Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-3.3

DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

June 1999

Method IO-3.3

Acknowledgments

This Method is a part of *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air* (EPA/625/R-96/010a), which was prepared under Contract No. 68-C3-0315, WA No. 2-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development, were responsible for overseeing the preparation of this method. Other support was provided by the following members of the Compendia Workgroup:

- James L. Cheney, U.S. Army Corps of Engineers, Omaha, NE
- Michael F. Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

Author(s)

- Bob Kellog, ManTech, RTP, NC
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Peer Reviewers

- David Brant, National Research Center for Coal and Energy, Morgantown, WV
- John Glass, SC Department of Health and Environmental Control, Columbia, SC
- Roy Bennet, U.S. EPA, RTP, NC
- Charles Lewis, EPA, RTP, NC
- Ray Lovett, West Virginia University, Morgantown, WV
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Method IO-3.3
Determination of Metals in Ambient Particulate Matter Using
X-Ray Fluorescence (XRF) Spectroscopy

TABLE OF CONTENTS

[This page intentionally left blank.]

Chapter IO-3
CHEMICAL SPECIES ANALYSIS
OF FILTER-COLLECTED SPM

Method IO-3.3
DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING
X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

1. Scope

1.1 During a span of more than two decades, the U. S. Environmental Protection Agency (EPA) has developed and applied x-ray fluorescence (XRF) to the analysis of ambient and source aerosols using both energy and wavelength dispersive spectrometers. Inorganic Compendium Method IO-3.3 briefly describes the agency's experience with XRF and informs the reader of its capability in elemental aerosol analysis and attempts to give a brief account of what is involved in its application. The procedures described have been in a continual state of evolution beginning with those in use on a special purpose spectrometer designed by Lawrence Berkeley Laboratory (LBL) and eventually applied to a commercially available instrument manufactured by Kevex. It is for the Kevex spectrometer to which this method applies.

1.2 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by Federal, state, and local governments is based on these data. Accurate measures of toxic air pollutants at trace levels is essential to proper assessments.

1.3 Suspended particulate matter (SPM) in air generally is considered to consist of a complex multi-phase system consisting of all airborne solid and low vapor pressure, liquified particles having aerodynamic particle sizes ranging from below 0.01 microns to 100 (0.01 Fm to 100 Fm) microns and larger. Historically, measurement of SPM has concentrated on total suspended particulates (TSP) with no preference to size selection.

1.4 The most commonly used device for sampling TSP in ambient air is the high-volume sampler, which consists essentially of a blower and a filter, and which is usually operated in a standard shelter to collect a 24-hour sample. The sample is weighed to determine concentration of TSP and is usually analyzed chemically to determine concentration of various inorganic compounds. When EPA first regulated TSP, the National Ambient Air Quality Standard (NAAQS) was stated in terms of SPM with aerodynamic particle size of < 100 Fm captured on a filter as defined by the high-volume TSP sampler. Therefore, the high-volume TSP sampler was the reference method. The method is codified in 40CFR50, Appendix B.

1.5 More recently, research on the health effects of TSP in ambient air has focused increasingly on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter of < 10 Fm. These particles are referred to as PM_{10}. It is now generally recognized that, except for toxic materials, it is this PM_{10} fraction of the total particulate loading that is of major significance in health effects. The reference method for PM_{10} is codified in 40CFR50, Appendix J and specifies a measurement principle based on extracting an ambient air sample with a powered sampler that incorporates inertial separation of PM_{10} size range particles and collection of these particles on a filter for a 24-hour period. Again, the sample is weighed to determine concentration of PM_{10} and is usually analyzed chemically to determine concentration of various inorganic compounds.

1.6 Further research now strongly suggests that atmospheric particles commonly occur in two distinct modes, the fine (< 2.5 µm) mode and the coarse (2.5 to 10.0 Fm) mode. The fine or accumulation mode (also termed the respirable particles) is attributed to growth of particles from the gas phase and subsequent agglomerization, whereas the coarse mode is made up of mechanically abraded or ground particles. Because of their initially gaseous origin, the fine range of particle sizes includes inorganic ions such as sulfate, nitrate, and ammonium as well as combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Samplers which separate SPM into two size fractions of 0-2.5 µm and 2.5-10 µm are called dichotomous samplers. In 1997, the EPA promulgated a new standard with fine particles. The new $PM_{2.5}$ standard replaced the previously NAAQS for PM_{10}.

1.7 Airborne particulate materials retained on a sampling filter, whether TSP, PM_{10}, $PM_{2.5}$, or dichotomous size fractions, may be examined by a variety of analytical methods. This method describes the procedures for XRF analysis as the analytical technique. The XRF method provides analytical procedures for determining concentration in ng/m^3 for 44 elements that might be captured on typical filter materials used in fine particle or dichotomous sampling devices. With the sample as a thin layer of particles matrix effects substantially disappear so the method is applicable to elemental analysis of a broad range of particulate material. The method applies to energy dispersive XRF analysis of ambient aerosols sampled with fine particle (< 2.5 µm) samplers, dichotomous and VAPS (versatile air pollution sampler) samplers with a 10 µm upper cut point and PM_{10} samples.

1.8 The analysis of ambient aerosol samples captured on filterable material should be performed by a scientist that has been trained in energy dispersive x-ray fluorescence spectroscopy and its associated data processing system. The training should be performed by a scientist with an advance degree in the physical sciences with a minimum of 5 years experience in x-ray spectroscopy.

2. Applicable Documents

2.1 ASTM Documents

- D4096 Application of High Volume Sample Method For Collection and Mass Determination of Airborne Particulate Matter.
- D1356 Definition of Terms Related to Atmospheric Sampling and Analysis.
- D1357 Practice For Planning the Sampling of the Ambient Atmosphere.

2.2 U.S. Government Documents

- U.S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance,* EPA-600/R-94/038a.
- U.S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- "Reference Method for the Determination of Particulate Matter in the Atmosphere," *Code of Federal Regulations*, 40 *CFR* 50, Appendix B.
- "Reference Method for the Determination of Particulate Matter in the Atmosphere (PM_{10} Method)," *Code of Federal Regulations*, 40 *CFR* 50, Appendix J.
- "1978 Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air." *Federal Register* 43 (194):46262-3.
- *Test Methods for Evaluating Solid Waste, Method 9022*, EPA Laboratory Manual, Vol. 1-A, SW-846.

2.3 Other Documents

- Kevex XRF TOOLBOX II Reference Manual
- Kevex 771-EDX Spectrometer User's Guide and Tutorial

3. Summary of Method

[Note: This method was developed using the Kevex spectrometer. EPA has experience in the use of the Kevex spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals over the last two decades. The use of other manufacturers of x-ray spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 12 through 14 of Method 10-3.3 are met. However, modifications to Compendium Method IO-3.3 procedures may be necessary if another commercial x-ray spectrometer is used.]

The method described is x-ray fluorescence applied to PM_{10}, fine (< 2.5 μm) and coarse (2.5-10 μm) aerosols particles captured on membrane filters for research purposes in source apportionment. The samplers which collect these particles are designed to separate particles on their inertial flow characteristics producing size ranges which simplify x-ray analysis. The instrument is a commercially available Kevex EDX-771 energy dispersive x-ray spectrometer which utilizes secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements. Spectra are acquired by menu-driven procedures and stored for off-line processing. Spectral deconvolution is accomplished by a least squares algorithm which fits stored pure element library spectra and background to the sample spectrum under analysis. X-ray attenuation corrections are tailored to the fine particle layer and the discrete coarse particle fraction. Spectral interferences are corrected by a subtractive coefficient determined during calibration. The detection limits are determined by propagation of errors in which the magnitude of error from all measured quantities is calculated or estimated as appropriate. Data are reported in ng/m^3 for all samples. Comprehensive quality control measures are taken to provide data on a broad range of parameters, excitation conditions and elements.

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by federal, state and local governments are based on these data.

4.2 Inhalable ambient air particulate matter (< 10 μm) can be collected on Teflon® filters by sampling with a dichotomous sampler and analyzed for specific metals by X-ray fluorescence. The dichotomous sampler collects particles in two size ranges - fine (< 2.5 μm) and coarse (2.5-10 μm). The trace element concentrations of each fraction are determined using the nondestructive energy dispersive X-ray fluorescence spectrometer.

4.3 The detectability and sensitivity of specific elements may vary from instrument to instrument depending upon X-ray generator frequency, multichannel analyzer sensitivity, sample interferences, etc.

5. Definitions

[Note: Definitions used in this document are consistent with ASTM Methods. All pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Accuracy. The agreement between an experimentally determined value and the accepted reference value.

5.2 Attenuation. Reduction of amplitude or change in wave form due to energy dissipation or distance with time.

5.3 Calibration. The process of comparing a standard or instrument with one of greater accuracy (smaller uncertainty) for the purpose of obtaining quantitative estimates of the actual values of the standard being calibrated, the deviation of the actual value from a nominal value, or the difference between the value indicated by an instrument and the actual value.

5.4 10 μm Dichotomous Sampler. An inertial sizing device that collects suspended inhalable particles (< 10 μm) and separates them into coarse (2.5-10 μm) and fine (< 2.5 μm) particle-size fractions.

5.5 Emissions. The total of substances discharged into the air from a stack, vent, or other discrete source.

5.6 Filter. A porous medium for collecting particulate matter.

5.7 Fluorescent X-Rays (Fluorescent Analysis). Characteristic X-rays excited by radiation of wavelength shorter than the corresponding absorption edge.

5.8 Inhalable Particles. Particles with aerodynamic diameters of < 10 μm which are capable of being inhaled into the human lung.

5.9 Interference. An undesired positive or negative output caused by a substance other than the one being measured.

5.10 Precision. The degree of mutual agreement between individual measurements, namely repeatability and reproducibility.

5.11 Standard. A concept that has been established by authority, custom, or agreement to serve as a model or rule in the measurement of quantity or the establishment of a practice or procedure.

5.12 Traceability to NIST. A documented procedure by which a standard is related to a more reliable standard verified by the National Institute of Standards and Technology (NIST).

5.13 Uncertainty. An allowance assigned to a measured value to take into account two major components of error: (1) the systematic error, and (2) the random error attributed to the imprecision of the measurement process.

5.14 Chi-square. A statistic which is a function of the sum of squares of the differences of the fitted and measured spectrum.

5.15 Fluorescer. A secondary target excited by the x-ray source and in turn excites the sample.

5.16 FWHM. Full width at half maximum, a measure of spectral resolution.

5.17 NIST. National Institute of Standards and Technology.

5.18 Shape. The actual shape of a background corrected pulse height spectrum for an element.

5.19 SRMs. Standard reference materials.

5.20 Teflo®. Trade name of a Teflon filter.

5.21 Unknown. A sample submitted for analysis whose elemental concentration is not known.

5.22 XRF. X-ray fluorescence.

6. Description of Spectrometer

The x-ray analyzer is a Kevex EDX-771 energy dispersive spectrometer with a 200 watt rhodium target tube as an excitation source. The machine has multiple modes of excitation including direct, filtered direct, and secondary which utilizes up to 7 targets or fluorescers. To minimize radiation damage to delicate aerosol samples only the secondary mode is used. Table 1 provides a listing of the fluorescers and the elements which they excite associated with energy dispersive spectrometers. Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background. The detector is cryogenically cooled lithium-drifted silicon with a 5 µm Be window and a resolution of 158 eV at Fe K_α and comes with two manually changeable collimators. A 16 position rotating wheel accommodates the samples and provides sample changing.

The machine is operated by procedure files (or programs) written in Kevex's proprietary Job Control Language (JCL) which runs in a Windows 3.1 environment and provides setting of the analytical conditions and data acquisition. Using the JCL language, procedures have been written in-house to perform all the

functions necessary to acquire spectra and to assign to them file names in a structured manner to facilitate future spectral processing. These procedures are invoked in menu form.

7. Caveats

7.1 The type of samplers mentioned in Section 1.7 must be operated in accordance with Inorganic Compendium Method IO-2.2 Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, or severe errors in x-ray analysis may occur. For example, errors in flow rate will not only give erroneous volumes but will cause a more serious condition of altering the cut points upon which the coarse particle x-ray attenuations are based. If samples are intended for x-ray analysis then the sampling protocol must conform to the constraints inherent within this method. Furthermore, the type of filter on which the sample is collected is very important. In general, thin membrane filters (Teflo® and Nuclepore®) are required so that the background is low and penetration of particles into the matrix of the filter is small. Thick depth filters such as quartz or glass fiber not only have high background but also allow particles to penetrate into the matrix of the filter - a condition which the spectral processing program cannot accommodate.

7.2 Some internal contaminations consisting of Sn, Ni, Cu and Fe are present which sometimes appear in blanks. Routine analysis of blanks with samples will give the magnitude of the correction necessary to compensate for this.

7.3 In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.

7.4 An inherent problem with a helium atmosphere is the diffusion of He through the detector window causing detector degradation and necessitating replacement. A lifetime of 3 to 4 years is expected.

7.5 Due to an x-ray leak around the anode area of the x-ray tube the head must be shielded with additional lead cladding to prevent unwanted excitation of internal parts. This leak posed no threat to personnel but caused high background when operating at the maximum voltage. The additional shielding proved very effective at improving detection limits.

7.6 Experience with wavelength dispersive spectrometers (WDXRF) has shown good agreement with energy dispersive instruments (EDXRF) over a broad range of elements. In spite of this agreement and the simpler spectral processing requirements of wavelength machines the preference remains with energy dispersive equipment for a variety of reasons. The very low power tubes in EDXRF machines leaves the sample intact and unaffected whereas in WDXRF the high power excitation embrittles the filter itself after 15 - 30 min exposure raising the possibility of altering particle morphology. This is a concern if electron microscopy is considered. Also, the vacuum environment, necessary for WDXRF, causes loss of some volatile materials.

8. Sample Preparation

8.1 Sample preparation begins with the correct operation of the samplers employed. Inorganic Compendium Method IO-2.2, Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, covering the option of the samplers in the field and subsequent collection of ambient air particles on 37-mm Teflon® filter for XRF analysis. One of the greatest advantages of analyzing aerosols by XRF is that the sample can, in theory, be collected in a manner most advantageous to XRF by sampling for a duration that produces an ideal mass loading on the filter. An approximate maximum target mass is about 100 μg/cm² although much less is often collected in many environments.

8.2 The types of filters used for aerosol sampling are 37-mm or 47-mm Teflo® with a pore size of 2 microns and, if electron microscopy is planned for the coarse fraction, then a 0.6 micron pore size Nuclepore® filter is used. The sample should be collected on the side of the Teflo® filter with the supporting ring to maintain the proper distance between the sample and detector during analysis. A properly collected sample will be a uniform deposit over the entire collection area of at least 25-mm in diameter. Samples which are not uniformly deposited over the whole collection area are not quantitatively analyzable.

8.3 All filter samples received for analysis are removed with tweezers from their container and are checked for any invalidating conditions such as holes, tears, or a non-uniform deposit which would prevent quantitative analysis. If such a condition is found the sample is noted as invalid on the XRF data entry form; data from such samples are not reported. Teflo® filters are easily handled because of the supporting ring, however, Nuclepore® filters must have a supporting ring applied to them (after gravimetric assay) to help maintain their flatness and to securely hold them in the frame. The sample is then placed in a custom-designed commercially available two-part sample frame which snaps together holding the filter securely in place.

9. Spectral Acquisition and Processing

9.1 Spectra are acquired in sets of 15 samples each. Up to 7 spectra are acquired for each sample depending on how many secondary excitation targets are selected. Utilizing all seven fluorescers requires approximately 4 hours machine time for 44 elements analyzed plus atmospheric argon.

9.2 Elemental intensities are determined by spectral deconvolution with a least squares algorithm which utilizes experimentally determined elemental shape functions instead of the mathematical Gaussian function. This approach has been successfully implemented for many years on an earlier machine and is described in Section 15, Citation 10. Since the spectral shape is not a pure Gaussian the experimental shapes are a more realistic representation of a spectrum. In addition to this library of elemental shape spectra there is also a background shape spectrum for each of the types of filters. It is assumed that the background on an unknown sample is due to the filter and not to the sample. (This is one of the reasons for avoiding heavily loaded filters.) The least squares algorithm synthesizes the spectrum of the sample under analysis by taking a linear combination of all the elemental shapes spectra and the background shape spectrum. The coefficients on the linear combination of elemental shapes and background spectra are scaling factors determined by minimizing chi-square thus producing the best fit possible by least square minimization. Values of the chi-square statistic are calculated for each sample and fluorescer to give an indication of the quality of the fit.

9.3 X-ray attenuation corrections are performed as described in Section 15, Citation 10 and are briefly described here. The mass absorption coefficients for the layer of fine particles is based on a typical composition of ambient aerosol particles so the actual x-ray attenuations on a given sample are simply a function of the mass loading. Coarse particle attenuations are more complex in that they are based on x-ray

attenuation by spherical particles with compositions of common crustal minerals with various size distributions. An average attenuation and uncertainty for each coarse particle element is based on this broad range of crustal minerals and is therefore a one-time calculation giving an attenuation factor useable for all subsequent coarse (2.5-10 µm) particle analyses. This treatment assumes low coarse particle loading so that the particles do not shadow one another - yet another reason for assuring that the sample mass loading is not too high. Attenuation corrections on PM_{10} particles are deduced from elemental concentration data from samples taken with collocated PM_{10} and dichotomous samplers.

9.4 The need for interference corrections arises from overlaps that are not deconvoluted by the least squares algorithm. This can best be illustrated by an example: Barium and titanium are analyzed by the gadolinium and iron fluorescers, respectively. The barium L x-rays overlap with the K x-rays of titanium and require an interference correction because the elements analyzed by gadolinium do not include titanium. The interference correction technique is described by Gilfrich in Section 15, Citation 29. The interference coefficient, determined during calibration, represents the fraction of the concentration of an affecting element (barium in the present example) which must be subtracted from the concentration of the affected element concentration (titanium) to compensate for the interference.

9.5 When samples are collected by the dichotomous or other samplers using virtual impaction, an additional correction must be employed because these type of samplers do not perfectly separate the fine and coarse particles. Due to virtual impaction requirements, about 10% of the fine particle mass is deposited on the coarse filter. Therefore, the attenuation corrections used for the particles on the coarse filter "over-correct" the attenuation because of these residual fines on the coarse filter. These effects are compensated for by the flow fraction correction.

10. Data Reporting

[Note: In other Inorganic Compendium methods, the authors have provided detailed examples of calculations involving final metal concentration (in terms of µg/m³) from filterable materials. However, due to the nature of overlapping spectra which is characteristic of energy dispersive spectormeters, calculations are required to be performed by computer due to the complexity of the deconvolution of the recorded spectra which uses least square algorithm involving experimentally determined elemental shape functions instead of the mathematical Gaussian function. To perform by hand would require second order calculus and considerable time and manpower. Thus, the application of a computer is mandatory to determine elemental intensities and the elemental concentrations by a polynomial fit using a model based on the fundamentals of x-ray physics process (see Section 11 for further explanation).]

The two most important data output files are an ASCII file which contains a recapitulation of the field data and the final sample concentrations in ng/m³ and a Lotus file with only the sample data. An example printout of a fine/coarse sample pair is shown in Table 3.

The uncertainty reported with each concentration is a 1F (68% confidence level) uncertainty and is determined by propagating the errors given in Section 12. Elements with concentrations below 3 times the uncertainty are flagged with an asterisk (*) on the printed record. If the true elemental concentration is zero then the fitting procedure implies that negative and positive results are equally probable. Therefore, negative numbers may be reported.

11. Calibration

11.1 Calibration is performed only when a change in fluorescers or x-ray tubes or detector is made or a serious malfunction occurs requiring significant repairs. Calibration establishes the elemental sensitivity factors and the magnitude of the interference or overlap coefficients. It takes approximately 2 weeks to complete a calibration.

11.2 Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. There are two types of calibration standards in use. One type consists of thin films deposited on Nuclepore substrates (Micromatter Co., Eastsound, WA). These standards are available for almost all the elements analyzed ranging in atomic number from 11 (Na) to 82 (Pb) with deposit masses gravimetrically determined to ± 5%. Another type consists of polymer films that contain known amounts of two elements in the form of organo-metallic compounds dissolved in a polymer and are not commercially available but their preparation is described in Section 15, Citation 9. These standards have been prepared for elements with atomic numbers above 21 (titanium and heavier). The same set of standards is used every time the spectrometer is calibrated. The standards are sufficiently durable to last many years, however occasionally one must be replaced due to accidents in handling. Approximately 200 calibration standards for 44 elements are in use (see Table 4.) and the acquisition of their spectra requires several days.

11.3 The background files which are used for background fitting are created at calibration time. Thirty clean Teflo® and Nuclepore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.

11.4 The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum. For this purpose it is not necessary for the concentration of the standard to be known - only that it be pure. A slight contaminant in the region of interest in a shape standard can have serious effect on the ability of the least squares fitting algorithm to fit the shapes to the unknown. For this reason the Se and elemental As standards, whose compounds are volatile, are kept in separate plastic bags in a freezer to prevent contamination of other standards; the Au standard, which will slowly amalgamate with atmospheric Hg, is kept in a desiccator. The shape standards are acquired for sufficiently long times to provide a large number of counts in the peaks of interest. It is these elemental shapes spectra that are fitted to the peaks in an unknown sample during spectral processing.

11.5 The spectra from the calibration standards are deconvoluted to get elemental intensities as described in Section 9.2. Using these intensities and the elemental concentration in the standards the sensitivities are determined by a polynomial fit using a model based on the fundamentals of the x-ray physics process as well as measurements on the calibration standards. This approach allows the calculation of sensitivities for elements for which there are poor or no standards such as volatile ones like Se and elemental As well as improving on elements with good standards.

11.6 The overlap coefficients are determined during calibration and represent the extent of interference that exists between overlapping spectral peaks. During calibration an affecting element (barium, to continue with the example of Section 9.4) is measured both at the analyte line peak for barium and at the titanium peak. The coefficient is expressed as the ratio of the concentration of the affected element (titanium) to the

concentration of the affecting element (barium). All elements requiring overlap coefficient determination are calculated in this manner.

12. Detection Limits

The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty ($\pm$ 5%); long term system stability ($\pm$ 5%); peak and background counting statistics; uncertainty in attenuation corrections; uncertainty in overlap corrections; uncertainty in flow rate; and uncertainty in coarse fraction due to flow fraction correction (paired samples only). Table 2 outlines typical 1F (68% confidence level) detection limits on a Teflo® blank for fine particles and a Nuclepore® blank for coarse (2.5 µm-10 µm) particles. These detection limits are defined in terms of the uncertainty in the blank. This ignores the effect of other elements which generally is small except for the light elements (potassium and lower) where overlapping spectral lines will increase the detection limit.

[Note: The difference in the detection limits between the two filters in Table 2 is due more to the difference in sensitivity to fine and coarse particles and less to the difference in filter material.]

Higher confidence levels may be chosen for the detection limits by multiplying the 1F limits by 2 for a 2F (or 95% level) or by 3 for 3F (or 99.7% level). To convert the detection limits to more useful units one can use the typical deposit areas for 37-mm and 47-mm diameter filters of 6.5 cm² and 12.0 cm² respectively.

13. Quality Control

13.1 A comprehensive quality control program is in effect consisting of many measured parameters covering all measurement conditions and automatically produces control charts for all such measurements. All plotted data are normalized to the mean to give a rapid assessment of relative change.

13.2 Run-time quality control gives an indication of instrument performance at the time of data acquisition by measurements on stable qualitative standards. The parameters which are measured and their significance are: peak areas (monitors change in sensitivity), background areas (monitors contamination or background changes), centroid (monitors gain and zero adjustment to insure that spectra are assigned the correct channel), and FWHM, (monitors degradation of the detector resolution). These four parameters are measured for elements ranging from sodium to lead and include atmospheric argon. An example of plots of run-time QC data are illustrated in Figures 1 through 4 and Table 5, for the target and tolerance values for the parameters measured.

13.3 In addition to the run-time quality control procedure the analysis results of Standard Reference Materials SRM1833 and SRM1832 are included in the data reports. These results provide an overall check of the spectral processing program for the elements which are certified in the standards. The sole purpose of the SRMs is to provide a quality control measure; the standards are not used for calibration. Typical results of these SRMs are documented in Tables 6 and 7, and plotted in Figure 5.

13.4 The run-time quality control procedures serve as an indicator of possible emerging problems by flagging deviations greater than 3 tolerance units as defined for each element in Table 5. Persistently increasing trends are investigated to determine their cause(s) before they impact the results of SRM analyses.

13.5 The acceptance criteria of results for the elements certified in the SRMs is that the uncertainty intervals for the analytical results and those of the certified values should overlap each other. If any element fails this then the run of unknowns is repeated. Repeated failures indicate the need for recalibration.

13.6 A value for chi-square is calculated and reported with the data to indicate the quality of the fit. Chi-square values that are much larger than 1.0 indicate a problem in the fitting procedure. Changes in detector resolution or gain in the amplifier produce large values for chi-square; however such changes would be detected by the run-time quality control procedure. Also, large chi-square values can accompany results for heavily loaded filters even though the relative errors are typical. In addition, elements analyzed by the titanium and the iron fluorescers may experience large chi-square values due to interferences from overlapping elements. Chi-square is a more useful measure of goodness-of-fit for the other fluorescers for this reason.

13.7 To acquire more information about fitting problems the fitted spectra can be viewed on the screen or a hard copy printed. Such plots can be compared to the unknown spectra, background spectra, or to the library shape standards to help elucidate the suspected problem. Various statistics such as the correlation coefficient can be calculated on the fitted and measured spectra as a additional measure of the goodness-of-fit. Fitted spectrum superposed on its measured spectrum along with the associated statistics is illustrated in Figure 6.

14. Precision and Accuracy

Precision varies with the element and concentration. At high concentrations (greater than 1 $\mu g/cm^2$) a precision of 7.1% can be expected for elements analyzed by one fluorescer and 5.0% can be expected for those analyzed by two. Refer to Table 1 for a listing of the elements and the fluorescers which analyze them. Based upon the analysis of NIST SRMs the accuracy is ± 10%.

15. References

1. Arinc, F., Wielopolski, L., and Gardner, R. P., *The Linear Least-Squares Analysis of X-Ray Fluorescence Spectra of Aerosol Samples using Pure Element Library Standards and Photon Excitation,* X-ray Fluorescence Analysis of Environmental Samples, ed. T. G. Dzubay, Ann Arbor Science, Ann Arbor, MI p.227.

2. Bevington, P.R., *Data Reduction and Error Analysis for the Physical Sciences*, McGrawHill Book Co., New York, N.Y.

3. Billiet, J., Dams, R., and Hoste, J., X-Ray Spectrum, 9:206-211, 1980.

4. Birks, L.S., and Gilfrich, J.V., "X-Ray Spectrometry," *Anal. Chem.*, 48:273R-28R, 1976.

5. Dzubay, T. G., *Analysis of Aerosol Samples by X-Ray Fluorescence,* Env. Science Research Lab, U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, April 1986.

6. Dzubay, T. G., "Chemical Elements Balance Method Applied to Dichotomous Sampler Data," *Annals New York Academy of Sciences*, 1980.

7.   Dzubay, T. G., *Development and Evaluation of Composite Receptor Methods, EPA Project Summary*, EPA-600/3-88-026, U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, September 1988.

8.   Dzubay, T. G., *Quality Assurance Narrative for SARB XRF Facility,* Env. Science Research Lab, U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, March 1989.

9.   Dzubay, T. G., et al., "Polymer Film Standards for X-Ray Fluorescence Spectrometers," *J. Trace and Microprobe Techniques,* 5(4):327-341, 1987-88.

10.   Dzubay, T. G., Drane, E. A., Rickel, D. G., and Courtney, W. J., "Computer Code for Analyzing X-Ray Fluorescence Spectra of Airborne particulate Matter," *Advances in X-Ray Analysis,* Vol. 23.

11.   Dzubay, T. G., Lamothe, P. J., and Yasuda, H., *Advances in X-Ray Analysis,* ed. H. F. McMurdie, C.S. Barrett, J. B. Newkirk, and C. O. Ruud, Plenum, New York, N.Y. 20:411-421, 1977.

12.   Dzubay, T. G., Morosoff, N., Whitaker, G. L., et al., "Evaluation of Polymer Films as Standards for X-Ray Fluorescence Spectrometers," Presented at Symposium on Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis.

13.   Dzubay, T. G., and Nelson, R. O., *Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols,* Advances in X-Ray Analysis, ed. W. L. Pickles, et al., Plenum Publishing Corp., New York, N.Y. 18:619, 1975.

14.   Dzubay, T. G., and Rickel, D. G., *X-Ray Fluorescence Analysis of Filter-Collected Aerosol Particles, Electron Microscopy and X-Ray Applications,* Ann Arbor Science, 1978.

15.   Dzubay, T. G., Stevens, R. K., Gordon, G. E., Olmez, I., Sheffield, A. E., and Courtney, W. J., "A Composite Receptor Method Applied to Philadelphia Aerosol," *Environmental Science & Technology,* 22:46, January 1988.

16.   Dzubay, T. G., Stevens, R. K., Gordon, G. E., Olmez, I., Sheffield, A. E., and Courtney, W. J., "A Composite Receptor Method Applied to Philadelphia Aerosol," *Environmental Science & Technology,* 22:46, January 1988.

17.   Giauque, R. D., Goulding, F. S., Jaklevic, J. M., and Pehl, R. H., "Trace Element Determination with Semiconductor Detector X-Ray Spectrometers," *Anal. Chem.,* 45:671, 1973.

18.   Goulding, F. S., and Jaklevic, J. M., *Fabrication of Monitoring System for Determining Mass and Composition of Aerosol as a Function of Time,* EPA-650/2-75-045, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1975.

19.   *Inhalable Particulate Network Operations and Quality Assurance Manual,* Office of Research and Development, Env. Monitoring Systems Lab, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711.

20.   Jaklevic, J. M., Landis, D. A., and Goulding, F. S., "Energy Dispersive X-Ray Fluorescence Spectrometry Using Pulsed X-Ray Excitation, *Advances in X-Ray Analysis,* 19:253-265, 1976.

21. Jenkins, R., and deVries, J. L., *Practical X-Ray Spectroscopy*, Springer-Verlag, New York, NY, 1967.

22. Loo, B. W., Gatti, R. C., Liu, B. Y. H., Chong-Soong, K., and Dzubay, T. G., "Absorption Corrections for Submicron Sulfur Collected in Filters," X-Ray Fluorescence Analysis of Environmental Samples, Ann Arbor Science, Ann Arbor, MI p. 187, 1977.

23. NBS Standard Reference materials Catalog 1986-87, National Bureau of Standards Publ. 260, U. S. Department of Commerce, Washington, DC p. 64, June 1986.

24. Rhodes, J. R., *X-Ray Spectrom.*, 6:171-173, 1977.

25. Wagman, J., Bennett, R. L., and Knapp, K. T., "Simultaneous Multiwavelength Spectrometer for Rapid Elemental Analysis of Particulate Pollutants," X-Ray Fluorescence Analysis of Environmental Samples, ed. T. G. Dzubay, Ann Arbor Science Publishers, Inc. Ann Arbor, MI, pp, 35-55, 1977.

26. *Volume II: Protocols for Environmental Sampling and Analysis,* Particle Total Exposure Assessment Methodology (P-Team): Pre-Pilot Study, EPA 68-02-4544, U. S. Environmental Protection Agency, Research Triangle Park, NC 27709, January 27, 1989.

27. Jaklevic, et al., *X-ray Fluorescence Analysis of Environmental Samples,* ed. T. G. Dzubay, Ann Arbor Science, Ann Arbor, MI, p. 63.

28. Cooper, J. A., Valdovinos, L. M., Sherman, J. R., Pollard, W. L., Sarver, R. H., and Weilder, J. K., "Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon® Membrane Filters by X-ray Fluorescence Analysis," NEA, Inc., Beaverton, OR, July 15, 1987.

29. Gilfrich, et al., *X-ray Fluorescence Analysis of Environmental Samples,* ed. T. G. Dzubay, Ann Arbor Science, Ann Arbor, MI, p. 283.

TABLE 1. EXAMPLE OF FLUORESCER USAGE

Element	Al	Ti	Fe	Ge	Ag	Zr	Gd
Na	x						
Mg	x						
Al	x						
Si	x						
P	x	x					
S	x	x					
Cl	x	x					
Ar	x	x					
K	x	x					
Ca	x	x					
Sc	x	x					
Ti			x	x			
V			x	x			
Cr			x	x			
Mn				x		x	
Fe				x		x	
Co				x		x	
Ni				x		x	
Cu				x		x	
Zn						x	
Ga						x	
Ge						x	
As						x	
Se						x	
Br						x	
Rb					x	x	
Sr					x		x
Y					x		
Zr					x		x
Mo					x		x
Rh							x
Pd							x
Ag							x
Cd							x
Sn							x
Sb							x
Te							x
I							x
Cs							x
Ba							x
La							x
W					x	x	
Au					x	x	
Hg					x	x	
Pb					x	x	

[Note: The 'x' marks the fluorescers that analyze each element.]

TABLE 2. METHOD DETECTION LIMITS (MDL) FOR
TEFLO® AND NUCLEPORE® BLANK FILTERS (1F)

Teflo® - fine element Method Detection Limits (MDL)			Nuclepore® - coarse element Method Detection Limits (MDL)		
	ng/cm^2	ng/m^3[1]		ng/cm^2	ng/m^3[2]
Na	5.3	1.59	Na	17.4	47.12
Mg	3.2	0.96	Mg	7.9	21.34
Al	17.6	5.29	Al	46.7	126.48
Si	8.0	2.41	Si	21.2	50.40
P	2.6	0.78	P	4.1	11.10
S	2.6	0.78	S	6.9	16.56
Cl	4.8	1.44	Cl	5.6	13.44
K	6.3	1.89	K	5.6	15.17
Ca	9.0	2.71	Ca	8.7	23.56
Sc	1.5	0.45	Sc	1.3	3.52
Ti	16.9	5.08	Ti	18.7	42.52
V	5.3	1.59	V	5.5	14.89
Cr	3.0	0.90	Cr	3.0	8.12
Mn	.8	0.24	Mn	.8	2.17
Fe	.7	0.21	Fe	1.0	2.71
Co	.4	0.12	Co	.4	1.08
Ni	.6	0.18	Ni	.7	1.89
Cu	.7	0.21	Cu	.8	2.17
Zn	1.0	0.30	Zn	1.1	2.98
Ga	1.6	0.48	Ga	1.5	4.06
Ge	1.1	0.33	Ge	1.0	2.71
As	.8	0.24	As	.9	2.44
Se	.7	0.21	Se	.6	1.62
Br	.6	0.18	Br	.7	1.89
Rb	.7	0.21	Rb	.7	1.89
Sr	1.1	0.33	Sr	.9	2.44
Y	1.2	0.36	Y	1.1	2.98
Zr	1.2	0.36	Zr	1.1	2.98
Mo	1.6	0.48	Mo	1.5	4.06
Rh	25.9	7.79	Rh	26.5	71.70
Pd	22.9	6.89	Pd	18.7	50.65
Ag	20.2	6.02	Ag	20.3	54.98
Cd	22.0	6.62	Cd	19.2	52.00
Sn	30.5	9.18	Sn	31.5	85.31
Sb	31.4	9.45	Sb	26.7	72.31
Te	26.3	7.91	Te	27.6	66.62
I	35.5	10.68	I	34.4	93.17
Cs	48.9	14.62	Cs	50.9	137.85
Ba	51.8	15.59	Ba	58.3	157.89
La	70.6	2.12	La	68.9	186.60
W	3.4	10.23	W	3.3	8.93
Au	1.7	0.51	Au	1.5	4.06
Hg	1.5	0.45	Hg	1.4	3.79
Pb	1.5	0.45	Pb	1.5	4.06

[1]Based upon dichotomous sampling for 24-hrs. using a 37-mm Teflo® filter at a sampling rate of 0.9 m^3/hr.
[2]Based upon dichotomous sampling for 24-hrs using a 37-mm Nuclepore® filter at a sampling rate of 0.1 m^3/hr.

TABLE 3. DATA REPORT FORMAT FOR A FINE/COARSE PAIRED SAMPLE

```
KEVEX SUMMARY: ADOBE FLATS URBAN PARTICULATE STUDY
        SITE         =    ADB
        DURATION (MIN) =     714.0      SAMPLE DATE  =  3/20/92 AND 1900 HOURS
        FLOW FRAC     = .0869           FLOW (L/MIN) =   37.105 +-  .500
        XRF ID        = 999906          XRF ID       = 999956
        SAMPLE ID     = T0033           SAMPLE ID    = NU0033
                      FINE, NG/M³                      COARSE, NG/M³
        MASS   77912.  +-   1962.       MASS   11347.  +-    812.
        *NA     211.9 +-    71.4        *NA      53.3 +-    27.1
         MG     564.6 +-    89.4         MG     443.9 +-    40.8
        *AL     162.2 +-    74.1         AL     539.9 +-   173.8
         SI     213.4 +-    40.4         SI     909.5 +-   232.7
        * P      12.1 +-    18.5        * P      -5.5 +-    11.3
          S    2653.4 +-   183.7          S     285.7 +-    84.9
         CL    1164.4 +-    79.3        *CL      34.8 +-    24.6
          K     193.6 +-    13.8          K      63.5 +-     8.9
         CA      43.4 +-     5.6         CA     181.7 +-    13.9
        *SC       3.6 +-     4.1        *SC      -1.3 +-     2.2
        *TI      17.6 +-     6.6         TI      54.7 +-     9.6
        * V       4.6 +-     2.3        * V       3.2 +-     1.7
        *CR       2.0 +-     1.0         CR       9.8 +-     1.6
         MN      10.0 +-     1.4         MN      10.1 +-     1.3
         FE     243.7 +-    21.9         FE     783.5 +-    78.2
        *CO       2.8 +-     1.8        *CO       4.8 +-     1.7
         NI       3.8 +-     1.2        *NI        .3 +-      .6
         CU      14.3 +-     1.9         CU       8.8 +-     1.3
         ZN     167.5 +-    14.9         ZN      27.6 +-     4.9
        *GA       2.4 +-     1.0        *GA      -.0 +-      .4
        *GE       3.3 +-     1.3        *GE       .0 +-      .6
         AS      24.7 +-     3.6        *AS       1.8 +-     1.2
         SE       4.7 +-      .8        *SE       .7 +-      .4
         BR      29.0 +-     2.8         BR       7.9 +-     1.1
        *RB       1.7 +-      .8        *RB       1.0 +-      .4
         SR       2.9 +-      .9         SR       2.2 +-      .5
        * Y      12.4 +-     6.1        * Y       3.9 +-     2.9
        *ZR       2.9 +-     4.8        *ZR       4.3 +-     2.6
        *MO       7.3 +-     4.8        *MO      -3.2 +-     2.2
        *RH        .0 +-     3.2        *RH      -1.2 +-     1.6
        *PD      -3.6 +-     3.1        *PD      -1.0 +-     1.7
        *AG      -6.4 +-     3.4        *AG       1.2 +-     1.9
        *CD       8.5 +-     4.5        *CD      -.7 +-      2.2
         SN      54.3 +-     9.4        *SN       2.3 +-     3.9
        *SB      -1.6 +-     6.4        *SB      -.6 +-      3.3
        *TE       2.5 +-     7.5        *TE      -7.2 +-     3.8
        * I      25.0 +-     9.6        * I       2.4 +-     4.7
        *CS      -4.0 +-    11.2        *CS      12.4 +-     5.9
        *BA      -7.7 +-    13.7         BA      25.1 +-     7.4
        *LA      -4.8 +-    34.5        *LA      22.6 +-    17.9
        * W      -1.1 +-     2.6        * W       1.5 +-     1.3
```

```
       *AU      -.9 +-      1.8        *AU        .2 +-       .9
       *HG      -.4 +-      1.9        *HG       1.5 +-      1.0
        PB     221.6 +-     19.7        PB       46.0 +-      6.2
 *  INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
   XRF DATE= 04/29/1992  16:35 RBK   (F):  04/29/1992  20:35 RBK   (C)
   SPECTRAL ANALYSIS DATE=  5/20/1992
```

TABLE 4. CALIBRATION STANDARDS AND CONCENTRATIONS

Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²
CaF237	F	18.00	CuS1124	S	31.90	Cr 85	Cr	85.00	RbNO311	Rb	69.00
CaF2 29	F	14.10	CuS58.6	S	16.50	Cr 84	Cr	84.00	RbNO322	Rb	12.90
CaF2 90	F	43.80	CuS57.6	S	13.90	Cr 75	Cr	75.00	RbNO3 a	Rb	24.90
CaF2 91	F	44.30	CuS58.2	S	14.00	Cr 74	Cr	74.00	RbNO3 b	Rb	24.90
CaF2102	F	49.60	NaCl 57	Cl	34.60	Cr 122	Cr	122.00	RbNO3 c	Rb	24.90
CaF2 66	F	32.10	NaCl 87	Cl	52.80	CrCu32a	Cr	9.19	SrF2 57	Sr	39.80
CaF2 28	F	13.60	NaCl446	Cl	27.10	CrCu26g	Cr	8.14	SbSr29z	Sr	4.97
CaF2 33	F	16.10	NaCl715	Cl	43.40	MnZn24b	Mn	8.57	SrF2 50	Sr	34.90
CaF2 39	F	19.00	NaCl497	Cl	30.20	Mn 57	Mn	57.00	SbSr31y	Sr	5.14
CaF2 54	F	26.30	NaCl501	Cl	30.40	Mn 183	Mn	183.00	SrF2137	Sr	95.60
CaF2291	F	14.10	NaCl 51	Cl	31.00	MnZn27x	Mn	9.10	SrF2184	Sr	12.80
CaF2 30	F	14.60	NaCl512	Cl	31.10	Mn 43	Mn	43.00	SrF2 92	Sr	64.20
CaF2 52	F	25.30	NaCl519	Cl	31.50	Mn 46.9	Mn	46.90	SrF2103	Sr	71.80
CaF2 48	F	23.40	KCl 45	Cl	21.40	Mn 44.5	Mn	44.50	YF3 46	Y	28.00
CaF2 45	F	21.90	KCl53.3	Cl	25.40	Mn 46.6	Mn	46.60	ZrCd24c	Zr	9.85
CaF2 36	F	17.50	KCl 70	Cl	33.30	Mn 43.7	Mn	43.70	ZrCd20w	Zr	10.77
CaF2134	F	65.20	KCl 49	Cl	23.30	Mn 69	Mn	69.00	MoO3145	Mo	96.70
CaF2110	F	53.50	KCl48.7	Cl	23.20	FePb37y	Fe	7.72	MoO3106	Mo	70.70
NaCl 57	Na	22.40	KCl47.9	Cl	22.80	Fe 107	Fe	107.00	MoO3110	Mo	73.30
NaCl 87	Na	34.20	KCl 48	Cl	22.80	Fe 127	Fe	127.00	MoO3 59	Mo	39.30
NaCl446	Na	17.60	KCl47.6	Cl	22.60	Fe 46	Fe	46.00	MoO3 54	Mo	36.00
NaCl715	Na	28.10	KCl 45	K	23.60	Fe 88	Fe	88.00	Rh 16	Rh	16.00
NaCl497	Na	19.60	KCl53.3	K	28.00	FePb38y	Fe	7.71	Pd 33	Pd	33.00
NaCl501	Na	19.70	KCl 70	K	36.70	Co 45a	Co	45.00	Pd 198	Pd	198.00
NaCl 51	Na	20.10	KCl 49	K	25.70	Co 45b	Co	45.00	Ag 35	Ag	35.00
NaCl512	Na	20.10	KCl48.7	K	25.50	RbCo29c	Co	7.43	Ag 132	Ag	132.00
NaCl519	Na	20.40	KCl47.9	K	25.10	RbCo25b	Co	7.65	Cd 83	Cd	83.00
Mg 81	Mg	81.00	KCl 48	K	25.20	Ni 54	Ni	54.00	ZrCd20w	Cd	9.15
Mg 41	Mg	41.00	KCl47.6	K	25.00	Ni 88	Ni	88.00	ZrCd24c	Cd	8.38
Mg 41.3	Mg	41.30	CaF2 37	Ca	19.00	NiV 21c	Ni	5.77	Cd 77	Cd	77.00
Mg 43	Mg	43.00	CaF2 29	Ca	14.90	Ni 101	Ni	101.00	Sn 40	Sn	40.00
Mg 43.8	Mg	43.80	CaF2 90	Ca	46.20	Cu 96	Cu	96.00	Sn 185	Sn	185.00
Mg 60.2	Mg	60.20	CaF2 91	Ca	46.70	Cu 104	Cu	104.00	Sn 97a	Sn	97.00
Al 57	Al	57.00	CaF2102	Ca	52.40	Cu 128	Cu	128.00	Sn 97b	Sn	97.00
Al 37.9	Al	37.90	CaF2 66	Ca	33.90	CrCu26g	Cu	7.65	Sn 79	Sn	79.00
Al 37.4	Al	37.40	CaF2 28	Ca	14.40	CrCu32a	Cu	8.63	Sb 194	Sb	194.00
Al 29	Al	29.00	CaF2 33	Ca	16.90	Cu 38	Cu	38.00	Sb 47	Sb	47.00
Al 43.2	Al	43.20	CaF2 39	Ca	20.00	Zn 51	Zn	51.00	Sb 147	Sb	147.00
Al 62	Al	62.00	CaF2 54	Ca	27.20	Zn 125	Zn	125.00	Sb 42	Sb	42.00
Al 75	Al	75.00	CaF2291	Ca	14.90	MnZn27x	Zn	8.46	SbSr29z	Sb	5.01
SiO 46	Si	29.30	CaF2 30	Ca	15.40	MnZn24b	Zn	7.97	SbSr31y	Sb	5.18
SiO 47	Si	29.90	CaF2 52	Ca	26.70	GaP 34	Ga	23.50	Te 53	Te	53.00
SiO 51a	Si	32.50	CaF2 48	Ca	24.60	GaP 40	Ga	27.70	KI 46	I	35.20
SiO 51b	Si	32.50	CaF2 45	Ca	23.10	GaP 70	Ga	48.50	CsBr 53	Cs	33.10
SiO 56	Si	35.70	CaF2 36	Ca	18.50	GaP 105	Ga	72.70	CsBr 54	Cs	33.70
SiO 80	Si	51.00	CaF2134	Ca	68.60	Ge 37	Ge	37.00	CsBr 51	Cs	31.90
SiO27.6	Si	17.60	CaF2110	Ca	56.50	TiGe33d	Ge	6.22	BaF2108	Ba	84.60
SiO46.1	Si	29.40	ScF3 57	Sc	25.10	TiGe29x	Ge	5.94	BaF2 48	Ba	37.60
SiO72.2	Si	46.00	Ti 39	Ti	39.00	Ge 140	Ge	140.00	BaF2 60	Ba	47.00
GaP 34	P	10.50	Ti 95	Ti	95.00	BaAs23y	As	5.60	BaF2 57	Ba	44.70
GaP 40	P	12.30	TiGe33d	Ti	2.46	BaAs36w	As	5.52	BaF2143	Ba	112.00
GaP 70	P	21.50	TiGe29x	Ti	2.36	CsBr 53	Br	19.90	BaF2114	Ba	89.40
GaP 105	P	32.30	V 45	V	45.00	CsBr 54	Br	20.30	BaAs23y	Ba	4.98

TABLE 4.   (continued)

Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²
CuS1052	S	30.80	V 53	V	53.00	CsBr 51	Br	19.10	BaAs36w	Ba	4.91
CuS 48	S	13.00	NiV 21c	V	6.64	RbNO346	Rb	26.60	LaF3157	La	111.30
CuS 136	S	33.00	Cr 30	Cr	30.00	RbCo25b	Rb	7.88	LaF3 62	La	44.00
CuS39.6	S	10.20	Cr 53	Cr	53.00	RbCo29c	Rb	7.65			

TABLE 5. TARGET AND TOLERANCE VALUES FOR QC RESULTS

(TARGET VALUES)

FILE: 0:QCBEGTGT					FILE: 0:QCENDTGT				
STDEL ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)	STD ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)
1833	Pb	31112.12	10.5449	207.4653	1832	Cu	17548.85	8.0411	174.1389
1833	Zn	31772.52	8.6306	179.6835	1832		5303.84	6.9247	167.1478
1833	Fe	313475.41	6.3935	159.4537	1832	Mn	86202.33	5.8891	154.6347
1833	Ti	216978.09	4.5037	142.4946	1832	Ca	217562.00	3.6847	135.3520
1833	Si	69021.60	1.7322	121.7406	1832	V	99761.96	4.9443	146.1904
1833	K	220344.80	3.3069	132.4137	1832	Al	16562.45	1.4779	119.5793
BLKt	Sn	111.52	0.0000	0.0000	1832	Si	67688.42	1.7319	118.4960
BLKt	Pb	85.82	0.0000	0.0000	1832	Na	10332.21	1.0256	114.4485
BLKt	Cu	497.06	0.0000	0.0000	BLKn	Ba	183.14	0.0000	0.0000
BLKt	Sr	72.92	0.0000	0.0000	BLKn	W	241.42	0.0000	0.0000
BLKt	Ni	648.99	0.0000	0.0000	BLKn	Zn	148.48	0.0000	0.0000
BLKt	Fe	459.10	0.0000	0.0000	BLKn	Sr	83.00	0.0000	0.0000
BLKt	S	266.76	0.0000	0.0000	BLKn	Ni	654.44	0.0000	0.0000
BLKt	Al	396.30	0.0000	0.0000	BLKn	Fe	603.55	0.0000	0.0000
BLKt	Ar	747.74	0.0000	0.0000	BLKn	S	3047.53	0.0000	0.0000
BLKt	Na	120.85	0.0000	0.0000	BLKn	Si	936.48	0.0000	0.0000
BaNa	Na	27711.44	1.0278	107.2698	BLKn	Ar	751.18	0.0000	0.0000
BaNa	Ba	7369.12	32.0701	670.6336	BLKn	Mg	3622.12	0.0000	0.0000
					BaSr	Sr	210871.20	14.1410	227.8625
					BaSr	Ba	7464.85	32.0692	671.0372

(TOLERANCE UNITS in %)

FILE: 0:QCBEGTOL					FILE: 0:QCENDTOL				
STDEL ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)	STD ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)
1833	Pb	1.66	0.0313	0.9901	1832	Cu	1.66	0.0104	1.9331
1833	Zn	1.66	0.0131	1.7328	1832	Co	1.70	0.0308	2.4345
1833	Fe	1.66	0.0224	0.9361	1832	Mn	1.66	0.0198	1.3536
1833	Ti	1.66	0.0259	0.9768	1832	Ca	1.66	0.0253	1.1311
1833	Si	1.66	0.0616	1.4120	1832	V	1.66	0.0243	1.1031
1833	K	1.66	0.0323	0.9235	1832	Al	2.02	0.1173	3.3722
BLKt	Sn	12.98	0.0000	0.0000	1832	Si	1.66	0.0481	0.8888
BLKt	Pb	8.93	0.0000	0.0000	1832	Na	1.78	0.1560	1.5333
BLKt	Cu	4.95	0.0000	0.0000	BLKn	Ba	9.92	0.0000	0.0000
BLKt	Sr	17.61	0.0000	0.0000	BLKn	W	8.20	0.0000	0.0000
BLKt	Ni	3.81	0.0000	0.0000	BLKn	Zn	11.45	0.0000	0.0000
BLKt	Fe	7.57	0.0000	0.0000	BLKn	Sr	10.88	0.0000	0.0000
BLKt	S	8.71	0.0000	0.0000	BLKn	Ni	6.55	0.0000	0.0000
BLKt	Al	7.23	0.0000	0.0000	BLKn	Fe	5.63	0.0000	0.0000
BLKt	Ar	17.39	0.0000	0.0000	BLKn	S	2.88	0.0000	0.0000
BLKt	Na	16.00	0.0000	0.0000	BLKn	Si	6.75	0.0000	0.0000
BaNa	N	1.66	0.1103	1.2599	BLKn	Ar	22.14	0.0000	0.0000
BaNa	Ba	2.53	0.0979	3.9782	BLKn	Mg	5.64	0.0000	0.0000
					BaSr	Sr	1.66	0.0073	0.4538
					BaSr	Ba	1.86	0.0279	2.8094

TABLE 6. EXAMPLE PRINTOUT OF SRM 1833

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

SITE	=				
DURATION (MIN)	= .0	SAMPLE DATE = 99/99/99 AND 9999 HOURS			
FLOW FRAC	= .0000	FLOW (L/MIN) = .000 + - .200			
XRF ID	= 112141				
SAMPLE ID	= SRM1833				

	FINE, NG/CM²			NIST CERTIFIED VALUES			
MASS	0.	+ -	398.	MASS	15447		
*NA	-801.2	+ -	326.4	NA	.0	+ -	.0
MG	161.3	+ -	18.2	MG	.0	+ -	.0
AL	1027.5	+ -	102.2	AL	.0	+ -	.0
SI	34806.8	+ -	3023.4	SI	33366.0	+ -	2163.0
P	79.8	+ -	19.9	P	.0	+ -	.0
*S	-28.2	+ -	782.8	S	.0	+ -	.0
*CL	-68.6	+ -	113.8	CL	.0	+ -	.0
K	16734.7	+ -	1018.7	K	17147.0	+ -	1699.0
*CA	-3.9	+ -	61.4	CA	.0	+ -	.0
*SC	-17.1	+ -	5.4	SC	.0	+ -	.0
TI	12852.9	+ -	822.1	TI	12821.0	+ -	1854.0
*V	46.0	+ -	52.2	V	.0	+ -	.0
CR	108.2	+ -	12.7	CR	.0	+ -	.0
MN	13.8	+ -	2.9	MN	.0	+ -	.0
FE	14332.4	+ -	872.4	FE	14212.0	+ -	463.0
*CO	-2.6	+ -	2.9	CO	.0	+ -	.0
NI	62.5	+ -	4.6	NI	.0	+ -	.0
*CU	3.8	+ -	1.5	CU	.0	+ -	.0
ZN	3800.9	+ -	327.7	ZN	3862.0	+ -	309.0
*GA	-30.9	+ -	7.7	GA	.0	+ -	.0
*GE	5.9	+ -	3.6	GE	.0	+ -	.0
*AS	5.7	+ -	14.6	AS	.0	+ -	.0
*SE	-2.0	+ -	2.6	SE	.0	+ -	.0
*BR	-2.3	+ -	2.5	BR	.0	+ -	.0
*RB	.5	+ -	1.4	RB	.0	+ -	.0
*SR	-5.0	+ -	2.9	SR	.0	+ -	.0
* Y	-2.6	+ -	7.5	Y	.0	+ -	.0
*ZR	-7.6	+ -	3.5	ZR	.0	+ -	.0
MO	45.4	+ -	5.6	MO	.0	+ -	.0
*RH	156.7	+ -	69.5	RH	.0	+ -	.0
*PD	79.2	+ -	67.1	PD	.0	+ -	.0
*AG	114.0	+ -	69.7	AG	.0	+ -	.0

TABLE 6.   (continued)

	FINE, NG/CM^2			NIST CERTIFIED VALUES		
*CD	24.7	+ -	66.3	CD	.0 + -	.0
*SN	-1496.1	+ -	188.1	SN	.0 + -	.0
*SB	88.2	+ -	96.2	SB	.0 + -	.0
*TE	240.8	+ -	93.8	TE	.0 + -	.0
* I	134.8	+ -	107.5	I	.0 + -	.0
*CS	-209.3	+ -	106.6	CS	.0 + -	.0
*BA	-5098.1	+ -	517.8	BA	.0 + -	.0
*LA	-1416.4	+ -	202.2	LA	.0 + -	.0
W	59.9	+ -	17.6	W	.0 + -	.0
*AU	8.7	+ -	6.8	AU	.0 + -	.0
*HG	-30.6	+ -	5.9	HG	.0 + -	.0
PB	16886.2	+ -	1028.1	PB	16374.0 + -	772.0

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
 XRF DATE= 28-SEP-93 10:58:37 RBK
  SPECTRAL ANALYSIS DATE= 12/14/1993

TABLE 7. EXAMPLE PRINTOUT OF SRM 1832

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

SITE   =
DURATION (MIN)   = .0   SAMPLE DATE = 99/99/99 AND 9999 HOURS
FLOW FRAC   = .0000   FLOW (L/MIN) =   .000 + - .200
XRF ID   = 112191
SAMPLE ID   = SRM1832

	FINE, NG/CM^2				NIST CERTIFIED VALUES		
MASS	0.	+ -	398.	MASS	16431		
NA	11891.5	+ -	1035.0	NA	11173.0	+ -	.0
MG	92.2	+ -	13.0	MG	.0	+ -	.0
AL	15856.5	+ -	1373.2	AL	14953.0	+ -	986.0
SI	34398.8	+ -	2964.2	SI	35491.0	+ -	1150.0
P	492.0	+ -	32.1	P	.0	+ -	.0
S	402.1	+ -	27.3	S	.0	+ -	.0
CL	156.8	+ -	15.9	CL	.0	+ -	.0
* K	18.5	+ -	18.0	K	.0	+ -	.0
CA	20011.7	+ -	1218.2	CA	19225.0	+ -	1315.0
*SC	-21.8	+ -	5.6	SC	.0	+ -	.0
*TI	-4.7	+ -	130.6	TI	.0	+ -	.0
V	4593.6	+ -	281.1	V	4272.0	+ -	493.0
*CR	7.4	+ -	7.3	CR	.0	+ -	.0
MN	4959.3	+ -	302.4	MN	4437.0	+ -	493.0
FE	30.5	+ -	3.9	FE	.0	+ -	.0
CO	1055.1	+ -	64.7	CO	970.0	+ -	66.0
*NI	-6.8	+ -	1.8	NI	.0	+ -	.0
CU	2400.1	+ -	146.3	CU	2300.0	+ -	164.0
ZN	9.3	+ -	2.7	ZN	.0	+ -	.0
*GA	2.1	+ -	2.1	GA	.0	+ -	.0
*GE	.3	+ -	2.4	GE	.0	+ -	.0
*AS	-3.7	+ -	2.2	AS	.0	+ -	.0
*SE	1.0	+ -	1.2	SE	.0	+ -	.0
BR	10.7	+ -	1.8	BR	.0	+ -	.0
*RB	-.2	+ -	.9	RB	.0	+ -	.0
*SR	2.8	+ -	2.3	SR	.0	+ -	.0
* Y	-5.0	+ -	1.6	Y	.0	+ -	.0
*ZR	-6.5	+ -	1.8	ZR	.0	+ -	.0
MO	26.8	+ -	4.2	MO	.0	+ -	.0
*RH	25.2	+ -	58.2	RH	.0	+ -	.0

TABLE 7.   (continued)

	FINE, NG/CM^2				NIST CERTIFIED VALUES		
*PD	-69.0	+ -	54.7	PD	.0	+ -	.0
*AG	151.2	+ -	63.4	AG	.0	+ -	.0
*CD	24.2	+ -	58.2	CD	.0	+ -	.0
*SN	-640.8	+ -	138.6	SN	.0	+ -	.0
*SB	-73.5	+ -	81.3	SB	.0	+ -	.0
*TE	-9.3	+ -	73.9	TE	.0	+ -	.0
* I	-46.6	+ -	91.6	I	.0	+ -	.0
*CS	3.6	+ -	96.7	CS	.0	+ -	.0
*BA	-2352.9	+ -	328.6	BA	.0	+ -	.0
*LA	-509.9	+ -	156.5	LA	.0	+ -	.0
W	40.0	+ -	12.9	W	.0	+ -	.0
*AU	-5.6	+ -	2.5	AU	.0	+ -	.0
*HG	-5.4	+ -	3.0	HG	.0	+ -	.0
*PB	-10.4	+ -	4.2	PB	.0	+ -	.0

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
  XRF DATE= 29-SEP-93 13:27:55 RBK
  SPECTRAL ANALYSIS DATE= 12/14/1993
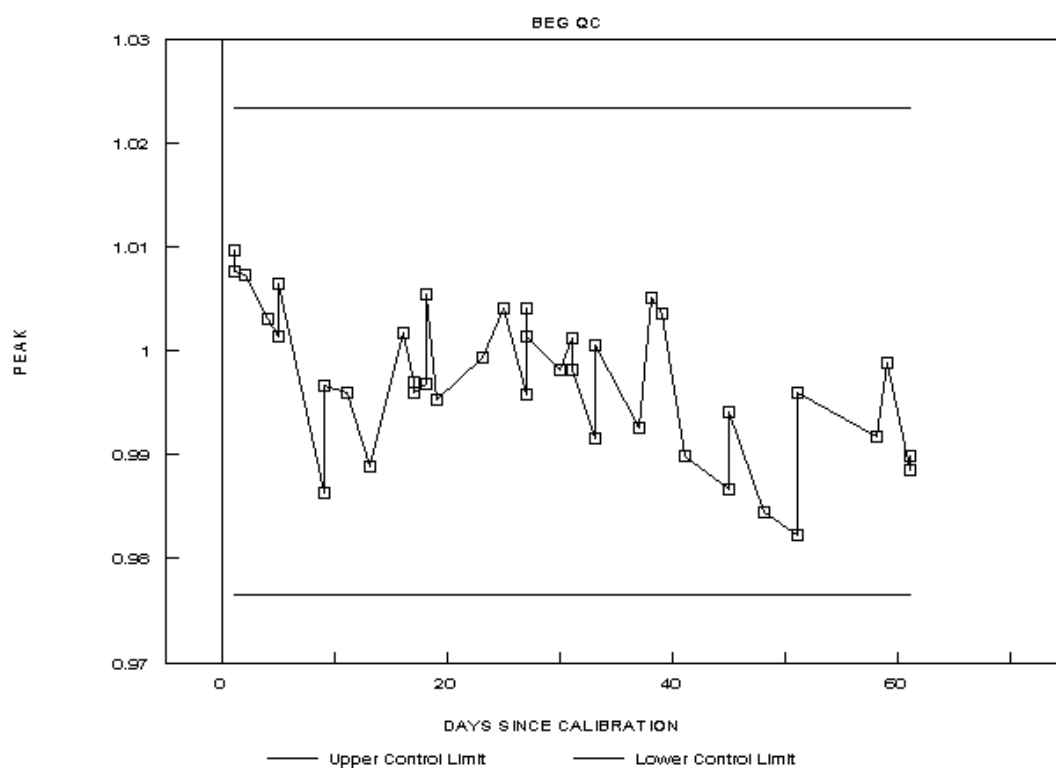
Figure 1. Quality control indicator associated with Fe peak area.
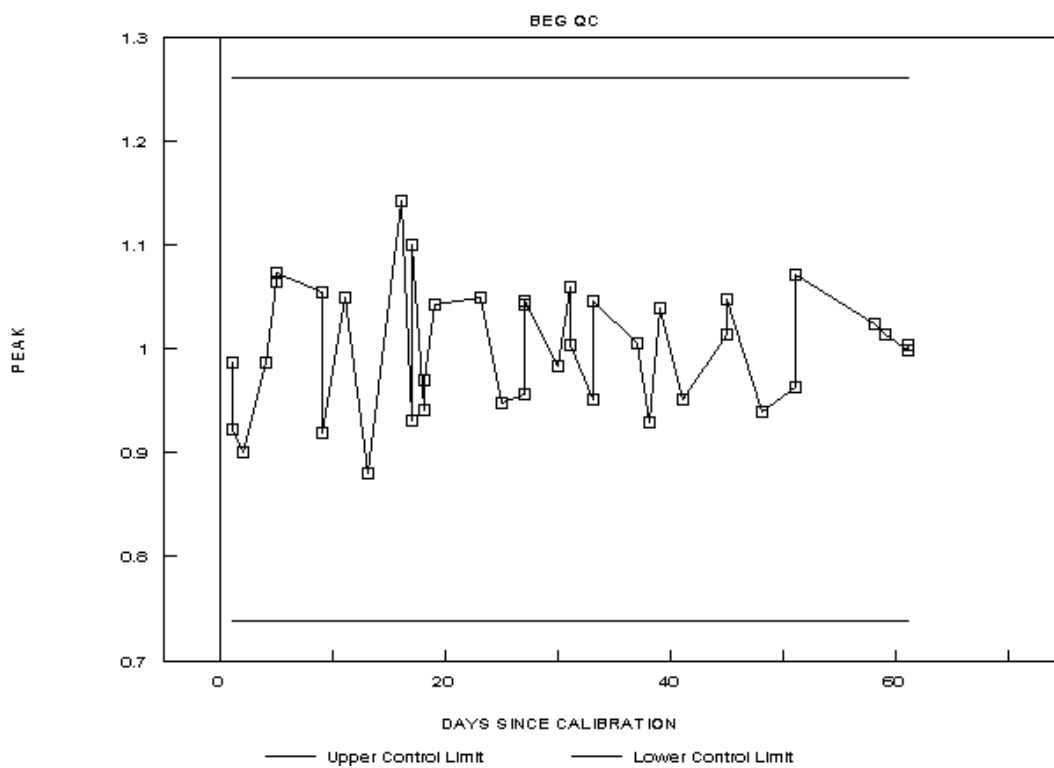
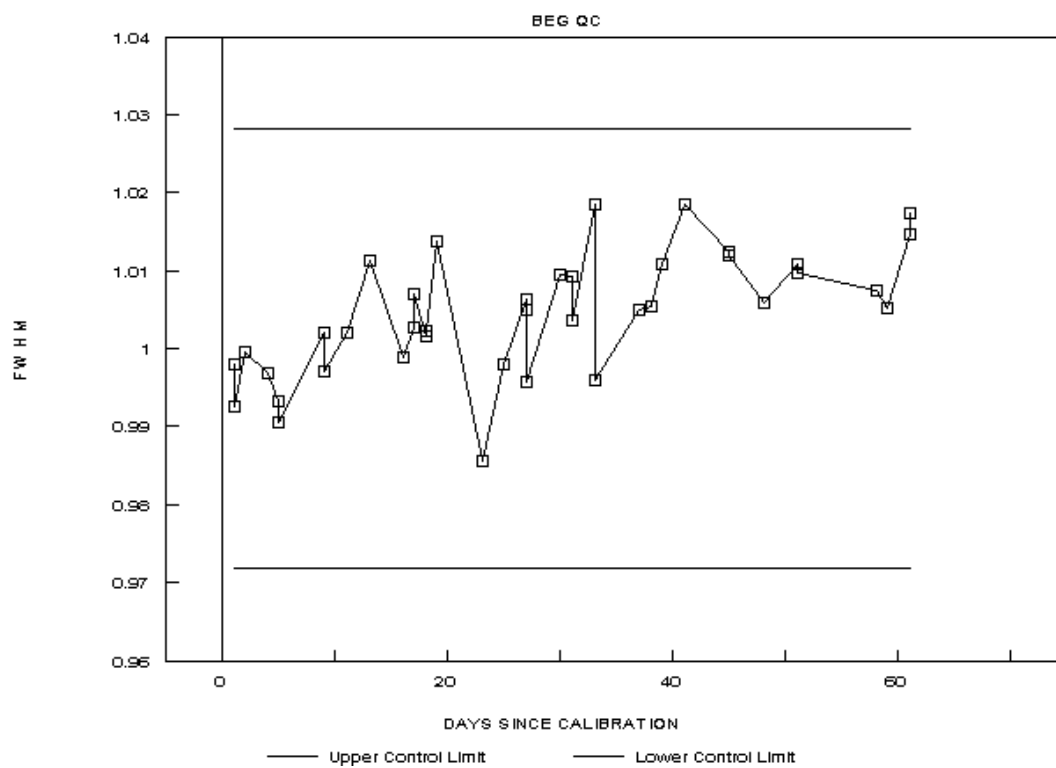Figure 2. Quality control indicator associated with S background area.

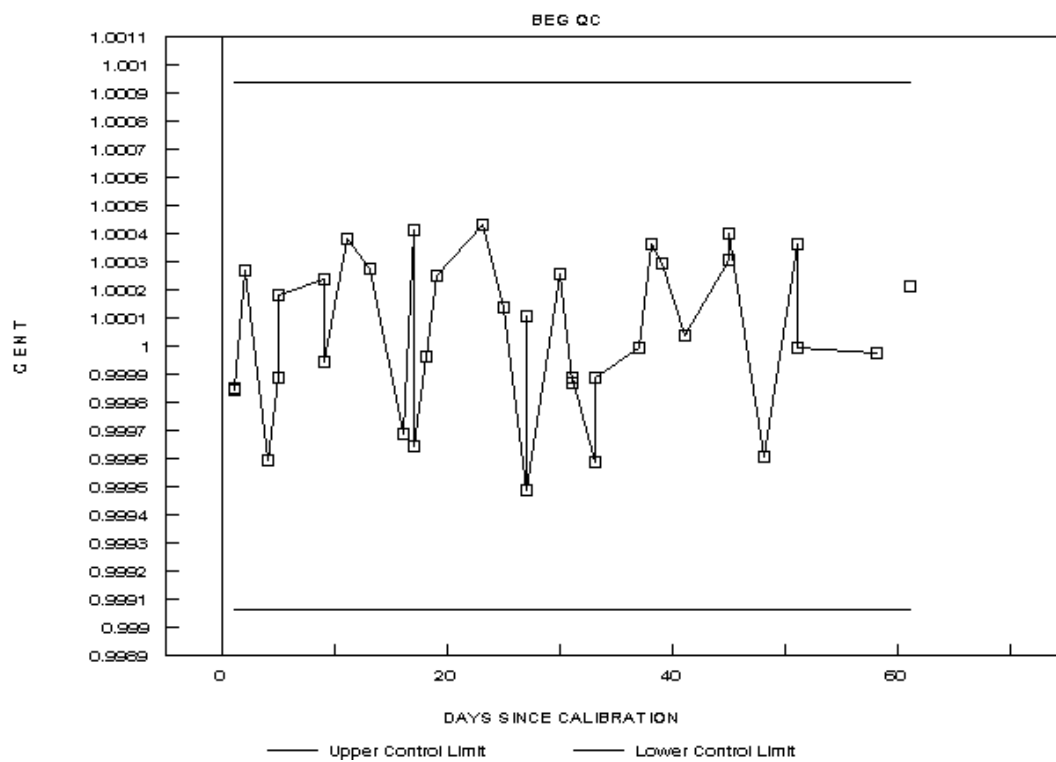Figure 3. Quality control indicator associated with Fe FWHM.

Figure 4. Quality control indicator associated with Pb centroid.
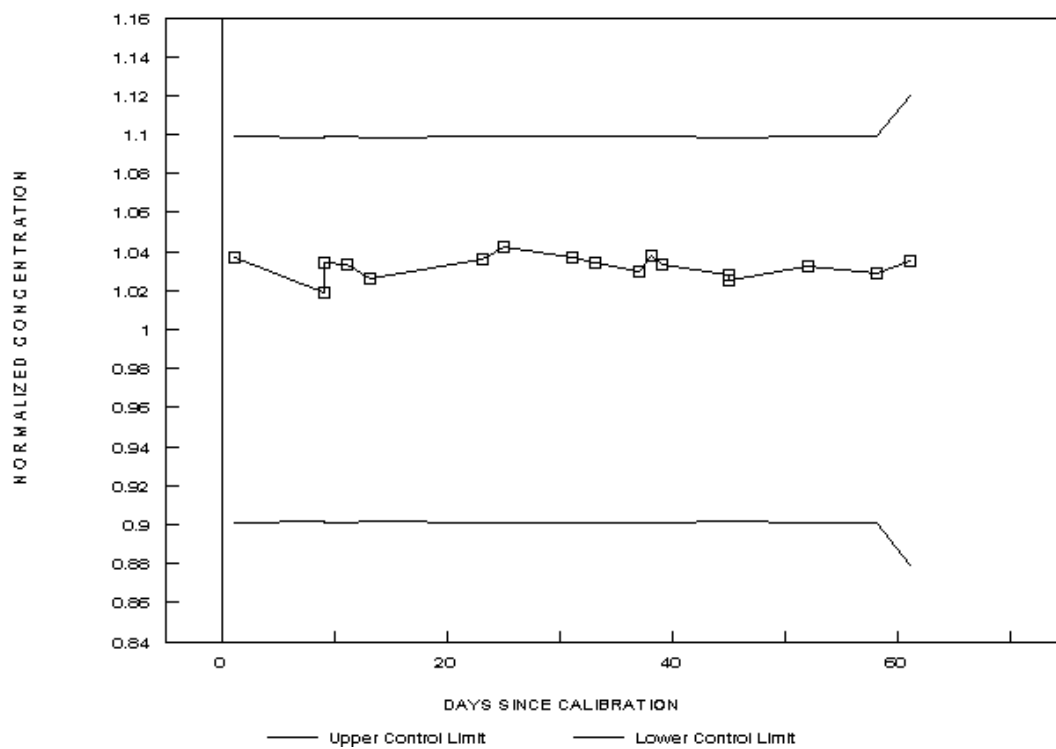
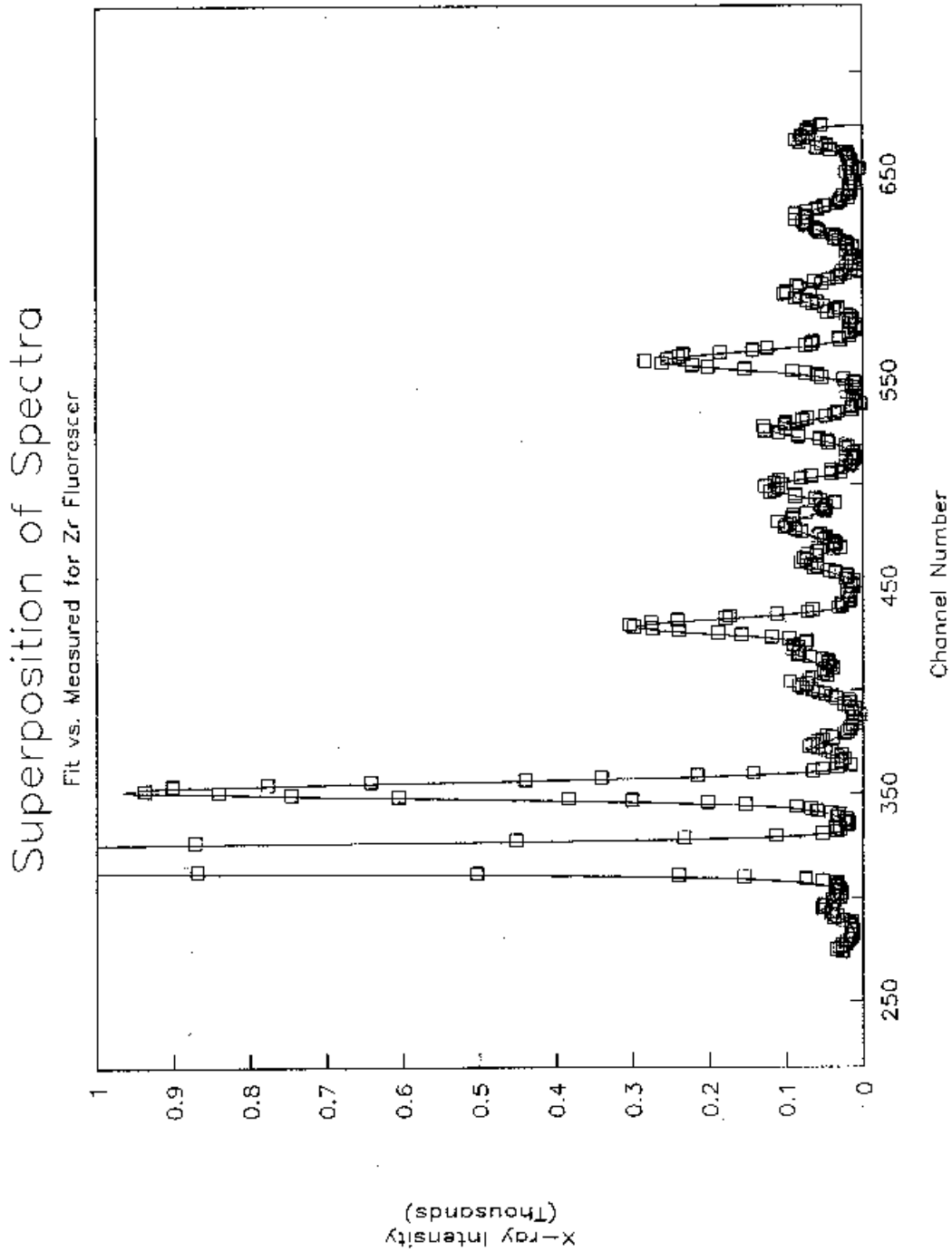Figure 5. Quality control indicator associated with Pb in SRMs.

Figure 6. Quality control indicator associated with superposition of fitted and measured spectrum.