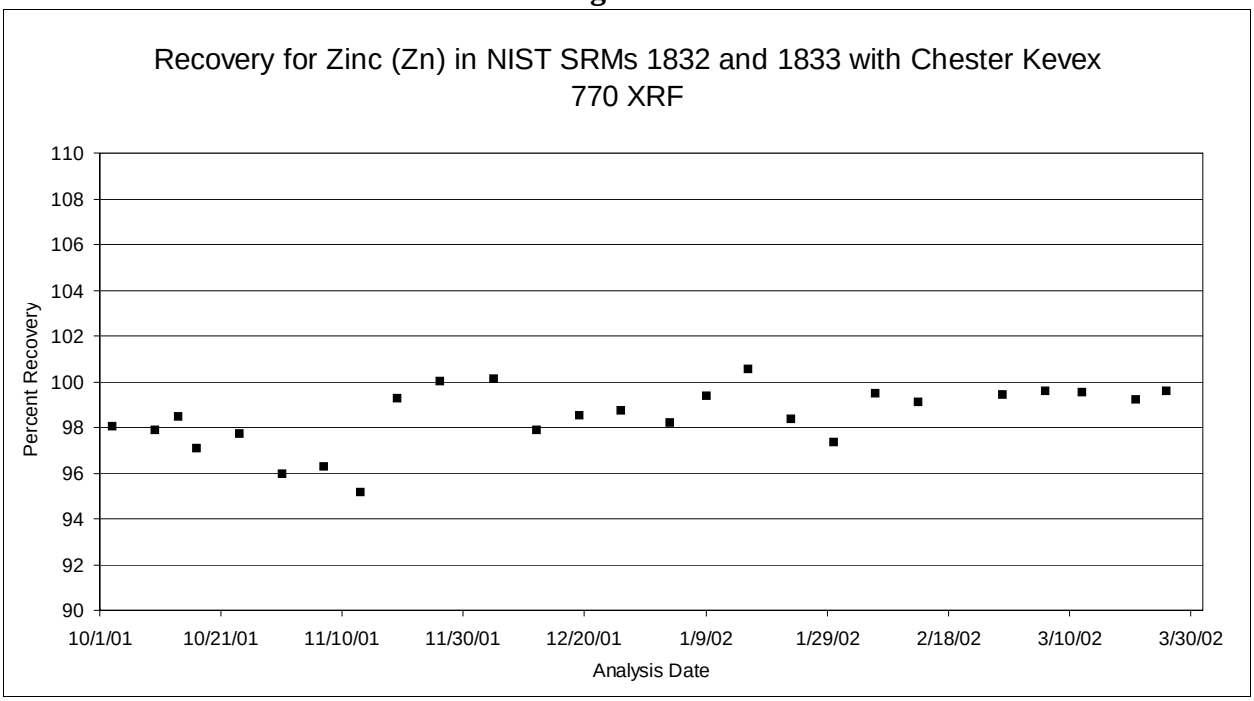


Figure 36



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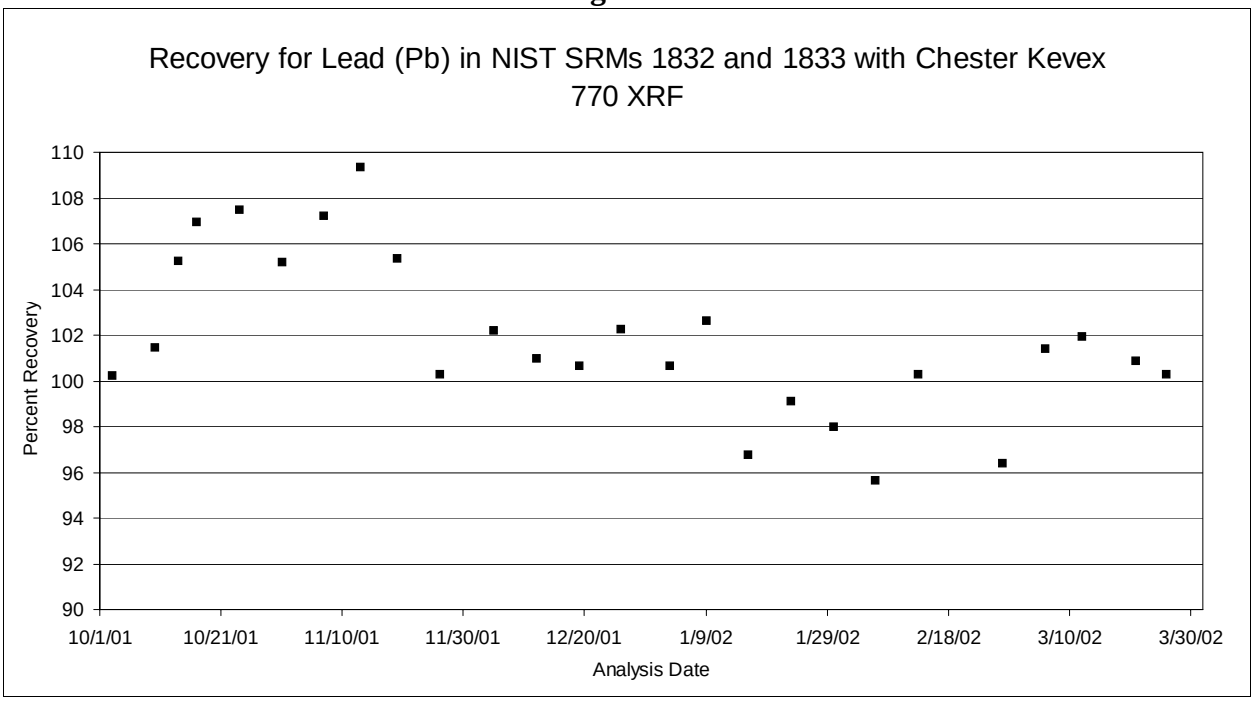


Figure 38

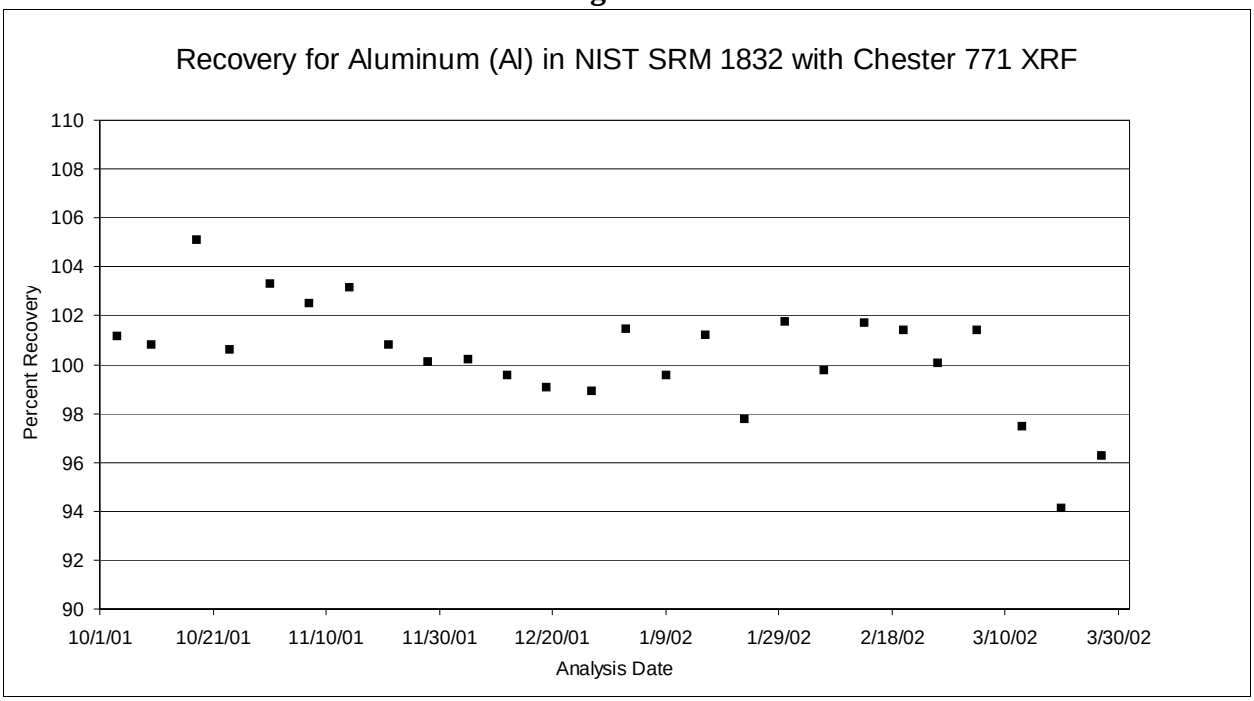


Figure 39

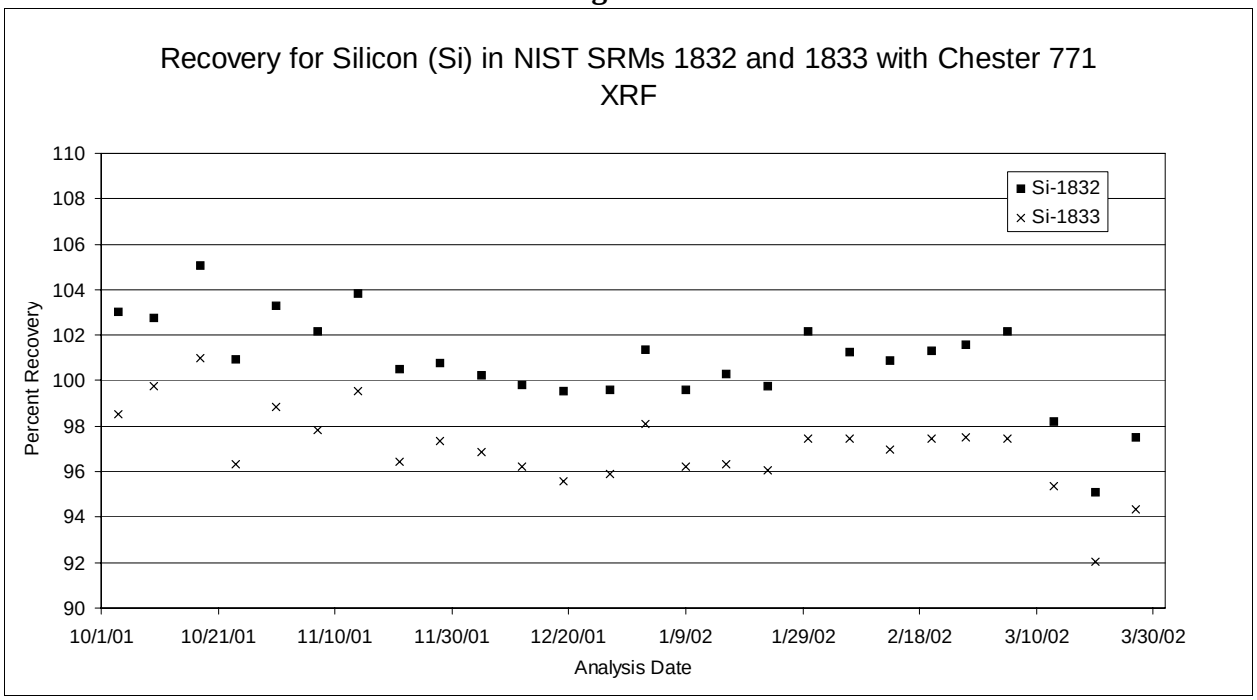


Figure 40

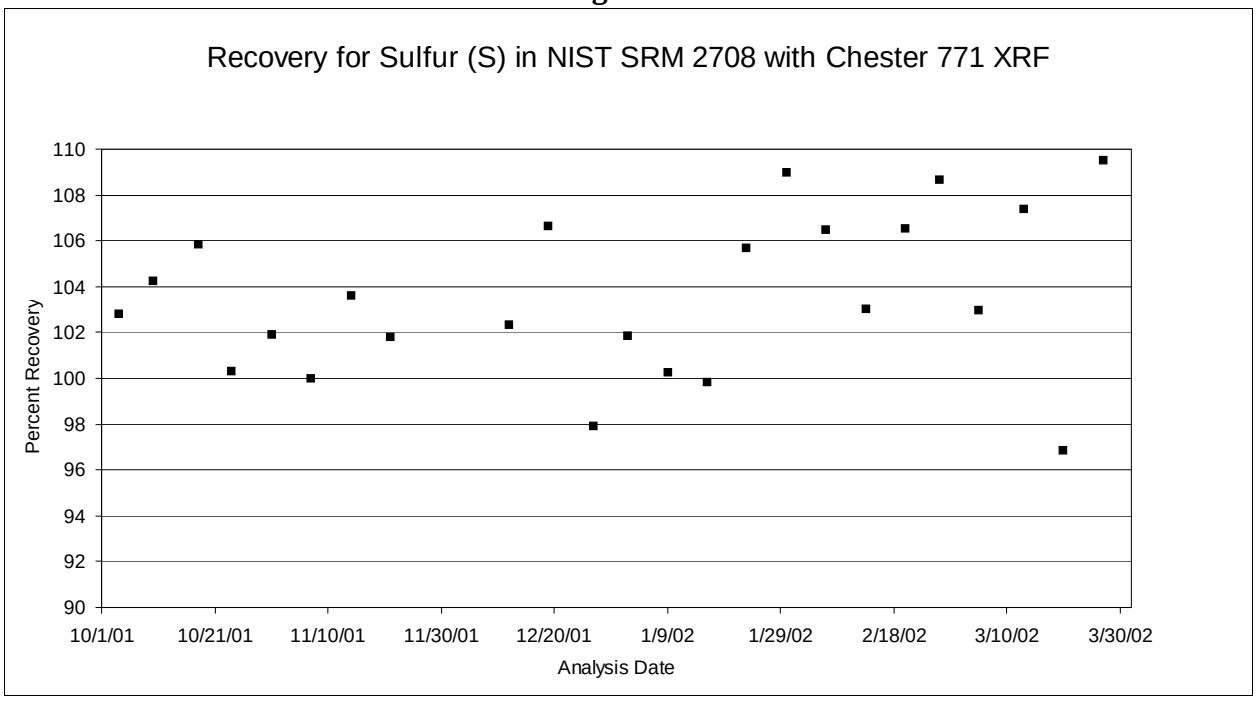


Figure 41

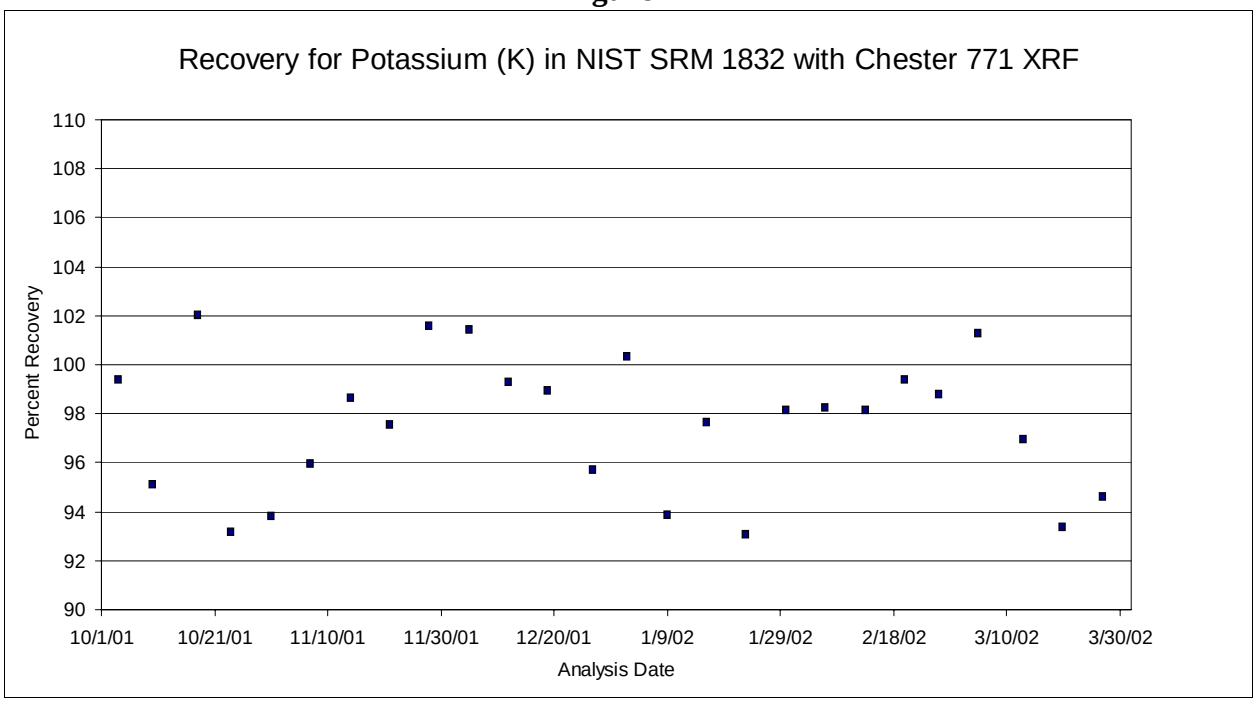


Figure 42

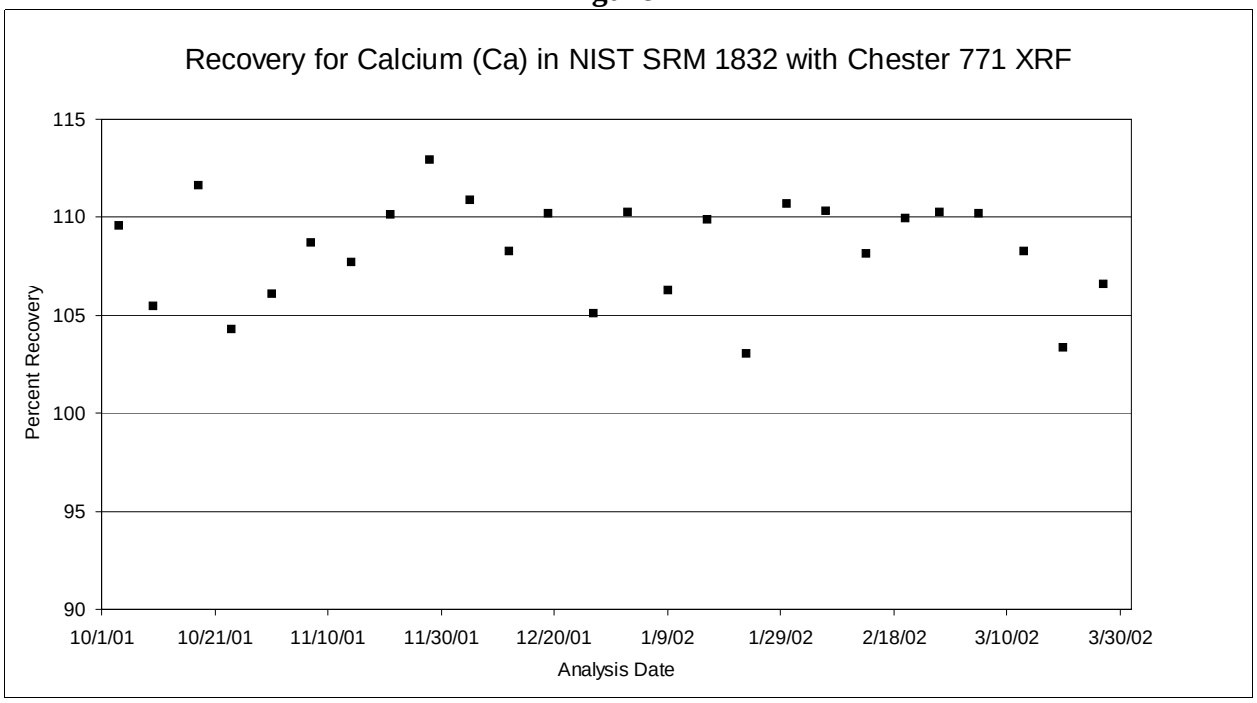


Figure 43

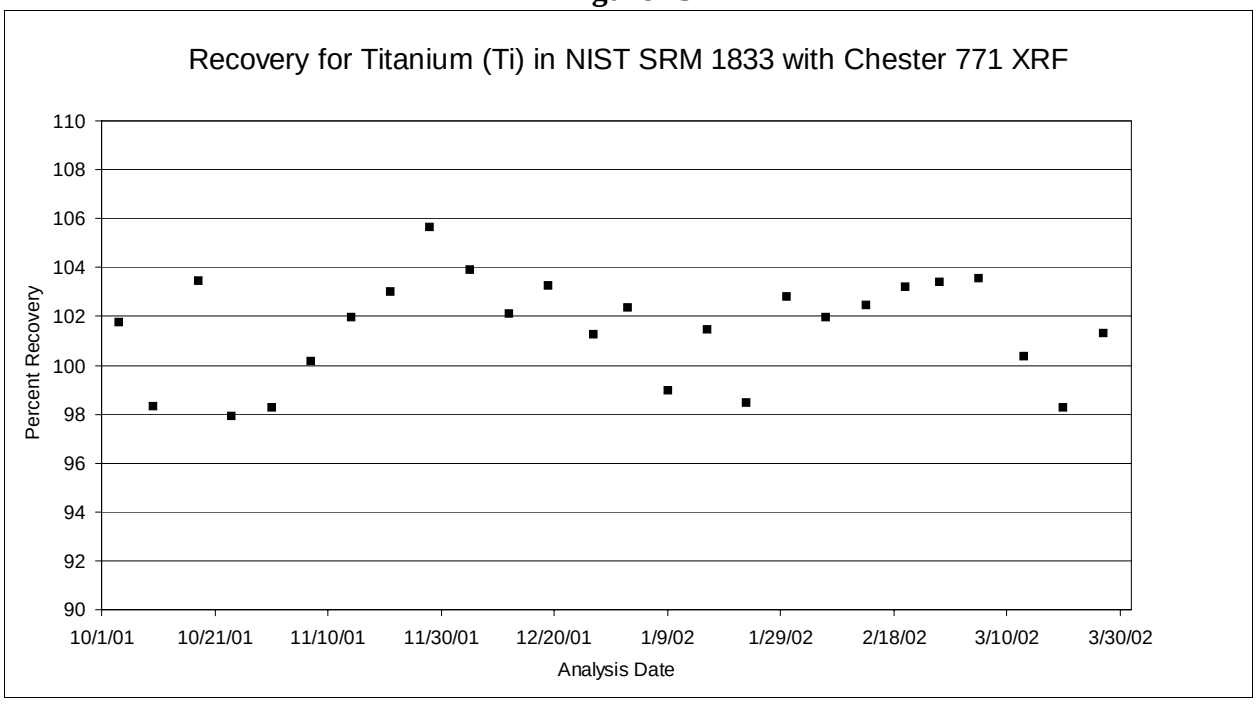


Figure 44

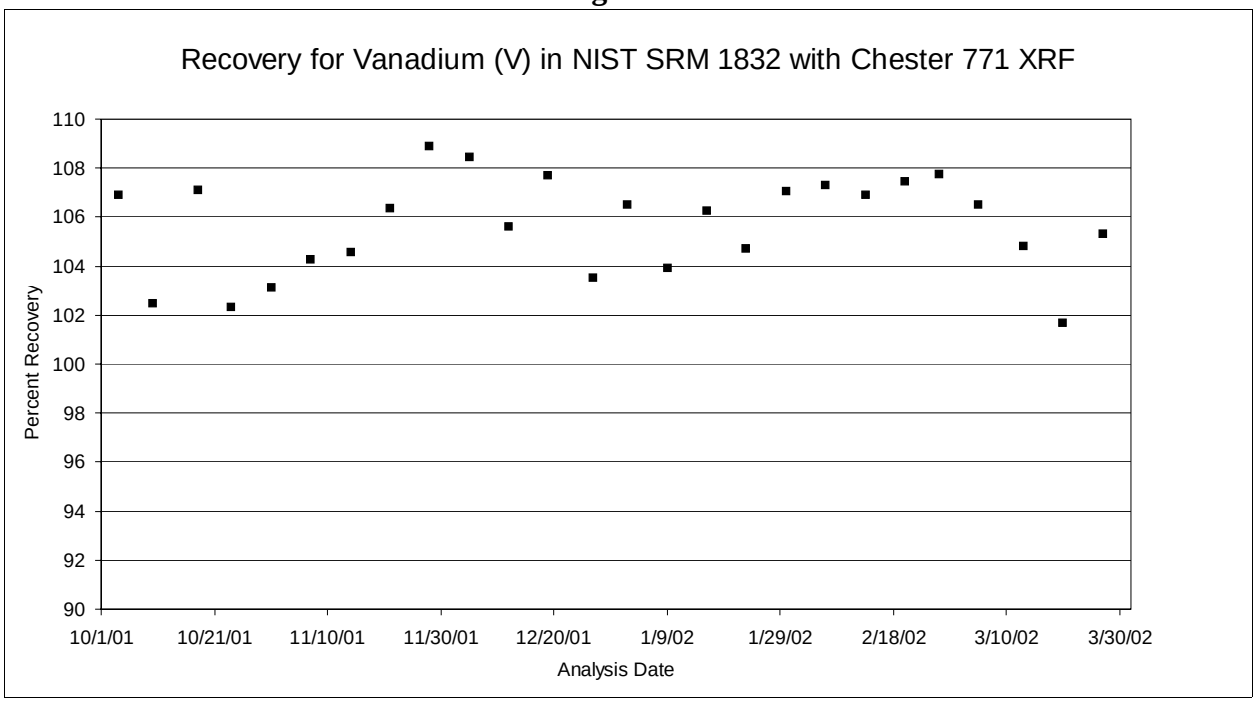


Figure 45

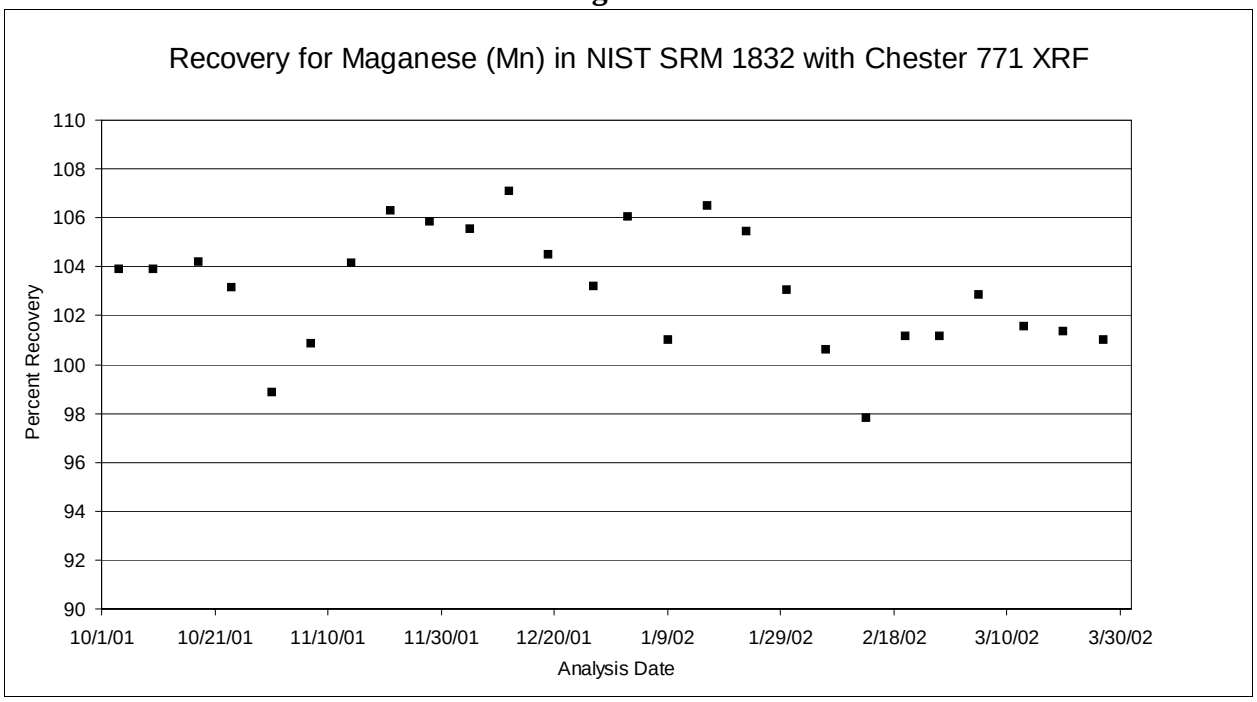


Figure 46

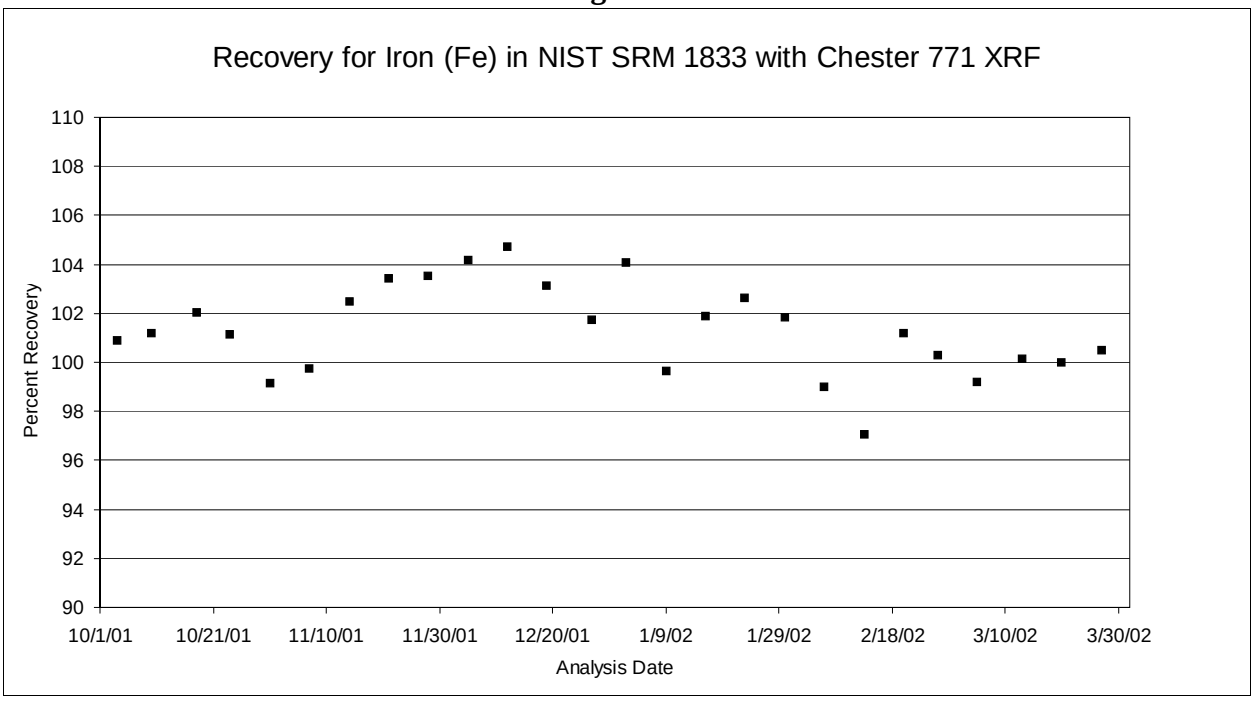


Figure 47

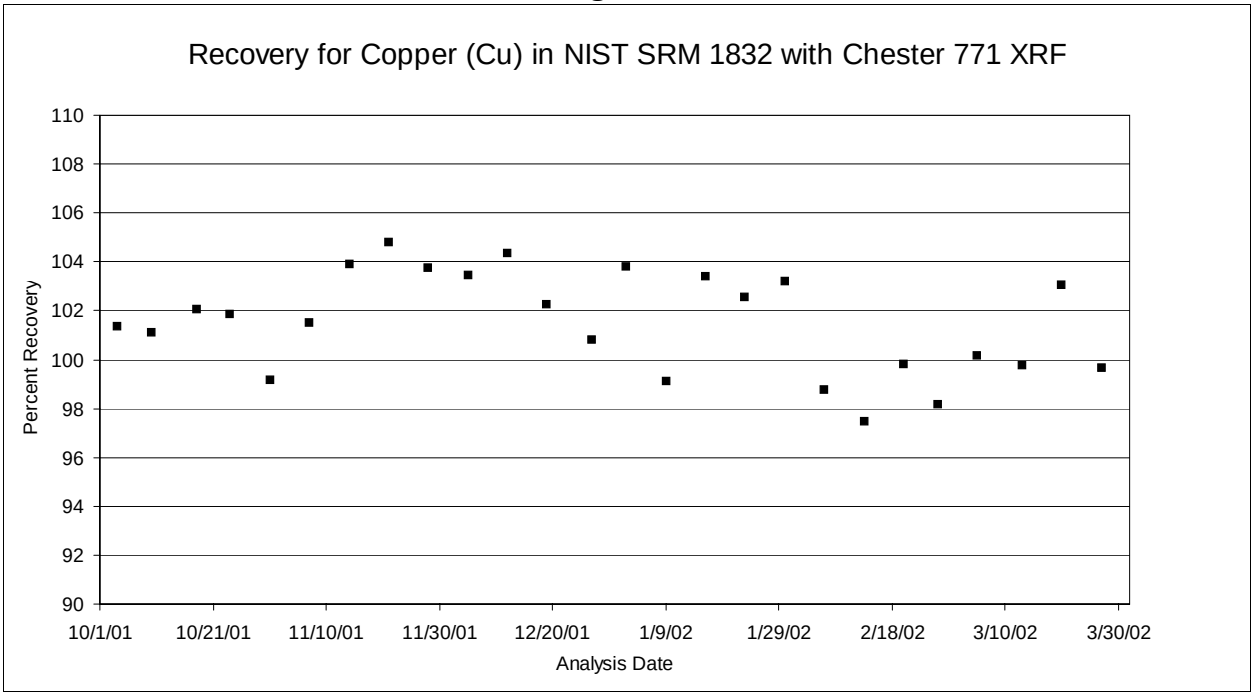


Figure 48

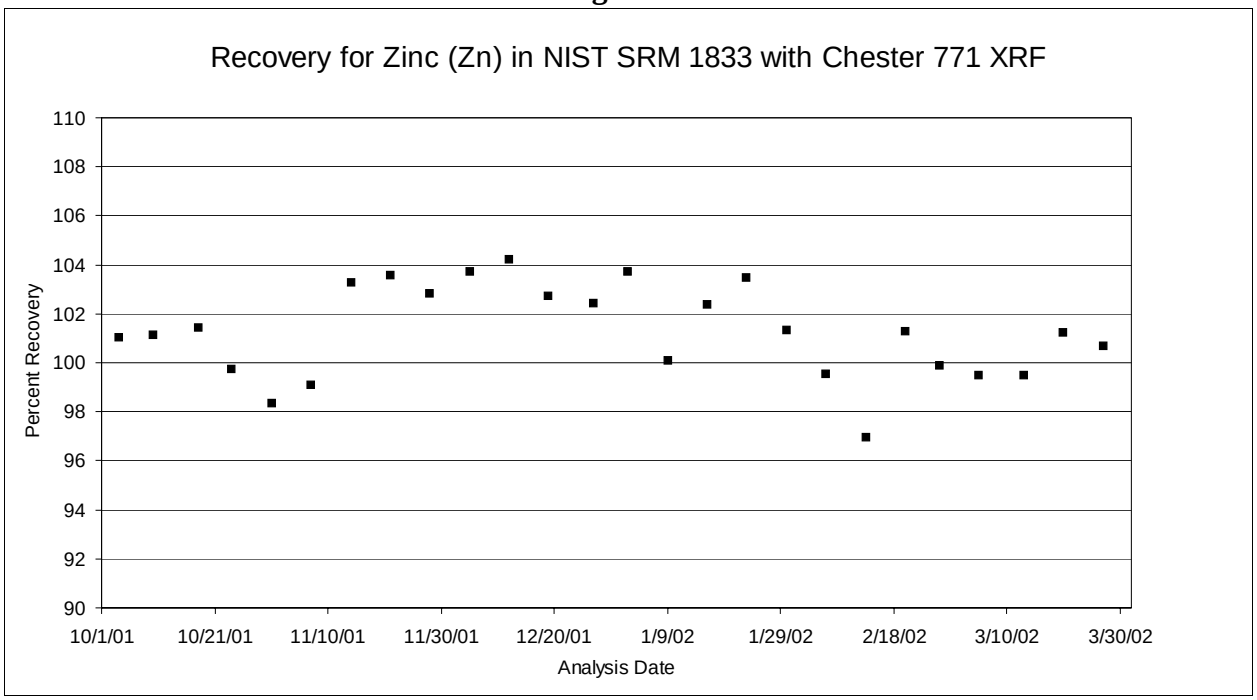
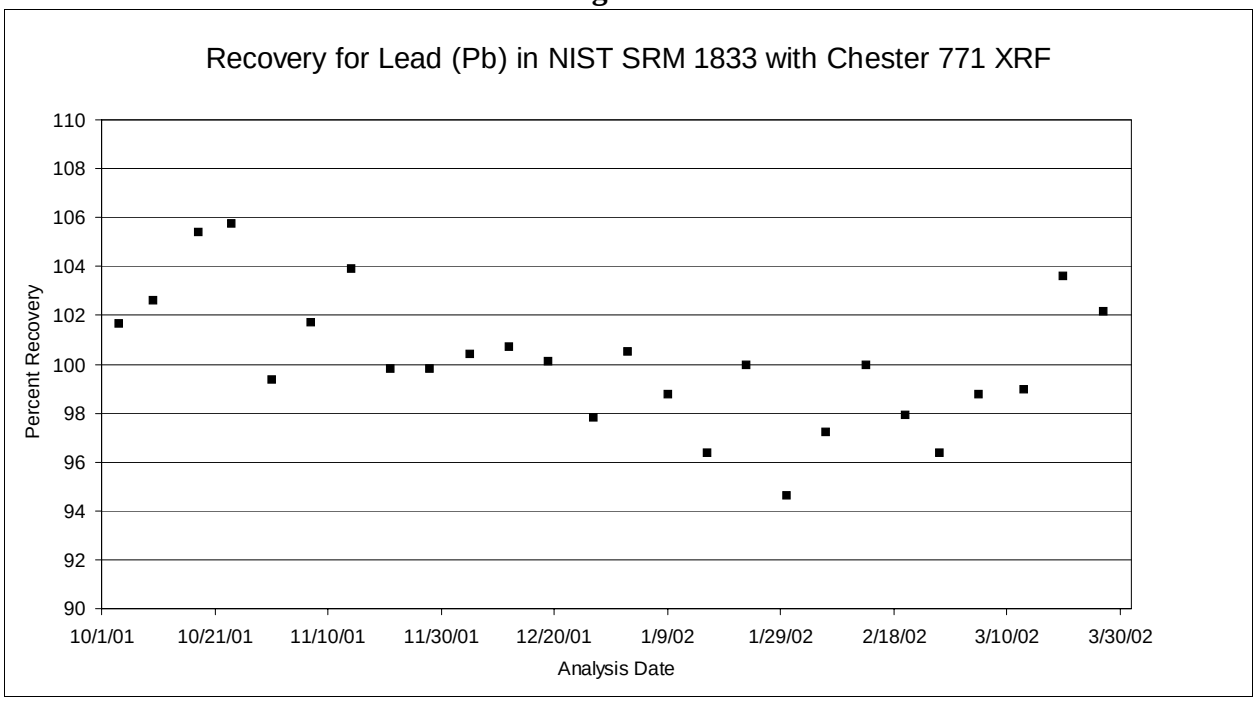


Figure 49



Replicates

Ten percent of the filters are reanalyzed and the results for select elements are compared. **Figures 50 through 61** compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.99 and correlation coefficients are all greater than 0.998 for the 770, indicating acceptable replication. Slopes for the 771 tended to be higher than for the 770. These values ranged from 0.980 to 1.11. Despite these higher values, the slope is still statistically indistinguishable from 1. The correlation coefficients are all greater than 0.996, indicating acceptable replication.

2.4.2.2 Data Validity Discussion

The data presented in Section 2.4.2 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters. These were minor, and not considered to have a significant impact on the analysis results.

2.4.2.3 Corrective Actions

No changes were made in the analytical procedures used by the Chester LabNet XRF laboratory.

2.4.3 Cooper Environmental Services (CES)

CES began analyzing STN samples on November 10, 2001.

2.4.3.1 Statistical Summary of QC Results

Precision

The precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for a select element are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of reproducibility or precision. The data used to monitor precision for individual elements are presented in **Figures 62 through 67**. **Table 20** shows the results of daily precision checks.

Recovery

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of a measured and expected values. **Figures 68 through 80** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 91.7 and 109.4 percent as shown in **Table 21**.

Figure 50

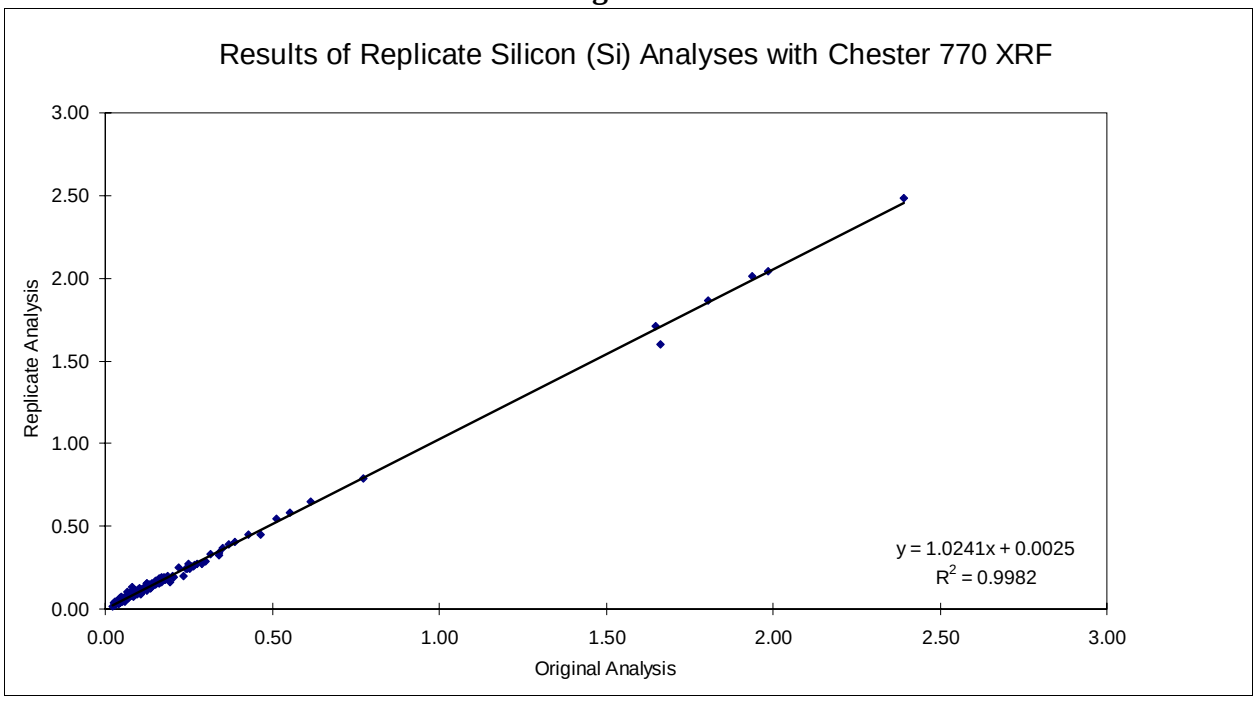


Figure 51

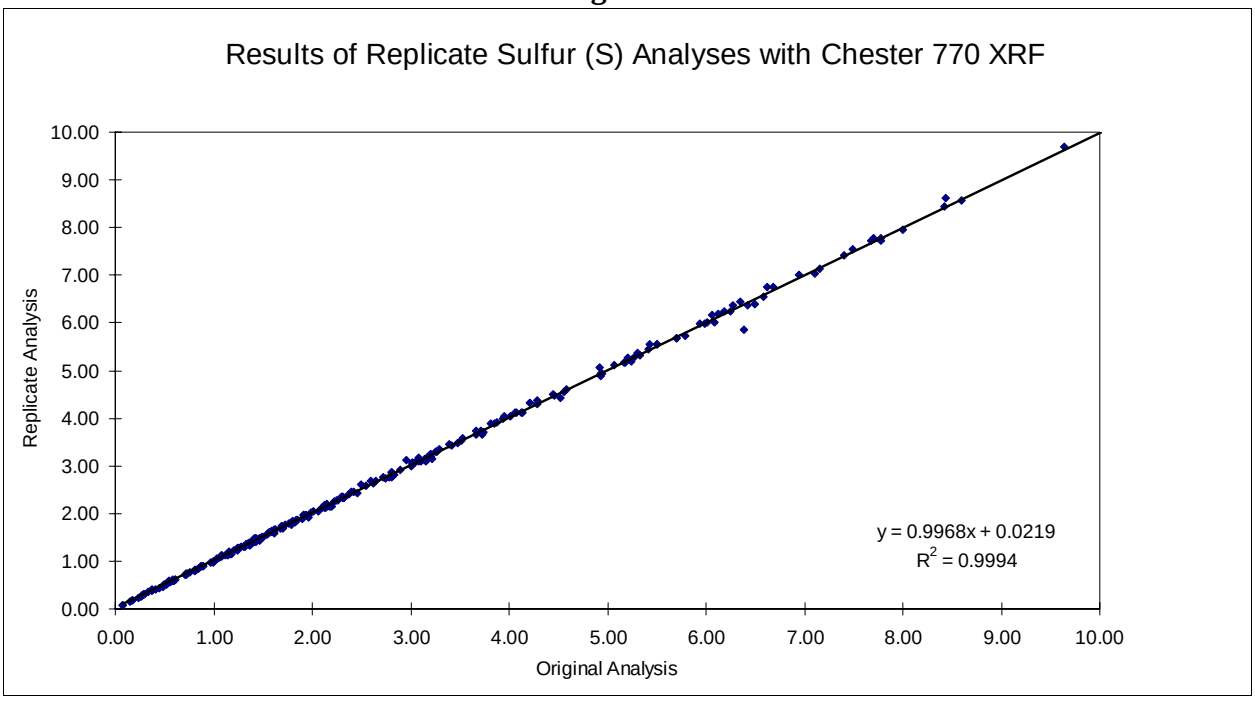


Figure 52

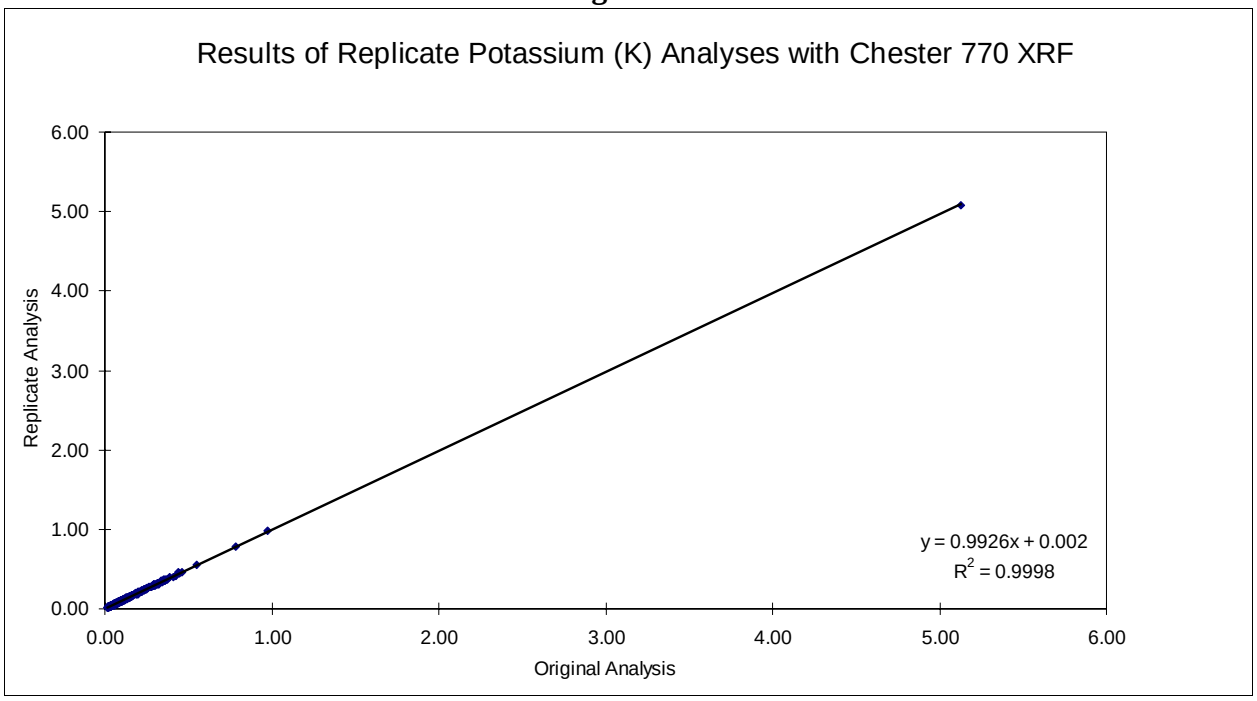


Figure 53

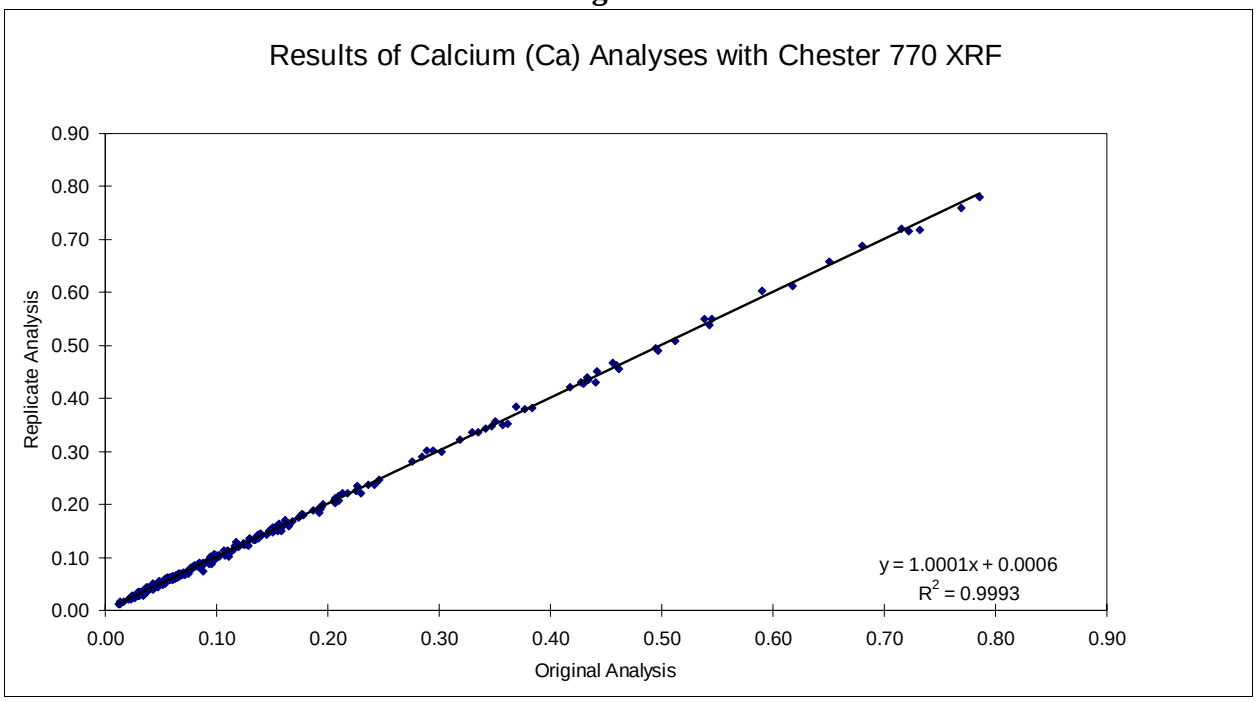


Figure 54

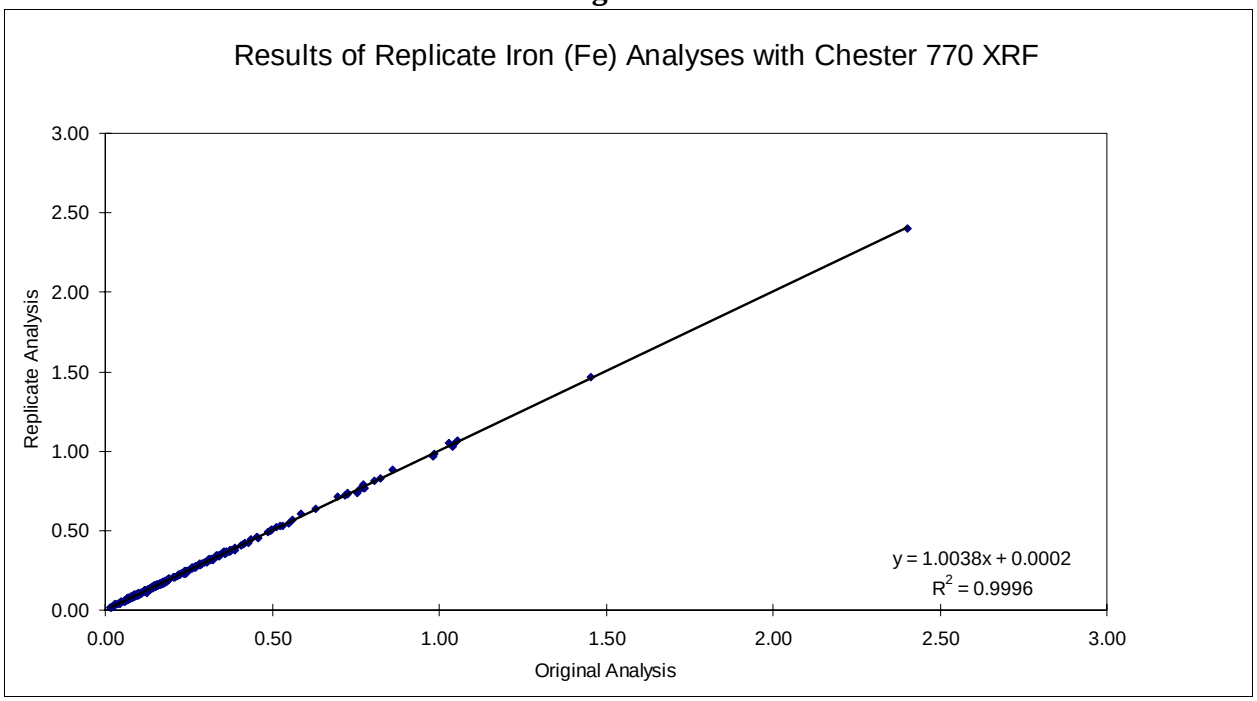


Figure 55

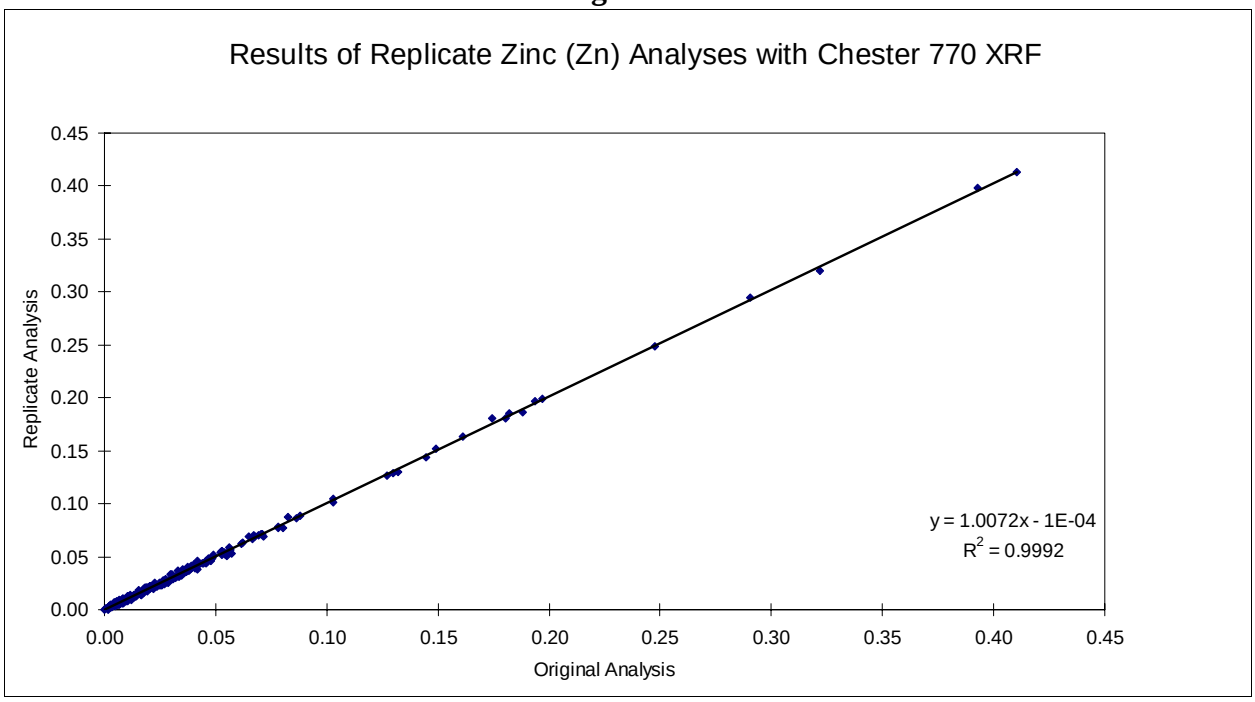


Figure 56

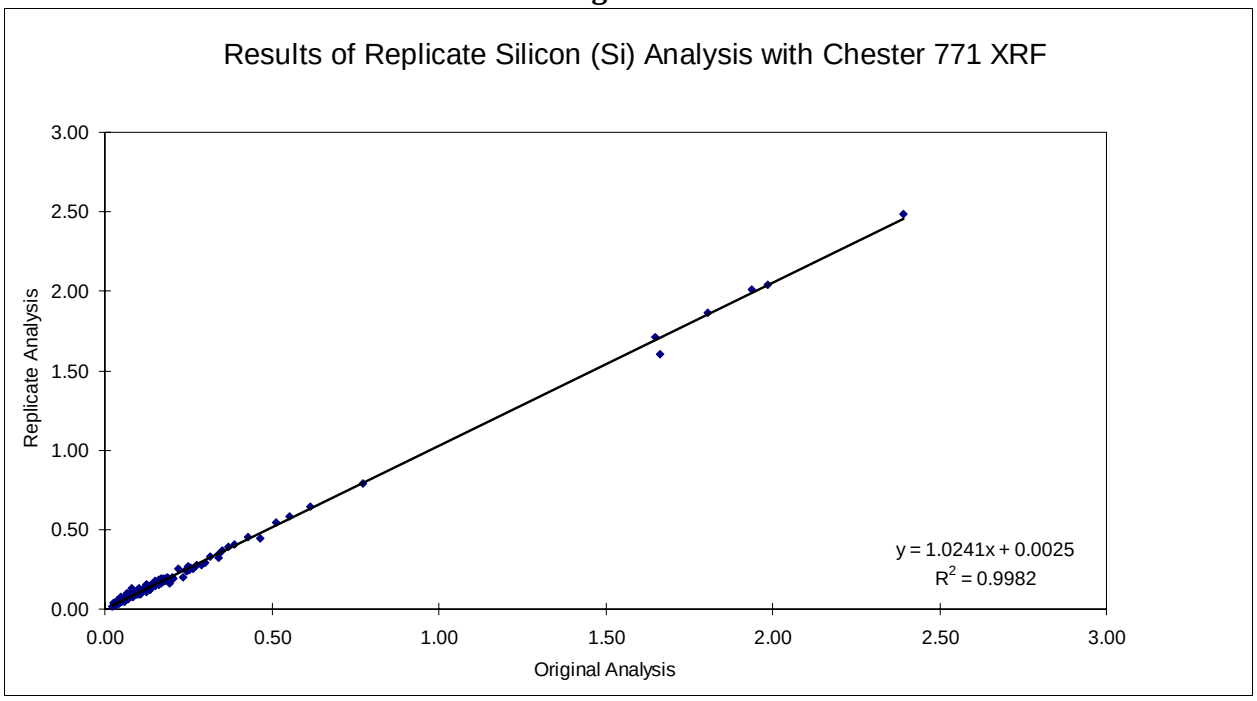


Figure 57

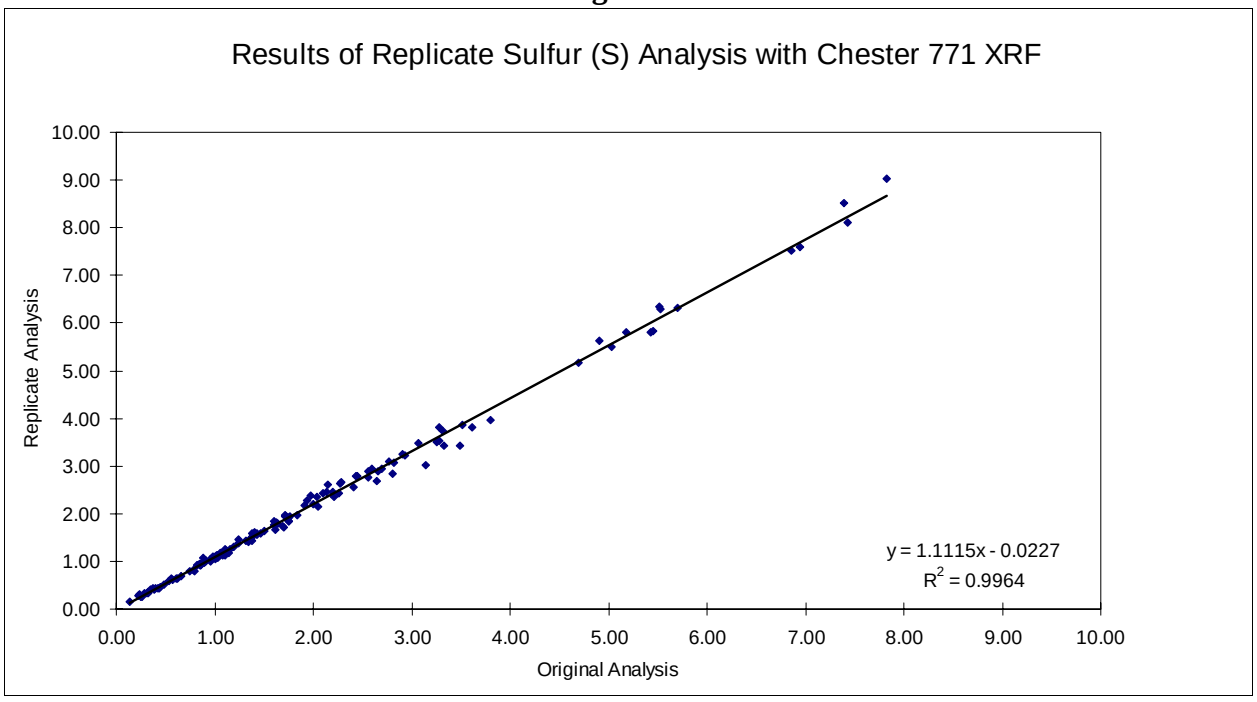


Figure 58

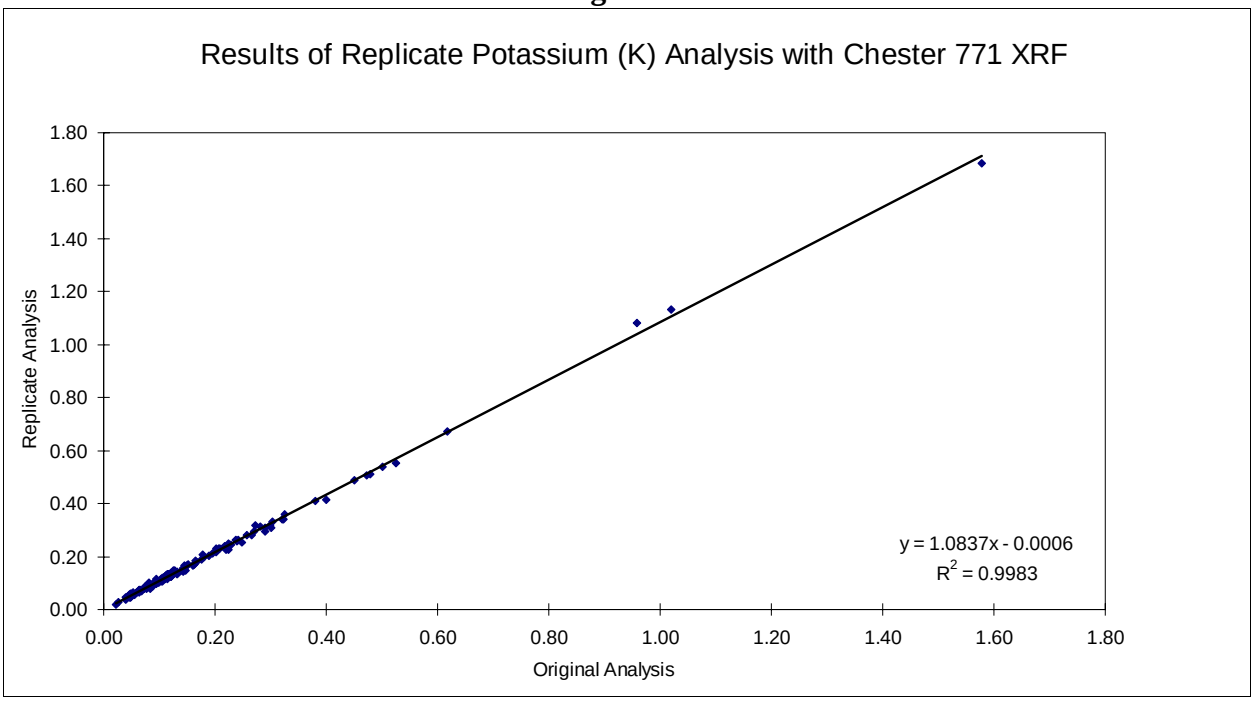


Figure 59

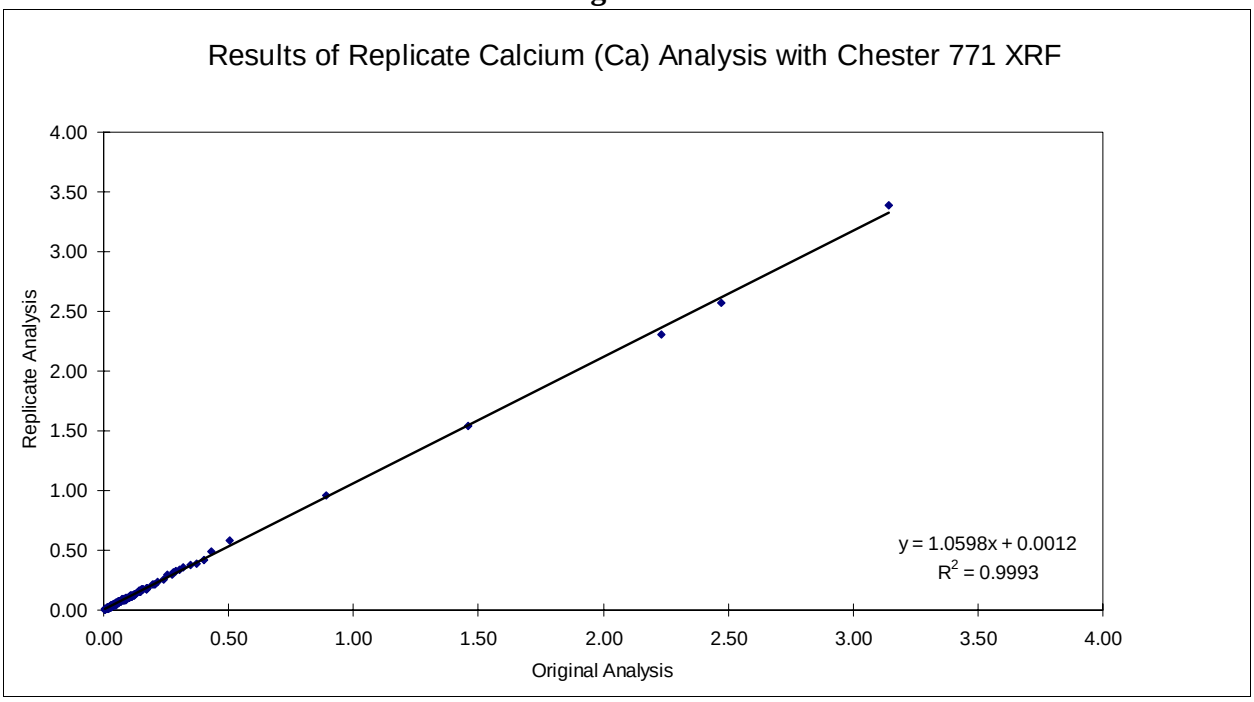


Figure 60

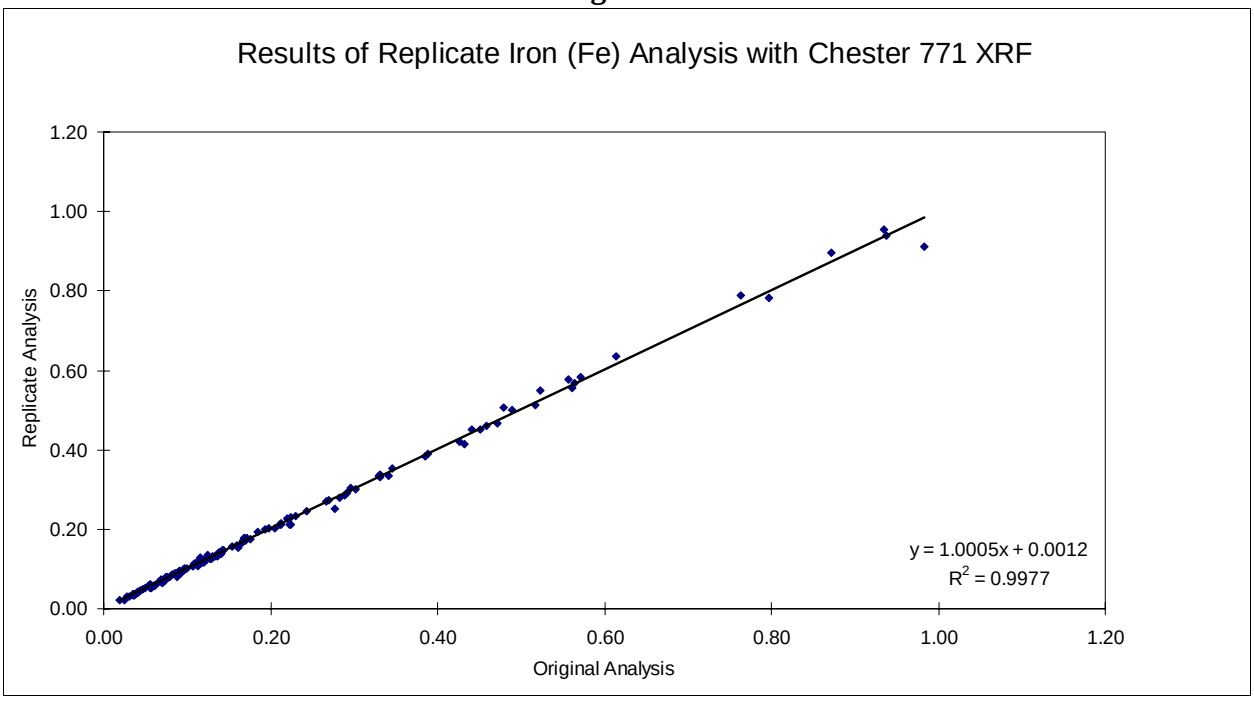


Figure 61

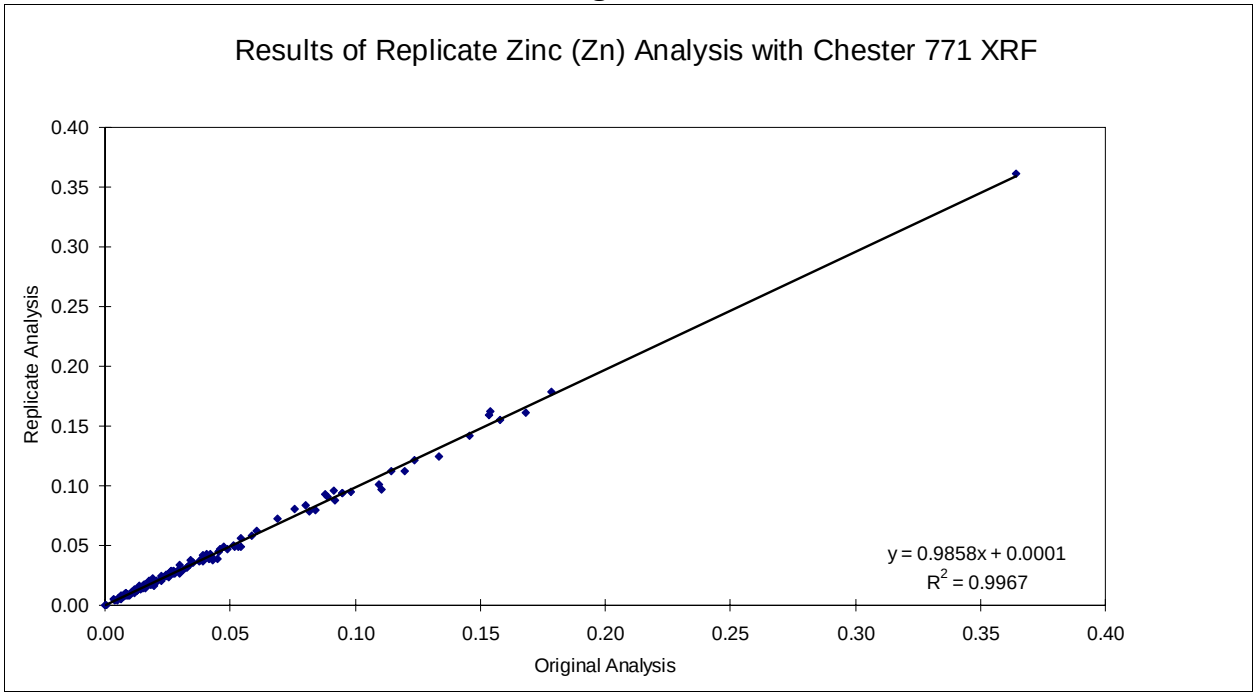


Figure 62

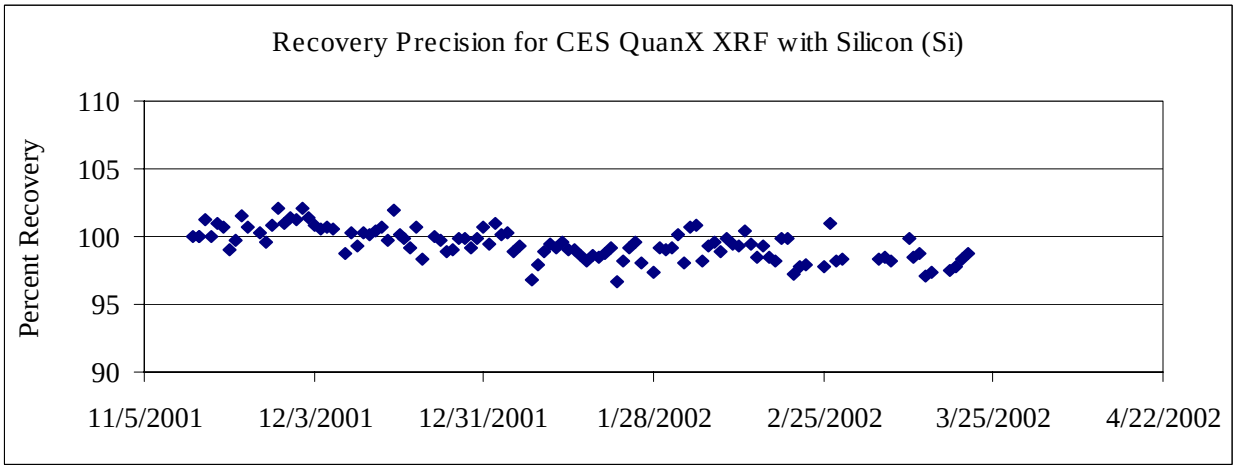


Figure 63

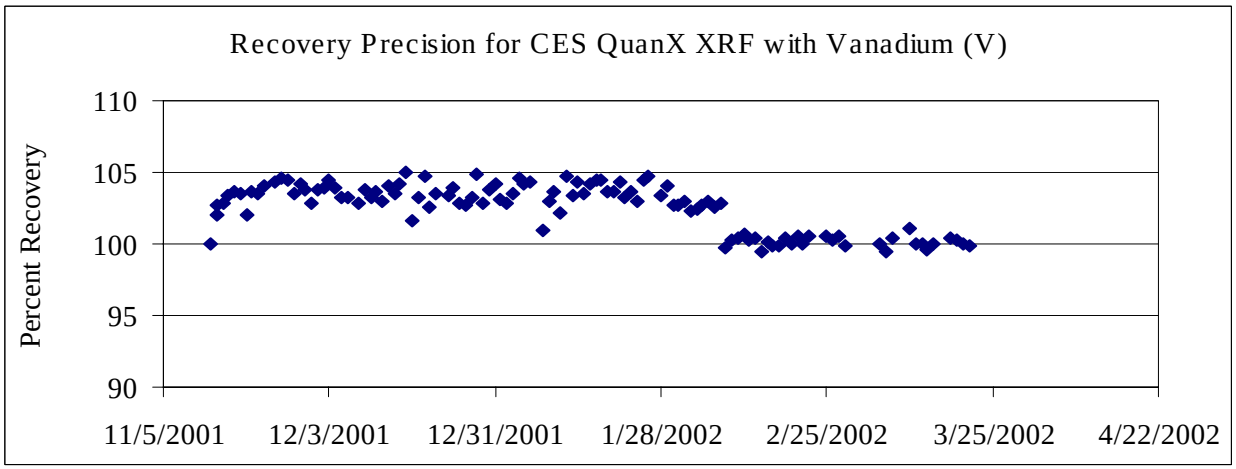


Figure 64

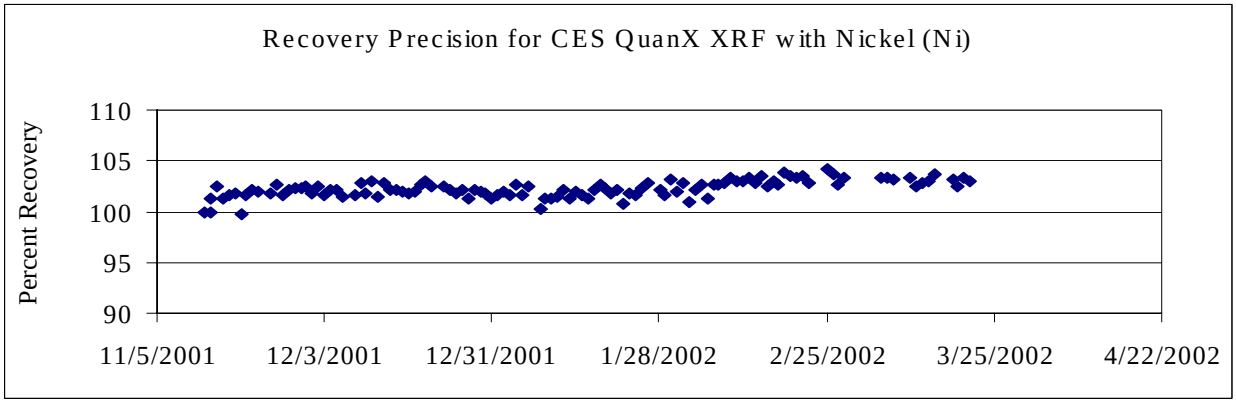


Figure 65

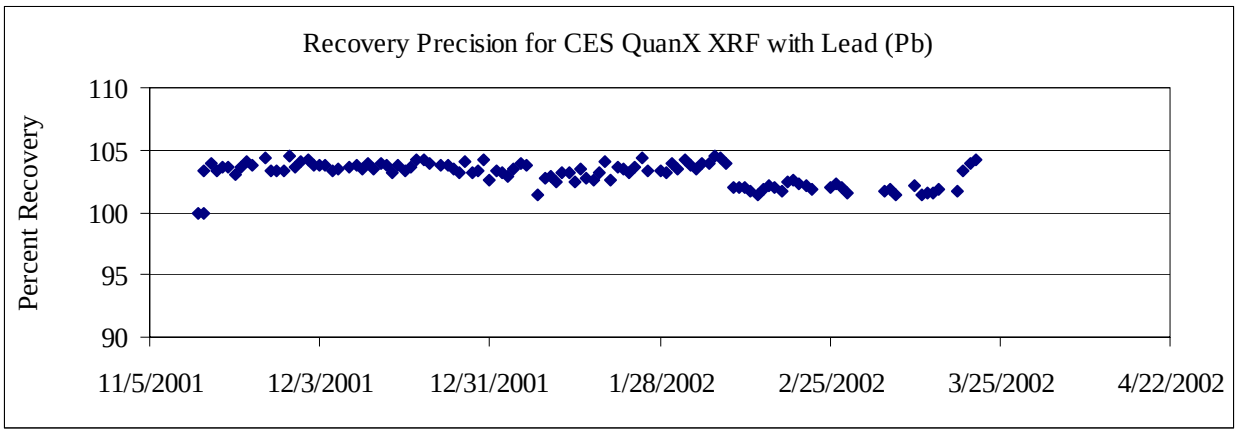


Figure 66

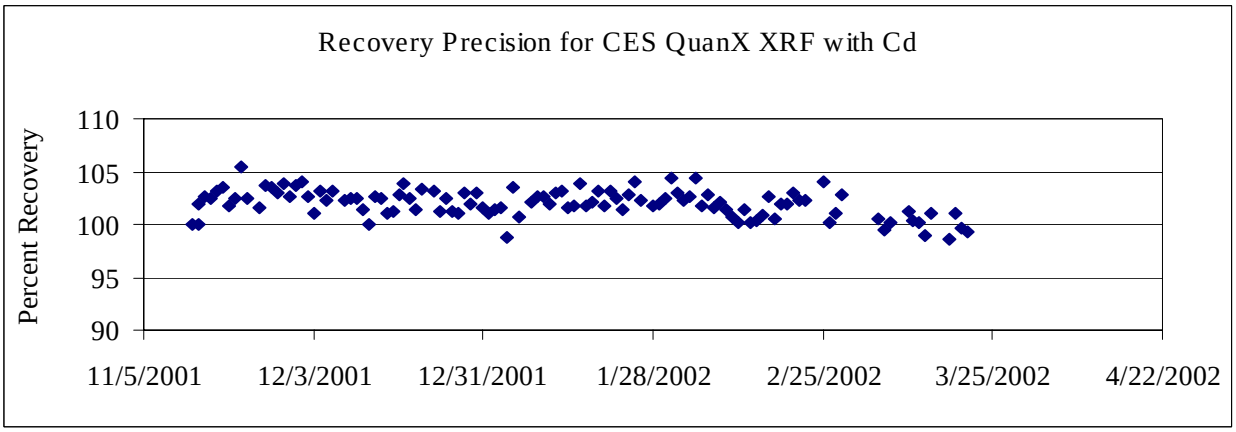


Figure 67

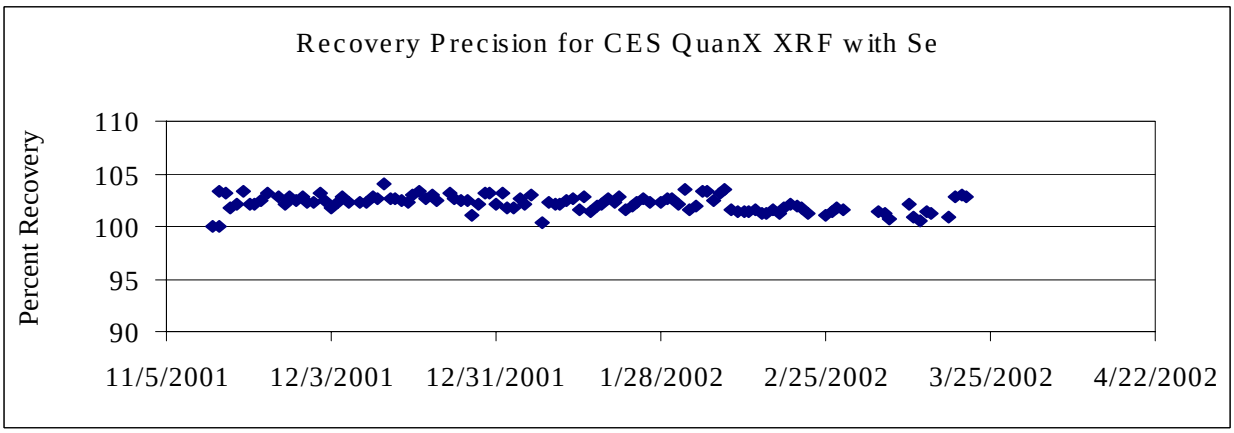


Table 20. Daily Replicate Measurement Results CES.

	Si	V	Ni	Pb	Cd	Se
Initial Calibration Value	9.11	10.17	10.2	20.53	5.15	3.86
V adjusted 2/8/2002	9.11	10.5	10.2	20.53	5.15	3.86
Cd Adjusted 2/28/2002	9.11	10.5	10.2	20.53	5.22	3.86
Average Daily Value	9.06	10.52	10.43	21.17	5.26	3.94
Standard Deviation	0.11	0.08	0.08	0.20	0.06	0.03
Rel Std Dev, percent	1.18	0.74	0.80	0.93	1.14	0.75
Percent Recovery						
AVG	99.4%	102.5%	102.2%	103.1%	102.0%	102.2%
SD	1.18	1.65	0.82	0.96	1.30	0.77
RSD	1.18	1.61	0.80	0.93	1.27	0.75

Figure 68

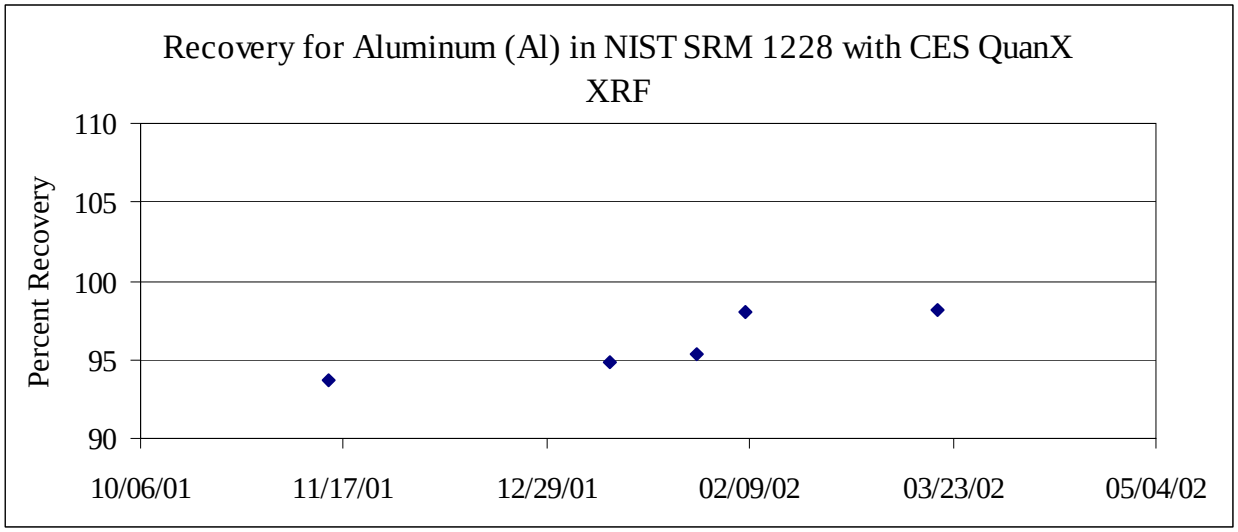


Figure 69

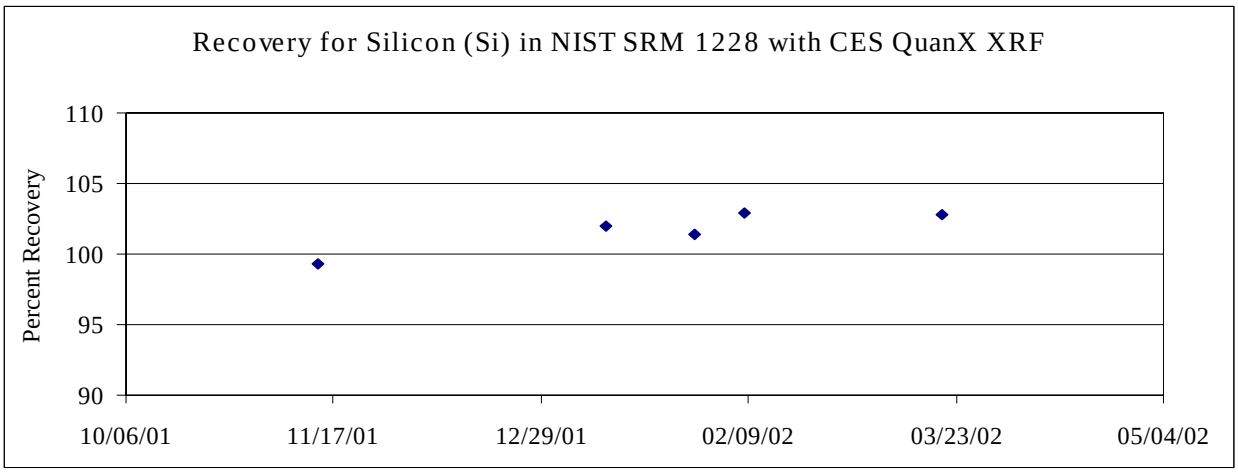


Figure 70

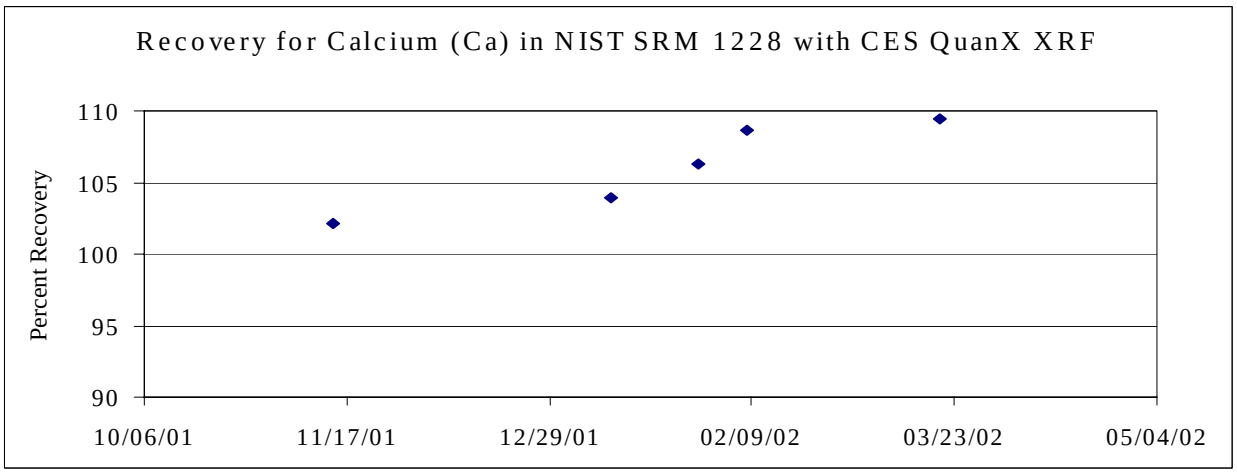


Figure 71

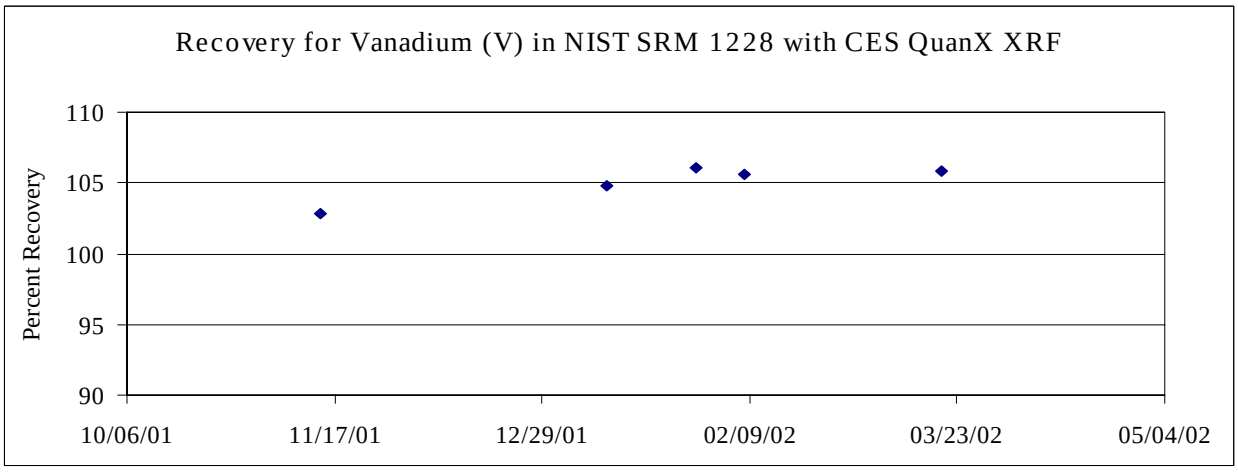


Figure 72

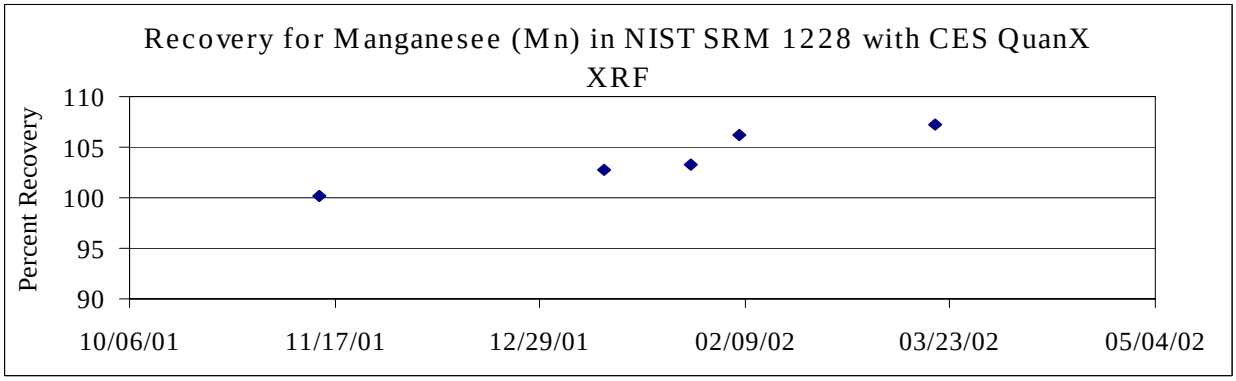


Figure 73

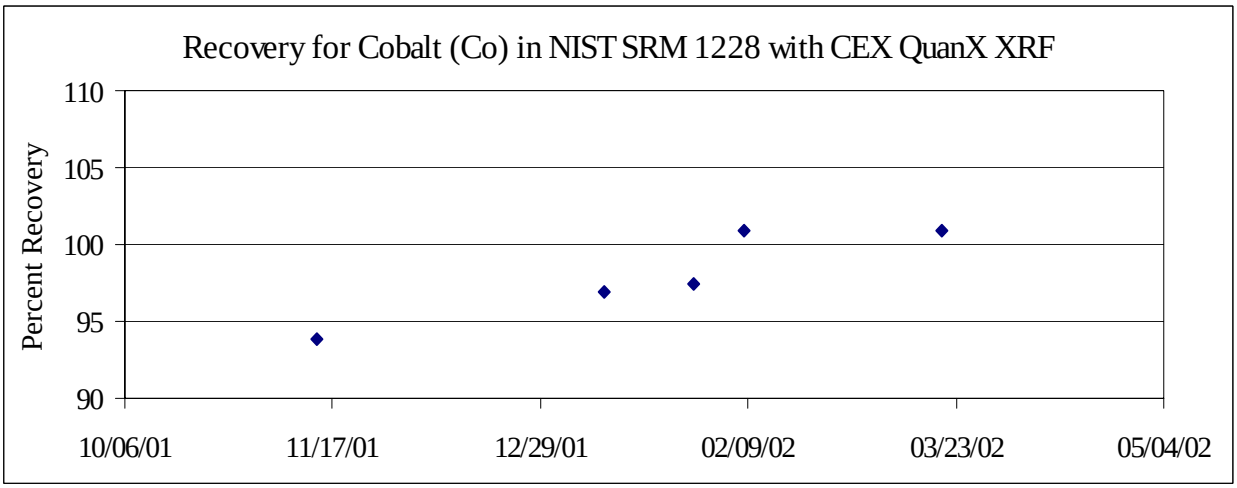


Figure 74

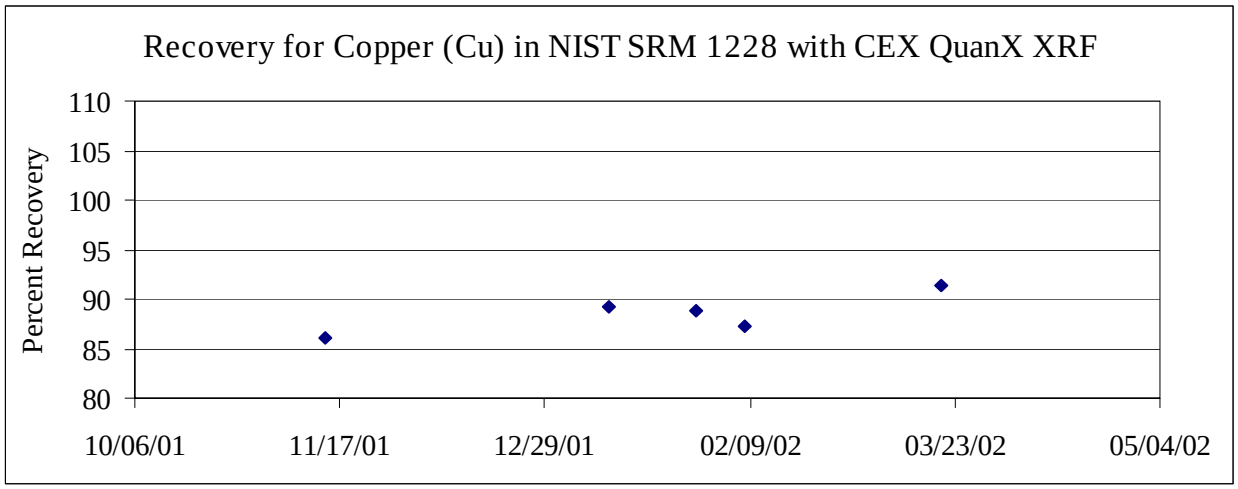


Figure 75

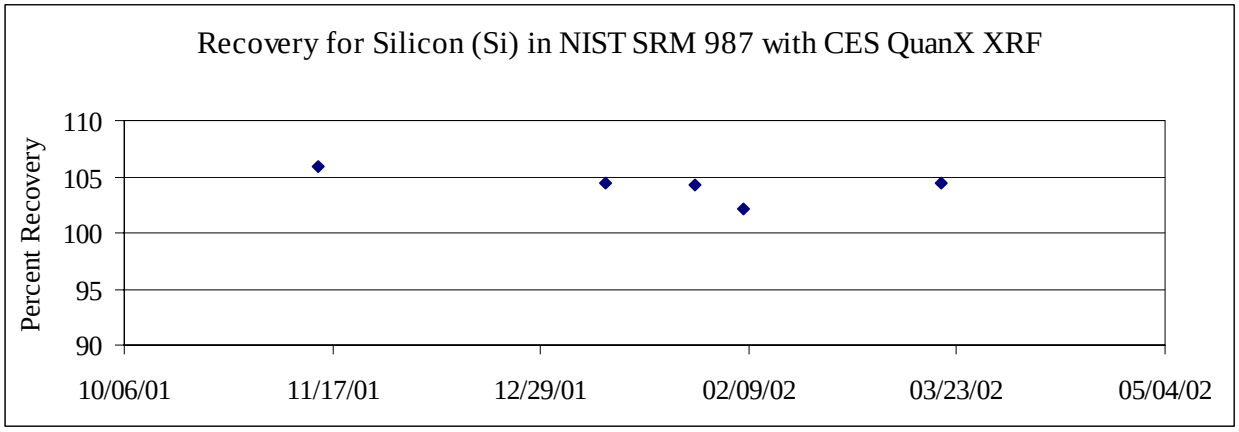


Figure 76

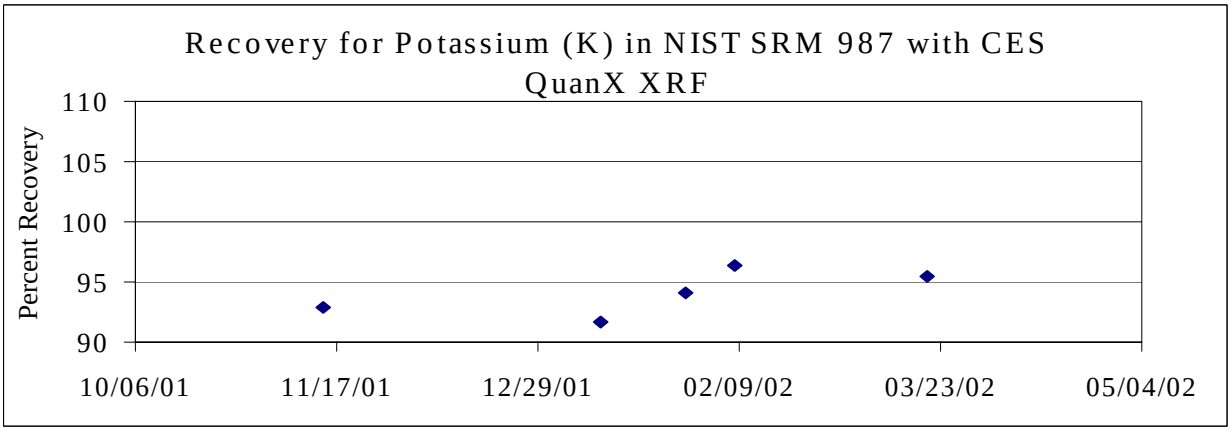


Figure 77

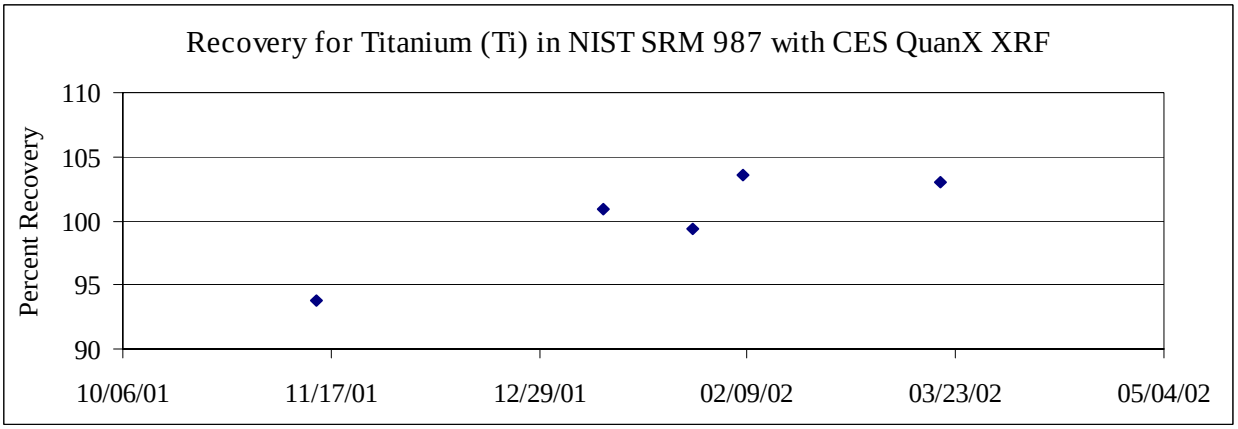


Figure 78

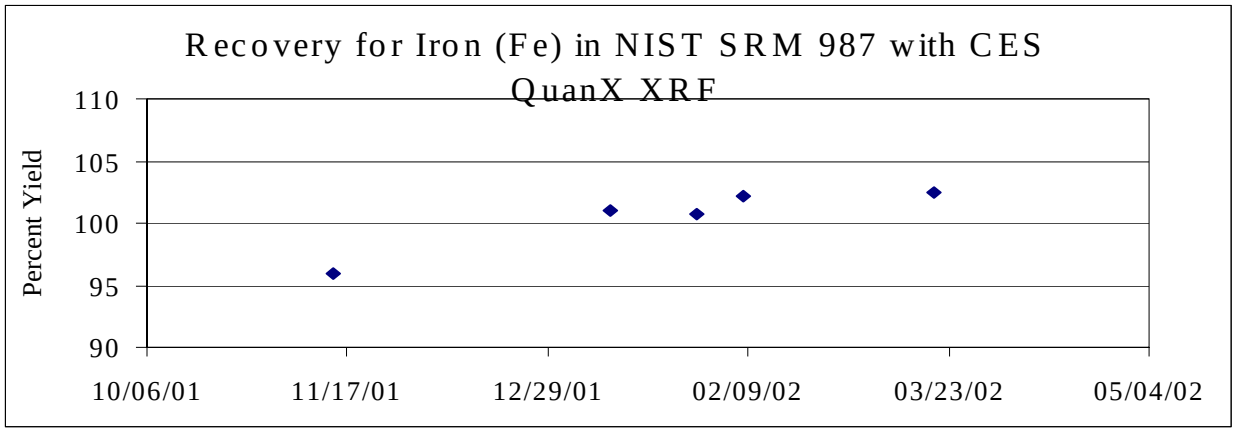


Figure 79

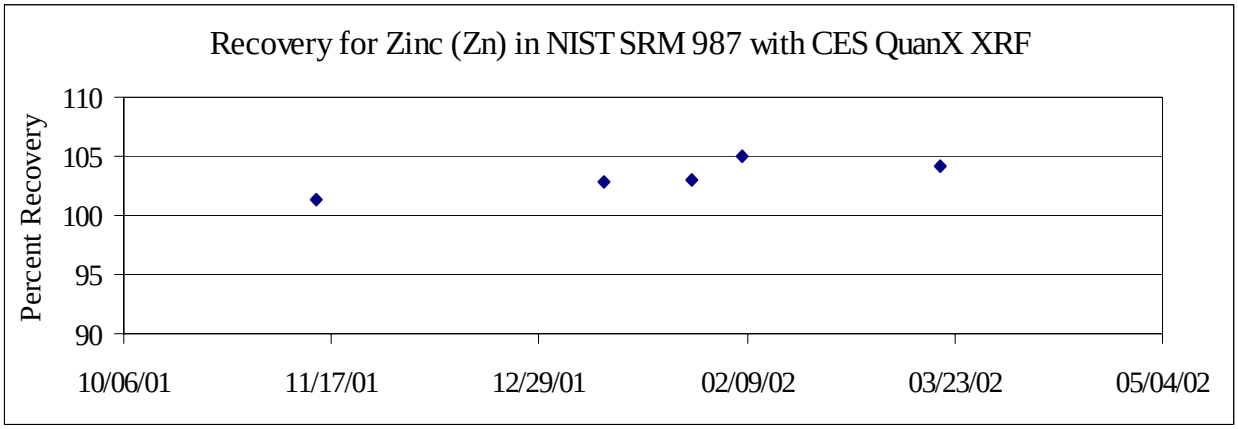


Figure 80

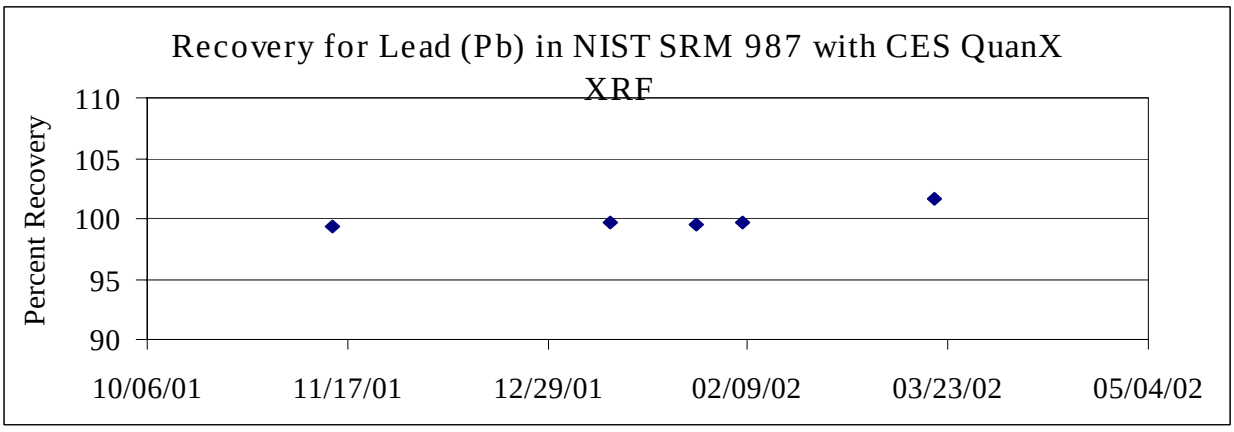


Table 21. Recovery Determined from Analysis of NIST Standard Reference Material Filters, QuanX.

Element	NIST/SRM 1228	NIST/SRM 987
	Range % Recovery	Range % Recovery
Al	93.7 - 98.1	----
Si	99.3 - 102.9	102.2 - 105.9
K	----	97.1 - 96.3
Ca	102.9 - 109.4	----
Ti	----	93.8 - 96.3
V	102.8 - 106.0	----
Mn	100.2 - 107.2	93.8 - 103.5
Co	93.9 - 100.9	----
Cu	93.9 - 100.9	----
Fe	----	95.9 - 102.5
Zn	----	101.3 - 105.0
Pb	----	99.3 - 101.7

Replicates

Ten percent of the filters are reanalyzed and the results for select elements are compared. **Figures 81 through 88** compare replicate values for eight elements through regression analysis. Note that slopes are all greater than 0.998 and correlation coefficients are all greater than 0.996, indicating acceptable replication.

Figure 81

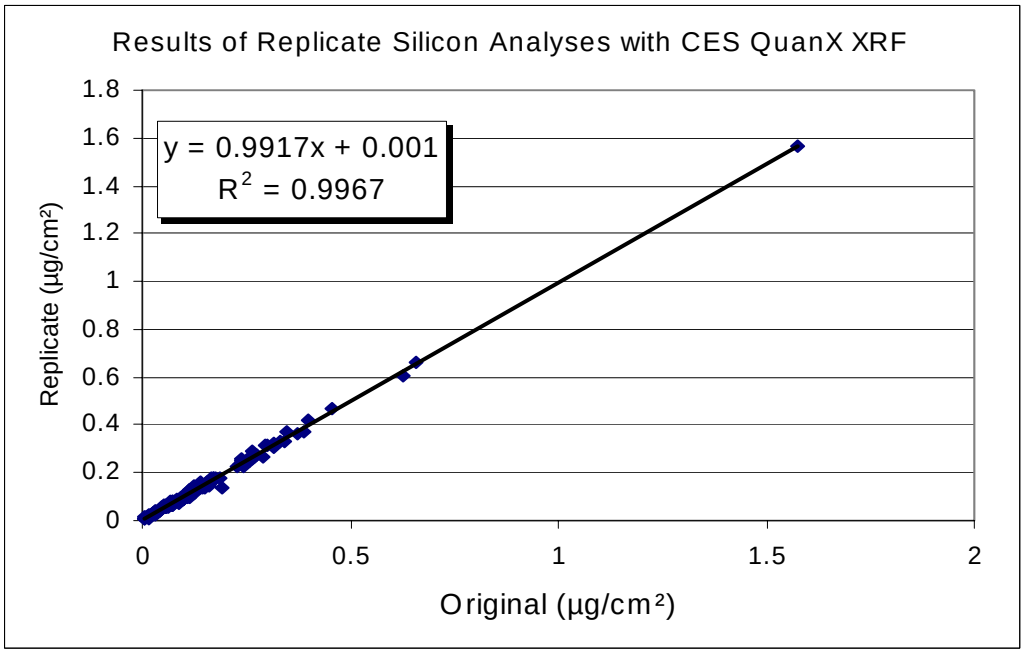


Figure 82

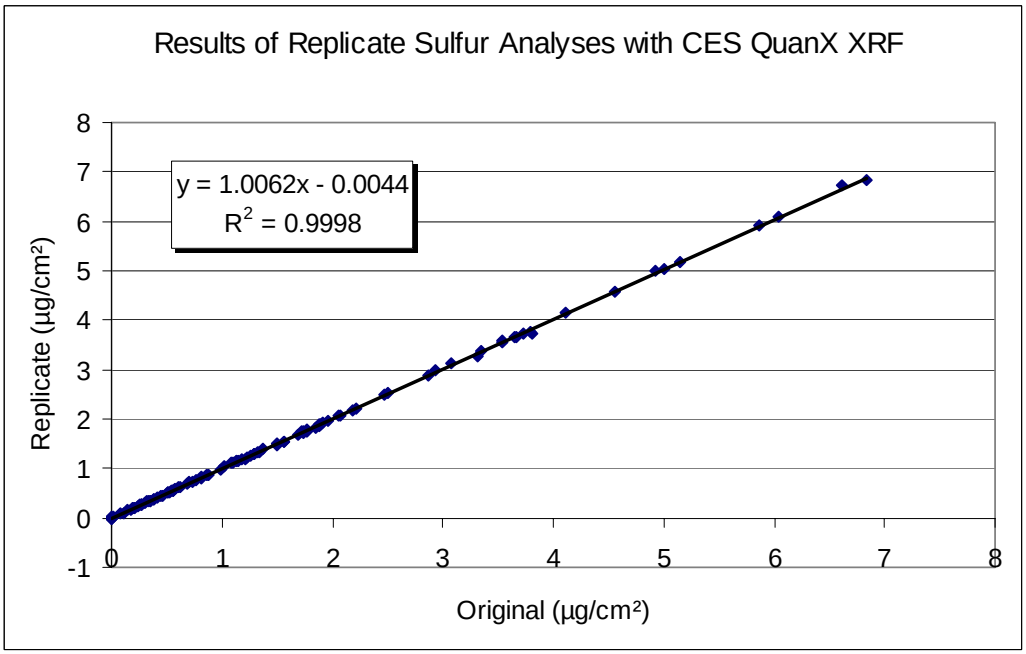


Figure 83

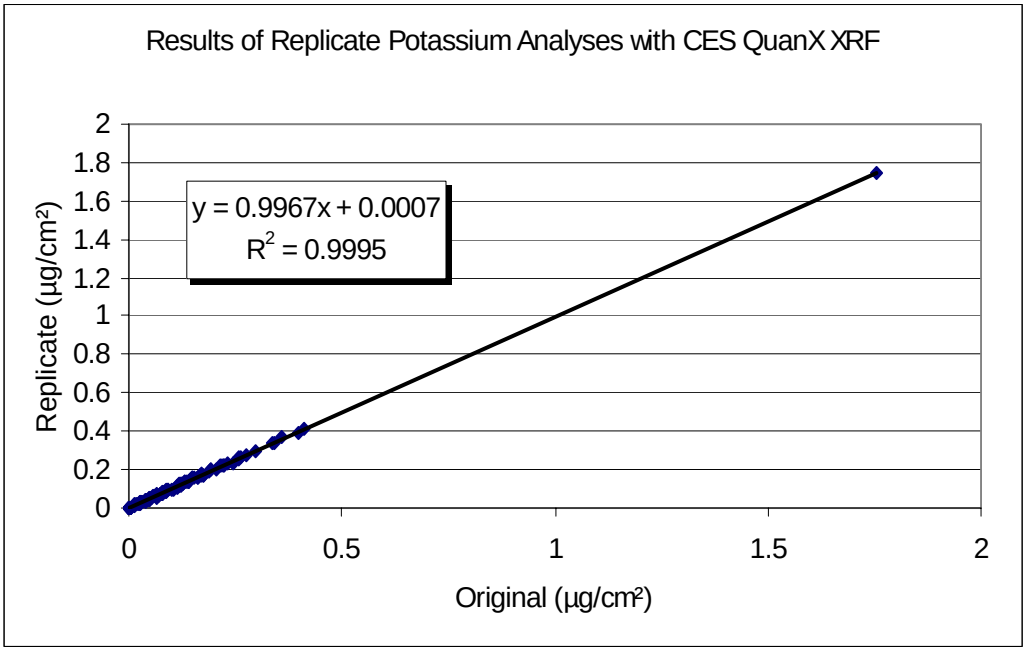


Figure 84

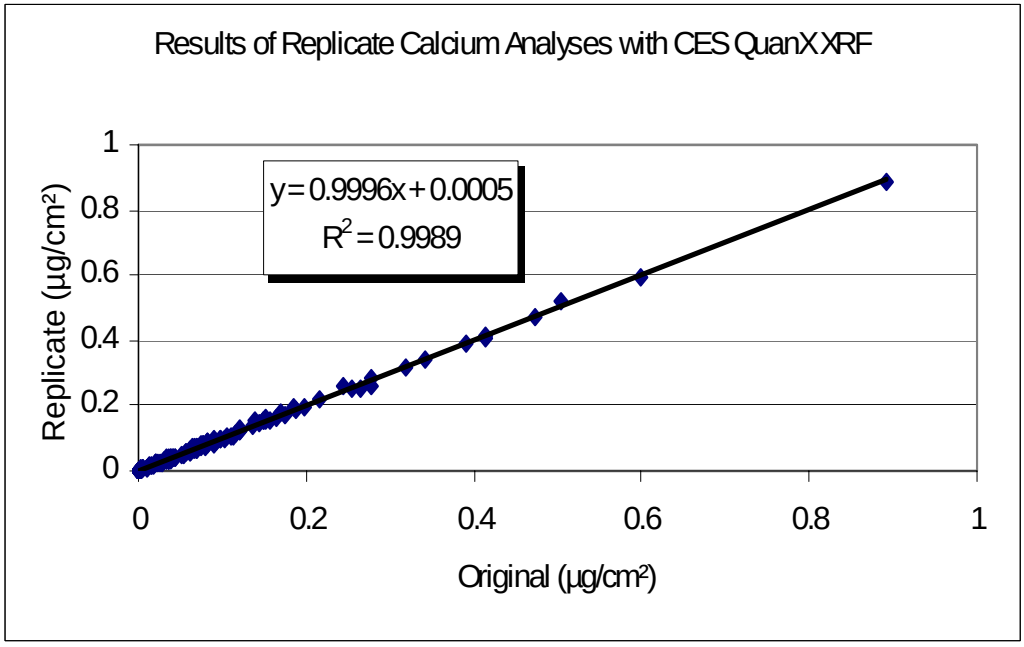


Figure 85

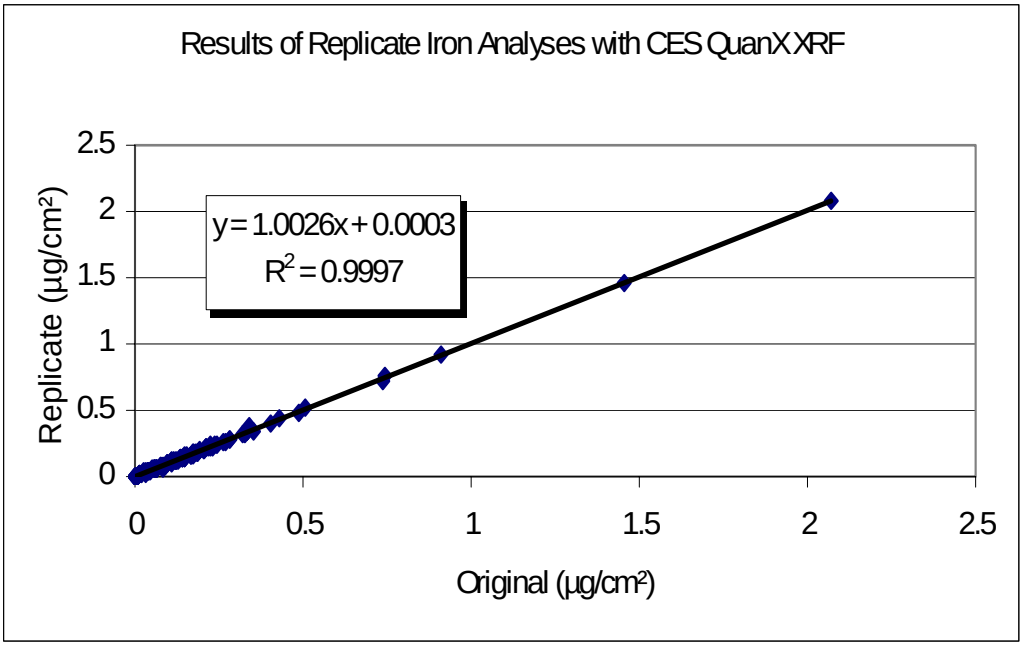


Figure 86

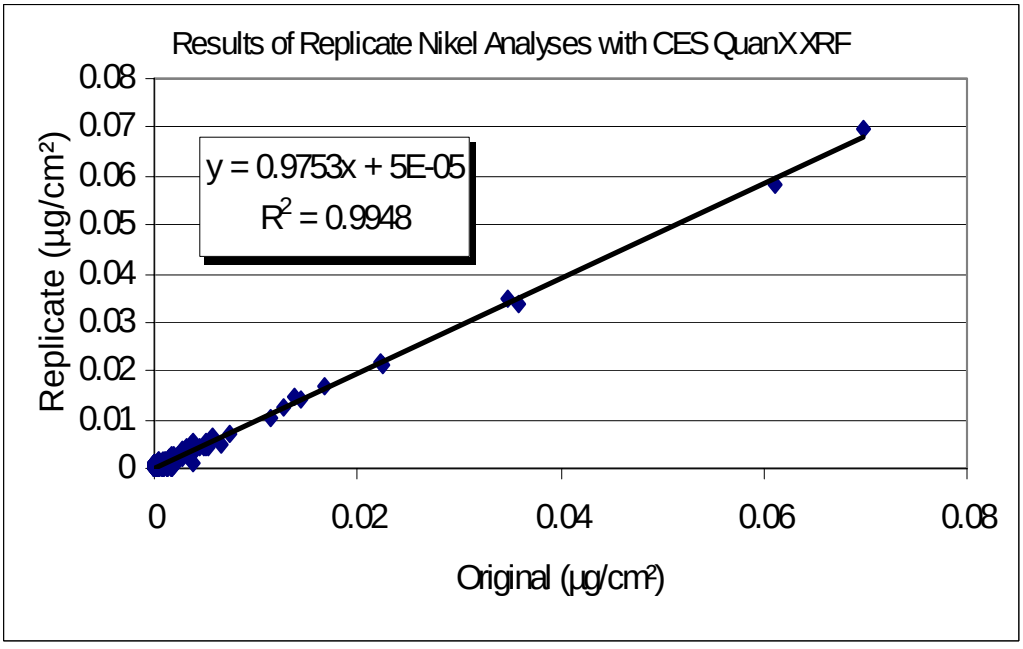


Figure 87

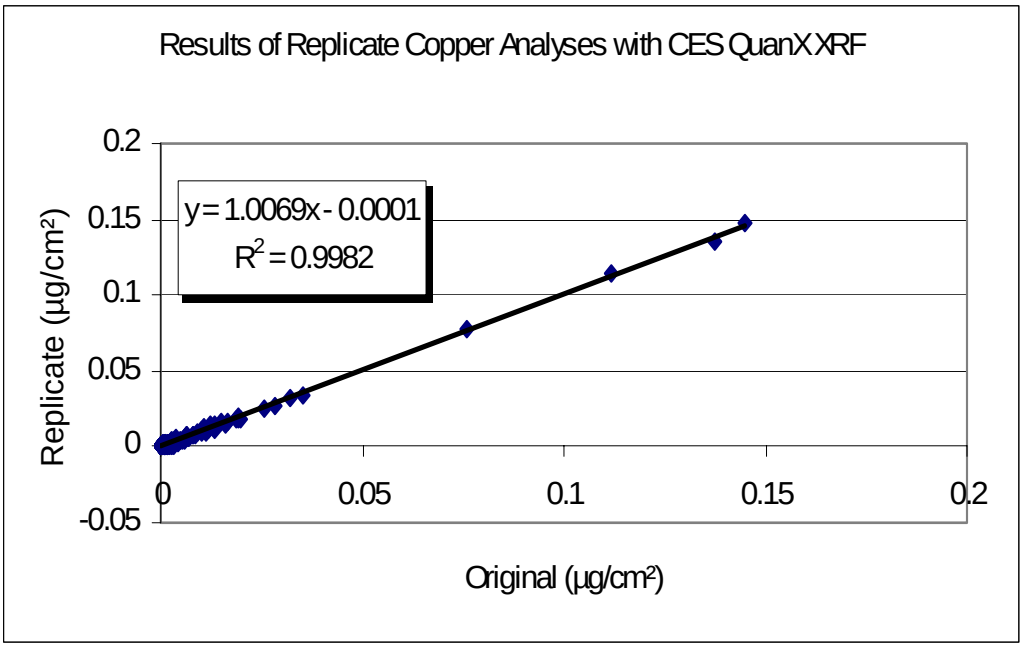
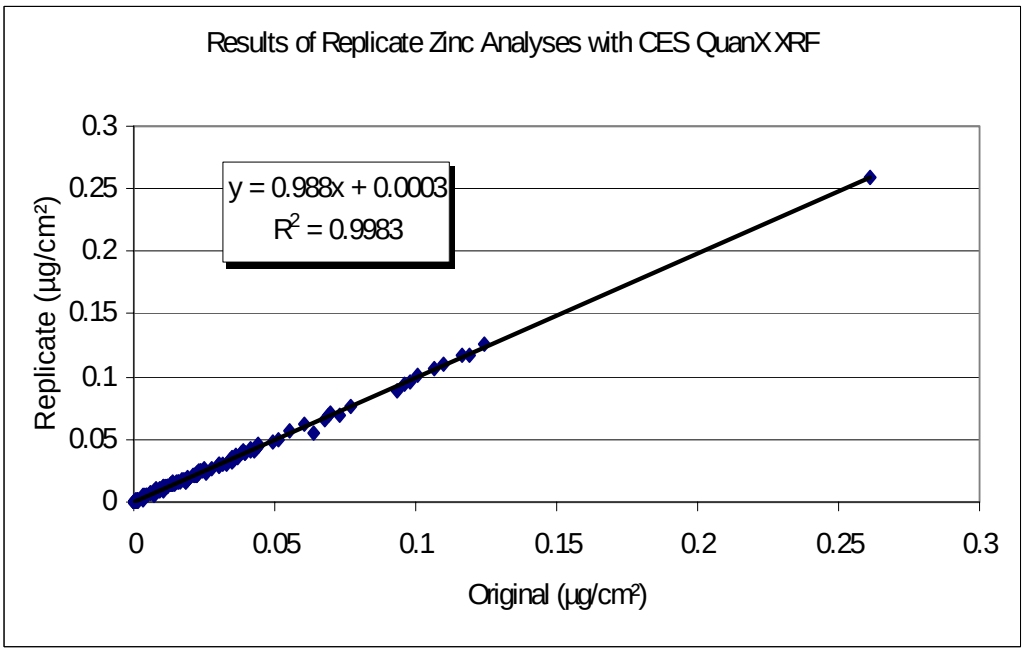


Figure 88



2.4.3.2 Data Validity Discussion

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

2.4.3.3 Corrective Actions

The XRF experience a sample wheel rotation problem on January 31, 2002. The problem was repaired, and the filters were reanalyzed.

The vanadium standard did not meet the 5% criteria on February 8, 2002, so the instrument was recalibrated.

The cadmium standard did not meet the 5% criteria on February 25, 2002, so the instrument was recalibrated.

2.4.4 RTI XRF Laboratory

RTI began analyzing STN by XRF samples on February 1, 2002.

2.4.4.1 Statistical Summary of QC Results

Precision

The precision is monitored by the reproducibility of the XRF signal in counts per second using standard samples. The counts for a select element are measured for each of the targets used. The comparison of the counts during calibration and during the run gives the measure of reproducibility or precision (**Table 22**). The data used to monitor precision are presented in **Figures 89 through 100**.

Table 22. Summary of RTI QC Precision Recovery Data, 02/01/2002 - 3/31/2002.

Element	n	Min	Max	Avg.	Std Dev	%CV
Si(1)	78	11.5	10.5	11.0	0.23	2.10
Ti(2)	78	10.5	8.56	10.2	0.28	2.77
Fe(3)	78	10.8	9.33	10.6	0.20	1.92
Se(4)	78	4.08	3.18	3.94	0.18	4.48
Pb(4)	78	5.90	5.34	5.71	0.10	1.74
Cd(5)	78	11.0	8.72	10.7	0.44	4.17

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 89

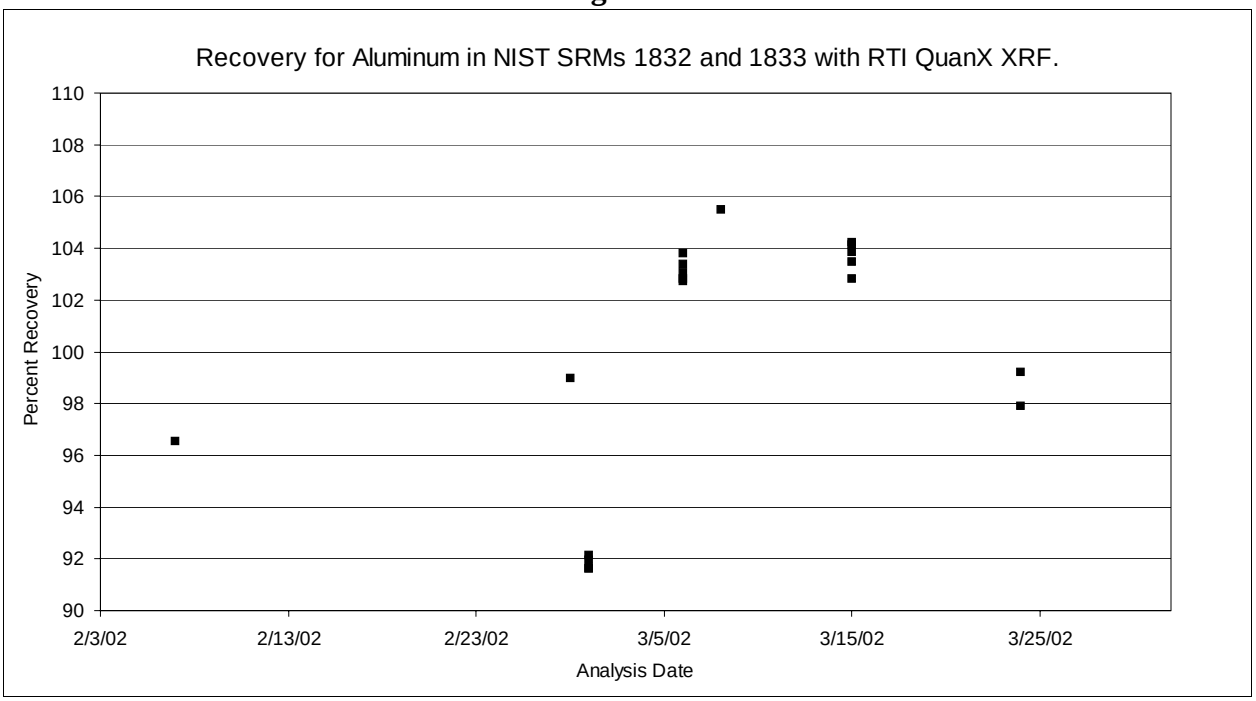


Figure 90

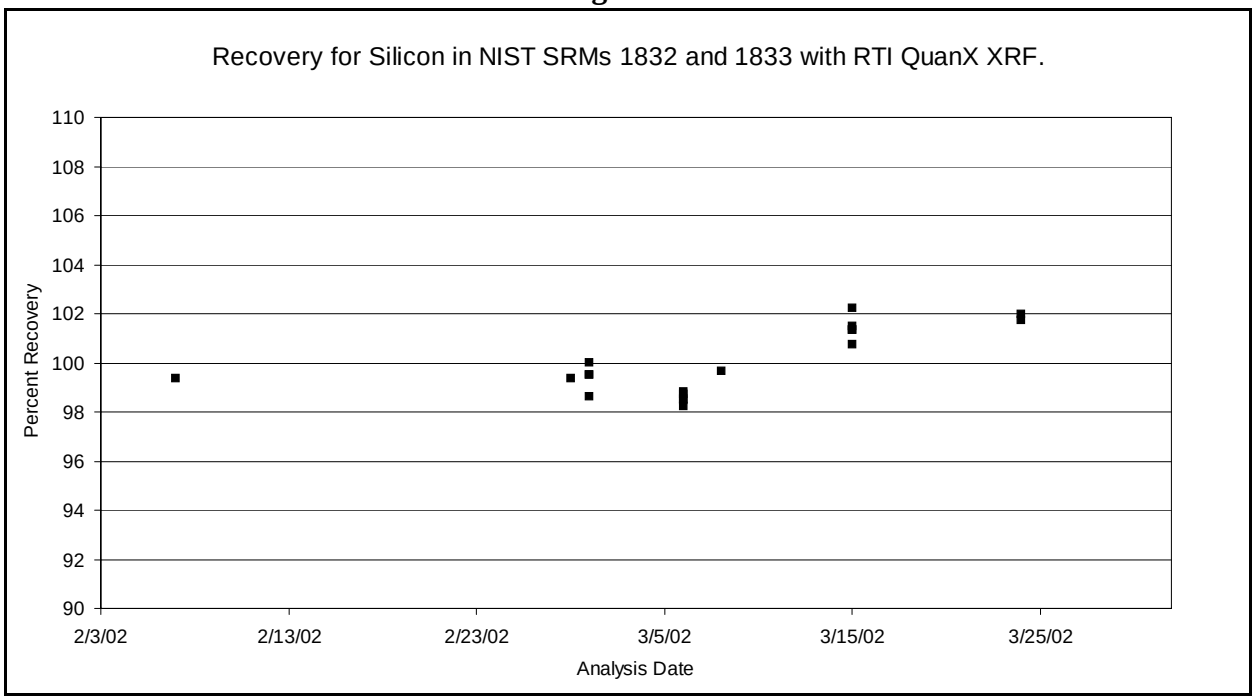


Figure 91

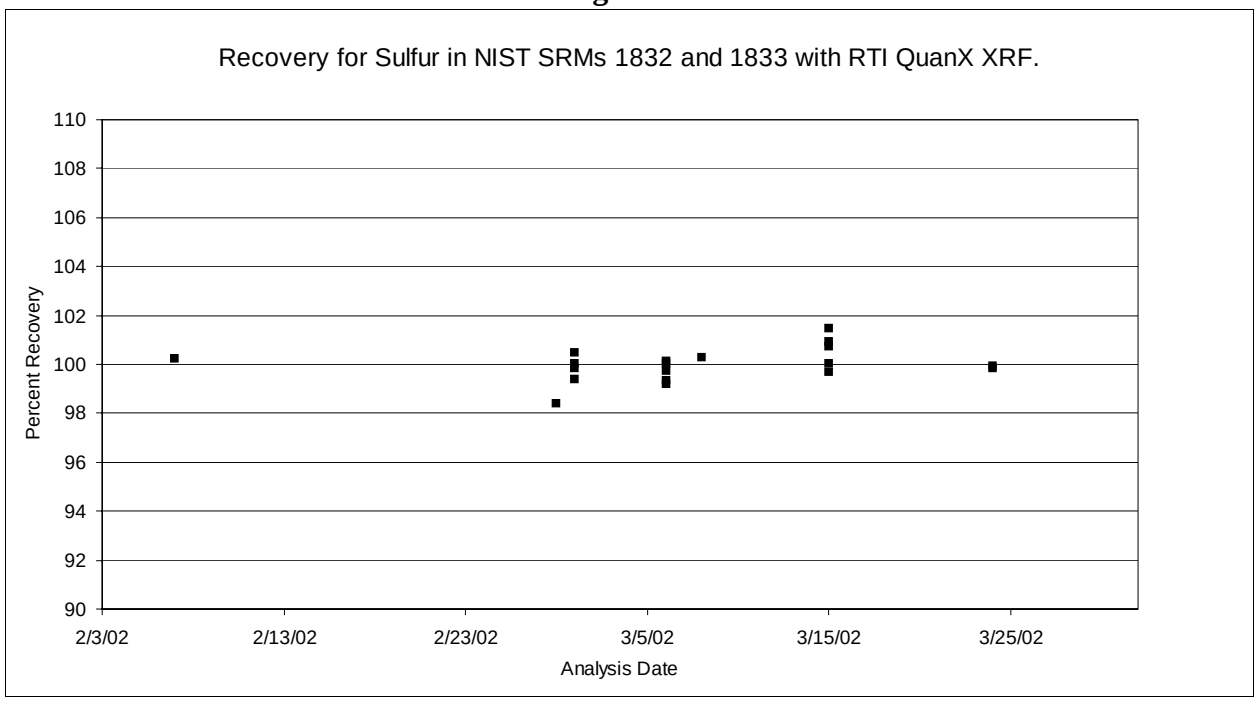


Figure 92

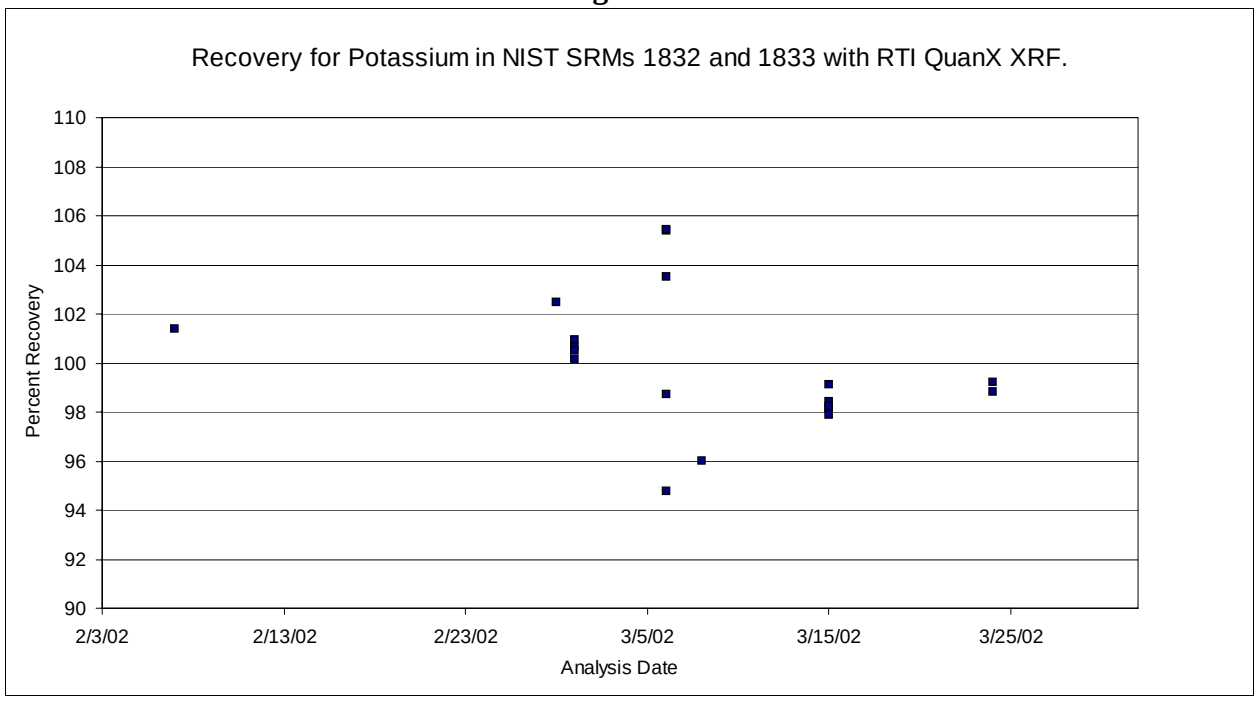


Figure 93

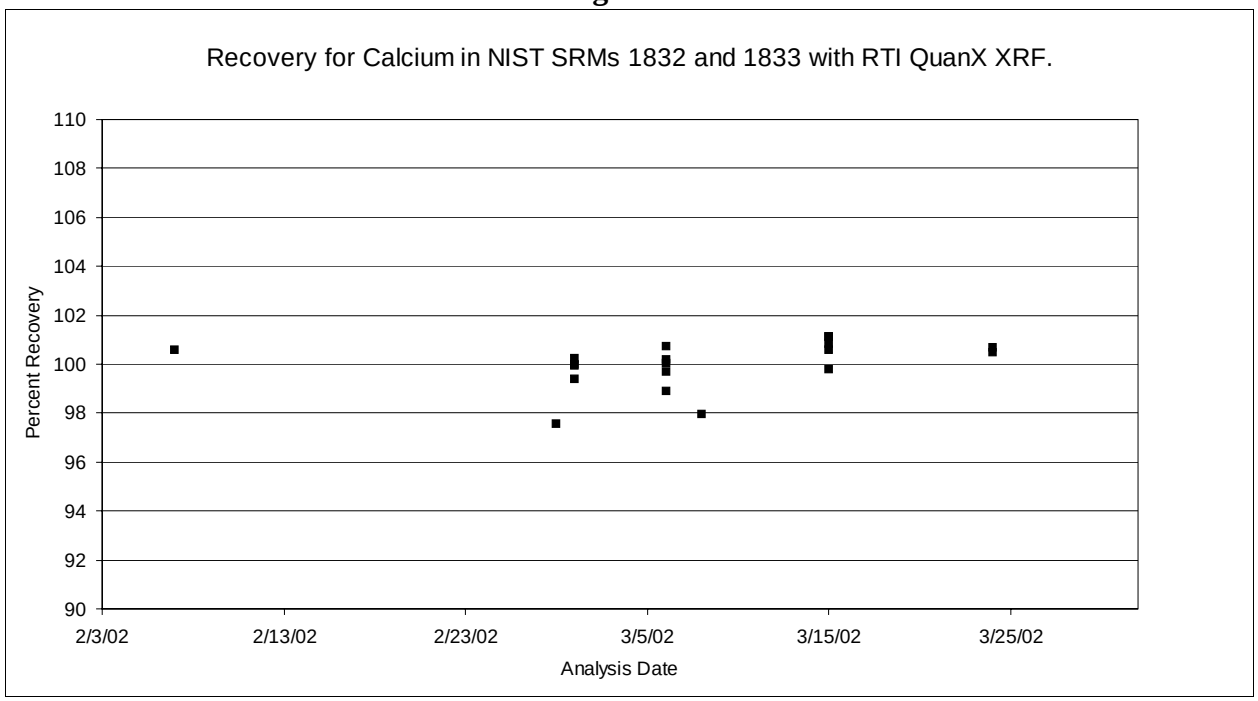


Figure 94

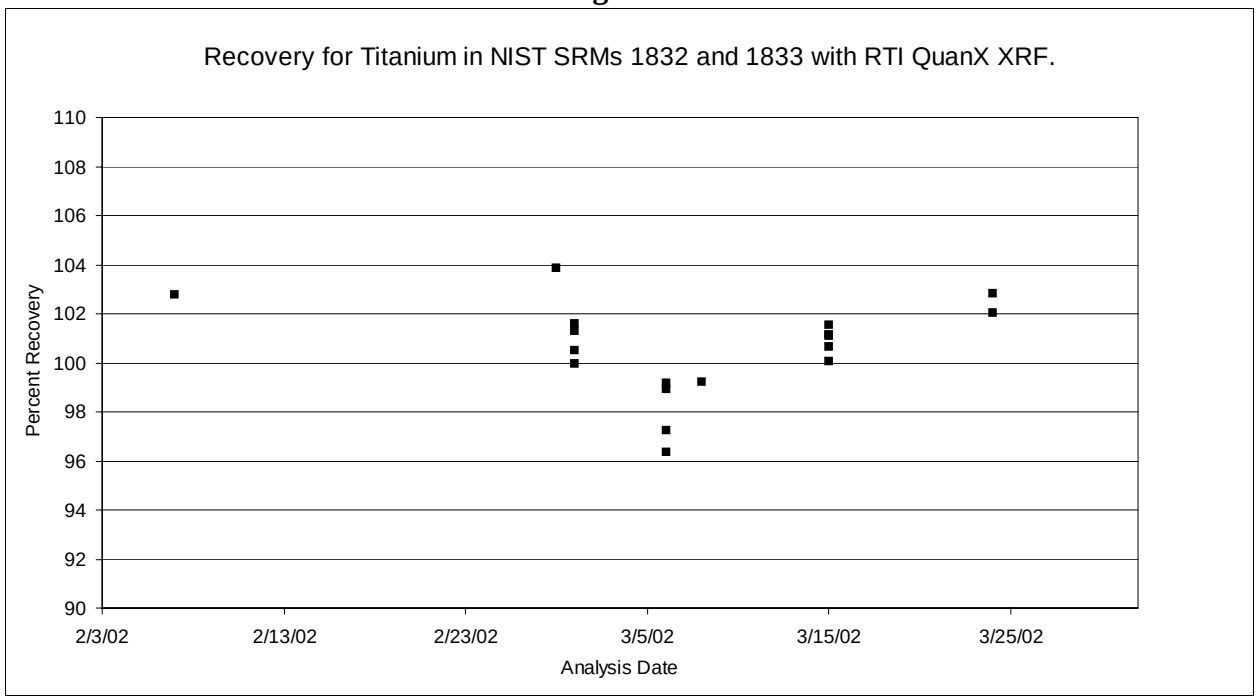


Figure 95

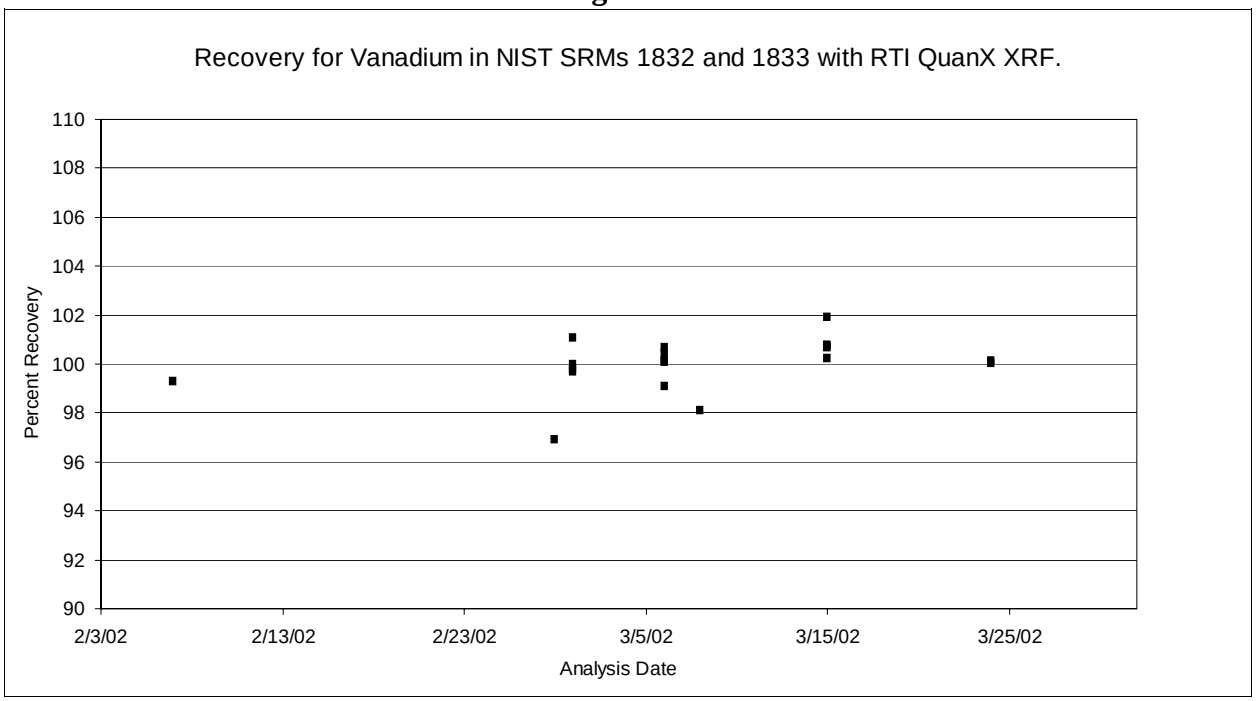


Figure 96

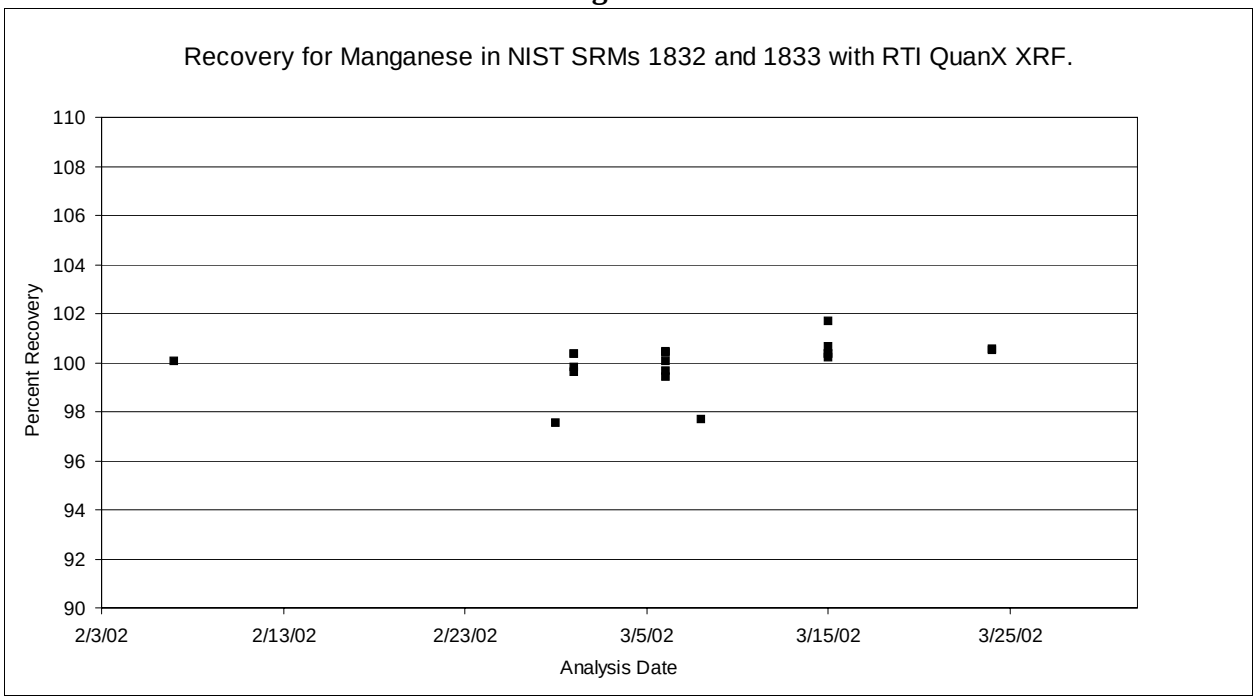


Figure 97

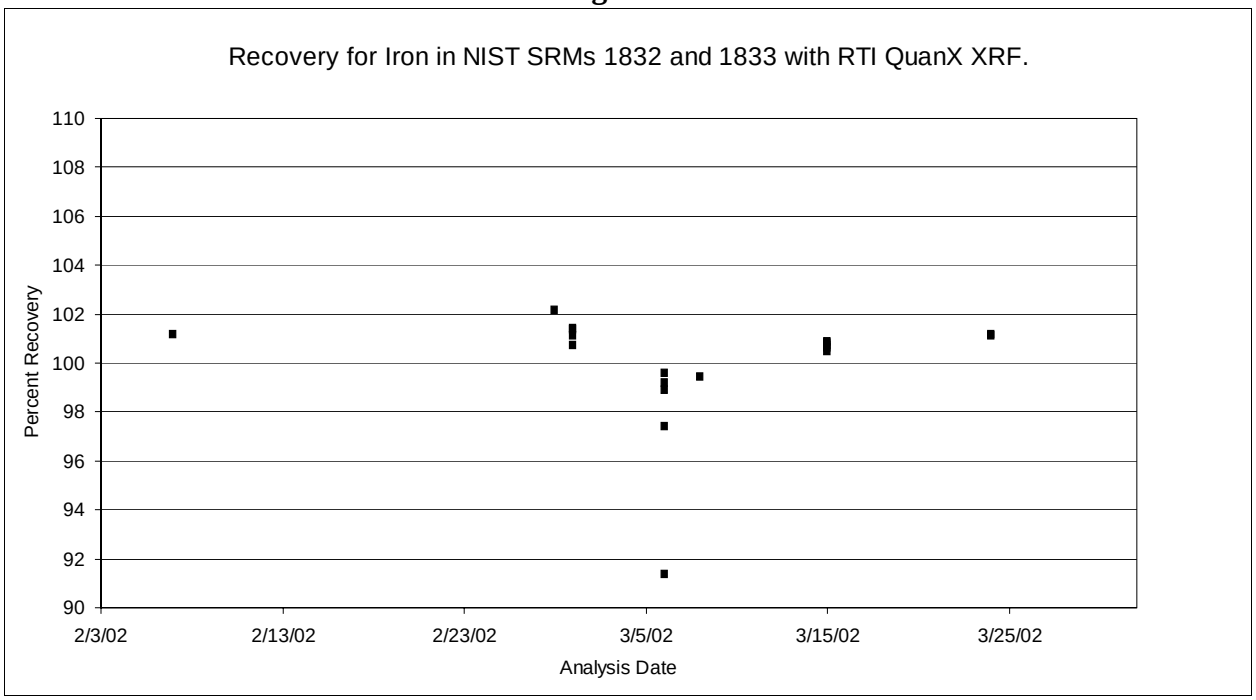


Figure 98

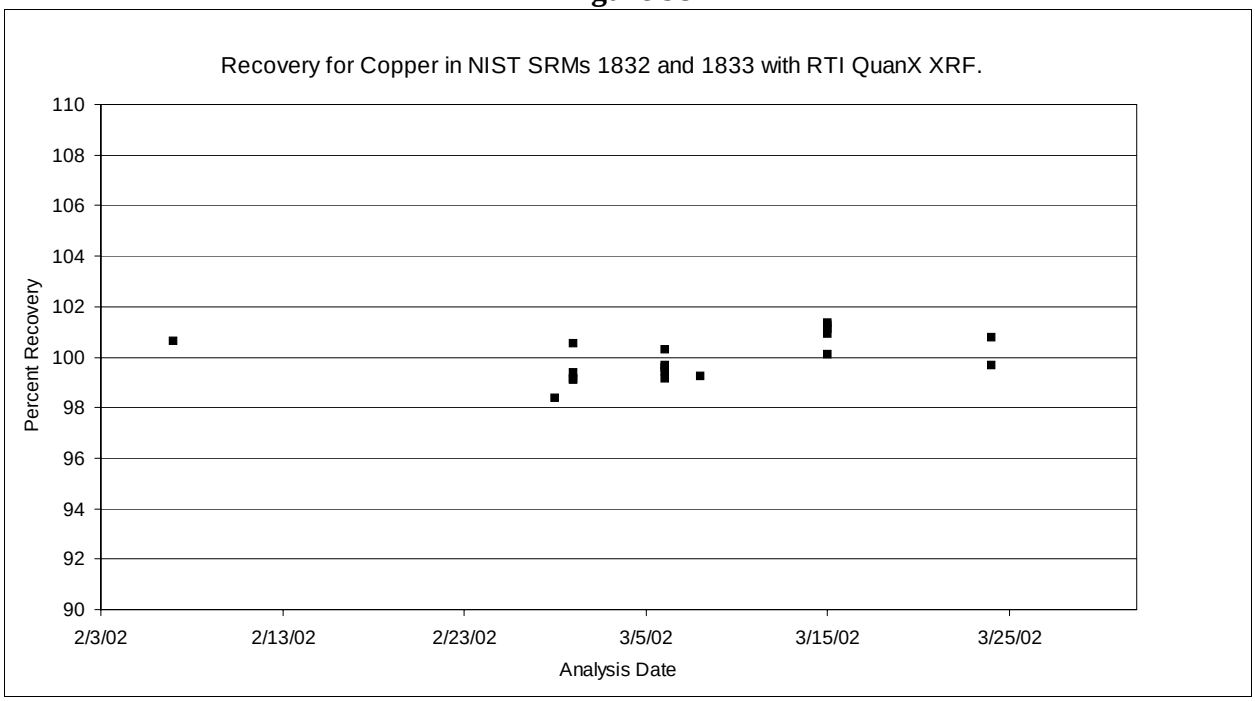


Figure 99

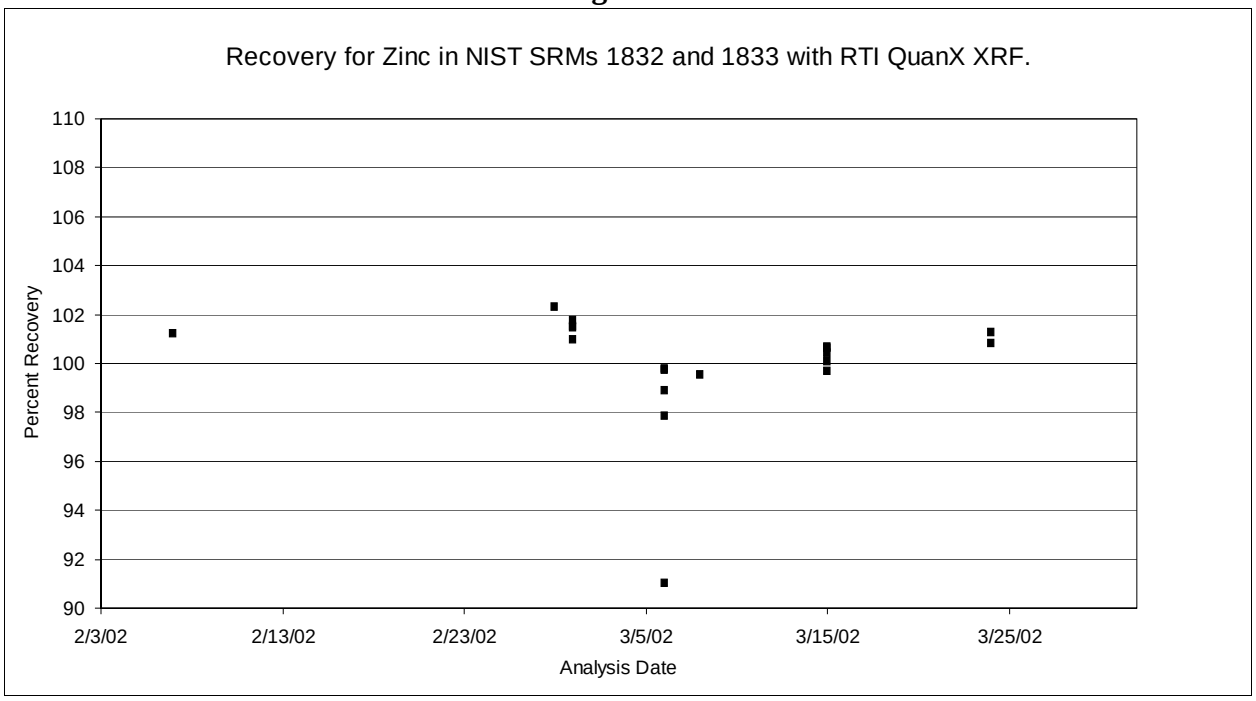
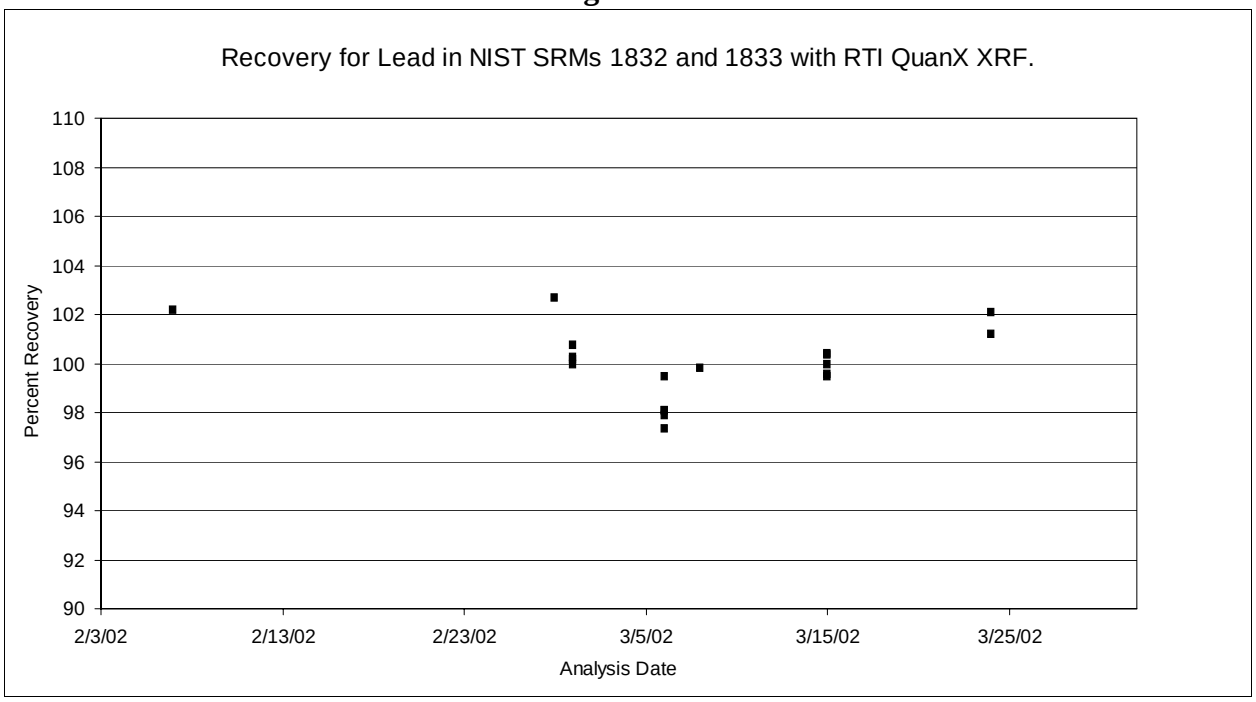


Figure 100



Recovery

Recovery or system accuracy is determined by the analysis of a series of NIST Standard Reference Materials filters. Recovery is calculated by comparison of a measured and expected values. **Figures 101 through 106** show recovery for 12 select elements spanning the range of the 48 elements normally measured. All recovery values for all elements ranged between 85 and 106 percent as shown in **Table 23**. It is noted that the Fe and Zn both have their lower values less than 90%. These values were acquired on one day; the average of five runs that day for Fe was 90% and Zn was 92%.

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

Element	Range % Recovery
Al	93 - 107
Si*	96 - 99
Si**	100 - 104
K	90 - 100
Ca	98 - 102
Ti	91 - 106
V	101 - 106
Mn	100 - 104
Fe	85 - 95
Co	102 - 105
Cu	96 - 99
Zn	86 - 96
Pb	99 - 104

*SRM 1832 *SRM 1833

Replicates

Ten percent of the filters are reanalyzed and the results for select elements are compared. **Figures 107 through 112** compare replicate values for six elements through regression analysis. Note that slopes are all greater than 0.989 and correlation coefficients range from 0.968 to 1.001, indicating acceptable replication.

2.4.4.2 Data Validity Discussion

The data presented in Section 2.4.4 indicate no problems with the XRF data. The only problems encountered were occasional tears and/or pinholes in the filters. These were minor, and not considered to have a significant impact on the analysis results.

Figure 101

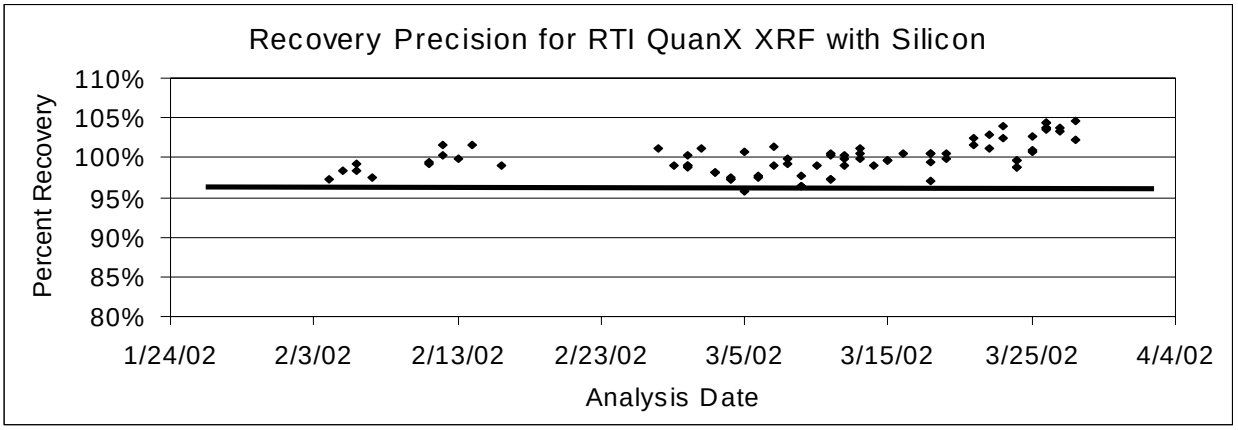


Figure 102

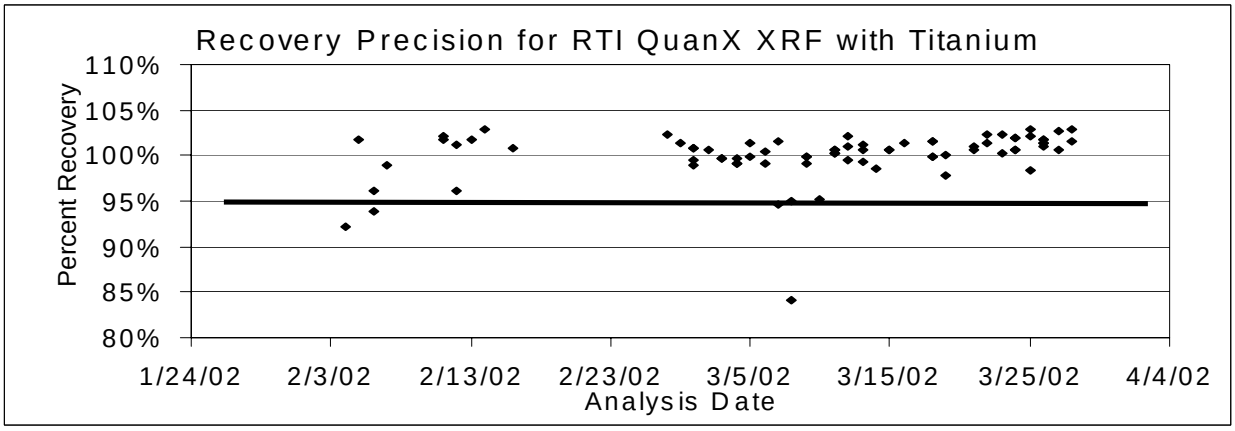


Figure 103

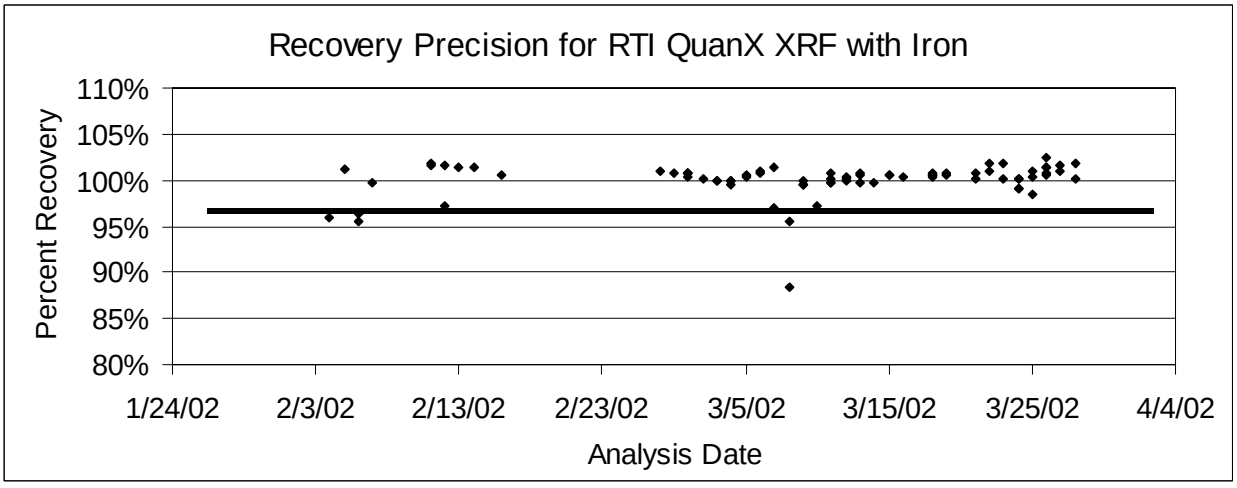


Figure 104

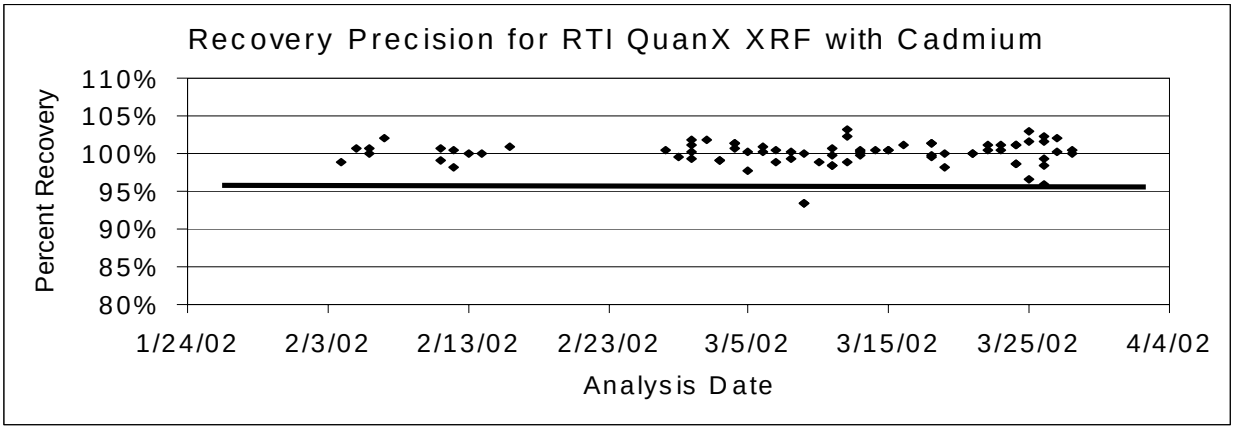


Figure 105

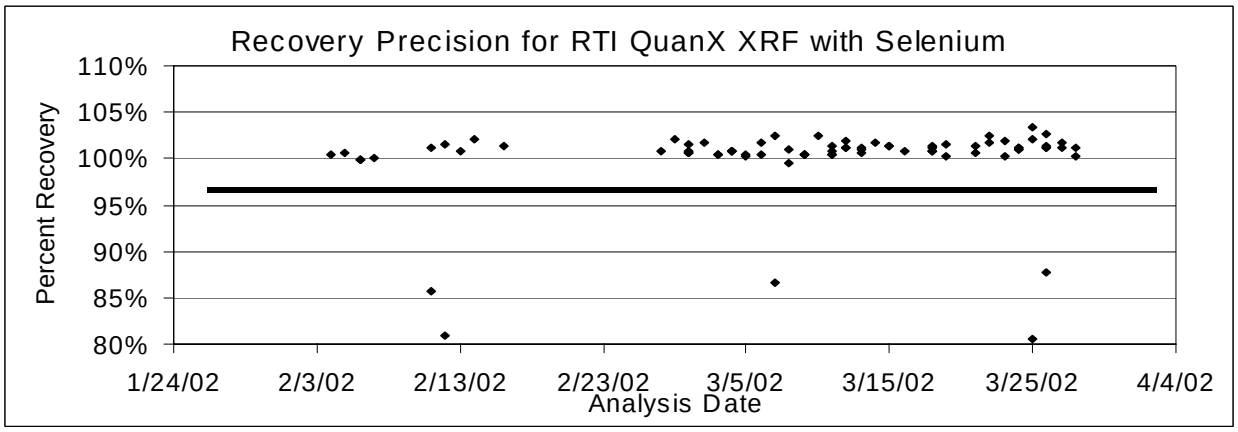


Figure 106

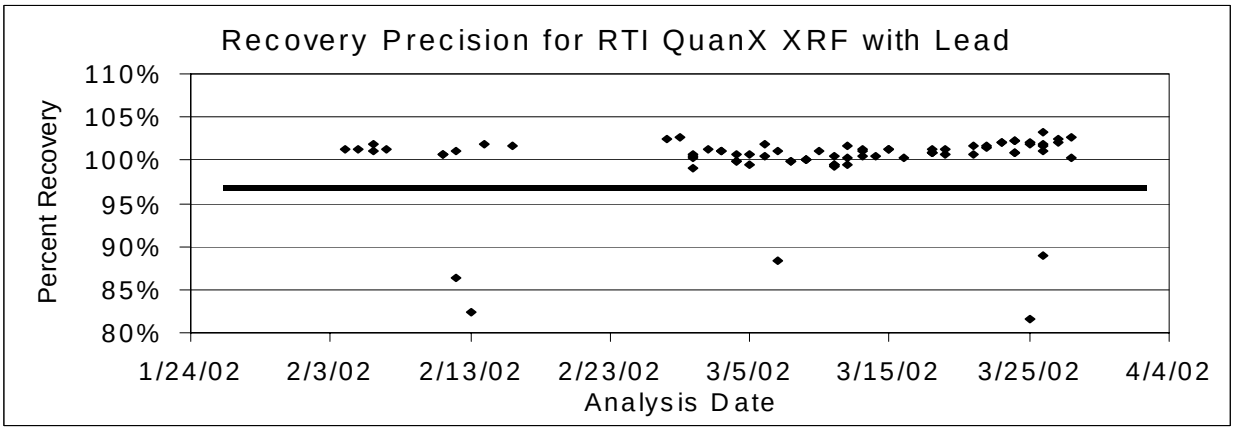


Figure 107

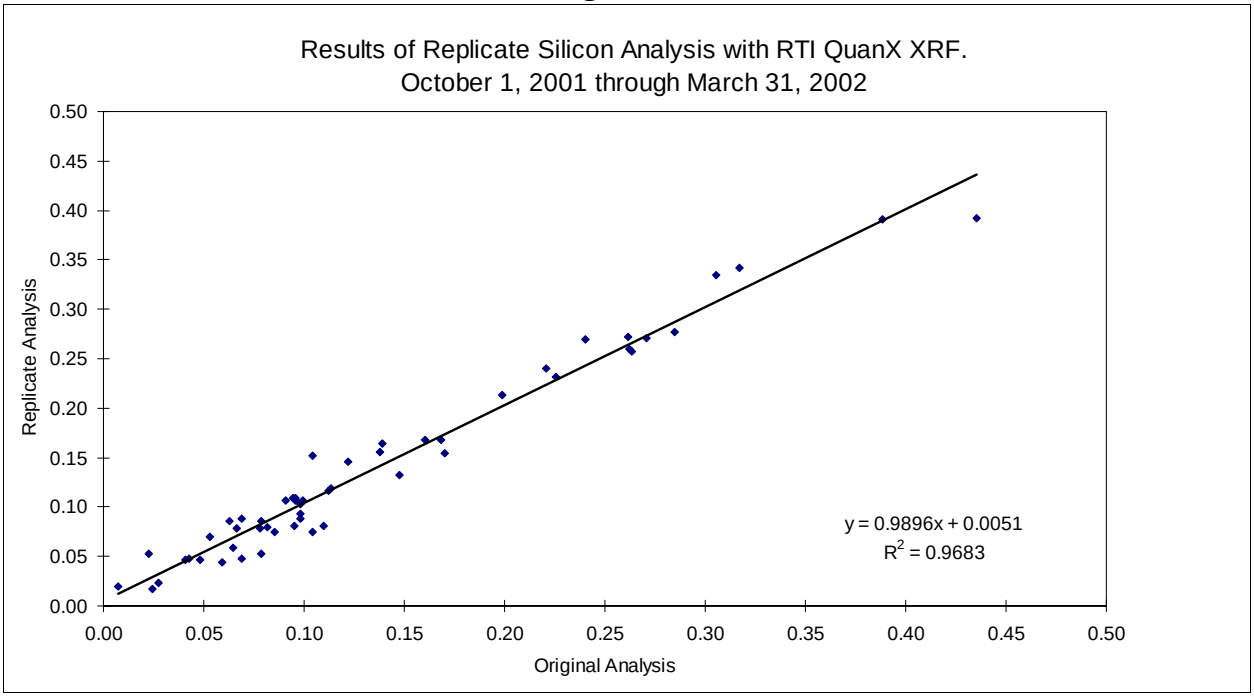


Figure 108

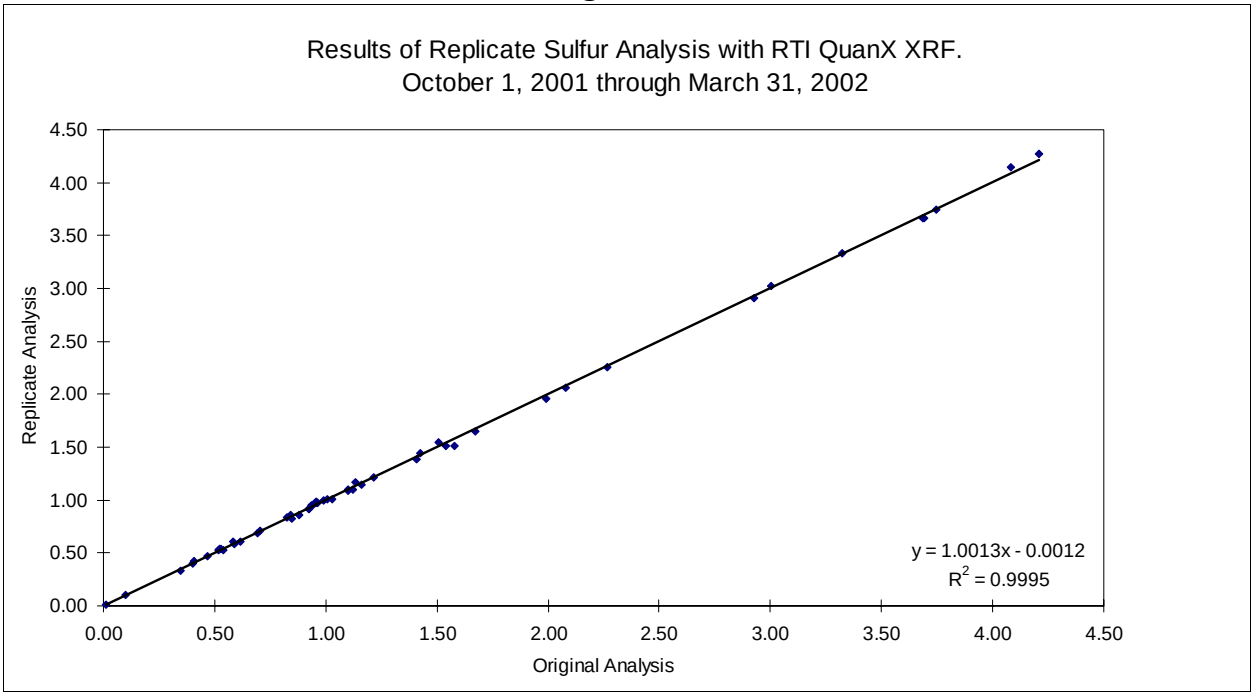


Figure 109

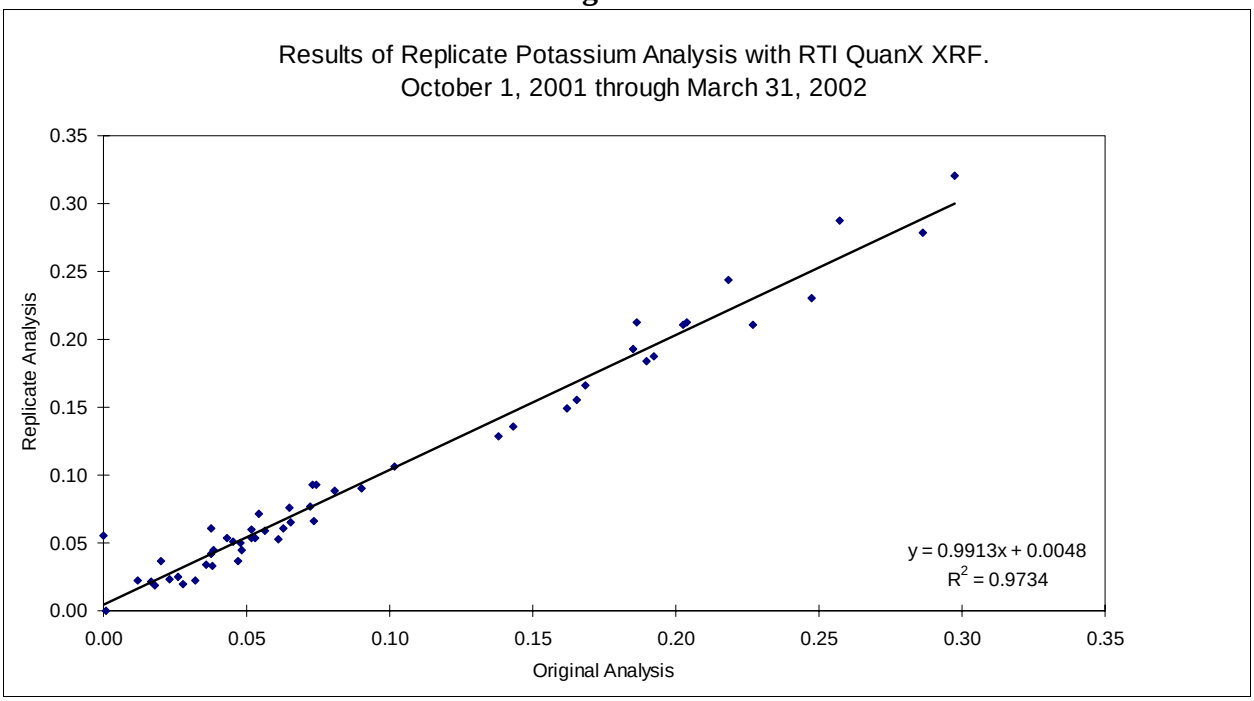


Figure 110

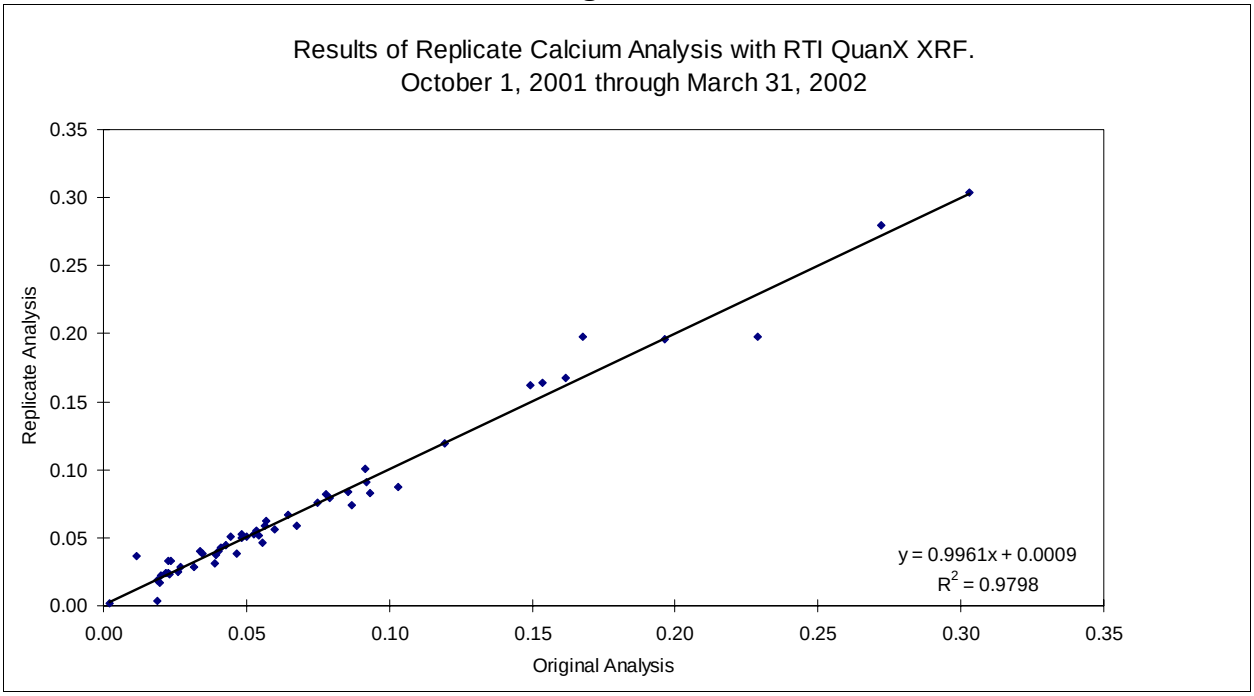


Figure 111

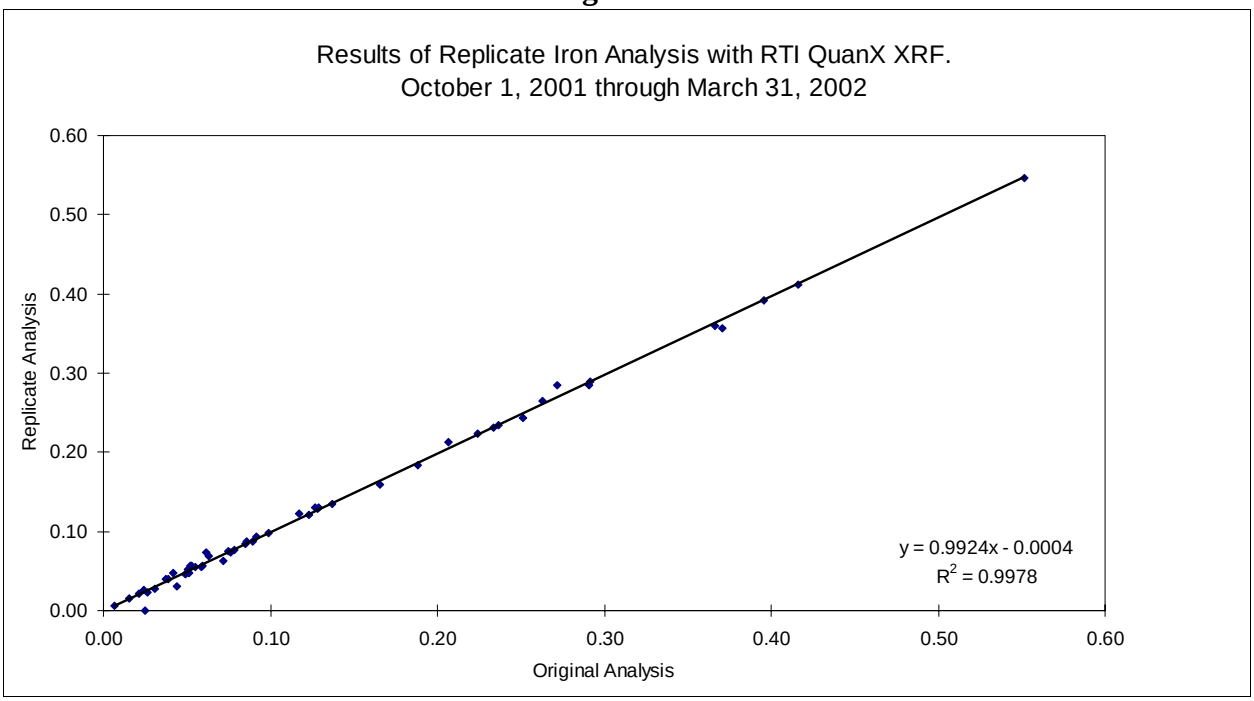
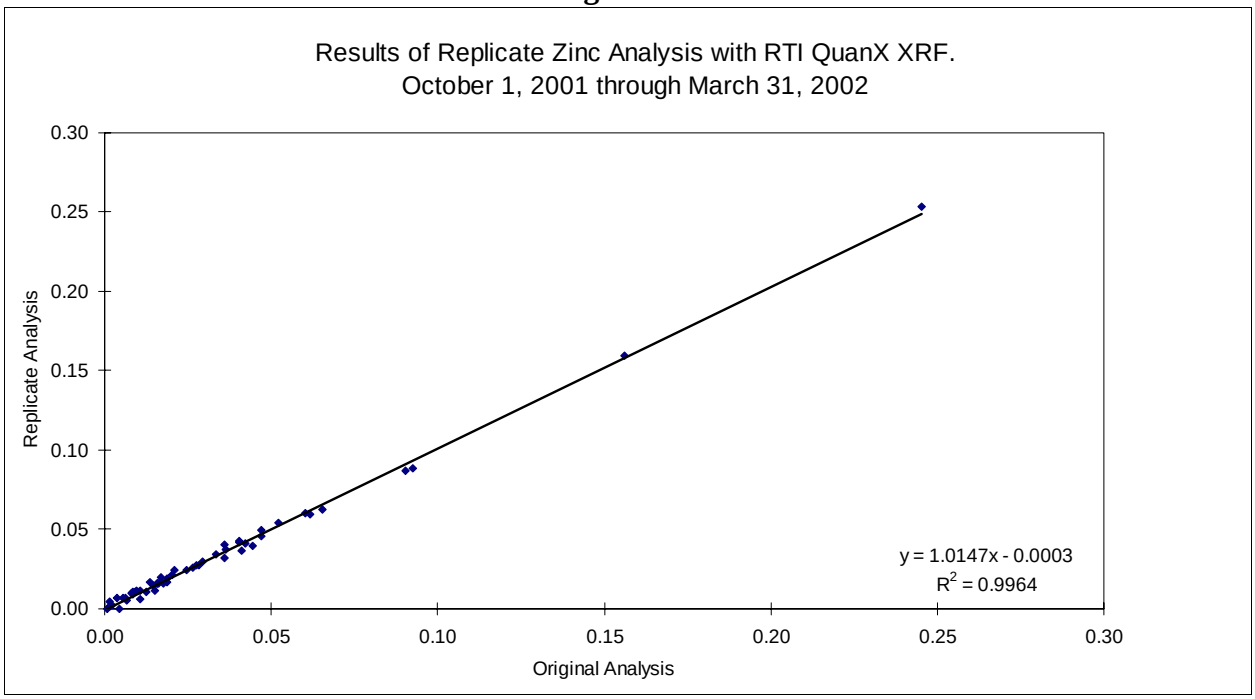


Figure 112



2.4.4.3 Corrective Actions

Several corrective actions were taken after the QuanX system was approved by EPA. First, the system was recalibrated several times when recovery standards fell outside the specified units. Second, the iron standard had to be rerun to obtain the spectrum shape when the iron analysis failed.

Finally, certain QC filters were observed to slide in the filter holders. Thereafter, care was taken to be sure they were secure before starting a run.

2.4.5 Round-Robin Intercomparison Results

Four different XRF instruments have been approved for use in this program. Each instrument was put through a series of tests using NIST reference materials and common, real-world air filter samples. The results were submitted to EPA and each XRF was accepted for use, that is, each XRF was accepted as equivalent to the others. It is important that this equivalency be tested on an ongoing basis. To do this, a set of field filters is being circulated among the laboratories. Approximately 43 filters are in circulation. **Figure 113** presents the results for the filters for each XRF versus the first values measured for these filters, which was done with the Chester Kevex 770 XRF. As noted, there is fairly even scatter around the 1:1 line. Also note that data are provided for the 772 XRF. This is Chester's third XRF, which has not yet been tested for acceptance in the program and, therefore, is not being used. **Figure 114** presents the median value for each element on all filters versus the values for each element on all filters measured with the individual XRFs.

As noted, the Chester Kevex 771 XRF falls below the 1:1 line. Reports of individual batches of field filters analyzed with this instrument show acceptance performance with precision and recovery tests, and also replicate tests. Acceptable performance is also indicated by the data in Section 2.4.1. Chester will address this apparent deviation for the 771 XRF.

2.5 Sample Handling and Archiving Laboratory (SHAL)

2.5.1 Description of QC Checks Applied

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

- Bar-code readers are used to input identification numbers from modules, bins, containers, 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.

Figure 113

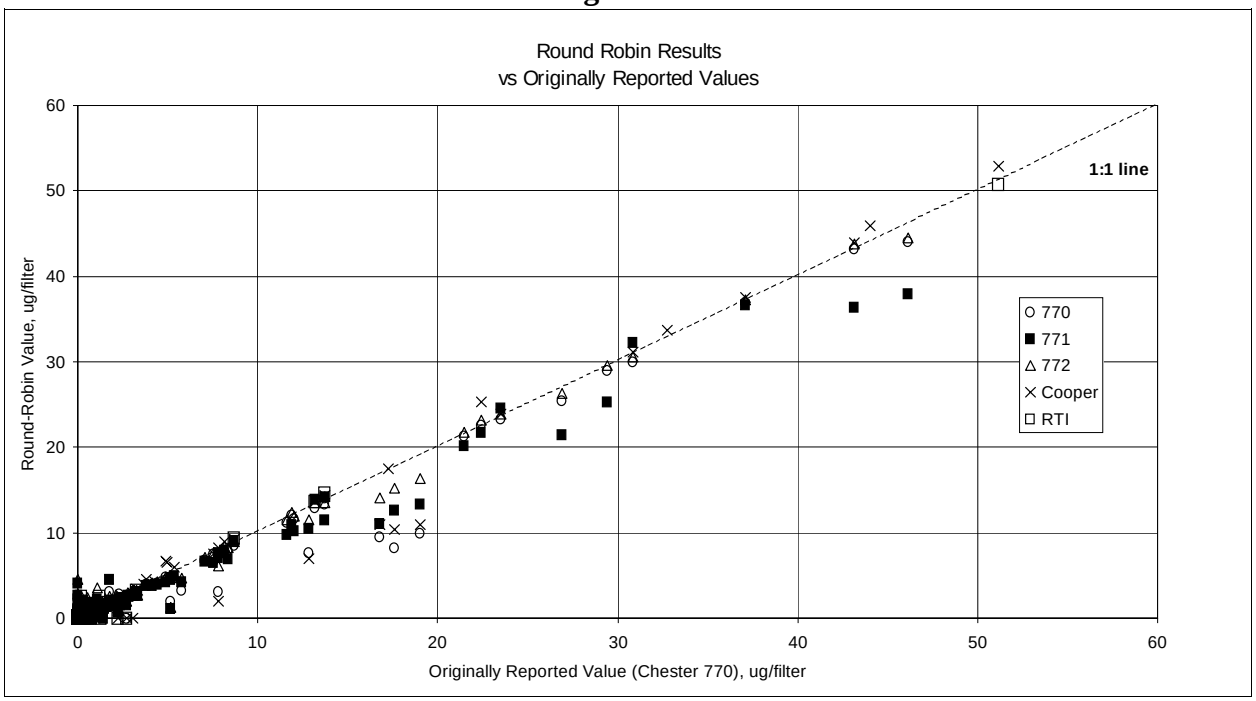
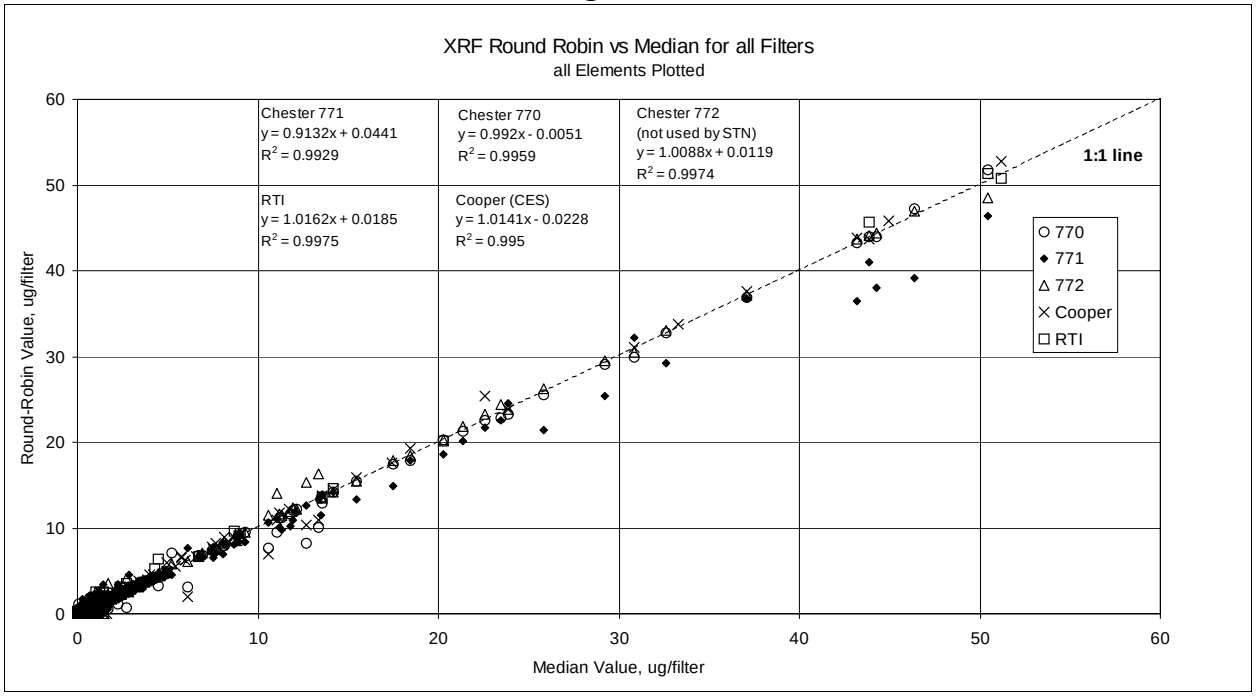


Figure 114



- The training of new employees includes a reciprocal check procedure, in which other SHAL technicians check the contents of each other's coolers before they are closed for shipment. This cross-checking procedure is also used when an excessive number of packing errors is reported.

- 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.

2.5.2 Corrective Actions Taken

Problem: The sites running on a 1-in-6 day schedule were not receiving coolers from RTI in time to swap out with the previous sampling event. **Corrective Action:** RTI modified the schedule for these sites. Now the site operator will receive the next sampling event from RTI prior to the end of the current sampling event. This will allow the site operator to retrieve one sampling event and install filters for the next sampling event all in one trip to the site.

Problem: EPA asked RTI to investigate the high mass values for blank filters. **Corrective Action:** In a continuing effort to lower the levels of analytes found on blank filers, the SHAL has made a significant effort to remove all sources of fibrous materials from the work area. Computers have been moved beneath the work tables. Kimwipes are no longer being used in the cleaning process. Plastic trays are no longer being used in the cleaning process. And the work area is now being cleaned more often.

Problem: Late coolers arriving at RTI causing undue effort to supply all sites on a timely basis. **Corrective Action:** RTI has begun to track late arriving coolers (see Appendix B). Sites that are shipping late on a continuous basis are contacted through the EPA DOPO.

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 the 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 coated with magnesium oxide. They are replaced at the sites at 3-month intervals. The last replacement was in early October 2001; the next scheduled change-out occurred in mid-January, 2002, and again in mid-April, 2002.

MetOne 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. A major change-out of MetOne denuders occurred in July, 2001, for those modules that had been in use for 18 months to that point. RTI ordered uncoated aluminum honeycomb denuder substrates from MetOne, cleaned them with solvent and deionized water, and then coated them with magnesium oxide. This change-out is the first where RTI-coated MetOne denuders were used; all earlier MetOne denuders had been supplied by the manufacturer.

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

No XAD-4 resin coated denuders (for removal of organic vapors) have been ordered thus far under the project by EPA/OAQPS.

The only significant problem encountered in the reporting period of operation has been the occasional receipt of broken or loose denuders. One URG denuder arrived at RTI broken with a note stating it was broken at the site. Arrangements were made to have it repaired at the site's expense.

2.7 Data Processing

2.7.1 Operational Summary

The data processing system has continued to operate with minimal problems, although minor improvements and modifications continue to be made. Significant delays in AIRS reporting resulted from EPA's introduction of the new AIRS AQS. As part of EPA's transition to the new system, there was a three month period in which RTI was unable to post data. In addition the new system required new import procedures and monitor record formats. Meeting these new requirements also introduced significant delays. Details of the problems and their successful resolution are provided in the next section.

2.7.2 Problems and Corrective Actions

2.7.2.1 Posting Delays due to EPA's AIRS Migration

As part of its plan to upgrade AIRS, EPA has implemented a completely new AIRS system. This was multi-year project that completely replaced the computer hardware (going from an IBM mainframe to network of UNIX systems), operating system (TSO to UNIX), database system (ADABASE to ORACLE), and user interface. To enable transfer of historical data from the old mainframe to the new system, EPA shut down the entire AIRS system for about two months (starting in December 2001). During this shutdown RTI was unable to post data to AIRS, resulting in a significant backlog of unposted data.

RTI was notified that AIRS had been restarted in mid February 2002. After starting the new system, RTI had repeated problems with user accounts, access, and passwords. These problems prevented reliable access for an additional month (until March 2002). In addition we have had problems with posting large batches of AIRS records in one job. We currently are posting our monthly reports in batches of around 18,000 records (this takes 5 to 6 batches to post each monthly report). RTI has been able to overcome these obstacles and has posted over 220,000 records into the new system between March and April of 2002. As of April 15, 2002, RTI had entirely caught up on posting all AIRS records for any sites that were in the program at the time of the new system implementation. The status of new sites is described in the next section.

2.7.2.2 Delays in posting new sites resulting from EPA changes in AIRS Monitor record formats

In order to post data from new sites, it is necessary to produce monitor records for each site and post those records in the new AIRS system. It should be noted that there are a set of multiple records required for each of the 64 or 66 parameters measured at each speciation site. In short, each new site added will require over 575 monitor records. With approximately 60 new sites added during the period between AIRS shutdown and resumption, RTI needed to post over 34,000 new monitor records. Although RTI had previously produced a program to generate monitor records for sites from the site information contained in our scheduling database, the new system changes have made this program unusable. While RTI could generate a set of records in the old format, EPA was not able to convert monitor records prepared in the old format to the new format. If this conversion had been possible, RTI would have had no delay in adding the new sites to AIRS (other than that imposed by the AIRS shutdown).

With the large number of monitor records needed for each site, a revised computer program to generate monitor records was clearly needed. Although RTI was hampered by a lack of documentation for the new system, it has successfully prepared such a program. During the

program preparation and testing, information on the site's monitoring objective (not needed for the old AIRS system) was found to be needed for new sites. To assist in obtaining this information, a report to list information needed for AIRS monitor records was prepared. Copies of the report were sent via the DOPO to the affected sites and information returned.

Additionally, during the software preparation, it was found that collection agency codes, which we had previously asked for on our laboratory service request, have been changed to new values in the new AIRS system. RTI obtained (from EPA) a crosswalk table from the old to the new codes and used this to update the information previously sent to us by sites before posting records for new sites.

With the assistance of the DOPOs to obtain the missing information, RTI (as of May 15, 2002) has been able to create monitor records and post all sampling data for 57 of the 60 new sites whose first AIRS data occurred during the AIRS shutdown. The remaining three sites all need either site creation (which must be done by the state) or other additional information to be supplied by the site before RTI can add their monitor records and data to AIRS.

EPA is currently working on obtaining this information and getting the states to create sites, where needed. RTI will post the data from these sites when the information is available and the sites have been created in AIRS.

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 (December 2001), 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 (December 2001).

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

2.8.3 Corrective Actions

No corrective actions were taken during the period October 1, 2001, through March 31, 2002.

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 22 through 27. **Table 24** 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 24. Delivery Batches by Delivery Date

Delivery Batch Number	Report Date	Earliest Sample	Last Sample
22	11/16/01	6/24/01	10/7/01
23	12/14/01	7/16/01	11/9/01
24	1/21/02	8/1/01	12/9/01
25	2/13/02	9/1/01	1/11/02
26	3/14/02	9/25/01	3/6/02
27	4/15/02	10/7/01	4/2/02

3.2 Trip and Field Blanks

The number of blanks run during this period are summarized in **Table 25**. Blank data are not submitted to AIRS, but are reported to the state monitoring agencies and to EPA for statistical analysis. As required by the QAPP, trip blanks are being scheduled at a frequency of one per 30 regular exposure events, and field blanks are scheduled at a rate of one per 10 regular exposures. However, use of the "alternate schedule" at sites where operators do not work on weekends has resulted in a larger proportion of Trip Blanks than required by the QAPP. Some routine samples that are not run are converted to additional Trip Blanks or Field Blanks provided that the site operator indicates that the correct SOP has been followed. Other unexposed samples are designated "unsampled blanks" when it is not clear what protocol the operator followed.

Table 26 summarizes the Trip and Field Blank results for the reporting period. High sodium values are seen starting with Batch 24. These are most likely the result of a manufacturer's batch of nylon filters that was found to be contaminated. RTI has instituted a new filter washing procedure that is contributing to the decline in sodium levels in recent batches. The values for Organic Carbon, which are typically above 10 micrograms per filter, are observed because of adsorption of carbon-containing compounds from the air during storage.

Table 25. Summary of Blanks Reported in Batches 22 through 27.

Blank Type	Delivery Batch	Count of Blanks
FIELD BLANK	22	85
FIELD BLANK	23	73
FIELD BLANK	24	197
FIELD BLANK	25	262
FIELD BLANK	26	294
FIELD BLANK	27	151
TRIP BLANK	22	15
TRIP BLANK	23	95
TRIP BLANK	24	45
TRIP BLANK	25	170
TRIP BLANK	26	79
TRIP BLANK	27	157
UNSAMPLED_BLANK	22	1
UNSAMPLED_BLANK	23	10
UNSAMPLED_BLANK	24	61
UNSAMPLED_BLANK	25	42
UNSAMPLED_BLANK	26	35
UNSAMPLED_BLANK	27	27

Table 26. Average Values for Trip and Field Blanks Summary for the Reporting Period

Trip Blanks							
ANALYSIS	**ANALYTE**	**22**	**23**	**24**	**25**	**26**	**27**
Cations	Ammonium	0.03	-0.01	0.05	0.00	0.06	0.01
Cations	Potassium	0.12	0.13	0.13	0.11	0.08	0.01
Cations	Sodium	0.21	0.56	4.66	5.62	2.41	1.55
Mass - PM2.5	Particulate matter 2.5µ	10.35	13.73	17.56	18.03	15.11	12.55
Nitrate - PM2.5	Nitrate	0.61	0.45	0.60	0.51	0.98	0.62
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.94	0.50	0.71	0.77	0.59	0.43
Nitrate - PM2.5 (MASS/teflon)	Nitrate	1.53	1.45	1.35	1.29	1.62	0.81
Sulfate - PM2.5	Sulfate	0.93	1.06	0.97	0.84	1.26	0.93
OC/EC	Carbonate carbon	0.00	0.00	0.00	0.00	0.00	0.00
OC/EC	Elemental carbon	1.10	1.53	1.88	1.50	1.83	1.61
OC/EC	OCX2	5.63	7.01	7.23	8.05	5.66	4.64
OC/EC	Organic carbon	14.32	12.99	13.70	14.80	13.36	10.95
Field Blanks							
ANALYSIS	**ANALYTE**	**22**	**23**	**24**	**25**	**26**	**27**
Cations	Ammonium	0.02	0.00	0.47	0.04	0.05	0.05
Cations	Potassium	0.07	0.03	0.15	0.05	0.06	0.07
Cations	Sodium	0.31	0.34	0.80	2.75	3.92	2.13
Mass - PM2.5	Particulate matter 2.5u	18.80	11.45	14.63	12.14	14.03	16.57
Nitrate - PM2.5	Nitrate	0.53	0.42	0.46	0.59	0.55	0.63
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.63	0.35	0.49	0.57	0.39	0.29
Nitrate - PM2.5 (MASS/teflon)	Nitrate	1.47	0.16	0.90	1.50	1.14	1.05
Sulfate - PM2.5	Sulfate	1.11	0.93	2.27	0.69	0.82	1.34
OC/EC	Carbonate carbon	0.00	0.00	0.00	0.00	0.00	0.00
OC/EC	Elemental carbon	1.42	2.15	2.08	1.64	1.60	1.69
OC/EC	OCX2	5.77	6.46	5.28	5.56	6.30	4.21
OC/EC	Organic carbon	11.97	12.61	10.83	11.61	13.61	10.15

3.3 Data Completeness and Frequency of AIRS Null Value Codes

Table 27 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). AIRS Null Value Codes indicate exposures that have been invalidated either in the field, in the laboratory, or by the state monitoring agency. Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval.

Table 27. Summary of Percent Valid AIRS Data by Delivery Batch.

LOCATION NAME	POC	22	23	24	25	26	27
20th St. Fire Station	5		100.0%	99.8%	86.7%	100.0%	100.0%
5 Points	5				80.0%	100.0%	99.7%
Air Monitoring, VA DEQ	5	100.0%	91.8%	99.9%	92.0%	100.0%	100.0%
Aldine	5	100.0%	81.8%	99.9%	85.8%	79.5%	95.8%
Allen Park	5	100.0%	100.0%	99.9%	77.1%	88.5%	89.2%
Alpine	5	51.3%	76.6%	91.6%	100.0%	88.0%	98.6%
APCD (Barret)	5				75.0%	100.0%	100.0%
Arendtsville	5	93.0%	100.0%				
Army Reserve Center	5	100.0%	100.0%	100.0%	92.3%	100.0%	100.0%
Arnold	5	41.9%	91.7%	98.8%	87.5%	100.0%	92.4%
Ashland Health Department	5				77.8%	85.7%	100.0%
Athens	5						54.7%
Augusta	5						100.0%
Bakersfield-California Ave	5	98.2%	100.0%	99.2%	91.7%	100.0%	93.5%
Bakersfield-California Ave (Collocated)	6	99.0%	100.0%	99.8%	91.7%	95.7%	93.0%
Bates House (USC)	5				80.0%	100.0%	84.7%
Baxter Water Treatment Plant	5	100.0%	93.3%				
Bayland Park	5	85.0%	82.2%	95.1%	84.2%	100.0%	100.0%
Beacon Hill	6	100.0%	78.8%	100.0%	88.2%	99.7%	100.0%
Bismarck Residential	5	100.0%	99.0%	98.4%	92.3%	100.0%	100.0%
Blair Street	6	100.0%	94.1%	99.7%	91.3%	100.0%	100.0%
Bountiful	5					100.0%	100.0%
Bowling Green-Kereiakes Park	5				84.6%	100.0%	100.0%
Boyd Park	5	100.0%	100.0%	86.3%	91.7%	94.7%	99.3%
Bristol	5				86.5%	99.6%	100.0%
Buffalo	6					100.0%	98.4%
Buncombe County Board of Education	5						100.0%
Burlington	5	100.0%	90.9%	89.9%	90.6%	100.0%	100.0%
Camden	5	100.0%	100.0%	91.7%	91.6%	100.0%	100.0%
Canton Health Dept.	5						100.0%
Capitol	5	75.8%	61.2%	88.8%	86.7%	94.4%	89.2%
Chamizal	5	100.0%	100.0%	94.7%	87.1%	99.4%	100.0%
Channelview	5	99.3%	40.1%	99.7%	72.0%	88.0%	86.2%
Cherry Grove	5					80.0%	100.0%
Chester	5	100.0%	100.0%	99.9%	91.7%	100.0%	100.0%
Chesterfield	5			33.3%	92.3%	100.0%	100.0%
Chickasaw	5						100.0%
Chicopee	5	100.0%	63.1%	93.9%	63.0%	96.2%	80.2%
Children's Park	5						97.9%
Chiwaukee Prairie Site	5						100.0%

LOCATION NAME	POC	22	23	24	25	26	27
Columbus	5						100.0%
Com ED	5	100.0%	100.0%	100.0%	80.0%	96.9%	100.0%
Commerce City	5	66.7%	84.6%	93.8%	87.0%	83.3%	100.0%
Conroe Airport	5	20.8%	51.6%	77.7%	81.7%	93.1%	87.6%
Cornell Elementary	5	98.7%	100.0%	99.8%	92.9%	100.0%	100.0%
Courthouse Annex-Libby	5						100.0%
Covington - University College	5				67.0%	100.0%	100.0%
CPW	5	100.0%	94.0%	99.7%	92.0%	100.0%	100.0%
Crossett	5						100.0%
Decatur	5						83.3%
Deer Park	6	66.7%	75.0%	77.8%	73.3%	85.0%	98.6%
Deer Park (Collocated)	7	52.6%	66.7%	74.7%	80.0%	90.9%	100.0%
Dona Park	5	99.8%	100.0%	93.5%	86.3%	90.6%	100.0%
Douglas	5						93.8%
Dover	5	66.7%	83.3%	99.8%	92.3%	100.0%	100.0%
Durango - Park School	5				66.7%	87.1%	87.2%
El Cajon	5	33.3%	85.7%	88.7%	90.9%	100.0%	100.0%
Elizabeth Lab	5	100.0%	100.0%	92.3%	91.3%	100.0%	100.0%
Ellis County WMA	5						100.0%
Essex	5	100.0%	99.4%	99.8%	91.7%	99.9%	100.0%
Essex - Met One	6					100.0%	91.5%
Fargo NW	5	100.0%	100.0%	98.2%	91.8%	100.0%	100.0%
Firearms Training (FT)	5				100.0%	100.0%	
Florence	5	100.0%	100.0%	99.5%	85.7%	100.0%	100.0%
Fort Meade	5	23.4%		100.0%	99.9%	100.0%	96.7%
Fort Meade - Met One	6						83.3%
Fresno - First Street	5	100.0%	90.4%	92.0%	83.6%	99.5%	82.9%
G.T. Craig	5	100.0%	100.0%	99.7%	91.3%	100.0%	100.0%
G.T. Craig - Collocated	6	100.0%	100.0%	99.6%	92.0%	91.5%	100.0%
Galveston Airport	5	89.6%	100.0%	99.4%	100.0%	99.9%	98.8%
Garden St.	5						100.0%
Garinger High School	5	100.0%	88.2%	86.4%	91.3%	100.0%	87.2%
General Hospital	5						99.2%
Georgetown	5	71.8%	100.0%	89.6%	79.5%	65.3%	100.0%
Grant School Site	5	80.0%	100.0%	99.8%	85.7%	100.0%	100.0%
Greensburg	5	99.4%	100.0%	99.7%	91.7%	100.0%	9.4%
Guaynabo	5	84.7%	91.7%	88.0%	80.0%	53.6%	65.5%
Guiding Hands School	5						57.1%
Gulfport	5	100.0%	100.0%	89.0%	80.3%	100.0%	100.0%
Guthrie	5			99.4%	91.7%	94.7%	100.0%
Hamshire	5	100.0%	95.3%	96.5%	84.2%	100.0%	93.9%
Hattie Avenue	5			100.0%	92.3%	100.0%	100.0%

LOCATION NAME	POC	22	23	24	25	26	27
Hattiesburg	5						100.0%
Hawthorne	5	87.2%	92.6%	91.5%	91.7%	100.0%	100.0%
Haynes Pt.	2		50.0%	97.9%	91.3%	100.0%	100.0%
Hazard - Perry County Horse Park	5				77.1%	100.0%	99.0%
Hazelwood	5	96.5%	100.0%			94.4%	
Head Start	5						100.0%
Hendersonville	5				50.0%	100.0%	100.0%
Hickory	5					100.0%	100.0%
Hinton	5	88.3%	100.0%	100.0%	87.9%	99.8%	100.0%
Houghton Lake	5					71.4%	100.0%
HRM 3#	5	95.1%	95.0%	96.2%	89.8%	100.0%	
IS 52	5		100.0%	91.3%	88.0%	94.1%	100.0%
Jackson Hinds Co.	5			99.5%	78.6%	100.0%	100.0%
Jefferson Elementary (10th and Vine)	5	100.0%	94.5%	93.5%	90.3%	94.0%	100.0%
JFK Center	5	100.0%	100.0%	99.6%	91.3%	100.0%	100.0%
Karnack	5	99.7%	100.0%	98.9%	92.7%	99.5%	100.0%
Kelo	5						49.2%
Kingsport	5				50.0%	100.0%	84.9%
Lake Clifton	5	92.7%	100.0%				
Lake Forest Park	6				81.3%	85.6%	95.8%
Laurel	5						84.7%
Lawrence County	5				100.0%	80.0%	100.0%
Lawrenceville	6	100.0%	83.3%	90.8%	95.7%	90.0%	46.9%
Lenoir Community College	5					100.0%	100.0%
Lewis	5	89.1%	100.0%	98.9%	92.0%	100.0%	100.0%
Lexington Health Department	5				77.8%	87.5%	100.0%
Liberty	5					100.0%	90.9%
Lindon	5	98.4%	100.0%	88.3%	92.2%	100.0%	100.0%
Lockeland School	5						100.0%
London-Laurel County	5						100.0%
Lorain	5						50.0%
Macon	5						93.8%
Mae Drive	5					66.7%	91.1%
Manchester	5					100.0%	100.0%
Manitowoc, Woodland Dunes site	5					100.0%	100.0%
Maple Canyon	6					9.4%	36.5%
Maple Leaf	6		100.0%	99.1%	84.6%	97.9%	100.0%
Mauriceville	5	100.0%	100.0%	100.0%	96.9%	99.5%	100.0%
Mayville Hubbard Township site	5			99.5%	85.7%	100.0%	94.1%
McMillan Reservoir	5	100.0%	100.0%	93.2%	87.2%	88.2%	85.9%
Mendenhall	5					80.0%	100.0%
Mesa County Health Department	5					100.0%	100.0%

LOCATION NAME	POC	22	23	24	25	26	27
Middletown	5				80.0%	99.6%	99.0%
Millbrook	5					100.0%	100.0%
Mingo	5	3.1%		40.6%	58.3%	71.5%	99.6%
MLK	5	100.0%	100.0%	99.8%	85.7%	100.0%	99.1%
MN - Rochester	5			74.2%	80.0%	100.0%	100.0%
MO Supersite Alton	5				77.6%	83.3%	100.0%
MOMS	5						100.0%
Nampa NNC	5		100.0%	98.7%	84.6%	100.0%	100.0%
New Baltimore SuperSite	5					50.0%	83.9%
New Brunswick	5	100.0%	100.0%	99.5%	92.0%	100.0%	100.0%
New Brunswick (Collocated)	6	100.0%	100.0%	99.8%	84.0%	100.0%	100.0%
NLR Parr	5						100.0%
North Birmingham	5	100.0%	100.0%	99.4%	92.0%	100.0%	100.0%
NY Botanical Gardens	6	95.3%	98.9%	93.5%	83.8%	100.0%	100.0%
OCUSA Campus	5						100.0%
Osborn	5	100.0%	69.4%	89.8%	59.1%	100.0%	76.2%
Owensboro - KY Wesleyan College	5				77.8%	100.0%	100.0%
Paducah Middle School	5				77.8%	100.0%	100.0%
Peoria Site 1127	5	100.0%	100.0%	99.9%	86.8%	100.0%	100.0%
PerkinstownCASNET	5				33.3%	100.0%	100.0%
PHILA - AMS Laboratory	7			99.9%	91.3%	94.4%	100.0%
Philips	5	100.0%	92.9%	99.8%	91.7%	100.0%	100.0%
Phoenix Supersite	7	100.0%	82.3%	89.1%	86.7%	94.4%	92.3%
Pinnacle State Park	5	62.5%	82.7%	97.4%	90.9%	100.0%	100.0%
Platteville	5					78.8%	100.0%
Portland - SE Lafayette	6	98.7%	84.1%	95.3%	87.0%	100.0%	100.0%
Portsmouth	5		100.0%	99.8%	81.6%	93.6%	93.6%
Providence	5				91.7%	100.0%	100.0%
Queens College	6	84.9%	93.0%	94.4%	80.2%	99.5%	100.0%
RBD	5					100.0%	100.0%
Reno	5	100.0%	100.0%	92.9%	99.6%	87.5%	100.0%
Riverside-Rubidoux	5	99.0%	100.0%	92.9%	92.0%	100.0%	99.8%
Riverside-Rubidoux (Collocated)	6	100.0%	100.0%	92.9%	91.7%	99.6%	100.0%
Roanoke	5				86.7%	100.0%	100.0%
Rochester Fire Headquarters	5	100.0%	90.9%	87.3%	91.3%	94.4%	100.0%
Rome	5						93.8%
Roxbury (Boston)	5	46.1%	72.7%	86.1%	92.3%	94.1%	100.0%
Roxbury (Boston) - collocated	6						90.0%
Sacramento - Del Paso Manor	5	66.7%	100.0%	99.4%	87.5%	93.8%	92.3%
San Jose - Fourth Street	5	85.7%	92.3%	99.8%	91.7%	100.0%	100.0%
Sault Ste Marie	5		66.7%	63.1%	90.9%	100.0%	100.0%
Savannah	5						93.8%

LOCATION NAME	POC	22	23	24	25	26	27
Searcy	5						100.0%
Seney NWR	5				87.6%	99.9%	96.7%
SER-DNR Headquarters	5	100.0%	100.0%	99.7%	92.0%	100.0%	100.0%
Shenandoah High School	5						100.0%
Simi Valley	5				84.1%	99.2%	100.0%
South DeKalb	5	83.9%	87.9%	98.2%	91.7%	94.1%	100.0%
Southfield	5	100.0%	80.0%	99.7%	81.8%	79.9%	100.0%
Southwick Community Center	5						97.2%
Springfield Pumping Station	5	98.0%	77.0%	98.2%	92.3%	100.0%	98.4%
St Theo	6					100.0%	100.0%
St. Paul Harding	5			99.5%	91.7%	100.0%	100.0%
Sun Metro	5	100.0%	100.0%	92.9%	100.0%	100.0%	95.2%
Taft	5				75.0%	97.3%	97.8%
Tallahassee Community College	5					100.0%	80.0%
Taylors Fire Station	5				83.3%	100.0%	100.0%
Toledo Airport	5						100.0%
TRNP - NU	5					100.0%	84.9%
UTC	5				66.7%	88.7%	100.0%
Washington Park	5	100.0%	100.0%	99.9%	91.3%	99.2%	100.0%
Waukesha, Cleveland Ave. Site	5					75.0%	100.0%
Whiteface	5	98.9%	99.2%	88.1%	87.8%	94.7%	100.0%
Wilbur Wright Middle School	5				83.3%	100.0%	100.0%
William Owen Elem. School	5					100.0%	100.0%
Woolworth St	5	97.5%	98.3%	97.1%	79.7%	91.5%	84.0%
Wylam	5				91.7%	100.0%	100.0%