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

Compendium Method IO-3.4

DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

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Method IO-3.4

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DISCLAIMER

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

Method IO-3.4
Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy

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

Method IO-3.4
DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

1. Scope

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

1.2 On July 1, 1987, the U. S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for ambient particulate matter. This new primary standard applies only to particles with aerodynamic diameters $\leq$10 µm (PM_{10}) and replaces the original standard for TSP. To measure concentrations of these particles, the EPA also promulgated a new federal reference method (FRM). This method is based on the separation and removal of non-PM_{10} particles from an air sample followed by filtration and gravimetric analysis of PM_{10} mass on the filter substrate. In 1997, the PM_{10} standard was replaced with the national ambient air quality standard (NAAQS) for $PM_{2.5}$.

1.3 The new primary standard (adopted to protect human health) limits $PM_{2.5}$ concentrations to 50 µg/m^3, averaged over a 24-h period. These smaller particles are able to reach the lower regions of the human respiratory tract and, therefore, are responsible for most of the adverse health effects associated with suspended particulate pollution. The secondary standard, used to assess the impact of pollution on public welfare, has also been established at 15 µg/m^3 for an annual average.

1.4 Ambient air SPM measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the NAAQS for $PM_{2.5}$. These measurements are obtained by the states in their state and local air monitoring station (SLAMS) networks as required under 40CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by EPA as either reference or equivalent methods.

1.5 The procedure for analyzing the elemental metal components in ambient air particulate matter collected on high volume filter material is described in this method. The high volume filter material may be associated with either the TSP or PM_{10} sampler, as delineated in Inorganic Compendium Method IO-2.1.

1.6 Filters are numbered, pre-weighed, field deployed and sampled, returned to the laboratory, extracted using microwave or hot acid, then analyzed by inductively coupled plasma (ICP) spectroscopy. The extraction procedure is accomplished by following Inorganic Compendium Method IO-3.1.

1.7 This method should be used by analysts experienced in the use of ICP, the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of 6-months experience with commercial instrumentation is required.

1.8 Those metals and their associated method detection limit (MDL) applicable to this technology are listed in Table 1.

2. Applicable Documents

2.1 ASTM Standards

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

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94/038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- *Reference Method for the Determination of Particulate Matter in the Atmosphere*, 40 CFR 50, Appendix J.
- *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)*, 40 CFR 50, Appendix B.
- *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air, Federal Register* 43 (194): 46258-46261.
- U. S. EPA Project Summary Document (1).
- U. S. EPA Laboratory Standard Operating Procedures (2).
- Scientific Publications of Ambient Air Studies (3-7).

3. Summary of Method

3.1 Instrument Description

3.1.1 The analytical system is an inductively coupled plasma atomic emission spectrometer, as illustrated in Figure 1. The plasma is produced by a radio frequency generator. The current from the generator is fed to a coil placed around a quartz tube through which argon flows. The oscillatory current flowing in the coil produces an oscillating magnetic field with the lines of force aligned axially along the tube. The argon is seeded with electrons by momentarily connecting a Tesla coil to the tube where the plasma forms inside. The ions in the gas tend to flow in a circular path around the lines of force of the oscillatory magnetic field and the resistance to their flow produces the heat. To avoid melting the silica tube, a flow of argon is introduced tangentially in the tube, which centers the plasma away from the walls of the tube. The plasma is formed in the shape of a toroid or doughnut, and the sample is introduced as an aerosol through the middle of the toroid. The hottest part of the plasma is in the ring around the center of the toroid, where temperatures of about 10,000 K are achieved. Through the center of the toroid where the sample is introduced, the temperature is somewhat lower, and the sample is subjected to temperatures of about 7,000 K. From the very hot region in the plasma and just above it, a continuum is radiated because of the high electron density. Above this

region, the continuum emission is reduced as the temperature falls and the spectral lines of the elements in the sample may be observed. Since this plasma is generated in an inert atmosphere, few chemical interferences exist.

3.1.2 The spectrum is resolved in a spectrometer. The relative intensities and concentrations of the elements are calculated by a small computer or processor. Samples containing up to 61 preselected elements can be analyzed by ICP simultaneous analysis at a rate of 1 sample per minute. The ICP technique can analyze a large range of concentrations. A single calibration curve can accomodate changes in concentration of 5 orders of magnitude.

3.2 Sample Extraction

Two extraction procedures may be performed: hot acid extraction or microwave extraction, as documented in Inorganic Compendium Method IO-3.1. Extraction involving hot acids is hazardous and must be performed in a well-ventilated fume hood.

3.3 Sample Analysis

A technique for the simultaneous or sequential multi-element determination of trace elements in an acid solution is described in this Compendium method (see Figure 2). The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency ICP. The spectra are dispersed by a grating spectrometer, and the intensities of the line are monitored by photo multiplier tubes. The photo currents from the photo multiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Data is processed by computer and yields micrograms of metal of interest per cubic meter of air sampled ($\mu g/m^3$).

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently, the use of receptor models has documented the need for elemental composition of atmospheric aerosol into components as a means of identifying their origins. The assessment of human health impacts, resulting in major control actions by federal, state, and local governments, is based on these data. Accurate measures of toxic air pollutants at trace levels are essential for proper assessments. The advent of inductively coupled plasma spectroscopy has improved the speed and performance of metals analysis in many applications.

4.2 ICP spectroscopy is capable of quantitatively determining most metals at levels that are required by federal, state, and local regulatory agencies. Sensitivity and detection limits may vary from instrument to instrument.

5. Definitions

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

5.1 Autosampler. Device that automatically sequences injections of sample solutions into the ICP.

5.2 Background Correction. Removing a high or variable background signal, using only the peak height of intensity for calculating concentration. Instruments measure background at one or more points slightly off the emission wavelength and subtract the intensity from the total intensity measured at the analytical wavelength.

5.3 Channels. Simultaneous ICPs have an array of photo multiplier tubes positioned to look at a fixed set of elements (wavelengths); each wavelength is a "channel," which varies by instrument.

5.4 Detection Limits. Determined by calibrating the ICP and determining the standard deviation of apparent concentrations measured in pure water. The result (F) is multiplied by a factor from 2 to 10 (usually 3) to define a "detection limit." Complex sample matrices result in a higher background noise than pure water, so actual detection limits vary considerably with sample type. It is recommended that an instrument detection limit (IDL) be determined in a standard whose concentration is about three times the expected detection limit.

5.5 Detectors. Photomultiplier tubes (PMTs).

5.6 Fixed Optics. The most crucial element in the optical design. If the grating moves during measurement, uncertainties in the results are inevitable.

5.7 Grating. The optical element that disperses light.

5.8 Integration Time. The length of time the signal from the PMT is integrated for an intensity measurement. The most precise measurements are taken at the peak intensity.

5.9 Inter Element Intereference. When emission lines from two elements overlap at the exit slit, light measured by the PMT is no longer a simple measure of the concentration of one element. The second element interferes with the measurement of the first at that wavelength. If lines free of interference can't be found, approximate concentrations of the element of interest can be calculated by calibrating that element and the interferent (inter element correction).

5.10 Linear Dynamic Range. The light intensity in an ICP source varies linearly with the concentration of atoms over more than 6 orders of magnitude (the linear dynamic range). This variation allows for determination of trace and major elements in a single sample, without dilution. Fewer standards for calibration are needed, often a high standard and a blank suffice.

5.11 Limit of Quantitation. The lowest level at which reliable measurements can be made. Defined as ten times the standard deviation of a measurement made in a blank (pure water), which is 3.3 times the "3F" detection limit.

5.12 Monochromator. The spectrometer design on a sequential ICP.

5.13 Nebulizer. A device creating a fine spray of sample solution to be carried into the plasma for measurement. Its performance is critical for good analyses.

5.14 Photomultiplier Tubes (PMTs). Light detectors in ICP instruments. When struck by light, the PMT generates a current proportional to the intensity.

5.15 Polychromator. The spectrometer design of a simultaneous ICP.

6. Ranges, Sensitivities, and Detection Limits

6.1 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on a particular instrument. All measurements must be within the instrument linear range where correction factors are valid. The analyst must verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data, i.e., confirming instrument performance and analytical results.

6.2 For comparison, Table 1 provides typical maximum element concentrations obtained on a Thermo Jarrell Ash Model 975 Plasma AtomComp ICP.

6.3 Calibration sensitivities are dependent upon spectral line intensities. For comparison, Table 1 provides typical sensitivities for the ICP mentioned in Section 6.2 for a Jarrell Ash Model 975 Plasma AtomComp ICP.

6.4 Detection limits vary for various makes and models. Typical detection limits achievable by the Thermo Jarrell Ash Model 975 ICP are given in Table 1. These are computed as 3.3 times the standard deviation of the distribution of outputs for the repeated measurement of a standard, which contains no metals and is used as the zero point for a two-point instrument standardization described in Section 11.3. The acid concentrations of this standard must match the acid concentrations of blanks and samples.

7. Precision and Accuracy

7.1 Accuracy for this procedure has not been determined. Spiked strips used for audits have been developed by the EPA. The main use of the audit results is to document chronologically the consistency of analytical performance. One multi-element audit sample should be extracted daily with normal ambient air samples. Audit samples can only approximate true atmospheric particulates, which contributes to the overall uncertainty. Attempts should be made to use National Institute of Standards and Technology (NIST) 1648 (urban particulate) to judge recovery. This material is not ideal because (1) there is no filter substrate; (2) relatively large amounts (100 mg) are required to overcome problems of apparent inhomogeneity, which in turn necessitates dilutions not required in normal application of this method; and (3) element ratios differ somewhat from those found in real samples. Typical recoveries experienced with the spiked strips and NIST 1648 are presented in Table 2.

7.2 Typical precision, bias, and correlation coefficients calculated from audit samples vs. blind replicate analyses are shown in Table 3. Treatment of the glass fibers during filter manufacture affects both recovery and precision of sample replicate pairs. This fact should be considered when studies are designed.

7.3 Good precision data does not imply accuracy; bias is still possible. Bias is nearly impossible to detect when a given type of sample is always analyzed by the same method using the same instrumentation. In this method, bias, if any, is most likely to arise during the sampling and sample preparation steps.

7.4 Quality assurance (QA) activities are discussed in Section 13 of this method. QA data for the method are composed of QA data for the instrument and for the sampling and sample preparation steps. The former are relatively easy to obtain by the analysis of known solutions and are usually quite good because of the inherent stability and linearity of the plasma and associated electronics. QA data for the sampling and sample preparation steps are nearly always poorer than for the instrument and thus dictate the QA data for the method as a whole. Consequently, a good instrumental calibration does not guarantee that the data produced are accurate. For instance, independent analysis (by neutron activation analysis) of real samples and of NIST SRM 1648 has revealed that Cr and Ti extractions are 25-75% efficient using the method described herein, yet both elements in solution are recovered very well by the plasma instrument.

8. Interferences

8.1 Spectral Interferences

Spectral interferences result when spectrally pure solutions of one element produce a finite output on channels assigned to other elements. Table 4 provides recommended wavelengths to monitor selected metals using ICP in order to minimize spectral interferences. When the quantitative correction is made, the order of correction is arranged so that only "true" (that is, interference-free or previously corrected) values are used in any quantitative correction of another element for comparison. The quantitative correction factors are listed in Table 10 in the order in which they are applied in the data-processing step for the analysis of ambient air using the Thermo Jarrell Ash Model 975 ICP. The correction relation for any affected element is:

$$\text{"true" concentration} = \frac{\text{(apparent conc.)} \times \text{(correction factor "true")}}{\text{(concentration of the affecting element)}}$$

[Note: The information in Table 10 was generated using a specific instrument and is presented only to provide an indication of potential interferences. Specific correction factors must be generated for each instrument during each analysis.]

8.2 Matrix Interference

Matrix interferences do exist. This problem has been minimized by matrix matching of standards and samples. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches were made in the development of this procedure.

9. Apparatus

[Note: This method was developed using the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880, as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

9.1 Desiccator. For cooling oven-dried chemicals.

9.2 Gravity Convection Type Drying Oven. Drying chemicals and glassware, Precision Scientific 31281 or equivalent.

9.3 Mechanical Convection Type Drying Oven. For drying plastic ware (Blue Island Electric OV 510A-2 or equivalent).

9.4 Inductively Coupled Plasma Emission Spectrometer. The ICP described in this method is the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880. EPA has experience in use of this equipment during various field monitoring programs. Other manufacturers' equipment should work as well. The instrument uses a Plasma Therm HFS 2000D R.F. generator as the power supply for the plasma. The excitation source is a three-turn inductively coupled plasma torch with a cross-flow pneumatic nebulizer for sample introduction. Samples are pumped to the nebulizer with a Gilson Minipuls II single channel peristaltic pump. The instrument is equipped to read 48 elements as identified in Table 4. A dedicated PDP-8E (Digital Equipment Corporation) minicomputer controls the instrument and yields a concentration printout. To achieve data storage capability, the PDP-8E has been interfaced with a PDP11/34.

9.5 Bottles. Linear polyethylene or polypropylene with leakproof caps for storage of samples. (500 mL, 125 mL, and 30 mL). Teflon bottles for storing multi-element standards.

9.6 Pipettes. Volumetric 50 mL, 25 mL, 20 mL, 15 mL, 10 mL, 9 mL, 8 mL, 7 mL, 6 mL, 5 mL, 4 mL, 3 mL, 2 mL, Class A borosilicate glass.

9.7 Pipettes. Graduated 10 mL, Class A Borosilicate glass.

9.8 Pipette. Automatic dispensing with accuracy of 0.1 mL or better and repeatability of 20 FL (Grumman Automatic Dispensing Pipet, model ADP-30DT, or equivalent).

10. Reagents

10.1 Hydrochloric Acid. Ultrex grade, 12.3 M (Baker 1-4800) for preparing standards.

10.2 Nitric Acid. ACS reagent grade, concentrated (16 M) for preparing 10% v/v nitric acid, to clean labware only (Fisher A-200). Add 100 mL of concentrated HNO_3 to ~ 500 mL of ASTM Type II water and dilute to 1 L.

[Note: This acid is not for sample preparation; it contains excessive metals].

10.3 Nitric Acid. Ultrex grade, 16 M (Baker 1-4801) for preparing standards.

10.4 Stock Calibration Standards. Multi-element and single-element plasma-grade stocks are used for the analysis. The stocks are purchased from Spex Industries, Inc., Inorganic Ventures, Inc., or equivalent. Working calibration standards are prepared by dilution of the concentrated calibration stocks. The calibration standard stocks used for instrument calibration and initial calibration verification (ICV) are purchased from different suppliers. The source (manufacturer and lot), concentration, expiration date, and acid matrix are recorded for all calibration standards used for the analysis. Stock solutions should be stored in Teflon bottles. The final concentration of nitric and hydrochloric acid in the calibration standards should be the same as those in the prepared samples.

10.5 Compressed Argon in Cylinders and Liquid Argon in Tanks, Purity 99.95%. Best source.

10.6 ASTM Type I water (ASTM D1193). Best source. The Type I water should have a minimum resistance of 16.67 milli-ohms, as evidenced by the reading of the resistivity meter during water flow.

11. Analysis

11.1 Standard Stock Solutions

11.1.1 All labware should be scrupulously cleaned. The following procedure is recommended: Wash with laboratory detergent or ultrasonic for 30 min with laboratory detergent. Rinse and soak a minimum of 4 hr in 10% V/V nitric acid. Rinse 3 times with deionized, distilled water, and oven dry.

[Note: Nitric and hydrochloric acid fumes are toxic. Prepare in a well-ventilated fume hood. Mixing results in an exothermic reaction. Stir slowly.]

11.1.2 Preparing Calibration Curve Standards. Mixed calibration curve standards are prepared by diluting appropriate volumes of the stock calibration standards in Class A volumetric flasks. Table 1 provides examples of typical concentrations used for calibration for several elements. Each working standard solution should be labeled with a name, an expiration date, and the initials of the preparer.

11.1.3 Prepare Initial Calibration Verification Standard (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared at the midpoints of the calibration curves. These standards are prepared from certified stocks having a different manufacturer than the calibration standards. The final concentration of the ICV should be in the range of 25 µg/mL for Al, Ca, Fe, Mg, K and Na. All other analytes should be in the range of 2 µg/mL.

11.1.4 Prepare Interference Check Standard (ICS). The interference check standards are analyzed at the beginning and end of the sample run and for every 8 hours of continuous operation. The ICS should contain approximately 200 µg/mL of Al, Ca, Fe, and Mg. In addition, the ICS should contain approximately 1 µg/mL of all other analytes, including Ag, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Se T, Y, Zn, and Bi.

11.1.5 Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The LCS is prepared for all analytes at the 2 µg/mL level and when analyzed, should be within 80% to 120% of actual concentration. If the results are not within this criterion, then the results must be qualified.

11.1.6 Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The MS should be at the 25 µg/strip level. The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

11.1.7 Prepare a Reagent Blank (RB). Prepare a reagent blank that contains all the reagents in the same volumes used in processing the routine samples. The reagent blank must be carried through the entire preparation procedure and analysis scheme. The final solution should contain the same acid concentration as sample solutions for analysis. The running frequency of analysis of a reagent blank is about 1 for every 40 real samples.

11.2 ICP Operating Parameters

A daily log of the operating parameters should be maintained for reference. Entries are made by the analyst of periodic intervals throughout the run. The following list of parameters are examples from the Thermo Jarrell Ash Model 975 Plasma AtomComp. Specific manufacturer's guidelines should be followed.

ICP HARDWARE	SPECIFICATIONS
• Plasma power	1.1 kW forward automatic control 11 W reflected (minimum possible)
• Argon coolant flow	18 1/min liquid argon source
• Argon nebulizer flow	16 psi (approx. 700 mL/min)
• Sample uptake	Avg. 1.85 mL/min
• Observation Zone	Centered 16 mm above the load coil
• Sample preflush time	45 s; preburn, 1 s
• Exposure	10 s
• H_2O Post Flush	10 s then proceed to next sample
• Slits	25-µm entrance slit; 75-µm exit slit
• Photomultiplier tube voltage	900 V

11.3 Instrumental Preparations

11.3.1 Calibration Curve Linearity. ICP spectrometers generally are considered to yield a linear response over wide concentration ranges; however, investigation for linearity for elements expected to exceed concentrations of about 25 µg/mL may be necessary. Linearity may vary among manufacturers and according to operating parameters. The method and conditions described in this procedure have imposed the following limitations:

- Ca response is linear to 40 µg/mL, becoming non-linear.
- Cr saturates the electronics at 50 µg/mL.
- Cu saturates the electronics at 40 µg/mL.
- Fe saturates the electronics at 230 µg/mL.

- Mg response is curvilinear to 40 µg/mL, becoming unuseable.
- Na response is curvilinear to 80 µg/mL, becoming unuseable.

The curvilinear nature of Mg and Na responses below the levels specified were made acceptable by programming the ICP computer with segmented calibration curves as described in the manufacturer's instructions.

11.3.2 Spectral Interferences. Section 8 described briefly spectral interferences. A thorough determination of spectral interferences is a lengthy, time-consuming study in itself. The following are some of the factors influencing the presence or absence and magnitude of interferences:

- Wavelength of lines being read;
- Expected concentrations of the elements involved;
- Quality and the stability of the system optics (i.e., minimal deterioration with time);
- Quality and stability of photo multiplier tubes and electronics; and
- Purity of chemicals in use.

A thorough study of interferences has been conducted by EPA in the development of this method and have been addressed in the data processing program listed in Table 5.

[Note: The spectral interference factors listed in Table 5 were determined by analyzing single element solutions of each interfering element. The concentration of each single element solution was within the linear dynamic range (LDR) of the analysis, usually 100 µg/mL. The criteria for listing a spectral interference was an apparent analyte concentration from the interfering single element solution that was outside the 95% confidence interval estimates for the determined method detection limit (MDL) of the analyte. The factors are presented as a guide for users of this method for determining interrelement interference effects. The user is cautioned that other analytical systems other than the Thermo Jarrell Ash Model 975 Plasma AtomComp described in this method may exhibit somewhat different levels of interference than those listed in Table 5 and that the interference effects must be evaluated for each individual system.]

11.3.3 Matrix Interferences. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches should be made in the use of this procedure.

11.4 Sample Receipt in the Laboratory

11.4.1 The sample should be received from the extraction laboratory in a centrifuge tube, as documented in Inorganic Compendium Method IO-3.1.

11.4.2 No additional preservation is needed at this time. Sample is ready for ICP analysis.

11.5 ICP Operation

[Note: This method was developed using the Thermo Jarrell Ash 975 Plasma AtomComp spectrometer. EPA has experience in the use of the Model 975 spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals using ICP over the last several years. The use of other manufacturers of ICP spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 13, Quality Control, are met. However, modifications to Compendium Method 10-3.4 procedures may be necessary if another commercial ICP spectrometer is used.]

11.5.1 Start and allow the instrument at least 45 min for warmup.

11.5.2 Profile following manufacturer's directions. Run 12 warmup burns of old high QC solution to exercise the photomultiplier tubes.

11.5.3 Standardize by opening the standardization buffers with a J command on the CRT operating off-line from the PDP-11/34. Flush for 2 min with the first working standard. Make two exposures, print the average ratio on the teletype, and identify the standard when queried. Repeat for all five working standards. Complete with an S command and answer the query "Enter LCN" with a carriage return (RTN). Calibration data are not stored in the PDP-ll.

11.5.4 Go on-line to the PDP-ll by typing "RUN JA" and answer PDP-ll queries to identify the operator, data storage, and operating condition codes.

11.5.5 The PDP-ll will automatically acquire gains and offsets (slopes and X-intercepts of the calibration curve) determined by the ICP standardization. Values falling outside a previously determined bandwidth will be reported by the computer. When this occurs, corrective action must be taken. Gain and offset values are element-specific.

11.5.6 Measure the sample-pump uptake rate which should be approximately 1.8 mL/min.

11.5.7 Select a QC solution for analysis. On the CRT, enter RTN "QC" RTN "21", RTN for high QC, or "QC" RTN "22", RTN for low QC. When "DSC" appears on CRT, type "HIQC" or "LOQC", as applicable, followed by its prep date and RTN. The number "1.0" will appear twice, indicating the multiplication and dilution factors have been set to 1.0. This step is followed by the query "OK?"

11.5.8 Begin pumping the QC solution selected in Section 11.5.7 from an aliquot. Start the stopwatch when the leading edge of the solution has just entered the nebulizer. Time for 45 s and press RTN on the CRT to begin the exposure. The end is signaled by the CRT bell. Transfer the pickup tube to deionized distilled water.

11.5.9 When the PDP-ll has acquired the data, it will query "QC SMP:." Type RTN, "STD," RTN "21," RTN to identify the zero standard (Working Standard No. 1; see Section 11.1). After "DCS:" As in Section 11.5.7, the multiplication and dilution factors will default to 1.0, and the query "OK?" will appear.

11.5.10 Begin pumping from an aliquot of the zero standard and time for 45 s, as in Section 11.5.8. Start the exposure with RTN on the CRT. At the bell, return the pickup to deionized, distilled water.

11.5.11 When the PDP-ll has acquired the data, it will query "STD SMP:." Type "1," RTN, RTN, and it will query "OK?" Type "NO," RTN and the cursor will move to the left end of the line.

11.5.12 Select the first sample. On the CRT, enter the Project I.D. from the label. Press RTN. Type numerical sample number and RTN. After "DCS:," type the four letter I.D. code and RTN. The computer next queries "MLT:" (for multiplication factor); enter "360", RTN. After "DIL:" (for dilution factor), enter "1," RTN. The computer then asks "OK?"

11.5.13 Begin pumping the sample from the sample bottle and time for 45 s before pressing RTN. At the bell, return the pickup to deionized, distilled water and select the next sample.

11.5.14 Enter second sample by typing the sample number, RTN, 4-letter I.D., RTN, and another RTN to begin the exposure.

11.5.15 Present 8 samples to the instrument.

11.5.16 Challenge the instrument with the QC solution that was not selected in Section 11.3.7. Repeat CRT entries and procedure in Sections 11.5.7 and 11.5.8.

11.5.17 Resume sample analysis. Repeat Sections 11.5.11 through 11.5.13.

11.5.18 Analyze nine samples.

11.5.19 Return to Section 11.5.6 and repeat through Section 11.5.17.

11.5.20 End the analytical session after about 3 to 3.5 h. Type "-1," RTN. The computer will query "DO YOU WISH TO SAVE THIS SESSION'S DATA?" Type "YES," RTN. The computer will back up the data and issue instructions. This terminates the RUN JA program.

11.5.21 Usually two sessions per day are attempted. Repeat Sections 11.5.2 through 11.5.20 for the second session.

11.5.22 Instrument operating parameters are recorded before and after every 20 burns. A typical day's record is shown in Figure 3.

11.5.23 With minimal experience, the instrument operator will be able to compress the above steps (i.e., process more than one sample at a time by overlapping the steps required for the different samples).

12. Data Processing

12.1 Filter Blanks and Discrimination Limit

Since individual blanks are not available from each filter used for sampling, the mean unexposed filter value is subtracted from the result for each exposed sample to obtain the best estimate of each element in the filter particulate material. A discrimination limit must be defined so that possible contributions from an individual filter are not falsely reported as being from the particulate material. Calculate the filter batch mean, F_m (see

Method IO-3.2), and the standard deviation of the F_m values for each filter. If F_m is greater than the instrumental detection limit, then F_m must be subtracted from the total elemental content for each particulate bearing filter when the net metal in the particulate material is calculated. Determine the smallest atmospheric concentration of the element that can be reliably distinguished from the filter's contribution by multiplying the standard deviation for the filter batch by 3.3 and dividing by the average volume of air sampled, usually 1700 m^3. The resulting value will be the discrimination limit for that element.

12.2 Metal Concentration in Filter

12.2.1 Calculate the air volume sampled, corrected to EPA-reference conditions:

$$V_{std} = V_s \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right)$$

where:

V_{std} = volume of ambient air sampled at EPA-reference conditions, m^3.
V_s = volume of ambient air pulled through the sampler, m^3.
T_{std} = absolute EPA-reference temperature, 298EK.
T_m = average ambient temperature, EK.
P_{bar} = barometric pressure during sampling measurement condition, mmHg.
P_{std} = EPA-reference barometric pressure, 760 mmHg.

12.2.2 Metal concentration in the air sample can then be calculated as follows:

$$C = [(\mu g \text{ metal/mL})(\text{final extraction volume (i.e., 20 mL)/strip})(9) - F_m]/V_{std}$$

where:

C = concentration, µg metal/std. m^3
µg metal/mL = metal concentration determined from Section 11.5.
Final extraction volume, mL/strip = total sample extraction volume, mL, from extraction procedure (i.e., 20 mL).

$$9 = \frac{\text{Useable filter area [20 cm x 23 cm (8" x 9")]}}{\text{Exposed area of one strip [2.5 cm x 20 cm (1" x 8")]}}$$

F_m = average concentration of blank filters, µg.
V_{std} = standard air volume pulled through filter, std m^3, (25EC and 760 mmHg).

13. Quality Assurance (QA)

13.1 Instrumental Tuning and Standardization

13.1.1 The instrument must be tuned by the manufacturer at installation. However, the element lines should be checked periodically to determine if they have maintained their positions relative to the mercury profile line. Follow the manufacturer's instructions.

13.1.2 The Thermo Jarrell Ash Company published directions for performing instrument diagnostic checks and pertinent acceptable data limits (Ward, 1978, 1979 a, b, 1980 a, b). Diagnostic checks should be run periodically at a frequency dictated by the "goodness" of instrumental QC checks.

13.2 Calibration For Quantitative Analysis

See Section 13.3.2.1.

13.3 Daily QA Check and Analytical Run Sequence

Data validation steps described in this section are primarily instrumental and do not guarantee extraction efficiency.

13.3.1 Real-Time Judgments: Standards, Gains, Offsets. This system requires virtually no data computations by the operator. However, the operator is required at several points to judge, based on historical experience, the validity of numbers generated and to decide whether to continue or stop. During the standardization, the operator must observe element response to determine if values are normal. The operator must watch for computer-generated messages reporting gains or offsets that exceed the tolerance limits. Proper corrective action is based on operator experience and is discussed in Section 14.5.

13.3.2 General Quality Control. The required general quality control requirements for ICP analysis are discussed below and summarized in Table 6.

13.3.2.1 Initial Calibration. At least two calibration standards and a calibration blank are analyzed at the beginning of an analysis run. The standards used to calibration are diluted from certified stock standards (see Section 11.1) and are used within the expiration dates. The calibration standards and blanks are prepared in the same nitric and hydrochloric acid matrix as the samples.

13.3.2.2 Initial Calibration Verification (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared from certified stocks having a different manufacturer than the calibration standards. The measured concentration should be within 90% to 110% of the actual concentration.

13.3.2.3 Initial Calibration Blank (ICB). The ICB is analyzed immediately following ICV and prior to the high standard verification. The acceptance criteria for the ICB is the same as for continuing calibration blank (CCB) verification.

13.3.2.4 High Standard Verification (HSV). Immediately after the analysis of the ICB, and prior to the analysis of samples, the HSVs are reanalyzed. The measured concentration should be within 95% to 105% of actual concentration.

13.3.2.5 Interference Check Standards (ICSs). The ICSs are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. The results for the analytes should be within 80% and 120% of the actual concentration. Samples containing levels of interferences above the levels in the ICS should be considered for dilution.

13.3.2.6 Continuing Calibration Verification (CCV). CCV standards are prepared from the calibration standard stocks at the midpoint of the calibration curve. The CCV standards are analyzed at the beginning of the run prior to samples, after every 10 samples, and at the end of the run prior to the last continuing calibration blank (CCB) analysis. The measured concentration should be within 90% and 110% of the actual concentration.

13.3.2.7 Continuing Calibration Blanks (CCBs). The CCBs are analyzed following each CCV. The results of the CCBs are evaluated as follows:

- The CCBs are compared to the method detection limits.
- The absolute value of the instrument response must be less than the method detection limits.-

- If not, then sample results for analytes < 5 times the amount in the blank must be flagged or analysis must be repeated.

13.3.2.8 Reagent Blank (RB). A RB sample is prepared and analyzed with each sample batch. This analysis is used to determine if concentrations reflect background levels from sample digestion. If the instrument measured response is greater than the method detection limits, then the sample results for the affected analyte(s) must be flagged. Samples may be considered candidates for redigestion and reanalysis for that analyte.

13.3.2.9 Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The results for the analytes should be within 80% to 120% of actual concentration. If the results are not within this criterion, then strips of the LCS and all samples should be redigested and reanalyzed.

13.3.2.10 Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

13.3.2.11 Duplicate and/or Spike Duplicate. Duplicate samples and/or matrix spike duplicates are prepared and analyzed with each sample batch. These samples are used to estimate method precision, expressed as relative percent difference (RPD). The RPD between the duplicate and/or matrix spike duplicate final concentrations should be < 20%.

13.3.2.12 Serial Dilution. The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90% and 110% of the undiluted sample results.

13.3.2.13 Sample Dilution. Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

13.4 Corrective Actions

13.4.1 The plasma must operate in a stable mode with a uniform sample feed rate. Failure to reproduce standards' responses or QC values usually is caused by a partially or totally plugged nebulizer. This condition may be verified by observing a decrease in the pump rate or the absence of a fog in the nebulizer spray chamber. A similar effect will be observed if the argon supply pressure or the RF power should change. Experience with the sample pump and the RF power supply has been excellent, and both appear to be very stable electronically.

13.4.2 Intermittent failure of QC solutions to fall within the tolerance band may be due to an intermittent failure in a spectrometer circuit or to a broken nebulizer needle. Both are difficult to detect without extensive testing or dismantling of equipment. Leaks in the argon supply lines are also likely causes of such problems. Leaks in the ground-glass joints of the torch-spray chamber can be eliminated by the light use of a good grade stopcock grease (not silicone-base) (see Section 13.5).

13.4.3 One intended purpose of the repeated analysis of QC solutions was to detect and correct instrument drift occurring within any 1 day. Experience has shown that drift is not a problem when the instrument is standardized twice daily. When drift has been detected, it has been attributed to thermal drift and corrected by repro filing (i.e., adjusting the optical alignment). The instrument must be restandardized after profiling.

13.4.4 Long-term drift is more difficult to detect. A gradual increase in the gains of short-wavelength elements over a period of weeks or months is probably due to degradation of mirror coatings. Washing the mirrors may help in the short term, but usually they must be replaced. Mirrors may be ruined if washed

improperly; manufacturer-approved procedures should be followed. Gradual degradation of electronic circuits will also cause long-term drift.

13.5 Routine Maintenance

13.5.1 The torch and spray chambers occasionally must be cleaned. Frequency of cleaning must be determined through experience, as a schedule and criteria have not been established. Ultrasonic the chambers in a hot detergent for at least 30 min, soak in aqua regia overnight, and rinse in deionized, distilled water.

[Note: Aqua regia is a strong oxidizing agent. Wear protective clothing and a face shield.]

13.5.2 The ground-glass joints of the torch-spray chamber should be greased with a good grade of non-silicone base stopcock grease. After reassembly, the torch must be optimized for maximum flux throughput according to manufacturer's instructions.

13.5.3 Should the plasma be extinguished during an analysis session, the session must be ended. Restandardization is necessary after the plasma is reignited. Restandardization must be delayed until the reflected power has been at a minimum for approximately 10 min.

14. Method Safety

The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

15. References

1. "Standard Operating Procedures for the ICP-DES Determination of Trace Elements in Suspended Particulate Matter Collected on Glass-Fiber Filters," EMSL/RTP-SOP-EMO-002, Revision, October, 1983.

2. "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," *Code of Federal Regulations*, Title 40, Part 50, Appendix B, pp. 12-16 (July 1, 1975).

3. "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air.," *Federal Register* 43 (194): 46262-3, 1978.

4. Rhodes, R. C., 1981, "Special Extractability Study of Whatman and Schleicher and Schuell Hi-Vol Filters," Memo to file, August 5, 1981, Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, NC.

5. Ward, A. F., *The Jarrell-Ash Plasma Newsletter*, Volumes I, II, and III.

6. Nygaard, D., and Sot, J. J., "Determination Near the Detection Limit: A Comparison of Sequential and Simultaneous Plasma Emission Spectrometers," *Spectroscopy*, Vol. 3(4).

7. "Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particulates," Harper, et. al., *Analytical Chemistry*, Vol. 55(9), August 1983.

TABLE 1. TYPICAL CONCENTRATIONS OF THE MOST CONCENTRATED WORKING STANDARD,[1] TYPICAL ICP CALIBRATING SENSITIVITIES AND TYPICAL METHOD DETECTION LIMITS[2]

Element	Most Conc. Working Std., mg/L	Calibrating Sensitivity, counts/Fg metal	Detection[3] Limit	
			mg/L	ng/m^3
Al	50.0	4,887	0.061	13.5
As	5.0	5,063	0.025	5.5
Au	5.0	11,683	0.009	1.9
B	10.0	42,892	0.030	6.6
Ba	10.0	13,430	0.003	0.7
Be	2.0	57,457	0.002	0.4
Bi	10.0	467	1.030	226.6
Ca	40.0	52,787	0.103	22.7
Cd	4.0	37,438	0.005	1.1
Ce	5.0	13,859	0.048	10.6
Co	5.0	2,787	0.015	3.3
Cr	4.0	76,772	0.012	2.6
Cu	20.0	159,213	0.010	2.2
Fe	50.0	16,985	0.034	7.5
Ge	5.0	1,645	0.079	17.5
Hg	5.0	9,031	0.055	12.1
In	5.0	520	0.081	18.5
K	20.0	253	0.205	45.1
La	2.0	44,468	0.007	1.5
Li	2.0	12,500	0.003	0.7
Mg	40.0	70,951	0.024	5.3
Mn	10.0	108,751	0.004	0.9
Mo	5.0	5,266	0.009	1.9
Na	80.0	186	inoperative	inoperative
Nb	2.0	59,859	0.11	2.4
Ni	5.0	4,306	0.014	3.1
P	20.0	2,941	0.104	22.9
Pb	25.0	10,324	0.032	7.0
Pd	5.0	7,996	0.130	7.0
Pt	5.0	847	0.107	23.5
Re	10.0	288	0.150	33.0
Rh	5.0	32,421	2.000	440.0
Ru	10.0	5,227	0.187	41.1
Sb	5.0	4,246	0.025	5.5
Se	5.0	930	0.156	34.3
Si	50.0	9,152	0.172	37.8
Sm	5.0	52,532	0.024	5.4
Sn	5.0	469	0.042	9.2
Sr	5.0	55,091	0.001	0.2
Ta	5.0	21,030	0.145	52.1
Te	5.0	4,676	0.021	4.6
Ti	5.0	58,777	0.003	0.7
Tl	5.0	3,063	0.152	33.4
V	5.0	107,250	0.007	1.5
W	5.0	1,170	0.057	12.5
Y	5.0	35,800	0.004	0.9
Zn	20.0	478	0.120	26.4
Zr	5.0	18,010	0.008	1.8

[1]The least concentrated working standard contains no metals.
[2]Data source is 48 determinations of standard No.1 made from 01/26/83--03/22/83 during analysis of 1982 NAMS filters.
[3]Based upon sampling rate of 1.13 m^3/min for 24-hr for a total sample volume of 1627.2 m^3; factor of 9 for partial filter analysis; digestion of 0.020 L/filter.

TABLE 2. RECOVERIES FROM SPIKED STRIPS[1] AND FROM NIST SRM 1648

Element	% Recovery	%RSD
Spiked Strips[1]		
As	96.5	2.7
Co	95.5	3.4
Cu	76.1	4.3
Fe	98.3	3.7
Mn	96.9	4.0
Ni	96.4	3.9
Pb	99.1	1.9
Sr	96.4	4.4
V	94.0	2.1
Zn	89.4	6.2
NIST SRM 1648		
Ba	80	0.8
Be	not listed by NIST	
Cd	114	8.5
Cu	100	1.4
Fe	68	1.4
Mn	88	1.6
Mo	not listed by NIST	
Ni	90	9.0
Pb	95	1.1
V	79	1.9
Zn	97	3.8

[1]Recovery values based on X-ray fluorescence analytical values taken as "true".

TABLE 3. TYPICAL PRECISION, BIAS, AND CORRELATION COEFFICIENTS OBTAINED BY SAMPLE/REPLICATE PAIR ANALYSIS[1]

Element	Pairs Found	Coefficient Variation (%)	Coefficient Bias (%)	Coefficient
B	32	10	1.0	0.95
Ba	32	9	0	1.0
Cd	17	11	0	1.0
Cu	32	4	-1.0	1.0
Fe	32	8	1.0	0.99
Mn	32	21	5.0	0.99
Ni	14	10	-2.0	1.0
Pb	31	3	0.0	1.0
Sb	4	5	3.0	0.99
Sr	32	7	1.0	1.0
V	25	6	-1.0	1.0
Zn	31	16	-3.0	0.94

[1]Based on the analysis of 32 sample/replicate pairs of 1982 NAMS filters from 01/26/83 - 03/22/83. Because these data were obtained from real samples, there was no control over the actual concentrations. Elements displaying a large coefficient of variation tended to have mean concentrations in the lower end of the quantifiable range.

TABLE 4. ICP SPECTROMETER ELEMENTS WITH WAVELENGTHS

Element	Wavelength	Element	Wavelength
Al	308.22	Nb	316.34
As	193.76	Ni	231.60
Au	242.80	P	214.91
B	249.77	Pb	220.35
Ba	493.41	Pd	363.47
Be	313.04	Pt	265.95
Bi	195.33	Re	209.24
Ca	396.85	Rh	343.49
Cd	226.50	Ru	297.66
Ce	446.02	Sb	206.84
Co	228.62	Se	196.09
Cr	357.87	Si	288.16
Cu	324.75	Sm	442.43
Fe	259.94	Sn	189.99
Ge	199.82	Sr	407.77
Hg	253.65	Ta	240.06
In	230.69	Te	214.28
K	766.49	Ti	334.90
La	379.48	Tl	351.92
Li	670.78	V	292.40
Mg	279.55	W	202.99
Mn	257.61	Y	371.03
Mo	202.03	Zn	206.19
Na	589.00	Zr	339.20

TABLE 5. CORRECTION FACTORS FOR SPECTRAL INTERFERENCES

Affecting Element	Affecting Factor	Affected Element	Affecting Element	Affecting Factor	Affected Element
Ta	0.0166	Co	Bi	0.0268	Rh
Ta	0.0026	Fe	Bi	0.0116	Se
Al	0.0141	Ta	Bi	0.0041	Si
Al	0.0375	V	Bi	0.0125	Sr
B	0.0181	Zr	Ge	0.0071	Al
Be	0.0020	Nb	Ge	0.0015	Be
Be	0.0025	V	Ge	0.0085	Mo
Ce	0.2313	V	Ge	0.0293	Nb
Hg	0.0574	Co	Ge	0.1489	Ta
Hg	0.0151	Fe	P	0.0017	Al
La	0.0028	Fe	P	0.0265	Cu
La	0.0122	V	P	0.0016	Fe
Pb	0.1104	Nb	P	0.0032	Mg
Pd	0.0247	Nb	P	0.0100	Nb
Pd	0.1649	Sm	P	0.0017	Si
Pd	0.0125	Ti	P	0.0010	Zn
Pt	0.0600	Cr	Re	0.0240	Al
Pt	0.0175	Nb	Re	0.0110	B
Pt	0.1300	Ta	Re	0.1609	Mn
Pt	0.0210	V	Re	1.2400	Mo
Si	0.0281	Nb	Re	0.0556	Pd
Si	0.1300	Ta	Re	0.0044	Si
Si	0.2495	Zr	Re	0.2146	V
Te	0.0254	V	Ru	0.0141	Fe
Tl	0.0607	Ce	Ru	0.0843	Mn
Tl	0.0229	Zr	Ru	0.0233	Mo
Zn	0.0132	Ta	Ru	0.0827	Nb
As	0.0119	A1	Ru	0.2531	Ta
As	0.1736	Pt	Ru	0.0364	Ti
As	0.0125	V	Ru	5.5170	V
Bi	0.0083	A1	Ru	0.4996	Zr
Bi	0.0212	Cr	W	0.0021	Al
Bi	0.0065	Fe	W	0.0039	Mg
Bi	0.0326	La	W	0.0027	Zn
Bi	0.0155	Mg	As	0.0218	Ge
Bi	0.0312	Mn			

TABLE 6. EXAMPLE REQUIRED QUALITY CONTROL REQUIREMENTS FOR ICP ANALYSIS

QC procedure	Typical frequency	Criteria
Initial calibration (IC)	At the beginning of the analysis	None
Initial calibration verification (ICV)	Immediately after initial calibrations	90-110% of the actual concentration
Initial calibration blank (ICB)	Immediately after initial calibration verification	Must be less than project detection limits
High standard verification (HSV)	Following the initial calibration blank analysis	95-105% of the actual concentration
Interference check standard (ICS)	Following the high standard verification, every 8 hours, and at the end of a run	80-120% of the actual concentration
Continuing calibration verification (CCV)	Analyzed before the first sample, after every 10 samples, and at the end of the run	90-110% of the actual concentration
Continuing calibration blanks (CCBs)	Analyzed following each continuing calibration verification	Must be less than project detection limits (MDLs)
Reagent blank (RB)	1 per 40 samples, a minimum of 1 per batch	Must be less than project detection limits
Laboratory control spike (LCS)	1 per 20 samples, a minimum of 1 per batch	80-120% recovery, with the exception of Ag and Sb
Duplicate and/or spike duplicate	1 per sample batch	RPD # 20%
Matrix spike (MS)	1 per 20 samples per sample batch	Percent recovery of 75-125%
Serial dilution	1 per sample batch	90-110% of undiluted sample
Sample dilution	Dilute sample beneath the upper calibration limit and at least 5X the MDL	As needed

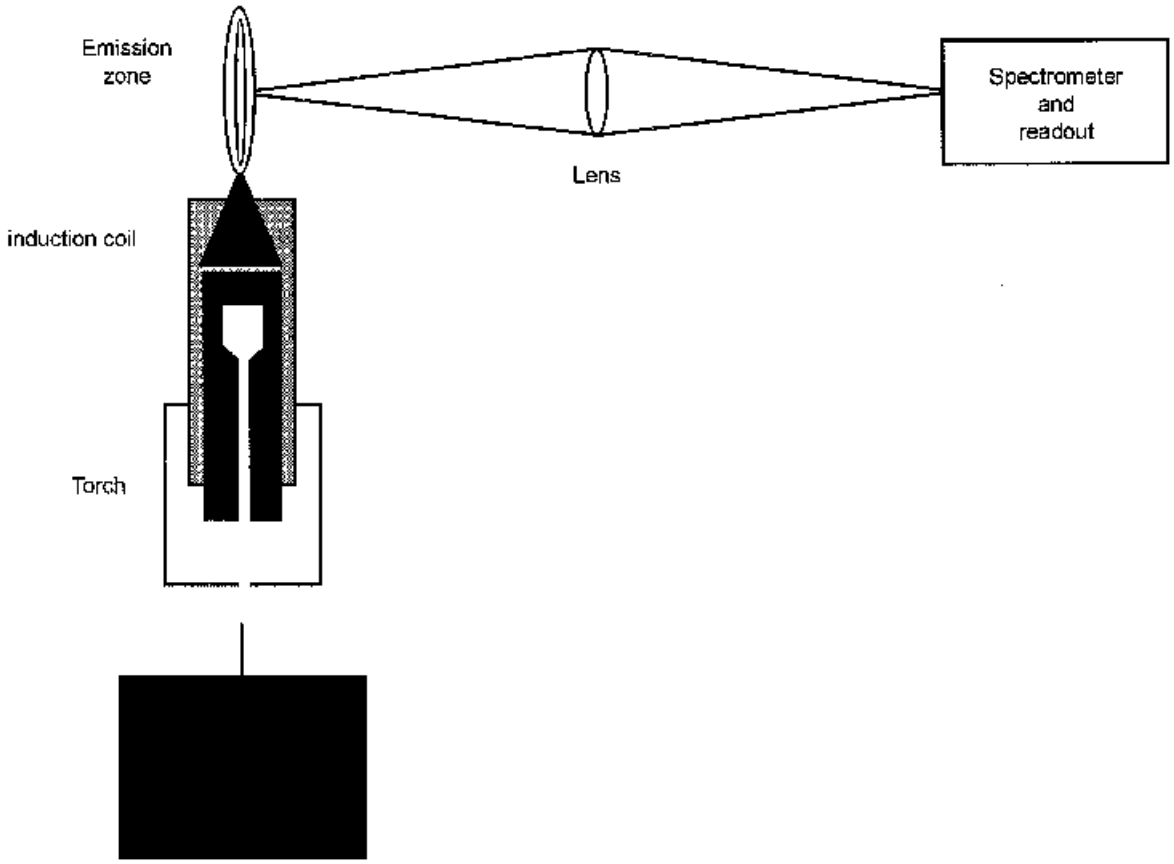

Figure 1. Schematic diagram of a typical inductively coupled plasma-optical emission spectroscopy instrument featuring parts of the instrument most important to the user.

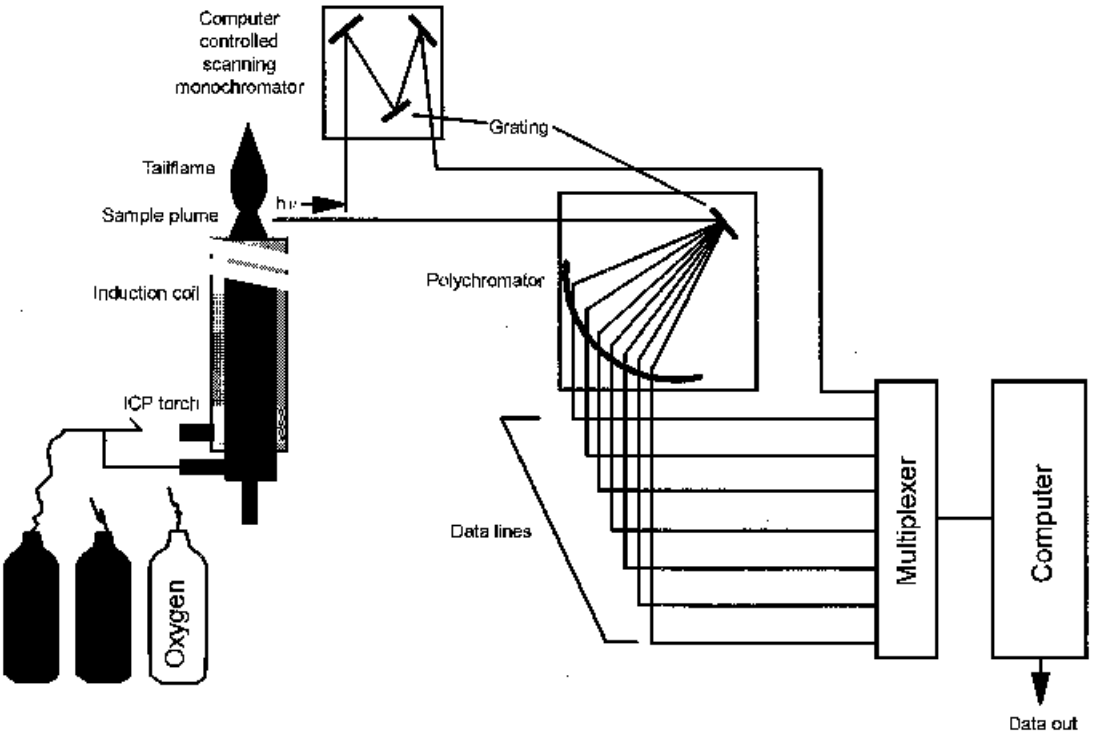

Figure 2. Simultaneous or sequential multi-element determination of trace elements by ICP.

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