QUALITATIVE X-RAY FLUORESCENCE ANALYSIS OF WORKPLACE SUBSTANCES

Method Number:	ID-204
OSHA Permissible Exposure Limit (PEL):	Provides qualitative element Exposure Limit (PEL) identification for the regulated substances listed in Section 4.1, Table 1.
Sampling Matrix:	Air filter, wipe filter, and bulk material
Sampling Procedure:	Samples are collected either as air samples on mixed-cellulose ester or polyvinyl chloride filters, as wipe samples using smear tabs, or as 10 to 20 mL of bulk material.
Air Volume:	Obtain full work-shift air samples when possible.
Sampling Rate:	2 L/min for personal samples. If possible, take area samples at 9 L/min.
Analytical Procedure:	All samples are analyzed with minimal sample preparation using an Energy Dispersive X-ray Fluorescence Spectrometer. This procedure may be adapted to Wavelength Dispersive Systems.
Qualitative Detection Limit:	
Air Samples:	Typically 0.1 to 30 µg. See Section 4.2, Table 2 for specific air sample detection limits.
Bulk Samples:	Typically 0.01 to 8%. Potential worst-case detection limits are derived from results presented in Section 4.3, Tables 3 and 4a-4c. These limits are presented in Section 4.3, Table 4d.
Status of Method:	Evaluated qualitative method
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1. Introduction

This method describes the sampling and semiquantitative X-ray fluorescence analysis of industrial hygiene air, wipe, and bulk samples. Samples are analyzed for element composition only, and up to 70 elements are possible. The substances listed in Section 4.1, Table 1 can be qualitatively and sometimes semiquantitatively analyzed by this method. (Note: Air sample filters are analyzed qualitatively only. For quantitation of collected particulate on a filter matrix, additional work is necessary to either prepare standards on filters which duplicate the particle size and mass distributions, or to extract the particulate from the filter samples.) The method also provides support to the industrial hygienist (IH) in evaluating potential exposure to other heavy elements.

1.1 History

1.1.1 Previously, samples submitted to the OSHA Laboratory for qualitation were analyzed manually using a Finnigan Model 8000 X-ray Spectrometer. This instrument was an Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer that used non-monochromatic X rays and support software which produced spectral scans of limited information (5.1).

1.1.2 Neutron Activation Analysis was also used for element identification. This analysis was non-routine, complicated, time consuming, expensive, and required a reactor-certified analyst (5.2).

1.1.3 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is generally used for quantitative analysis. All or a portion of the sample is destroyed or altered in the process of analysis. With proper selection of analytical lines, ICP-AES can provide qualitative element identification, but is typically limited to metal analyses. Simultaneous ICP instruments generally analyze fewer elements than EDXRF instruments, and are not routinely used at the OSHA Salt Lake Technical Center (OSHA-SLTC) for qualitative analysis (5.3).

1.1.4 This method was evaluated using the OSHA Laboratory's XRF system. It consisted of a Kevex 770 X-ray generator, its associated satellite box, vacuum system, helium flush system, firmware-based 8000 keyboard console, computer monitor, Digital Equipment Corporation (DEC) 11/73 computer, graphics memory, Kevex spectrum analyzer, and Toolbox II software. This method can be adapted to other systems.

1.2 Principles

1.2.1 X-ray fluorescence relies upon the excitation of atoms in a sample by the application of X rays of sufficient energy to cause the promotion or escape of inner orbital electrons and subsequent decay accompanied by characteristic fluorescence.

In an EDXRF spectrometer, X-ray photons are counted and their corresponding energies (kV) are measured. The resultant data set is displayed as a spectrum.

The approximate relationship between an element's atomic number and the energy of individual emission lines for each specific X-ray line series (e.g., the K_α line or the L_β line) is given by Moseley's law:

$$E = a(Z - \sigma)^2$$

where:
E = energy of X ray
a = proportionality constant
Z = atomic number
σ = constant for each line series

Moseley's law indicates that an element's spectral lines are a smooth function of the atomic number. The spectral lines for elements with low atomic number (light elements) occur at lower energies than the corresponding lines for elements with high atomic number (heavy elements). The peak energies and spectral group patterns provide for qualitative identification.

1.2.2 Data workup depends on the manner of sample preparation - thin films or thick dusts.

a) Thin films

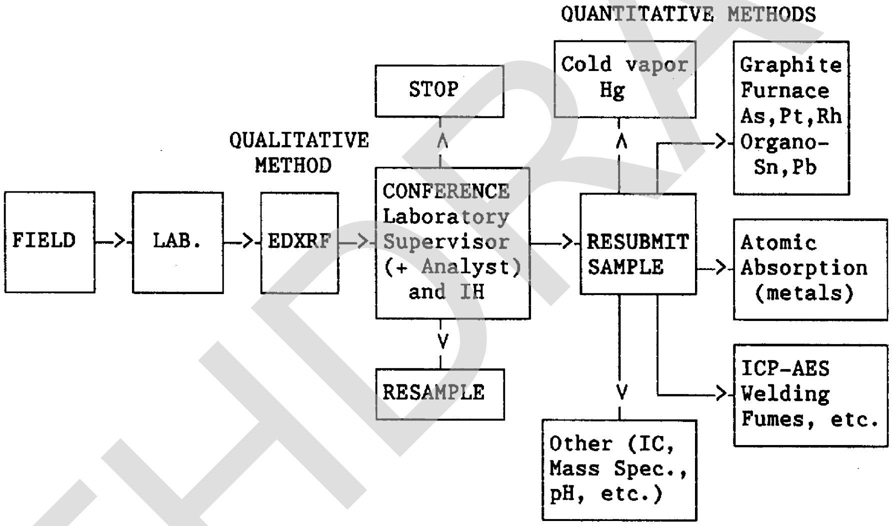
For uniform thin deposits of material on a support medium that is transparent to X rays, EDXRF produces signal intensities that are proportional to the amount of analyte present.

b) For thick samples and powders consisting of a few grams of material approximately a centimeter deep, non-linear calibration curves or fundamental parameters approaches can be used to account for sample self-absorption and inter-element enhancement effects. By monitoring the Compton and Rayleigh X-ray scatter from a sample, additional corrections may be made for unanalyzed light elements. Most samples analyzed by this method are treated as thick samples and powders.

c) Non-linear calibration curves can also be used to correct for other instrumental realities (e.g., fluorescing support medium or non-linear effects due to close instrument-sample geometry).

1.2.3 The results from EDXRF analyses are used for analytical support and fit into the following scheme:

SAMPLE FLOWCHART



This approach screens air samples of unknown composition to identify elements in dusts listed in Section 4.1, Table 1. It is also used to make a semiquantitative determination of the composition of bulk samples. The information obtained during the screening is used to determine whether additional time and resources are necessary to quantitatively identify the constituents in bulk, wipe, or certain air samples. Samples analyzed by XRF take only minutes to prepare, are not destroyed in the process, and do not require analytical standards for each screening or semiquantitative determination.

1.3 Method Performance

The detection limits reported in this method are based upon the optimization of the instrument for the maximum practical signal. The microgram detection limits reported for air samples are for analyte elements dispersed as aerosols concentrated near the center on the surface of polyvinyl chloride (PVC) membranes. PVC membranes were selected over mixed-cellulose ester (MCE) membranes because the detection limit experiment involved determining the weight of the substance on the membrane. The PVC membrane has shown greater stability during weighing. Membranes composed of MCE, however, give better detection limits than PVC.

1.3.1. Analytical detection limit

Detection limits for filter samples are listed and discussed in Section 4.2, Table 2.

a) Aerosol samples

The approach used to calculate detection limits is attributed to Birks (5.4) and is given in Bertin (5.5). The following equation (based on Poisson counting statistics) was used to estimate detection limits (DL):

$$DL = 3\sqrt{B}\left(\frac{A}{C}\right)$$

where:
A = analyte mass, (µg)
B = blank counts
C = analyte counts

The blank counts were determined in the same energy region used for profile-fitting the analyte counts. The analyte counts were determined from a peak profile fit of either:

1) The blank- and background-subtracted analyte peak.
2) The background-subtracted analyte peak in cases where blank subtraction would yield negative counts.

For aerosol air samples collected on PVC membranes, the detection limit ranged from about 30 µg for elements with atomic numbers below 17 (chlorine) to less than 4 µg for elements with atomic numbers above 17. When determining these detection limits (Section 4.2, Table 2), X-ray tube currents were set to values that give a maximum of 50% dead time on a Lucite monitor. Sample analysis time was 200 s for both blanks and samples. Sub-microgram detection limits are possible for many heavy elements. The use of mixed-cellulose ester (MCE) membranes offers better detection limits than PVC membranes.

b) For powdered bulk samples, matrix effects can have a profound effect on the lower levels of detection. A wide range of sample types was evaluated in the bulk tests. Based on the data shown in Section 4.3, Tables 4a-4c, the quantitative detection limit of the analytical procedure extends from about 8% for aluminum down to 0.01% for most elements with atomic numbers above 23 (vanadium). Elements that can be quantitated at levels of 0.01% in light matrices may be non-detected at levels of 1% in matrices with severe interferences. Potential worst-case detection limits for powdered bulk samples are presented in Section 4.3, Table 4d.

1.3.2 Instrument response to the analyte

The instrument response is sample and matrix dependent. For air and bulk samples, the lower qualitative limit is the detection limit. For homogeneous powdered bulk samples, the semiquantitative working range extends from the detection limit to near 100% of an analyte.

1.3.3 Recovery

Recoveries are matrix dependent. Typical recoveries for elements in powdered bulk samples are listed in Section 4.3, Tables 4a-4c and portrayed in Section 4.3, Figure 1.

1.4 Advantages

Provides rapid, non-destructive analyses
Affords qualitative information for a large number of elements
Can be semiquantitative
Can identify unexpected elements
Requires no sampling reagents

1.5 Disadvantages

Analysis requires expensive instrumentation and support software
Requires experienced analyst(s)
Limited use in quantitative analysis
Analysis is matrix dependent
Requires information about the sample matrix, chemistry, and suspected elements to achieve the most accurate analysis

2. Sampling

2.1 Safety Precautions

2.1.1 Attach the sampling equipment to the worker such that it will not interfere with work performance or safety.

2.1.2 Follow all safety practices that apply to the work area being sampled.

2.2. Equipment

2.2.1 Air sampling

a) Mixed-cellulose ester (MCE) filters, 0.8-µm pore size, cellulose backup pads, and cassettes, 37-mm diameter (part no. MAWP 037 A0, Millipore Corp., Bedford, MA).

b) Low-ash PVC membrane filter (use for gravimetric determinations or when quartz determinations are necessary), 37-mm, 5-µm pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA].

c) Cellulose back-up pads (support pads) (MSA, Pittsburgh, PA).

d) Clear polystyrene, 37-mm inside diameter, closed-face cassette, (two-section, SKC part no. 225-2 or three-section, SKC part no. 225-3, SKC, Fullerton, CA).

e) Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.

f) Sampling pump

Personal samples: Use a personal sampling pump that can be calibrated to within ±5% of 2 L/min with the sampling device attached.

Area samples: Use a higher volume sampling pump capable of 5 to 9 L/min.

g) Cyclone (only if respirable dust sampling is necessary); Nylon, 10-mm (BDX-99R, part no. 7010048-1 Sensidyne Inc., Largo, FL, or part no. 456243, MSA, Pittsburgh, PA). (A flow rate of 1.7 L/min is used.)

h) Assorted flexible tubing

i) Stopwatch and bubble tube or meter for pump calibration

j) Analytical balance (0.01 mg).

k) Desiccant (Drierite or similar material) and desiccating chamber. (Note: Use only if weights of air samples are desired).

2.2.2. Bulk sampling

a) Scintillation vials, 20-mL, (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners. If possible, submit bulk or wipe samples in these vials. Tin or other metal cap liners should not be used since a chemical reaction with the sample can occur. Glass scintillation vials and vinylite cap liners may not be appropriate for some liquids (e.g., strong bases). In these cases, use containers appropriate for the substance.

2.2.3 Wipe sampling

(Note: Wipe samples are not an optimum medium for this method - See Section 2.3.3 for further details.)

a) Smear tabs (part no. 225-24, SKC Inc., Eighty Four, PA, or Whatman no. 41 or no. 42 filters, Whatman LabSales Inc., Hillsboro, OR). Filters composed of PVC or MCE (Section 2.2.1.) can also be used to take wipe samples.

b) Scintillation vials, 20-mL (as described above).

2.3 Sampling Techniques

See Section 4.1, Table 1 for additional sampling information regarding substances having specific dust PELs.

2.3.1 Air sample collection

If sample weights are of interest, desiccate and then weigh any PVC filters before sampling.

Due to the nature of substances collected and analyzed using this method, it is recommended that samples taken for compliance purposes are pre- and post-weighed, and an exposure assessment is made based on the sample weight before submission for analysis.

For XRF analyses, MCE filters are preferred over PVC because they are more transparent to X-rays and blank intensities are less significant. However, sample weights are better determined using the PVC filter because moisture retention is minimal. Use PVC membrane filters for gravimetric analyses.

1) Place a cellulose backup pad in a cassette. Place the membrane filter (either MCE or PVC) on top of the backup pad. If large loadings are expected and the membrane has a smooth and a rough side, place the membrane in the cassette with the smooth side against the backup pad and use a three-section cassette to help produce a more adherent deposit. Assemble the cassette.

2) Attach a Tygon tube between the pump and a flow calibration cassette so that the air will be drawn through the filter membrane. Do not place any tubing in front of the cassette.

3) Calibrate each sampling pump to within ±5% of the recommended sampling rate with the calibration cassette attached in-line. A cyclone should also be attached during calibration if necessary for quartz or respirable dust sampling (also see Step 9 below).

4) Attach a prepared cassette to the calibrated sampling pump and place in the employee's breathing zone.

5) If possible, take a full shift sample at the recommended sampling rate.

6) Place plastic end caps on each cassette after sampling.

7) If weights are of interest, remove any PVC filters from the cassettes, dessicate, and then post-weigh. Replace the filters in their cassettes.

8) Attach an OSHA-21 seal around each air and blank sample in such a way as to secure the end caps of the cassettes.

9) Submit at least one blank sample with each set of air samples.

10) Gravimetric analyses in the field should suffice when the 5 mg/m³ respirable dust PEL for a substance is evaluated. Any respirable dust samples suspected of containing quartz should be submitted to the laboratory for quartz analysis. Also, situations may arise where the IH needs further information to characterize a respirable dust exposure. In these cases, respirable dust samples can be submitted for laboratory analysis.

2.3.2 Bulk sample collection

In order of laboratory preference, bulk samples may be one of the following:

a) a high-volume filter sample,
b) a representative settled dust (rafter) sample,
c) a sample of homogeneous dust (or powdered) bulk material in th workplace.

1) Collect between 10 to 20 mL of dry bulk sample to provide for optimum detection of minor components in bulk samples. Samples of at least 10-mL volume are recommended. This provides sufficient material for other analyses, if necessary. If samples are liquids or very low-density (fluffy) dusts, **contact the laboratory.** Liquids that evolve corrosive gases or that dissolve support membranes may damage the XRF spectrometer. Some very low density dusts are poorly analyzed.

2) Transfer the bulk material into a 20-mL scintillation vial, seal with a cap having an inert plastic liner, and wrap with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise (top to bottom) around the vial.

3) The type of bulk sample should be stated on the OSHA 91 and cross-referenced to the appropriate air sample(s).

2.3.3 Wipe sample collection

Wipe samples are not an optimum medium for this method; increased background signal noise results in high detection limits and irreproducible blank corrections. Substances collected on wipes are unevenly distributed. If necessary, qualitative scans of a portion of the wipe sample can be performed.

1) Wear clean, impervious, disposable gloves when taking each wipe sample.

2) Moisten the wipe filters with deionized water prior to use.

3) If possible, wipe a surface area covering 100 cm².

4) Fold the wipe sample with the exposed side in.

5) Transfer the wipe sample into a 20-mL scintillation vial, seal with a cap having an inert plastic liner, and wrap with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise (top to bottom) around the vial.

2.4 Sample Shipment

2.4.1 Document the operation and indicate any known or suspected elements and compounds. If possible, indicate whether components that volatilize may be present.

Any information regarding suspected sample composition, industrial operation, etc. will aid in obtaining the most accurate analysis. These details can assist the analyst when optimizing the instrument and call attention to potential interferences.

2.4.2 Request QUAL-XRF analysis and any appropriate follow-up quantitative analysis.

2.4.3 Ship air and blank samples to the laboratory with appropriate paperwork.

2.4.4 Bulk and wipe samples should be shipped separately from air samples. They should be accompanied by Material Safety Data Sheets (MSDS) if available. Check current shipping restrictions and ship to the laboratory by the appropriate method.

3. Analysis

The user must decide upon the applicability of available equipment and software when using this method. This method is performed using an EDXRF; however, the analyses can be conducted using wavelength dispersive X-ray fluorescence (WDXRF) spectrometers. The type of sampling media used may also be a major consideration. Membranes made of PVC rapidly decompose when irradiated with the high intensity X-ray fluxes present in most WDXRF spectrometers. The decomposition releases corrosive HCl gas and produces a mechanically-weakened membrane consisting of an organic char.

3.1 Safety Precautions

3.1.1 Chemical

Handle reagents and bulk samples carefully. Use protective equipment such as: Gloves, laboratory coats, safety glasses, and an exhaust hood. Use a fit-tested respirator if necessary. Clean up spills immediately.

3.1.2 Radiation

a) When samples are suspected of containing radio-nuclides, first scan the samples using a radiation survey monitor to determine if additional precautions are necessary.

b) Follow established laboratory safety guidelines. Modern X-ray fluorescence spectrometers have built-in safety devices and interlocks to prevent X-ray exposure. **WARNING: These devices should not be adjusted, removed, or overridden for any reason.**

c) Radiation monitors are worn by X-ray equipment operators. These monitors consist of badges and finger rings which are periodically analyzed to detect exposure to low-level radiation.

d) There should be a red or yellow warning light which, when lit, indicates the X-ray generator is powered up. The instrument may be checked for radiation leaks using a sensitive radiation survey meter. Radiation leaks, if present, will be most easily detected when the X-ray tube is operated at the highest power design specification.

e) Periodically have safety mechanisms checked to determine satisfactory operation. A sensitive, fixed-position radiation alarm may be used as an area monitor, but damaging radiation exposures can occur in collimated beams that do not intersect the monitor's probe.

f) Avoid inserting fingers into the sample compartment. Use forceps to change samples.

3.2 Equipment

3.2.1 X-ray fluorescence spectrometer

The spectrometer should be equipped with appropriate monitors, collimators, and secondary targets. The spectrometer at the OSHA Laboratory included the following:

Lucite monitor
Tantalum collimator
Gadolinium secondary target with gadolinium filter
Silver secondary target with silver filter
Zirconium secondary target with zirconium filter
Germanium secondary target
Titanium secondary target

3.2.2 Sample holders for cups

3.2.3 Sample holders for air filters

3.2.4 Sample cups

3.2.5 Kapton window film, 0.33 mil thick (part no. 3511, SPEX Industries, Edison, NJ)

3.2.6 Mylar window film, 0.25 mil thick (part no. 3517, SPEX Industries)

3.2.7 Mylar window film, 0.14 mil thick Ultra-thin Mylar, (part no. D12-202, Kevex Corporation, San Carlos, CA)

3.2.8 Polypropylene window film, 0.20 mil thick (part no. 3520, SPEX Industries)

3.2.9 Microporous window film, polypropylene (part no. D12-203, Kevex Corporation)

3.2.10 Radiation safety monitor (model Monitor 4, S.E. International Instrumentation Division, Summertown, TN)

3.2.11 Platform balance capable of 0.01 g precision and at least 50 g range

3.2.12 Vacuum desiccator - use for sample preparation (model no. F42020, Bel-Art Products, Pequannock, NJ)

3.2.13 Vacuum pump - use for sample preparation (model no. DD 20, Precision Scientific, Chicago, IL)

3.3 Reagents (use reagent grade or better powders for calibrations).

3.3.1 Boric acid

3.3.2 Graphite

3.3.3 Sodium bicarbonate

3.3.4 Aluminum oxide

3.3.5 Ammonium sulfate

3.3.6 Titanium dioxide

3.3.7 Zinc oxide

3.3.8 Yttrium oxide

3.3.9 Aluminum sheet, 1 mm thick

3.3.10 Copper sheet, 1 mm thick

3.4 Instrument Calibration

This method is optimized for the analysis of powdered bulk samples. Use appropriate materials and manufacturer recommendations when calibrating specific instrumentation and software. For the purposes of this method, calibration Sections 3.4.2 to 3.4.5 should be performed only once for a properly maintained instrument. Examples of the calibrations performed on the equipment described above are given in the Standard Operating Procedure (SOP) (5.6) and in Section 4.4, Table 5a.

3.4.1 Prepare appropriate standard(s) and perform an energy calibration of the EDXRF spectrometer.

3.4.2 Determine the peak-width at half-maximum for calibrating the peak deconvolution (profile fitting) software. (This is typically performed when the instrument is installed and then checked periodically during preventive maintenance.)

3.4.3 If necessary, calibrate the instrument for fundamental parameters-type determinations according to instrument manufacturer instructions.

3.4.4 Calibrate the instrument for light element corrections. For example, the following powder samples might be selected and prepared as bulks in appropriate sample holders:

Graphite
Boric acid
Sodium bicarbonate
Ammonium sulfate
Aluminum oxide

When obtaining scatter data, use an energy scale range appropriate to include the X-ray scatter data.

3.4.5 Run a variety of known powdered materials and perform adjustments as necessary to improve recoveries.

3.5 Sample Preparation

Check the sample documentation for information regarding composition. Knowledge of the composition provides a basis for handling potential interferences and assists in selecting the appropriate computer model to account for any matrix effects.

Perform assembly of sample holders on a clean dust-free surface. **Use sample holders appropriate for the instrument.** (Note: The instrument mentioned in the method and evaluation had the following sample/detector/target geometry: The analytical surface is horizontal to and above the detector and target. Samples placed "dust side down" are placed with the dust side oriented towards the target and detector.)

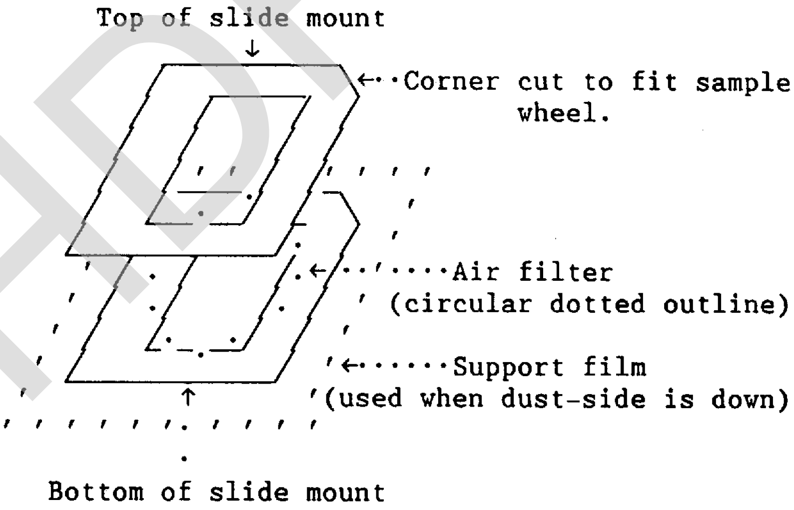
3.5.1 Air sample preparation - MCE and PVC filters

1) Decide how to present the sample for analysis.

   a) Filters with **ADHERENT DUST** are non-destructively analyzed **DUST-SIDE UP** in the sample holder. For enhanced sensitivity of elements lighter than Ti, the filter containing an **ADHERENT DUST** may be prepared with the dust-side down with an optional 0.2-mil (5.1-μm) polypropylene support film.

   b) Loose dust on filters can be analyzed dust side up, but only if great care is taken. There is a potential for contaminating the sample chamber.

2) Assemble the filter holders. The air sample holders used in the evaluation of this method are shown below.



Air sample mount used on Kevex 8000/770

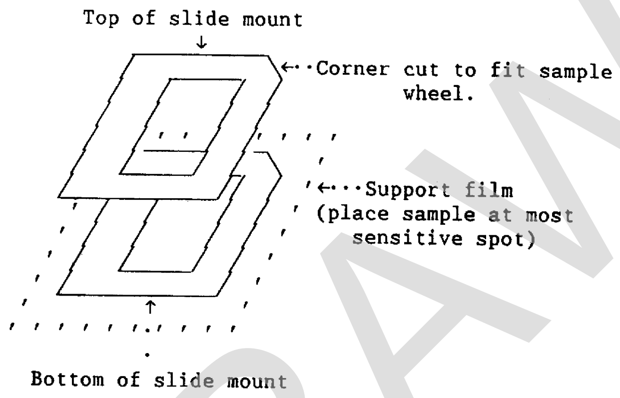
3.5.2 Bulk samples

Samples in the liquid state are generally not analyzed. The liquid phase can be evaporated and the non-volatile residue analyzed; however, element loss in volatile compounds may occur. A vacuum is normally applied to the sample during part of the analysis and may cause the loss of volatile components.

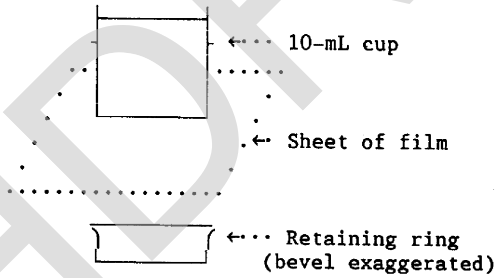
1) Film support selection

For this method, bulk samples may be analyzed on 0.14-mil (3.6-µm) Mylar film. Other materials are available and can be used if samples are chemically incompatible with Mylar, but light element recoveries and Compton to Rayleigh scatter ratio data will be affected. These materials and compatibilities are more fully described in the SOP (5.6).

2) The bulk sample holders used during the evaluation of this method are shown below.



Bulk sample mount used on Kevex 8000/700



Sample cup used for powdered bulk samples

(Optional Microporous film may be used with an additional retaining ring on top to cover the sample.)

a) Liquid bulk or small amounts of dry bulk samples

A qualitative analysis should only be performed if a sample consists of:

evaporated deposits
small quantities of powder
small solid pieces having a total weight less than about 0.5 g

An attempt should be made to prepare this type of sample as a thin, even layer on the support film. This reduces sample matrix effects; however, increased detection limits due to decreased sensitivity are noted. When a sample cannot be spread evenly, position the sample at the most sensitive location on the sample holder. This location can be determined by trial and error using copper peak intensities from a small ring of fine copper wire and a sample holder containing a support film. Mark the location of the ring center on the support film with a felt-tipped pen, and reposition the sample on the membrane until a maximum signal is obtained. Use the resulting template to position samples at the most sensitive spot. Samples which do not cover the entire film or which cannot be made homogeneous produce poor estimates of the amount of non-analyzed material present.

Liquid bulk or small amounts of dry bulk samples are prepared by the following procedure:

1) Select a film material chemically compatible with the sample. The films most often used are made of Mylar, Polypropylene, or Kapton. Further information regarding specific incompatibilities is listed in the SOP (5.6.) and manufacturer catalogs.

2) Assemble the sample holder.

3) Position a small volume of the powdered bulk specimen or several drops of liquid sample at the most analytically sensitive location on the film. For liquid samples, place the film holding the liquid sample in a vacuum desiccator with a liquid nitrogen trap to catch vapors. Evaporate the liquid to dryness and then slowly let air into the desiccator so as not to disturb the dried material. Some oxidizing agents or organic substances may attack all three films mentioned above. For this reason, it is important to reduce the time that solvents are in contact with the film; therefore, begin evaporation as soon as possible after spotting the film. Substances such as sulfuric acid and sodium hydroxide become more concentrated and reactive after evaporation. Ammonium carbonate or boric acid can be added to neutralize acids or bases respectively. If not neutralized, a rapid analysis and removal from the sample chamber is desirable.

b) Large quantities of bulk dust (thick) samples If a sufficient amount (> 0.5 g) of finely powdered dust is available, a semiquantitative analysis can be performed. These bulks are best presented as a thick layer of dust in a sample cup. This greatly improves detection limits and minor component identifications; however, increased matrix effects are also noted. The sample should be homogeneous because the entire contents of the cup are not analyzed.

1) Assemble bulk sample cups and place in sample holders. Use 0.14-mil Mylar film unless it is chemically incompatible with the sample. An excellent substitute support medium is 0.20-mil polypropylene film. The 0.20-mil polypropylene has lower levels of trace light elements and is more transparent to X rays from the light elements present, but it has less mechanical strength than 0.14-mil Mylar film and is more likely to rip. For semiquantitative analyses, always use the same film for standards, samples, and blanks.

2) If manufacturer software requires sample mass thickness data(mg/cm²), perform the following:
Tare the sample cup on a balance capable of 0.01 g precision. Pour some of the powdered bulk into the cup until the depth reaches 1 to 2 cm (approximately 5 mL). Record the weight of the powder. Calculate the sample mass thickness by dividing the sample mass (in mg) by the area (in cm²). To obtain the mass thickness for samples contained in 2.54-cm inside-diameter cups, multiply the mass (in g) by 197.35 mg/(g●cm²). This conversion constant was calculated by:

$$197.35\ \mathrm{mg/g{\bullet}cm^2} = \frac{1000\ \mathrm{mg/g}}{3.1416 \times (2.54\ \frac{\mathrm{cm}}{2})^2}$$

Record the mass thickness for each sample.

3) If it is necessary to perform light element analyses on dusty bulks, protect the instrument sample chamber and vacuum pump from dust cloud contamination by either sealing the top of the sample cups with Microporous polypropylene film (using a retaining ring) or by substituting He for the vacuum. Coal dust is a common example of a dust that tends to form a dust cloud when a vacuum is drawn. Check for potential dust cloud generation by first subjecting each sample to a vacuum in the vacuum desiccator.

4) For bulk blanks, use an air filter sample holder to analyze the support medium used in the assembly of the sample cup. This is performed in order to avoid detecting

scattered and fluoresced radiation from an empty bulk sample cup. (Normally when analyzing bulk material, the sample cup walls are blocked by the sample.)

3.6 Analysis

3.6.1 Analytical conditions

Use X-ray excitation conditions appropriate for the system and software being used. Always use the same analytical and calibration conditions. If X-ray tube currents are modified to optimize detector efficiency, use a monitor sample (such as Lucite) to make corrections for changing sensitivities. Operational parameters used during the evaluation of this method are listed in Section 4.4, Tables 5a-5b. For further instruction regarding analysis, consult the SOP (5.6) or specific instrument manuals.

3.6.2 Desirable analyte sensitivities

See Section 4.2, Table 2 and Section 4.4, Table 5a for examples of integrated peak areas obtained using the instrumentation specified in Section 1.1.4.

3.7 Interferences

3.7.1 Positive interferences (non-analyte signal-augmenting phenomena) include background signals; instrument artifacts from electronics, collimators, target, and filter fluorescence; target and filter Compton and Rayleigh scatter peaks; escape peaks; sum peaks; overlapping sets of M, L, and K spectral lines (MLK peaks) from elements other than those of interest; matrix specific enhancement; and closer sample placement. Many interferences can be resolved through software, by blank subtraction, or by identification of blank contaminants. Sum and escape peaks are further discussed:

a) Sum peaks occur when more than one photon arrive coincident at the detector. The problem of sum peaks can be reduced by decreasing the X-ray flux so that the count rate achieves "low % dead time." Alternately, some manufacturer software programs can correct for minor sum peaks.

b) An escape peak is generated by the low-probability quantum excitation of the K-shell electrons in the silicon atoms of the detector producing a small peak at 1.76 thousand electron volts (kV) below a fluorescence line. Fluorescence lines below 1.76 kV are unaffected, whereas those just above 1.76 kV are most strongly affected. This phenomenon is easily modeled, so software can readily correct for it.

Alternative analytical lines are often available to resolve interferences.

3.7.2 Negative interferences (signal-decreasing phenomena) include matrix absorption effects and displacement of the sample away from the secondary target and detector. Matrix absorption effects can be addressed using sample information provided by the IH. Sample displacement errors can be reduced by using care to prepare flat membrane support surfaces.

3.7.3 Peak location in a spectrum is not proof of the identity of an element. Analysis of other peaks for that element and profile fitting (also called deconvolution), if necessary, provide further evidence of identity. Qualitative analysis requires experience and analyst interaction.

3.8. Calculations

The sequence of steps in evaluating the data depends on software requirements. Alternate sequences may be necessary when using different software. The steps below assume certain software features are available to the user. Other software products may be used. Qualitative analysis consists of Sections 3.8.1-3.8.8. Semiquantitative analysis includes Sections 3.8.1-3.8.14.

3.8.1 Perform escape peak corrections.

3.8.2 Perform sum peak corrections, if available.

3.8.3 Perform blank corrections for membrane support (or air blank).

3.8.4 Perform automated identification of elements. Note: This is an optional step. Automated identification may suggest possible elements that the analyst may not have considered.

3.8.5 Perform background modeling and subtraction.

3.8.6 Identify the elements and interferences present using the systems graphic terminal and peak markers (which indicate MLK spectral locations). However, neither automated identification nor a trained analyst may be able to identify elements whose major peaks occur as shoulders on the peaks of other elements present in the matrix. When characterizing a sample, also consider the particular elements indicated on the sample documentation. Input the identified elements into the software.

3.8.7 Deconvolute (profile-fit) the identified elements to obtain integrated (area) counts for the analytical peaks.

3.8.8 Check for residual peaks. Uncorrected sum peaks and the peaks of unidentified elements may remain. This is an opportunity to identify elements that are subject to significant interferences, e.g., analyte peaks that occur only as shoulders on the peaks of other elements in a particular matrix. Repeat Sections 3.8.6 and 3.8.7 until all peaks are accounted for.

3.8.9 Determine the Compton to Rayleigh scatter ratio.

3.8.10 Perform the fundamental parameters estimation including the sample mass thickness and Compton to Rayleigh scatter data. [Note: This latter approach is especially useful when analyzing light matrices.]

3.8.11 Repeat 3.8.10. without the Compton to Rayleigh scatter data. [Note: This approach is useful when the sample matrix is unknown.]

3.8.12 Repeat 3.8.11. and force the results to total 100%. This approach is useful when all major elements in the sample have been accounted for.

3.8.13 Include any known (or suspected) chemistry (e.g., whether the sample consists of geological material, oxides, sulfides, alloys, organic, or other light element composition). Also include any known chemical stoichiometry of the analyzed elements to help account for unanalyzed elements such as the light elements Na, O, C, and H. Chemistry information places constraints on how the results are calculated and generally improves the reliability of the semiquantitative estimates. For example, for many mineral dusts, it may be appropriate to represent the analyzed elements as oxide compounds such as Fe_2O_3, TiO_2, SiO_2, CaO (or $CaCO_3$), and BaO. More specific knowledge about the matrix may be used. For example, if a sample theoretically consists of primarily anhydrous sodium sulfate and sodium chloride, represent the analyzed elements S and Cl as Na_2SO_4 and NaCl to account for the unanalyzed Na and O contents. Repeat Sections 3.8.10 through 3.8.12 to include the chemistry constraints.

3.8.14 The semiquantitative results from the operations above may differ significantly. Analyst experience and matrix information provided about the sample must be used to select the results that represent the most realistic physical and chemical assessment.

3.8.15 Re-analyze at least 10% of the samples submitted for semiquantitative XRF analysis by validated ICP-AES or atomic absorption (AA) methods. These samples can serve the function of quality assurance samples.

3.9 Reporting Results

Results for the following samples are generally reported as qualitative:

Air or wipe filter samples
Liquid bulk samples
Insufficient amount of bulk material (usually < 0.5 g)

3.9.1 Qualitative results

Report the elements identified by XRF analysis using element symbols. Rank the element symbols based on atomic number without regard to amounts.
The element symbols may be further qualified as follows:

1) "+" to indicate detected and confirmed present (e.g., "+ Fe")

2) "-" to indicate that a requested analyte was specifically looked for, but was not detected (e.g., "- Br")

3) "?" to indicate that a signal was present indicating that the element may be present, but it could not be confirmed on alternate peaks in this matrix (e.g., "? As" in a matrix containing Pb)

All of the identified elements need not be reported. Unreported elements may include those near the detection limit or those having significant interferences on all major analytical lines.

3.9.2. Semiquantitative results

All semiquantitative results are approximate. It is important to consider the limited accuracy of this method. The method evaluation indicated that errors in quantitation by a factor of 2 are not uncommon. Additional work can be performed to improve analytical results and some suggestions are mentioned in the Appendix.

Semiquantitative results may be reported two different ways:

a) In cases where samples were analyzed as homogeneous powders of uniform thickness, rank the element symbols (and qualifiers) from highest to lowest estimated concentration. This is the most restrained (or conservative) representation of the semiquantitative information.

b) Numerical semiquantitative results (with units of "%" or "µg/g") can be added to the list of identified substances in Section 3.9.2.a. Although reported to two significant figures, these results should be considered as "order of magnitude" estimates.

3.9.3 When routing samples for re-analysis by another method, include a copy of the semiquantitative numerical results. While not as detailed as an MSDS, these results provide useful information to those who must handle the bulk. Results also assist in bulk sample preparation to select both appropriate digestion techniques and aliquot sizes. Also request that the results obtained by the re-analysis be copied and returned to the analyst who performed the XRF analyses. This provides quality assurance information.

4. Backup Data

An evaluation of this method was conducted to address qualitative support for aerosol (air) and bulk samples, and the potential for analyzing bulk materials semi-quantitatively without the use of specific calibration standards. Samples were prepared and analyzed during this evaluation as described in Section 3. of the method. Fourteen air samples on PVC and twenty-one bulk samples were analyzed; results are presented in Sections 4.2 and 4.3 respectively. An outline of this Backup Data follows:

4.1 PELs Supported
Table 1 (Regulated Dusts)

4.2 Estimation of Aerosol Detection Limits
Experimental design
Table 2a (Aerosol Source Materials)
Table 2b (Estimated Detection Limits)
Table 2c (Estimated Aerosol Detection Limits - Conservative)
Calculations of aerosol detection limits
Discussion of aerosol detection limits

4.3 Evaluation - Bulk Sample Determinations
Experimental design
Calculations used in software

Table 3 [Pure Substances - $(NH_4)_2SO_4$ and Al_2O_3]
Table 4a (Homogeneous Light Element Matrices - TEG50-B and TEG50-C)
Table 4b (Heterogeneous Intermediate Matrices - NIST SRMs 635, 636, 637, 1881, and 2704)
Table 4c (Heterogeneous Mixed Matrix Types - V1 through V12)
Table 4d (Potential Worst-Case Bulk Detection Limits)
Discussion of bulk sample determinations (Figure 1)
Recovery results and outliers
Bulk detection limits
Non-certified trace element composition

4.4 Kevex Operating Conditions Used in Evaluations
Experimental design
Table 5a (Condition Code Definitions)
Table 5b (Element Ranges for Secondary Targets)

4.5 Conclusions

4.6 Appendix
Additional recommendations to improve aerosol detection limits
Additional recommendations to improve semiquantitative estimates

4.1 PELs Supported

Listed below are those compounds that may be characterized using this method; however, when the analysis of a specific compound is requested, an elemental analysis is performed and reported as the compound.

Table 1
Regulated Dusts

Substance characterized	Total mg/m^3	Respirable mg/m^3	Qualitative analyte(s)
Group I			
Aluminum	15	5	Al
Bismuth telluride, undoped	15	5	Bi, Te
Calcium carbonate	15	5	Ca
Calcium silicate	15	5	Ca, Si
Calcium sulfate	15	5	Ca, S
Gypsum	15	5	Ca, S
Limestone	15	5	Ca
Marble	15	5	Ca
Particulates not otherwise requlated	15	5	
Perlite	15	5	Si
Plaster of Paris	15	5	Ca, S
Group II			
Alpha-alumina	10	5	Al
Ammonium sulfamate	10	5	S
Emery	10	5	Al, Fe
Kaolin	10	5	Al, SI
Portland cement	10	5	Ca, Si
Rouge	10	5	Fe
Silicon	10	5	Si
Silicon carbide	10	5	Si
Group III			
Barium sulfate	10	5	Ba, S
Dicyclopentadienyl iron	10	5	Fe
Molybdenum, insoluble	10	5	Mo
Titanium dioxide	10	5	Ti
Zinc stearate	10	5	Zn

For all three groups listed, respirable dust samples are normally analyzed gravimetrically in the field. If crystalline silica is suspected, submit respirable samples to the lab for analysis.

Group I:

Sample analysis is based on a gravimetric determination performed in the field for total dust, because these PELs are the same as listed for "Particulates, not otherwise regulated". Additional analysis can be performed if necessary.

Group II:

Contact the laboratory before submitting samples, because methods may not be able to speciate the analyte.

4.2 Estimation of Aerosol Detection Limits

Experimental Design (Table 2a)

The detection limits for 21 elements were evaluated using aerosol air samples collected closed-face on tared PVC membranes. Element and reagent selection was based on the following considerations:

a) Elements found in dusts regulated by OSHA (Table 1) were included in order to provide estimates of detection limits for qualitative confirmations.

b) Toxic elements which may be found while screening air samples were also included. If detected, samples containing these elements may be routed for appropriate analyses.

c) Additional elements were selected to span the widest possible analytical range for each of the five secondary targets (Table 5b). In order to obtain estimates of the worst and best detection limits for each secondary target, analyses were performed on the least and most sensitive analytes. The analytical sensitivity for thin films is a smooth function of atomic number. This smooth function makes it possible to interpolate and extrapolate conservative detection limit estimates for elements not included in Table 2b (See Table 2c).

d) When possible, realistic matrices were included. For example, the National Institute of Standards and Technology (NIST) Portland Cement Standard Reference Material #635 (SRM-635) was used as the reagent for estimating the detection limits for six elements. Pure TiO_2 was included as a check on the detection limit estimate made using the trace Ti contained in the SRM-635 [shown as Ti(TiO2) and Ti(Blue) respectively in Table 2b]. Both detection limit estimates were similar for the two Ti determinations. Also, lead chromate was considered a representative matrix for both Pb and Cr.

e) Aerosol particles tend to concentrate in the center of air filters when samples are collected using closed-face cassettes.

The estimations of microgram detection limits for closed-face sampling were based on aerosols of reference materials containing one or more analyte elements deposited at approximately 2 L/min onto tared (approximately 12 mg) 37-mm PVC membranes (5-µm pore size) supported by cellulose back-up pads (using 3-piece cassettes). In order for accurate weights to be determined, PVC filters were used instead of MCE. The PVC filters were re-weighed after deposition and the analyte mass was calculated using the known percentage composition of the aerosol. The elements analyzed are listed below in order of increasing atomic number. They are paired with the corresponding source materials.

Table 2a
Aerosol Analyte Detection Limit Determinations
(Aerosol Source Materials)

Element	Source	Element	Source	Element	Source
Al	$AlPO_4$	Cr	$PbCrO_4$	Ag	Ag
Si	SRM-635	Mn	SRM-635	Cd	Cd
P	$AlPO_4$	Fe	SRM-635	Ce	$Ce(OH)_4$
S	SRM-635	Zn	ZnO	Ho	Ho_2O_3
K	SRM-635	As	As_2O_3	W	WO_3
Ca	SRM-635	Sr	$SrCO_3$	Hg	HgO
Ti	TiO_2, SRM-635	Zr	ZrO_2	Pb	$PbCrO_4$

Table 2b
Aerosol Analyte Detection Limit Determinations
(Estimated Detection Limits)

Element	kV Range		Micrograms	Analyte Counts	Blank Counts	Detection Limits, µg	Secondary Target
	from	to					
Al	1.330	1.640	194.0	967	1673	24.62	Ti
Si	1.540	1.920	176.6	1070	3999	31.31	Ti
P	1.800	2.250	222.8	4817	8017	12.42	Ti
S	2.100	2.600	58.1	3440	115906	17.25	Ti
K	3.120	3.460	7.7	2066	193	0.16	Ti
Ca	3.420	3.890	877.4	173044	248	0.24	Ti
Ti(TiO_2)	4.280	4.730	140.3	5157	41	0.52	Ge
Ti(Blue)	4.360	4.650	3.9	156	31	0.42	Ge
Cr	5.180	5.650	222.4	14631	69	0.38	Ge
Mn	5.740	6.070	1.3	164	57	0.18	Ge
Fe	6.140	6.650	37.5	7418	62	0.12	Ge
Zn	8.380	8.880	46.6	2184	25	0.32	Zr
As	10.360	10.700	6.8	84	15	0.94	Zr
Sr	13.840	14.440	38.6	932	20	0.56	Ag
Zr	15.360	16.120	299.8	9226	20	0.44	Ag
Ag	21.680	22.480	36	612	159	2.22	Gd
Cd	22.640	23.560	201	2783	158	2.72	Gd
Ce(Lα)	4.600	5.050	202.6	3768	41	1.03	Ge
Ho(Lα	6.440	7.000	644.3	36032	36	0.32	Ge
W(Lα)	8.120	8.660	508.3	6213	58	1.87	Zr
Hg(Lα)	9.620	10.320	1041.9	47456	38	0.41	Zr
Pb(Lα)	10.160	10.900	886.0	28014	36	0.57	Zr

Note: Membranes composed of PVC absorb low-energy X rays from the light elements more strongly than high-energy X rays from the heavy elements. For this reason, samples containing the light elements Al, Si, P, S, K, and Ca were analyzed without a support film and with theadherent dust side of the filter sample directed towards the secondary target and detector. Fluorescence from the element chlorine contained in the PVC membrane is largely responsible for the high background in the analytical region used when analyzing elements having a lower atomic number than Cl (Z = 17).

Table 2c
Conservative Estimated Aerosol Detection Limits (µg)

Periodic Table

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
												30	30	20	20		
K	Ca	Sc	[Ti]	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	[Ge]	As	Se	Br	Kr
2.	2.	1.	.5	.5	.4	.2	.1	.1	.1	.1	1.	1.	1.	1.	1.	1.	
Rb	Sr	Y	[Zr]	Nb	Mo	Tc	Ru	Rh	Pd	[Ag]	Cd	In	Sn	Sb	Te	I	Xe
1.	.6	.5	.4	.4	.4		6.	5.	4.	3.	3.	3.	3.	3.	3.	3.	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
3.	3.	3.	3.	2.	2.	2.	2.	1.	1.	.8	.6	.6	.6	.5			
Fr	Ra	Ac															

Between La and Hf:

Ce	Pr	Nd	Pm	Sm	Eu	[Gd]	Tb	Dy	Ho	Er	Tm	Yb	Lu
1.	1.	1.		.8	.7	.6	.5	.4	.3	4.	4.	3.	3.

After Ac:

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
.5		.5											

Microgram detection limits for elements in aerosols collected on PVC are shown above. The detection limits are listed below the symbol for each element that can be analyzed by this method. Results from Table 2b were used to make conservative estimates for the 21 elements evaluated (shown as **bolded** symbols). Detection limits for the remaining elements that can be analyzed were next obtained by interpolation and conservative extrapolation. All limits shown are estimates. The noble gases, elements lighter than Al, and chlorine cannot be analyzed on PVC membranes. (Chlorine and chlorine compounds can be analyzed on MCE membranes.) Note: This method is not appropriate for the radioactive elements Tc, Po-Ac, Pa, and Np-Lw. The secondary target elements used in this method are enclosed in [ ].

Calculation of aerosol detection limits (Table 2b)

Detection limit calculations were performed as indicated in Section 1.3.1 of the method. [Note: Although widely used as an estimate of the qualitative detection limit, this theoretical approach assumes a model that does not consider effects from interferences. Also, special care was used when performing appropriate blank subtraction, background modeling, and profile fitting in order to isolate the light element fluorescence peaks.]

Discussion of aerosol detection limit results (Tables 2b-2c)

The analytical detection limits in Tables 2b-2c above were determined using K_α analytical peaks, except as noted. Analyte counts shown in Table 2b are rounded to the nearest whole count. With the exception of the four lightest elements, the detection limits for most of the elements are very low. Compared to loadings needed to qualitatively analyze heavy elements on PVC membranes, relatively large loadings are necessary for light elements. Because MCE membranes are more transparent to X rays than PVC membranes, lower sample loadings can be used and better detection limits for light elements are achieved. Additional recommendations for improving aerosol detection limits can be found in the Appendix.

4.3 Evaluation - Bulk Sample Determinations

Experimental design (Table 3 and Tables 4a-4d)

Recoveries for 37 elements in powdered heterogeneous and homogeneous bulk samples were evaluated in order to model typical samples that are sent to the laboratory. The following elements were incorporated in the study (listed in order of increasing atomic number):

Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, Sn, Te, Ba, La, W, Hg, Tl, Pb, and Bi

The accuracy of this method is particularly sensitive to sample matrix effects, because standard matrices are not matched to sample matrices. For that reason, a wide variety of matrix types were used in the evaluation study. Homogeneous samples (Tables 3 and 4a) are useful in evaluating optimum conditions for analyses.

Heterogeneous samples (Tables 4b-4c) are useful in evaluating the effect of errors associated with packing and particle-size effects. They also have the additional error associated with obtaining representative samples of mixtures of solids. The evaluation samples consisted of seven known reference materials (Tables 4a-4b) and 12 evaluation bulk samples (Table 4c) prepared in a blind test of the method.

a) The results in Table 4a are for an organic (gelatin) matrix containing trace elements in two standard reference materials (TEG50-B and TEG50-C from Kodak Industries, Rochester, NY). These were light matrix materials accompanied by certificates of analysis.

b) The results in Table 4b are for standard reference materials (SRMs) from NIST. These mineral samples were accompanied by certificates of analysis and represented intermediate weight element matrices.

c) The results in Table 4c are for unknowns that were prepared in a manner to provide stable, challenging, and realistic samples of uniform composition. These mixtures were prepared by an independent chemist who ground and mixed the chemically compatible reagents. The majority of analytes were oxides. They included light, intermediate, and heavy matrices.

The major component of each of the evaluation bulk samples in Table 4c was a matrix consisting of one or more of the following:

boric acid (representing a light element matrix)
starch (representing a light element matrix)
zinc oxide (representing a heavy element matrix)
ferric oxide (representing a heavy element matrix)
silicon dioxide (Celite, representing an intermediate-weight
element matrix comparable to river sediment and Portland cement).

Except for the ferric oxide, all the matrices were white; this reduced the analyst's ability to immediately assess the major components of each bulk. As the data began to accumulate, the analyst judged that the matrices could be arranged in groups of three. The analyst's observations during the blind experiments were:

a) Three samples (V4 through V6 listed below) tended to clump and gave strong signals for Zn.

b) Three samples (V7 through V9) gave a strong signal for Si. The matrix identity of V1 through V3 and V10 through V12 could not be assessed from observations made by the analyst.

The identities of the matrices were revealed after the results of the analyses were reported:

Samples	Matrix	Type
V1 V2 V3	Boric acid	light element
V4 V5 V6	Zinc oxide	heavy element
V7 V8 V9	Silicon dioxide	intermediate
V10 V11 V12	Corn Starch	light element

Prior to the analyses the analyst knew that oxides of the elements were the major materials used for the components. This information provided chemistry information during data workup. The analyst prepared an additional sample consisting of powdered aluminum oxide to check analytical sensitivity. Aluminum was the lightest element attempted in the analyses of samples V1 through V12.

Results were determined using three different software routines that streamline the following calculations:

Calculations used in software

The three approaches described in Sections 3.8.10-12 of the method were used to obtain quantitative estimates of the composition of bulks presented in Tables 3-4c. Three in-house custom procedures (QUANT - Section 3.8.10, NORMQUANT - Section 3.8.11, and MARSQUANT - Section 3.8.12) were used to implement the three approaches and obtain estimates of sample composition. These procedures allow the option of including chemistry information (e.g., reporting as oxides if appropriate). Details of these routines are described below:

a) A custom procedure (results indicated by "QUANT" in Tables 3-4c) which calculated estimates only on detected elements. This procedure calls the proprietary Kevex fundamental parameters function QUANT/EXACT/FILM which takes into account the analytical data and the sample mass thickness. It performs an estimate of the composition of the sample in terms of analyzed elements (including any chemistry).

b) A custom procedure (results indicated by "NORMQUANT" in Tables 3-4c) calls the proprietary Kevex function QUANT/EXACT/FILM/NORM which takes the result above and proportions the results so that the composition sums to 100%.

c) A custom procedure (results indicated by "MARSQUANT" in Tables 3-4c) calls the proprietary Kevex software function QUANT/EXACT/FILM/MARS. Portions of the routine are iterative.

It uses Compton and Rayleigh scatter data and MARS (described below) calibration data to correct for the presence of unanalyzed light elements. Warning messages are displayed when the scatter data are outside the calibration range or when the process does not converge (This occurs when the process fails to estimate a reasonable light element composition for the sample due to matrix effects).

The MARS function accessed through the procedure "MARSQUANT" is a proprietary Kevex software function that is similar to the previously available Kevex CEMAS function. Portions of the routine are iterative. It appears to operate in the following sequence:

1) The function QUANT/EXACT/FILM is called as described above producing an initial estimate of the sample composition in terms of analyzed elements (including optional chemistry).

2) The mean atomic number of analyzed elements (including optional chemistry, e.g., oxygen content in oxides) is next determined.

3) Using the calibration information and the Compton and Rayleigh scatter information, an estimate is made of the mean atomic number of all elements (analyzed and unanalyzed) in the sample.

4) The results from 2) and 3) above are used to estimate the mean atomic number of unanalyzed light elements (MZ_u).

5) Two light elements (E_1 and E_2) that bracket the mean atomic number of unanalyzed light elements are selected. The elements E_1 and E_2 need not be present in the actual sample; they are representative light elements used in computations only.

6) The corresponding atomic weights of these representative light elements, E_1 and E_2, are used to give a representative total weight fraction for the unanalyzed elements.

7) The remainder of the weight fraction is attributed to the analyzed fraction.

8) The analytical results of analyzed elements (including optional chemistry) from operation 1) are then scaled to equal the sum of the analyzed fraction obtained from operation 7).

The overall composition includes the light elements that could be present in the sample. The analytical task was to determine the amount of each analyzed constituent relative to the overall composition of the sample. Test materials were analyzed using the three software routines listed above. For example, a test material consisting of a single analyzable constituent (e.g., Fe as Fe_2O_3) in a light element matrix might give disparate results consisting of:

100% by QUANT   100% by NORMQUANT   3.1% by MARSQUANT

For a single analyzable constituent, both QUANT and NORMQUANT always normalize to 100%; therefore, neither would be selected. If the MARS scatter data was within the calibration range, and MARSQUANT was able to converge, then the 3.1% result would be selected. If not, the analyst should consider reporting only qualitative results.

Results from only one of the three routines was selected for each test material based on the criteria indicated below each of the following tables of results. The reported results from that routine were compared to the theoretical values for the test material. The recovery for each analyzed element in each test material was calculated. Statistics were evaluated for the recoveries for each test material (where appropriate) and for all test materials. The recovery data did not follow a normal distribution. A log-normal distribution better described the observed distribution of recoveries. For a log-normal distribution the measure of scatter equivalent to 1SD is a factor (SD_f). Log-normal statistics are often useful when a wide range of results is encountered. The overall SD_f was found to be 2. Listed below are the results for two pure samples (Table 3), the results for a variety of bulk sample mixture analyses (Tables 4a-4c), and the summary of bulk detection limits (Table 4d).

The following characters, symbols, or nomenclature (in bold-type for illustration) are used in Tables 3-4c:

RECOVERY = ratio of FOUND/THEORETICAL amounts

P = results in parts per million (µg/g)

1% = 10,000 µg/g

ND = None Detected

SD_f represents the factor used to determine the log-normal recovery range equivalent to 1 standard deviation in the recovery. As an example where SD_f = 1.493 and the mean recovery = 0.956:

The low end of the recovery range for this analysis is obtained from:

Mean recovery × SD^{-1f} = 0.956 × 1/1.493 = 0.640

The high end of the recovery range is obtained from:

Mean recovery x SD^{1f} = 0.956 x 1.493 = 1.427

Detected elements in the tables with recoveries in error by more than a factor of 4 are flagged with the symbol "▿".

Table 3

Sample ELEMENT	$(NH_4)_2SO_4$ MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
S	34.49	(100)	(100)	24.27	1.421
Total	34.49			24.27	

QUANT and NORMQUANT both normalize to 100% when presented with result files having only one analyzed component. MARSQUANT operated without issuing error warnings and these results were selected. The compound stoichiometry was not given to the software.

Sample ELEMENT	Al_2O_3 MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
O	26.77	15.88	47.04	47.09	0.998
Al	30.08	17.84	52.83	52.91	0.998
Fe	197 P	244 P	655 P		
Zn	24 P	27 P	81 P		
Ga	124 P	143 P	424 P		
Zr	50 P	58 P	173 P		
TOTAL	56.89	33.77	100.00	100.00	

The MARS scatter corrections for light elements gave a mean atomic number (for all elements in sample) less than 0.5 Z above the highest MARS calibration standard (an arbitrary cut off at 11.15). However, no residual light elements were found by the MARS program. The results from either the QUANT or the NORMQUANT approaches better approximated this sample's composition; the sample was also known to be composed mainly of Al_2O_3. The NORMQUANT approach appeared most suitable in providing estimates of all constituents in the sample. This is representative of the utility of the method in estimating trace element composition when the major constituent is known and can be analyzed. This approach is used on some field samples, but it is not a strong test of the system.

Table 4a
Evaluation Bulk Sample Mixture Determinations
Homogeneous Light Element (Gelatin) Matrix

SAMPLE KODAK **TEG50-B**:

ELEMENT	MARSQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Na		397 P	ND
Mg		256 P	ND
Al		60 P	ND
S	0.52		-
Cl	0.91		-
K	88 P		-
Ca	0.55	0.2025	2.716
Ti	12 P		-
V	6 P		-
Cr	48 P	47 P	1.021
Mn	49 P	48 P	1.021
Fe	81 P		-
Co	50 P	46 P	1.087
Ni	46 P	52 P	0.885
Cu	46 P	51 P	0.902
Zn	41 P	53 P	0.774
As	70 P	115 P	0.609
Se	29 P	39 P	0.744
Ru	12 P		-
Ag	55 P		-
Cd	42 P	45 P	0.933
Sb	41 P	57 P	0.719
Te	40 P	45 P	0.889
Ba	-	50 P	ND
Hg	62 P	55 P	1.127
Tl	56 P	46 P	1.217
Pb	91 P	59 P	1.542
Bi	22 P	49 P	0.449

MARS software ran without issuing error messages. Statistics for heavy certified elements (those beyond Ti) are shown as mean recovery data.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 0.956, SD_f = 1.493

Table 4a (continued)
Evaluation Bulk Sample Mixture Determinations
Homogeneous Light Element (Gelatin) Matrix

SAMPLE KODAK **TEG50-C**:

ELEMENT	MARSQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Li		47 P	ND
Be		42 P	ND
B		51 P	ND
Na		185 ±32 P	ND
Mg		73 P	ND
S	0.51		-
Cl	1.45		-
K	200 P	94 ±32 P	2.128
Ca	1800 P	570 ±53 P	3.158
Ti	13 P		-
V	57 P	52 P	1.096
Cr	54 P	47 P	1.149
Mn	56 P	45 P	1.244
Fe	72 P	64 P	1.125
Ni	2 P		-
Cu	60 P	49 P	1.224
Ga	51 P	48 P	1.062
Rb	39 P	46 P	0.848
Sr	52 P	48 P	1.083
Zr	48 P	45 P	1.067
Mo	44 P	59 P	0.746
Ag	111 P	56 P	1.982
In	38 P	48 P	0.792
Sn	37 P	47 P	0.787
Ba	23 P	44 P	0.523
Bi	46 P	43 P	1.070

MARS software ran without issuing error messages. Statistics for heavy certified elements (those beyond Ti) are shown as mean recovery data.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 1.128 , SD_f = 1.531

Table 4b
Evaluation Bulk Sample Mixture Determinations
Heterogeneous Intermediate Element (Mineral) Matrices

SAMPLE **SRM-635** (NIST Portland Cement "Blue"):

ELEMENT	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Volatiles		3.24	ND
B		< 0.01	-
F		0.04	ND
Na as Na_2O		0.07	ND
Mg as MgO	0.77	1.23	0.626
▿Al as Al_2O_3	0.72	6.29	0.114
Si as SiO_2	7.28	18.	0.396
P as P_2O_5		0.17	ND
S as SO_3	8.15	7.07	1.153
Cl		< 0.01	-
K as K_2O	1.17	0.45	2.600
Ca as CaO	80.08	59.83	1.338
Ti as TiO_2	0.17	0.32	0.531
V	19 P	< 0.01	-
Cr as Cr_2O_3	0.01	0.01	1.000
Mn as Mn_2O_3	0.05	0.09	0.556
Fe as Fe_2O_3	1.41	2.61	0.540
Ni	31 P	< 0.01	-
Cu	12 P	< 0.01	-
Zn as ZnO		0.01	ND
Sr as SrO	0.16	0.21	0.762
Y	14 P		-
Zr		< 0.01	-
Mo		< 0.01	-
Ag		< 0.01	-
Sn		< 0.01	-
Ba	0.02	< 0.01	-
Pb		< 0.01	-

This sample matrix was too heavy for successful MARSQUANT operation. Because the sample was known to be geological, normalized oxide results from NORMQUANT were selected as most representative. Sum peaks from strong Ca signals may be responsible for producing weak lines near Co and Ni analytical peaks (Small signals were noticed in the vicinity of the Co spectrum; however, results for Co were ND). The representation of analytes listed under the ELEMENT heading are as indicated in NIST certification documents.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 0.677 , SD_f = 2.217

Table 4b (continued)
Evaluation Bulk Sample Mixture Determinations
Heterogeneous Intermediate Element (Mineral) Matrices

SAMPLE **SRM-636** (NIST Portland Cement "Yellow"):

ELEMENT	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Volatiles		1.16	ND
B		< 0.01	-
F		0.06	ND
Na as Na_2O		0.11	ND
▿Mg as MgO	0.73	3.95	0.185
Al as Al_2O_3	1.03	3.02	0.341
Si as SiO_2	9.88	23.22	0.425
P as P_2O_5		0.08	ND
S as SO_3	2.33	2.31	1.009
Cl		< 0.01	-
K as K_2O	1.38	0.59	2.339
Ca as CaO	83.48	63.54	1.314
Ti as TiO_2	0.11	0.18	0.611
V	0.01	< 0.01	-
Cr as Cr_2O_3	0.00	0.01	ND
Mn as Mn_2O_3	0.06	0.12	0.500
Fe as Fe_2O_3	0.86	1.61	0.534
Ni	27 P	< 0.01	-
Cu	31 P	< 0.01	-
Zn as ZnO	0.01	0.03	0.333
Rb	9 P		-
Sr as SrO	0.03	0.04	0.750
Y	15 P		-
Zr	85 P	< 0.01	-
Mo		< 0.01	-
Ag		< 0.01	-
Sn		< 0.01	-
Ba	0.06	< 0.01	-
Pb	0.01	< 0.01	-

This sample matrix was too heavy for successful MARSQUANT operation. Because the sample was known to be geological, normalized oxide results from NORMQUANT were selected as most representative. Sum peaks from strong Ca signals may be responsible for producing weak lines near Co and Ni analytical peaks (Small signals were noticed in the vicinity of the Co spectrum; however, results for Co were ND). The representation of analytes listed under the ELEMENT heading are as indicated in NIST certification documents.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 0.596 , SD_f = 2.028

Table 4b (continued)
Evaluation Bulk Sample Mixture Determinations
Heterogeneous Intermediate Element (Mineral) Matrices

SAMPLE **SRM-637** (NIST Portland Cement "Pink"):

ELEMENT	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Volatiles		1.69	ND
B		< 0.01	-
F		0.04	ND
Na as Na_2O		0.15	ND
Mg as MgO		0.67	ND
Al as Al_2O_3		3.28	ND
Si as SiO2	9.04	23.07	0.392
P as P_2O_5		0.24	ND
S as SO_3	1.72	2.38	0.723
Cl		< 0.01	-
K as K_2O	0.97	0.25	3.880
Ca as CaO	87.00	66.04	1.317
Ti as TiO_2	0.09	0.21	0.429
V	0.01	< 0.01	-
Cr as Cr_2O_3	0.01	0.01	1.000
Mn as Mn_2O_3	0.04	0.06	0.667
Fe as Fe_2O_3	0.94	1.80	0.522
Co	18 P		-
Ni	38 P	< 0.01	-
Cu	16 P	< 0.01	-
Zn as ZnO	0.00	0.01	ND
Sr as SrO	0.07	0.09	0.778
Y	20 P		-
Zr		< 0.01	-
Mo		< 0.01	-
Ag		< 0.01	-
Sn		< 0.01	-
Ba	0.10	< 0.01	-
Pb		< 0.01	-

This sample matrix was too heavy for successful MARSQUANT operation. Because the sample was known to be geological, normalized oxide results from NORMQUANT were selected as most representative. Sum peaks from strong Ca signals may be responsible for producing weak lines near Co and Ni analytical peaks. The representation of analytes listed under the ELEMENT heading are as indicated in NIST certification documents.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 0.820 , SD_f = 2.012

Table 4b (continued)
Evaluation Bulk Sample Mixture Determinations
Heterogeneous Intermediate Element (Mineral) Matrices

SAMPLE **SRM-1881** (NIST Portland Cement "White"):

ELEMENT	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Volatiles		2.01	ND
B		< 0.01	-
F		0.09	-
Na as Na_2O		0.04	-
Mg as MgO	0.84	2.62	0.305
▿Al as Al_2O_3	0.83	4.19	0.198
Si as SiO_2	9.83	22.25	0.442
P as P_2O_5		0.09	ND
S as SO_3	4.57	3.65	1.252
Cl		< 0.01	-
K as K_2O	2.23	1.17	1.906
Ca as CaO	78.71	58.68	1.341
Ti as TiO_2	0.12	0.23	0.522
Cr	28 P	< 0.01	-
Mn as Mn_2O_3	0.15	0.26	0.577
Fe as Fe_2O_3	2.60	4.68	0.556
Co	68 P		-
Ni	12 P		-
Cu	12 P		-
Zn as ZnO	ND	0.01	ND
Rb	4 P		-
Sr as SrO	0.09	0.11	0.819
Y	11 P		-
Zr	63 P	< 0.01	-
Ba	83 P	< 0.01	-

This sample matrix was too heavy for successful MARSQUANT operation. Because the sample was known to be geological, normalized oxide results from NORMQUANT were selected as most representative. Sum peaks from strong Ca signals may be responsible for producing weak lines near Co and Ni analytical peaks. The representation of analytes listed under the ELEMENT heading are as indicated in NIST certification documents.

Log-statistics (all detected analytes having theoretical values):

Mean recovery = 0.641 , SD_f = 2.010

Table 4b (continued)
Evaluation Bulk Sample Mixture Determinations
Heterogeneous Intermediate Element (Mineral) Matrices

SAMPLE **SRM-2704** (NIST Buffalo River sediment):

ELEMENT	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
Li		(50 P)	ND
C		3.348 ±0.016	ND
Na		0.547 ±0.014	ND
Al	5.10	6.11 ±0.16	0.835
Si	24.44	29.08 ±0.13	0.840
P		0.998 ±0.0028	ND
S	1.08	(0.4)	2.700
Cl		(<0.01)	-
K	7.36	2.00 ±0.04	3.68
Ca	9.90	2.60 ±0.03	3.808
Sc		(12 P)	ND
Ti	0.73	0.457 ±0.018	1.597
V	144 P	95 ±4 P	1.516
Cr	190 P	135 ±5 P	1.407
Mn	963 P	555 ±19 P	1.735
Fe	7.51	4.11 ±0.10	1.827
Co		14.0 ±0.6 P	ND
Ni	65 P	44.1 ±3.0 P	1.474
Cu	206 P	98.6 ±5.0 P	2.09
Zn	941 P	438 ±12 P	2.148
Ga		(15 P)	ND
As		23.4 ±0.8 P	ND
Se	4 P	(1.1 P)	3.636
Br	7 P	(7 P)	1.000
Rb	254 P	(100 P)	2.540
Sr	352 P	(130 P)	2.708
Y	79 P	-	-
Zr	797 P	(300 P)	2.657
Nb	35 P	-	-
Cd		3.45 ±0.22 P	ND
Sn		(9.5 P)	ND
Sb		3.79 ±0.15 P	ND
I		(2 P)	ND
Cs		(6 P)	ND
Ba	904 P	414 ±12 P	2.184
La		(29 P)	ND
Ce		(72 P)	ND
Sm		(6.7 P)	ND
Eu		(1.3)	ND
Dy		(6 P)	ND
Yb		(2.8 P)	ND
Lu		(0.6 P)	ND
Hf		(8 P)	ND
▿Hg	53 P	1.44 ±0.07 P	36.8
Tl		1.2 ±0.2 P	ND
▿Pb	674 P	161 ±17 P	4.186
Th		(9.2 P)	ND
U		3.13 ±0.13 P	ND

Noncertified theoretical values supplied by NIST are shown in parentheses.
This sample matrix was too heavy for successful MARSQUANT operation. The MARS approach failed on this geological material, so this material was analyzed as oxides and normalized to 100%. Error ranges are as indicated in NIST certification.

Log-statistics (all detected analytes less Hg):
Mean recovery = 2.009 , SD_f = 1.617
Log-statistics (all detected analytes including Hg):
Mean recovery = 2.308 , SD_f = 2.201

Table 4c
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample ELEMENT	V1 MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
B				11.61	ND
O	7.81	14.37	40.05		
Na				1.84	ND
Al				1.37	ND
P	0.96	1.05	2.92	3.26	0.294
K	0.11	0.15	0.43		
V	6.91	12.56	35.02	7.17	0.964
Fe	1.82	5.79	16.13	1.42	1.282
W	0.30	1.15	3.22	0.29	1.034
▿Hg	0.19	0.77	2.14	0.83	0.229
Total	18.14	35.87	100.00		

The MARS scatter corrections for light elements gave a mean atomic number (for all elements in sample) less than 0.5 Z above the highest MARS calibration standard (an arbitrary cut off at 11.15). Therefore, the results from the MARSQUANT approach were selected.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 0.612 , SD_f = 2.216

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample ELEMENT	V2 MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
B				15.80	ND
O	1.89	13.94	28.02		
Al				2.62	ND
P	0.20	0.32	0.65		
S	0.20	0.64	1.30		
Ca	474 P	0.24	0.48		
Cr	0.75	4.27	8.58	0.98	0.765
Mn	77 P	450 P	905 P		
Fe	346 P	0.22	0.44	442 P	0.783
Y	162 P	0.16	0.32		
Zr	1.70	19.69	39.58	1.53	1.111
Mo	0.49	5.93	11.92	0.45	1.089
Hf	614 P	0.41	0.83		
Pb	0.52	3.87	7.79	.046	1.130
Total	5.92	49.74	100.00		

No warnings were issued during the MARS scatter corrections for light elements. Therefore, results from the MARSQUANT approach were selected.
Log-statistics (all detected analytes having theoretical values):
Mean recovery = 0.961 , SD_f = 1.219

Sample	V3				
ELEMENT	MARSQUANT%	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
	(REPORTED)				
B				15.20	ND
O	2.11	9.39	27.58		
Al				2.22	Nd
V	0.18	0.48	1.42	0.20	0.900
Cr	85 P	240 P	705 P		
Mn	29 P	110 P	323 P		
Fe	4.05	17.00	49.90	4.34	0.933
As	0.16	1.29	3.79	0.21	0.762
W	0.42	2.96	8.68	0.37	1.135
Hg	0.38	2.91	8.54	1.48	0.257
Total	7.31	34.07	100.00		

The MARS scatter corrections for light elements gave a mean atomic number (for all elements in sample) less than 0.5 Z above the highest MARS calibration standard (an arbitrary cut off at 11.15). Therefore, results from the MARSQUANT approach were selected.
Log-statistics (all detected analytes having theoretical values):
Mean recovery = 0.715 , SD_f = 1.802

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample	V4				
ELEMENT	MARSQUANT%	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
			(REPORTED)		
O	7.75	18.46	21.01		
Ti	0.83	1.53	1.75	1.84	0.951
V	0.10	0.19	0.22	0.22	1.000
Cr	0.36	0.69	0.78	0.81	0.963
Mn	33 P	64 P	73 P		
Co	29 P	59 P	67 P		
Ni	140 P	286 P	325 P		
Cu	116 P	270 P	308 P		
Zn	26.16	63.49	72.25	73.39	0.984
Zr	0.34	0.90	1.02	0.79	1.291
Mo	0.81	2.13	2.42	1.66	1.458
Pb	0.16	0.41	0.47	0.41	1.146
Total	36.54	87.86	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.100 , SD_f = 1.182

Table 4c (continued)
Evaluation Bulk Sample Determinations
Hetrogeneous Mixed Matrix Types (Blind Test)

Sample ELEMENT	V5 MARSQUANT%	QUANT%	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
O	6.88	17.21	19.90		
Al			8.27		
Cr	730 P	0.14	0.16	0.15 (221 P)	1.067
Mn				(36 P)	
▿Fe	483 P	936 P	0.11	93 P (0.33)	11.828
Ni	146 P	291 P	337 P	(425 P)	
Zn	27.17	67.96	78.59	65.46 (69.51)	1.201
As	0.20	0.54	0.63	0.70	0.900
Zr	0.18	0.50	0.58	0.37	1.568
Mo				(578 P)	
Cd				(86 P)	
Hg				1.05	ND
Total	34.58	86.47	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

This sample was digested using mineral acids and reanalyzed by ICP-AES. Results for those elements detected by the ICP analysis are shown in parentheses.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.845 , SD_f = 2.881

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample ELEMENT	V6 MARSQUANT%	QUANT%	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
O	7.05	17.39	19.82		
Na				4.37	ND
Si				1.31	ND
P				2.94	ND
Fe	243 P	471 P	537 P		
Ni	174 P	346 P	394 P		
Zn	28.31	69.36	79.06	66.43	1.190
Br	135 P	355 P	405 P		
Zr	0.13	0.33	0.38	0.25	1.520
Mo	0.20	0.33	0.61	0.31	1.968
Hg				0.19	ND
Total	35.78	87.74	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.527 , SD_f = 1.286

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample	V7				
ELEMENT	MARSQUANT%	QUANT%	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
O	36.57	35.16	46.70		
Al				7.54	ND
Si	28.18	26.08	34.65	31.34	1.106
K	0.54	0.59	0.79		
Ca	0.39	0.43	0.57		
Ti	719 P	793 P	0.11		
Mn	181 P	214 P	284 P		
Fe	8.08	9.69	12.87	9.24	1.393
Ni	78 P	104 P	138 P		
Cu	21 P	28 P	37 P		
Zn	96 P	127 P	169 P		
As	0.70	0.94	1.25	1.88	0.665
Sr	1.61	2.25	2.99	1.79	1.670
Ba	113 P	132 P	176. p		
Total	76.18	75.28	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15 and residual light elements represented less than 50% of the sample. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.144 , SD_f = 1.490

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample	V8				
ELEMENT	MARSQUANT%	QUANT%	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
O	33.65	32.46	46.74		
Al				3.61	ND
Si	27.65	25.60	36.85	37.47	0.983
K	0.61	0.78	1.12		
Ca	0.48	0.62	0.90		
Ti	626 P	819 P	0.12		
V	41 P	54 P	78 P		
Cr	46 P	61 P	87 P		
Mn	24 P	32 P	46 P		
Fe	0.69	0.93	1.34		
Ni	1.87	2.67	3.84	3.68	1.043
Zn	144 P	216 P	312 P		
Sr	1.59	2.63	3.79	2.01	1.886
Zr	37 P	63 P	91 P		
Mo	1.11	2.03	2.92	1.39	2.101
Ba	47 P	65 P	93 P		
W	0.26	0.40	0.57	0.34	1.676
Hg	0.32	0.49	0.71	1.61	0.441
Pb	0.46	0.72	1.03	0.65	1.585
Total	68.79	69.45	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15 and residual light elements represented less than 50% of the sample. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.442 , SD_f = 1.816

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample V9

ELEMENT	MARSQUANT%	QUANT%	NORMQUANT% (REPORTED)	THEORETICAL%	RECOVERY
O	38.54	37.40	47.03		
Na				1.14	ND
Si	31.03	29.28	36.82	36.02	1.022
P				0.97	ND
K	0.66	0.76	0.96		
Ca	0.51	0.59	0.74		
Ti	1.42	1.68	2.11	1.51	1.397
Cr	0.43	0.52	0.65	0.53	1.226
Mn	99 P	122 P	154 P		
Fe	0.70	0.87	1.09		
Ni	1.18	1.50	1.88	1.98	0.949
Zn	73 P	94 P	119 P		
Rb	25 P	35 P	44 P		
Sr	0.51	0.71	0.90	0.57	1.579
Zr	2.02	2.89	3.63	2.34	1.551
La	0.78	0.96	1.21	1.16	1.043
Hf	416 P	529 P	665 P		
Hg	1.73	2.29	2.88	6.51	0.442
Total	79.56	79.53	100.00		

The MARS program extrapolated considerably beyond a mean atomic number = 11.15 and residual light elements represented less than 50% of the sample. The analyst decided that the results from either the QUANT or the NORMQUANT approaches adequately approximate this sample's composition. NORMQUANT was selected because the sample was known to be primarily oxides of the analyzed elements, and the MARSQUANT results suggested that the matrix did not have a large amount of unanalyzed light elements.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.082 , SD_f = 1.507

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample V10

ELEMENT	MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
O	0.51	5.43	17.10		
Mg				0.23	ND
Al				0.74	ND
Ti	582 P	0.30	0.94		
Cr	0.44	3.26	10.27	0.51	0.863
Sr	0.61	9.62	30.31	1.04	0.587
Ba	0.42	5.35	16.87	0.56	0.750
La	0.60	7.77	24.51	0.84	0.714
Total	2.63	31.72	100.00		

No warnings were issued during the MARS scatter corrections for light elements. Therefore, results from the MARSQUANT approach were selected.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 0.772, SD_f = 1.173

Sample V11

ELEMENT	MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY

O	1.76	10.77	17.53		
Mg				0.26	ND
Ti	1.60	6.21	10.11	1.39	1.151
Fe	474 P	0.37	0.60	0.049	0.967
Sr	0.44	3.97	6.47	0.36	1.222
Zr	0.48	4.50	7.33	0.39	1.231
Ba	3.59	35.44	57.70	4.16	0.863
Hf	199 P	0.16	0.26		
Total	7.94	61.42	100.00		

The MARS scatter corrections for light elements gave a mean atomic number (for all elements in sample) less than 0.5 Z above the highest MARS calibration standard (an arbitrary cut off at 11.15). Therefore, results from the MARSQUANT approach were selected.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 1.076 , SD_f = 1.170

Table 4c (continued)
Evaluation Bulk Sample Determinations
Heterogeneous Mixed Matrix Types (Blind Test)

Sample V12

ELEMENT	MARSQUANT% (REPORTED)	QUANT%	NORMQUANT%	THEORETICAL%	RECOVERY
O	0.92	10.48	18.45		
Ti	0.11	0.56	0.99		
Sr	0.94	10.87	19.13	0.84	1.119
Zr	1.27	15.50	27.29	1.11	1.144
Ba	1.01	11.96	21.06	1.18	0.856
La	0.61	7.06	12.42	0.81	0.753
Hf	417 P	0.37	0.66		
Total	4.89	56.80	100.00		

No warnings were issued during the MARS scatter corrections for light elements. Therefore, results from the MARSQUANT approach was selected.

Log-statistics (all detected analytes having theoretical values):
Mean recovery = 0.953 , SD_f = 1.228

Table 4d
Worst-Case Bulk Detection Limits (µg/g)

Periodic Table

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
												8%	4%	3%	1%	.5%	
K	Ca	Sc	[Ti]	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	[Ge]	As	Se	Br	Kr
800	600	400	200	100	70	60	60	50	50	50	50	50	50	120	50	50	
Rb	Sr	Y	[Zr]	Nb	Mo	Tc	Ru	Rh	Pd	[Ag]	Cd	In	Sn	Sb	Te	I	Xe
50	50	50	50	50	50		50	50	50	50	50	50	100	60	50	50	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
50	50	50	200	200	100	100	100	100	100	100	1%	50	100	50			
Fr	Ra	Ac															

Between La and Hf:

Ce	Pr	Nd	Pm	Sm	Eu	[Gd]	Tb	Dy	Ho	Er	Tm	Yb	Lu
900	900	800		700	700	600	600	500	500	400	400	300	300

After Ac:

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
100		100											

Bulk detection limits

Worst case percent detection limits for elements in bulk samples are shown above. The detection limits are listed below the **bolded** symbol for each element that was analyzed by this method. Results from Tables 4a-4c were used to make conservative estimates for the elements evaluated. The detection limit was not closely approached for many of the elements analyzed. Interpolation and extrapolation were used to provide estimates for DLs of elements not included in the evaluation. The detection limits shown are tentative estimates. The secondary target elements are enclosed in [ ].

Discussion of bulk sample determinations Recovery results and outliers:

Generally, recoveries were excellent for pure compounds (Table 3) and the trace elements in the gelatin standard reference materials (Table 4a samples TEG50-B and TEG50-C). A wider range of recoveries were found for the mineral standard reference materials (Table 4b), and the blind samples (Table 4c). Two features of the analyses suggested that log-normal statistics were more appropriate than normal (Gaussian) statistics.

a) The results had a large dynamic range.
b) Errors in this analysis tend to accumulate not as the sum of many small errors, but as the product of many small relative errors (factors differing slightly from one).

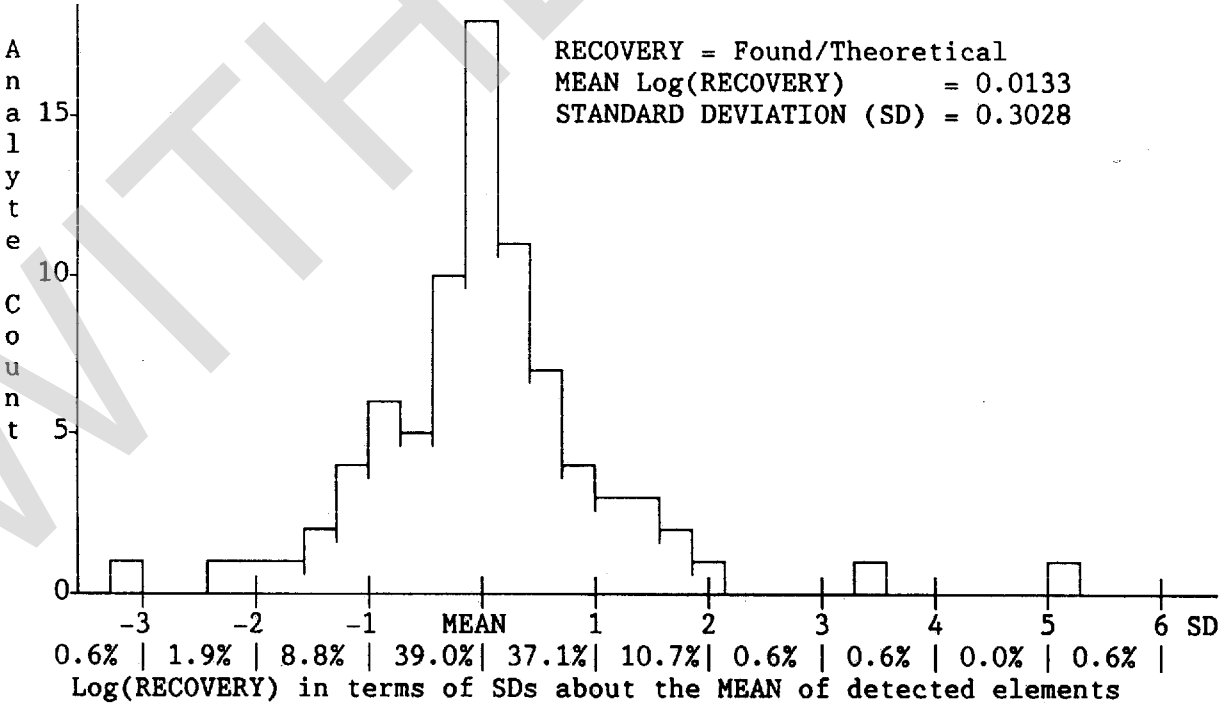
A test of log-normality was performed. The standard deviation found in the log(RECOVERY) was 0.3028 corresponding to a SD_f factor of 2.008 for recovery scatter. If ideal recovery at concentrations in the working range is taken as 1, a SD_f factor of 2 has the following statistical consequences:

$\pm SD_f$ Factor	Recovery range Ideal = 1	Error range Ideal = 0%	% of Samples (Frequency)* Theory	Found
1 SD_f = 2	½ to 2	-50% to +100%	68.3%	76.1%
2 SD_f = 4	¼ to 4	-75% to +300%	95.5%	95.6%
3 SD_f = 8	⅛ to 8	-88% to +700%	99.7%	98.1%

* frequency of samples, or area under the curve as designated by $\pm nSD_f$

The following figure is a histogram describing the spread in recoveries for detected analytes having theoretical values:

Bulk Analysis - Recoveries of Detected Analytes



As examples:

Eighteen of the analytes were near the mean log(RECOVERY) of 0.0133, while one analyte was somewhat further than 3SD below this mean.

An attempt was made to estimate confidence limits for the results. The log(found µg/g) was fit as a linear function of the log(theoretical µg/g) shown in the following equation:

(i) $(\text{found } \mu g/g) = 1.673 \times (\text{theoretical } \mu g/g)^{0.9391}$

This equation indicates that results at low µg/g values (less than 4,767 µg/g) tend to err high, and higher µg/g results tend to err low.

The standard deviation in the calculated log(found µg/g) about the linear regression line obtained in this operation was approximately 0.2929. This corresponds to a SD_f factor of 1.963 for the scatter in recovery comparable to 1SD (calculated from $10^{0.2929}$). Because equation (i) has no significance other than described above and is not used to make any secondary corrections, the scatter associated with the following relation was evaluated:

(ii) $(\text{found } \mu g/g) = 1.000 \times (\text{theoretical } \mu g/g)^{1.000}$

The scatter of data about the line represented by equation (ii) was evaluated by obtaining the standard deviation in the log (found µg/g) about the individual log(theoretical µg/g) values. The SD of 0.3023 corresponds to a SD_f factor of 2.006 (calculated from $10^{0.3023}$). When rounded to two significant figures, both approaches give the same factor of 2.0 with the same statistical consequences as noted in the table above. Two standard deviations is a common criterion for determining outliers. In eight instances, recoveries exceeded this criterion. These seven outliers (flagged with the symbol "▿" in the tables) represent 4.4% of the 159 results used to evaluate recovery. These results were not excluded when determining the statistics above. The outliers included the two light elements Mg and Al and the three heavy elements Fe, Hg, and Pb. Poor recoveries were noted also for K and Ca in sample SRM-2704 ($> 1.84 \times SD_f$). The reasons for these outliers and poor recoveries are discussed below:

The light elements Mg through K had poor recoveries in general (samples SRM-635, SRM-636, SRM-1881, and SRM-2704). Light element recoveries are generally low because matrix effects are more significant for light elements than for heavy elements. Occasionally, light elements were identified when they were not theoretically present. Instrument noise (micro-phonics, thermal, 1/F, shot, etc.), escape peaks, and background are strongest in the spectral range of the light elements and if not sufficiently corrected by the software, increase the spread of recoveries and mimic analyte signals. Automatic background correction is frequently poor in this low energy region. Low energy M and L lines from the heavy elements present in a sample complicate deconvolution.

Results from ICP-AES support the higher level of Fe found by EDXRF (sample V5 in Table 4c). The mortar and pestle used in grinding and mixing the materials in Table 4c were unexpectedly difficult to clean. This outlier may be due to Fe contamination from this source.

The Hg outlier results were for sample SRM-2704 in Table 4b and sample V1 in Table 4c. Analysis of sample SRM-2704 gave a very high recovery for Hg (36.8). The level of Hg found in SRM-2704 (53 µg/g) was at the detection limit for Hg in mineral samples; whereas, the certification indicated a much lower amount (1.44 µg/g). Trace levels of other elements with peaks in the same region (e.g., Ga and As) were not identified. Presumably at these low levels, the count data for these elements in the same region were incorrectly identified as Hg. Sample V1 had a low Hg recovery (0.229). Peak deconvolution apparently did not adequately correct for the overlap of W and Hg peaks.

The Pb outlier result was also for sample SRM-2704 in Table 4b. This outlier overestimated by slightly more than the +2SD limit used to define an outlier. The presence of the unidentified trace element As was probably responsible.

In general, the recoveries were as expected for semiquantitative analysis for the elements heavier than calcium (excluding Hg as described above).

Bulk Detection Limits:

Detection limits are strongly influenced by matrix effects and instrumentation. The following are examples:

1. The 1% DL for Hg shown in Table 4d is for a matrix containing ZnO; in the gelatin matrix Hg can be quantitated at 50 µg/g.

2. The DL for As is large to compensate for the common interference from Pb.

3. The DLs for Sn and Sb are large to compensate for an instrument artifact at the Sn Kα line.

4. The DLs can change abruptly between elements using different secondary targets and line series. For the analysis of La, the Gd secondary target and K_α line are used; for the analysis of Ce, the Zr secondary target and L_α line are used.

Non-detected elements heavier than Mg were present at levels exceeding 50 µg/g in some of the matrices. These included the following seven elements (Theoretical values are in parentheses):

Al(7.51%), Si(1.31%), P(2.94%), Cr(70 P), Zn(80 P), Ce(72 P), Hg(1.05%)

Aluminum, Silicon, and Phosphorus:

Table 4c shows a large amount of undetected Al in sample V7 (7.54%) that is comparable to the amount found in V5 (8.27%) which was not known to contain any Al. The Al peak is a small shoulder on the strong Si peak in sample V7; Al is poorly resolved in this Si matrix. Once identified as present, the Al content changes from ND to 3.72%. Due to the low sensitivity for light elements, the small peak found in sample V5 near the Al spectrum calculates out to a large amount of Al due to the heavy (Zn) matrix.

The detection limits for Si and P are 4 and 3%, respectively, and the results for the two elements (V6 in Table 4c) are well below their detection limits for the matrices tested.

Chromium and Zinc:

Table 4b shows a Cr-containing sample (SRM-636) with Cr non-detected. Table 4b also shows another Zn-containing sample (SRM-635) with Zn non-detected. The Cr and Zn certified values on the NIST certificate are both 0.01% expressed as the oxides. When gravimetric factors are applied to these rounded values, the results indicate levels above 50 P. Because of rounding error, the true values may actually be below the 50 P level.

Cerium:

Table 4b shows a sample (SRM-2704) containing the rare-earth elements (Ce to Lu). In general, rare earth elements are found in the same part of the spectrum where the common first transition series elements (Ti to Zn) occur. Additionally, the rare earth elements generally occur naturally as a complex mixture. As a result, the detection limits for the rare earth elements in common matrices may be orders of magnitude greater than 50 P.

Mercury:

Mercury represents an exceptional heavy metal; several samples contained Hg. While it performed well in the light matrix sample TEG50-B (Table 4a, recovery = 1.127), the recovery spread for Hg was wide ranging from ND (V5 and V6 in Table 4c) to 36.8 (SRM-2704 in Table 4b). Volatilization is not expected to be a major cause of losses, because a vacuum is drawn only after the Hg data are collected. Several matrix effects are possible. The Hg detection limit of 1.05% is appropriate for sample V5 (in Table 4c) which consists of a ZnO matrix containing As. The analytical peaks for Zn and As both strongly overlap the Hg major analytical peaks; only a very minor broad peak of Hg remains to help identify Hg. Mercury was not identified. If Hg were identified, the peaks deconvoluted, and quantitated, the Hg estimate present in sample V5 would change from ND to 0.43%.

If the seven outliers described above are excluded, the standard deviation in LOG(RECOVERY) was 0.2297. This corresponds to a SD_f factor of 1.697 with the following statistical consequences:

$\pm SD_f$ Factor	Recovery range Ideal = 1	Error range Ideal = 0%	% of Samples (Frequency)* Theory	Found
1 SD_f = 1.667	½ to 2	-41% to +70%	68.3%	69.5%
2 SD_f = 2.880	¼ to 4	-65% to +188%	95.5%	94.0%
3 SD_f = 4.888	⅛ to 8	-80% to +389%	99.7%	100.0%

* frequency of samples, or area under the curve as designated by $\pm nSD_f$

Non-certified Trace Element Composition:

Additionally, non-certified trace elements were detected in the bulk materials at levels exceeding 50 µg/g. These elements (listed in order of increasing atomic number) included the following:

Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Br, Y, Zr, Ag, Ba, Hf

The trace elements in the reagents complicated the analyses. Some of the observations are mentioned:

a) Hf was present in the reagent used to provide Zr.

b) Trace contaminants were discovered in the Celite reagent. An EDXRF scan of the "pure" Celite material indicated that it had the following approximate composition:

SiO_2	94.84%	NiO	0.03%
Fe_2O_3	2.18%	MnO_2	0.02%
K_2O	1.35%	SrO	0.01%
CaO	1.25%	ZrO_2	0.01%
TiO_2	0.25%	CuO	(< 0.01% = trace)
V_2O_5	0.04%	Rb2O	(< 0.01% = trace)

c) The pure Al_2O_3 (Table 3) contained detectable amounts of Fe, Zn, Ga, and Zr.

d) The ZnO was contaminated with several first transition elements.

e) The light matrices (boric acid and starch) are relatively free of trace contaminants.

4.4. Kevex Operating Conditions used in Evaluation

Experimental design (Table 5a-5b)

The conditions and data below are provided as suggested analytical conditions for routine sample analyses using this method and to describe overall instrument response. For non-routine samples, analytical conditions may differ significantly.

Kevex firmware and software use the term condition code (abbreviated Cond. Code below). Each of the condition code numbers 1 - 5 is associated with a set of instrument parameters and is used to facilitate routine analyses under different conditions.

Analytical preset times were all 200 s. Longer count times can be used if lower detection limits are necessary. The 12.5 µs time constant was used in order to obtain the best resolution for peak deconvolutions.

Reference elements (Ref) for fundamental parameters setup shown are the pure sheet materials listed in Section 3.3 and analyzed at the "Prescan mA" currents; the corresponding counts (Cts) are integrated Gaussian peak areas for the escape-peak and background corrected K_α data. The reference elements were analyzed without an intervening membrane.

Also shown in the table are integrated K_α peak intensities in counts (at the "Prescan mA" setting) for the same reference materials that were used in the fundamental parameters (EXACT) calibration for the various condition codes. These reference materials were selected because they produced satisfactory quantitative estimates of bulk powder samples that were used in preliminary experiments. Other materials can be used.

Table 5

Cond. Code	kV	Lucite mA	Prescan mA	Secondary Target	Atmos.	Range (kV)	Preset Time	Fund. Parameters Ref	Fund. Parameters Cts
1	60	0.830	0.130	Gd	Air	40	200	Cu	47,546
2	35	0.470	0.200	Ag	Air	40	200	Cu	315,627
3	25	2.360	0.550	Zr	Air	20	200	Cu	362,694
4	15	3.300	0.450	Ge	Vacuum	10	200	Cu	642,744
5	10	3.300	3.300	Ti	Vacuum	10	200	Al	28,900

Conditions for Air Samples:

Air samples typically give lower count rates than the Lucite monitor used in the analyses. The current settings in the "Lucite mA" column produce the maximum practical count rate for the Lucite monitor (not exceeding a 50% dead-time). The current was set to the "Lucite mA" values in order to produce the maximum feasible count rate in analyzing the filter samples.

Conditions for Bulk Samples:

Bulk samples can give count rates greater than that of the monitor. The prescan currents in the column "Prescan mA" shown were selected so that the majority of unknown bulk samples would give dead-times less than 50%. In practice, the monitor and bulks are prescanned in order to find the sample with the highest count rate. The mA current settings for bulk sets are then optimized (typically increased above the "Prescan mA" settings shown) so that the sample with the highest count rate at the starting current produces the highest count rate not exceeding a 50% dead-time. Reduced currents may be employed to resolve sum peak interferences. The design specifications for this instrument limit the maximum settings to 60 kV and 3.3 mA.

The following is a rough guide to select the appropriate analytical ranges when deconvoluting elemental spectra for the different condition codes:

Table 5b
Widest Element Ranges for secondary Targets

Condition Code	Target Element	Kα Range	Lα Range
1	Gd	Zr to La	
2	Ag	Cu to Rh	Hf to U
3	Zr	Cr to Rb	La to Bi
4	Ge	K to Cu	Sb to Ho
5	Ti	Al to Ca	Br to Sb

Optimum (non-overlapping) Element Ranges for Secondary Targets

Condition Code	Target Element	Kα Range	Lα Range
1	Gd	Ru to La	
2	Ag	Sr to Tc	Tl to U
3	Zr	Zn to Rb	Ho to Hg
4	Ge	Sc to Cu	Sb to Dy
5	Ti	Al to Ca	Br to Sn

4.5 Conclusions

Every attempt was made to mimic both air and bulk samples commonly received for qualitative analysis. The DLs and recoveries estimated for this method depend on how closely the samples resemble actual field samples. Analytical performance can be strongly influenced by interferences, sample matrix effects, and analyst experience.

For air samples, this method provides a useful tool to the industrial hygienist in confirming the presence of Table 1 substances in support of gravimetrically determined exposures. Other regulated elements may be identified in the process.

The method also provides a quick screen for up to 70 elements in powdered bulk samples. Under certain circumstances it can also provide quantitative estimates. Energy dispersive X-ray fluorescence is a powerful tool for which many additional uses are possible.

5. References

5.1 Occupational Safety and Health Administration Analytical Laboratory: Finnigan Standard Operating Procedure. Salt Lake City, UT. 1979 (unpublished).

5.2 Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method and Backup Report No. ID-114). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.

5.3 Occupational Safety and Health Administration Technical Center: Metal and Metalloid Particulates in Workplace Atmospheres (ICP Analysis) (USDOL/OSHA-SLTC Method No. ID-125G). Salt Lake City, UT. Revised 1991.

5.4 Birks, L.S.: X-Ray Spectrochemical Analysis; 2nd ed., New York: Interscience Publishers, 1969.

5.5 Bertin, E.P.: Principles and Practice of X-Ray Spectrometric Analysis; 2nd ed., New York: Plenum, 1975. p. 471.

5.6 Occupational Safety and Health Administration Analytical Laboratory: Standard Operating Procedure, Inorganic Analysis by X-Ray Fluorescence Spectrometry (Semiquant-XRF). Salt Lake City, UT. 1989 (unpublished).

Appendix

Additional recommendations to improve aerosol detection limits

Detection limits for some elements may be improved by redepositing dust from the PVC sample medium onto 0.45-μm pore size, 25-mm diameter Ag membranes. This can be accomplished using tetrahydrofuran (THF) to dissolve the PVC filter, suspending the particulate with ultrasound, and then filtering the particulate onto the Ag membrane. This deposit results in a more concentrated sample distribution. However, the options available to use the same sample in subsequent analytical methods are limited. The L-lines from Ag need to be considered as potential interferences when analyzing for light elements such as Al, Si, P, and S. The K-lines of Cl in PVC filters and the L-lines of Ag occur in the same spectral region and may present problems similar to those encountered in the analysis of light elements in this study. By producing thin even deposits, this approach also provides the opportunity to quantitate elements that are present in chemical forms that are insoluble in THF.

Longer integration times can also be used to reduce detection limits or to improve the precision in quantitation. The quality of analytical performance tends to be proportional to the square root of the analysis time.

Requests for the qualitative analysis of specific elements can sometimes be given special attention; the instrument may be set up with excitation conditions tailored to optimize for specific elements. For example, an Fe secondary target may be used (instead of a Ge secondary target) to give enhanced sensitivity for Cr. These non-routine situations generally place additional constraints on how calculations may be performed; semiquantitative analysis may not be feasible.

Additional recommendations to improve semiquantitative estimates

Semiquantitative XRF estimates can often be improved. Because XRF analysis is non-destructive, field samples may also be re-analyzed by wet reference methods such as ICP-AES or atomic absorption spectrometry (AAS). X-ray fluorescence can be used to estimate more elements than the several that can be analyzed by both techniques. Results for elements analyzed by both XRF and a wet reference method can be used to evaluate recoveries and can function as quality assurance samples. Results obtained for samples that are completely digested and analyzed using a validated wet method are often more reliable than results by XRF without extensive matrix modification or sample preparation. Due to resource limitations, not all elements analyzed by XRF can be readily analyzed by another technique. For this reason, another use for wet reference methods is to improve the XRF estimates of elements not analyzed by the reference method. This is accomplished by rescaling the results obtained by XRF to results obtained by the reference method using an element that was analyzed by both methods. Iron occurs in most bulks and can often function as an internal standard. Other approaches to internal standards can be used provided these materials can be homogeneously added. This approach can often resolve XRF matrix problems (such as the presence of non-analyzed elements).

Additional improvements may be unnecessary in cases of well-characterized matrices (such as when the major element composition is known or when analyzing homogeneous light-element matrices).