The Arizona Border Study

An Extension of the
Arizona National Human Exposure Assessment Survey (NHEXAS)Study
Sponsored by the Environmental Health Workgroup of the Border XXI Program

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 824719

Standard Operating Procedure **SOP-BCO-L-7.1**

Title: Operation, Calibration, and Maintenance of the Jobin-Yvon Model 70 Inductively Coupled Plasma Atomic Emission Spectrometer

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Exposure & Dose Research Branch

Title: Operation, Calibration, and Maintenance of the Jobin-Yvon Model 70 Inductively Coupled Plasma Atomic Emission Spectrometer	
Document No. BCO-L-7.1	APPROVALS
⎕ Full SOP ⎕ Working SOP #pages 14	On Site Principal Investigator:
Issue Date: August 7, 1995	Project QA Director:
Revision No. 0	Independent Reviewer:
Revision No: 1 Revision Date: July 25, 1997 Revision Made: Modified QC procedures; calculation	On Site PI: Project QA Director: Independent Reviewer:
Revision No: Revision Date: Revision Made:	On Site PI: Project QA Director: Independent Reviewer:

Distributed To:	Revision No.					
	1	2	3	4	5	6

Operation, Calibration, and Maintenance of the Jobin-Yvon Model 70 Inductively Coupled Plasma Atomic Emission Spectrometer

1.0 Purpose and Applicability

1.1 This standard operating procedure (SOP) details the operation and maintenance of an Instruments, SA Inc., Jobin-Yvon Model 70 (JY-70) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

1.2 The JY-70 is capable of simultaneously determining the concentrations of up to 31 elements: Al, Ag, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn, and Zr. The JY-70 is also capable of sequential determinations for these and other elements.

2.0 Definitions

2.1 Method Blank - all reagents (and a blank filter or wipe, when appropriate) carried through the same digestion procedure as the samples.

2.2 Method Detection Limit (MDL) - that concentration of a given element which produces a signal three times the standard deviation of the method blank signal.

2.3 Method of Standard Additions (MSA) - a method for mathematically compensating for chemical interferences in a given sample.

2.4 Laboratory Post-Preparation Spiked Sample (LPF) - a known amount of a given element spiked into an already digested sample solution. The volume of the spiking solution must not exceed 2% of the volume of the sample it is being added to. The amount of the spiked element should be between 50 and 200% of the sample concentration.

2.5 Laboratory Pre-Preparation Spiked Sample (LSF) - a known amount of a given element spiked into a sample before digestion. The amount of the spiked element should be between 50 and 200% of the sample concentration.

2.6 Relative Percent Difference (RPD) - the absolute value of the difference of the concentration values of two replicate injections from one sample, as expressed as a percentage of their mean.

2.7 Zero Standard - a solution acidified similarly to the digested samples and other calibration solutions. This solution is not spiked with any analytes, nor digested.

2.8 Initial Calibration Verification (ICV): standard used to determine whether an instrument is calibrated to within a preset limit (±15%).

2.9 Continuous Calibration Verification (CCV): analytical standard run every 10 to 20 samples to verify that the instrument is calibrated to within a preset limit (±15%).

3.0 References

3.1 "JY-70 ICP," Operator's Manual, August 1989.

3.2 "Plasma Therma HFD 1500 ICP," Operator's Manual, 1981.

3.3 "Sample Analysis by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry," Section 4.3, Exhibit D, US EPA Contract Laboratory Program Statement of Work for Analysis of Ambient Air (AA), Rev. IAIR01.2, October 1993.

3.4 "Standard Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy," Standard D 1109, American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 12.01, 1993.

3.5 "Standard Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectroscopy," Standard C 1111, American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 12.01, 1993.

3.6 I.B. Brenner and H.E. Taylor, "A Critical Review of Inductively Coupled Plasma-Mass Spectrometry for Geoanalysis, Geochemistry, and Hydrology; Part 1. Analytical Performance," Crit. Rev. Anal. Chem. **23**, 355-367 (1992).

4.0 Discussion

4.1 For ICP-AES, the sample digestates are pumped into a pneumatic nebulizer, the resulting aerosol is transported into an inductively coupled plasma, and the valence electrons of the metal(s) are excited into higher energy levels. Atomic and ionic line emission spectra characteristic of the metal(s) are produced when the electrons decay back to the lower energy levels.

4.2 The spectra are dispersed by a spectrometer and the intensity of specific line radiation(s) is monitored simultaneously or sequentially by a photomultiplier tube(s). The photocurrent produced by the photomultiplier tube(s) will increase in direct proportion to the concentration of the element(s) in the sample within the linear range of a specific emission line(s).

4.3 The photocurrent is processed by a computer system and related to the concentration of the metal(s) in the solutions through a calibration procedure.

5.0 Responsibilities

5.1 The sampling and shipping will be performed by University of Arizona personnel, according to SOPs UA-F-8.1 and UA-F-9.1. The extractions, according to SOP BCO-L-3.1, and analyses will be performed within the Atmospheric Sciences and Applied Technology Department at Battelle.

5.2 Samples will be logged into Battelle upon receipt from Arizona by the Sample Custodian. The Sample Custodian will document the date the sample is retrieved by Battelle personnel for subsequent digestion.

5.3 Sample digestion will be carried out and recorded in the inorganic NHEXAS laboratory record book (LRB) by the inorganic sample preparation technician. The inorganic sample technician is responsible for delivering sample and any related QA digestates to the analyst, together with a photocopy of the LRB page on which any sample weights or other pertinent information was recorded.

5.4 The analyst is responsible for calculating zero standard and method blank corrected target metals content for all samples, field blanks, and QA samples. Dust and soil metals concentrations will be reported as micrograms of metal per gram of dust/soil (μg/g). Wipe and filter metals concentrations will be reported as micrograms (μg) per sample.

5.5 The Project Laboratory Director is responsible for data review and submission of reviewed results to the data coordinator.

5.6 Should this SOP require revision, all changes must be reviewed and approved by the Project Laboratory Director prior to their adoption into practice.

5.7 After changes have been reviewed and admitted by the Project Laboratory Director, the SOP must be revised and reissued under the proper revision number.

6.0 Materials and Equipment

6.1 Materials

6.1.1 Instruments, SA,. Inc. Jobin-Yvon Model 70 ICP-AES, Ser. No. 209.

6.1.2 386DX IBM-compatible computer, or substitute, with JY-70 software, version 4.0.

6.1.3 Hewlett-Packard LaserJet III printer (or equivalent).

6.1.4 High purity argon, 99.99% purity.

6.1.5 Six 100 mL Class A volumetric flasks, used to prepare calibration and quality control standards.

6.1.6 Eppendorf air displaced adjustable volume pipetters, 5-100 µL, 100-1,000 µL, 1,000-5,000 µL, 5,000-10,000 µL.

6.2 Reagents

6.2.1 Concentrated nitric acid, (HNO_3), trace metals analysis grade, J.T. Baker (or equivalent).

6.2.2 Concentrated hydrochloric acid, (HCl), trace metals analysis grade, J.T. Baker (or equivalent).

6.2.3 Commercially-available single element stock solutions (1,000 and 10,000 µg/mL), traceable to NIST, J.T. Baker, or equivalent.

6.2.4 ASTM Type II water (ASTM D 1193).

7.0 Procedure

7.1 Safety

7.1.1 Radiation

7.1.1.1 Radio frequency (RF) radiation is generated within the ICP torch enclosure, but is shielded to meet FCC regulations. Door interlocks prevent exposure to harmful RF radiation by inadvertent observation of plasma.

7.1.1.2 High intensity ultraviolet (UV) radiation is emitted by the plasma. Observe plasma only through the welding glass window on the front of the enclosure. Avoid viewing plasma directly without proper eye protection.

7.1.2 General

Instrument exhaust gases contain the combustion products of the plasma, and the metal vapor generated from the sample, and therefore are definite personnel hazards. Instrument exhaust gases shall be mechanically vented from the laboratory.

7.2 Startup

7.2.1 Switch the RF power generator breaker "ON."

7.2.2 Open the GP45 argon valve to 60 psi.

7.2.3 Turn the water valve on.

7.2.4 Turn the mass flow controller on.

7.2.5 Turn the preset gas flow, nebulizer, and auxiliary buttons on. They are located on the torch box.

7.2.6 Turn the instrument control computer on, and wait for the DOS operating system to boot.

7.2.7 From the DOS prompt, type "F" <RETURN> to load the JY-70 automation software.

7.2.8 Type "F1" to begin the instrument self-test procedure.

7.2.9 After ca 5 min of gas purge, turn the nebulizer gas flow off.

7.2.10 Push the "RF ON" button, and then the "ICP IGNITE" button.

7.2.11 As soon as the plasma forms, turn the nebulizer gas on and start the peristaltic pump.

7.3 Calibration and Analysis Procedures

7.3.1 The instrument must be calibrated with elemental stock solutions diluted and acidified to the same acid content and strength as the digested samples being quantified.

7.3.2 Prepare no fewer than three calibration solutions at different concentration levels that bracket the expected concentration of the metal in the samples by aliquotting known amounts of stock standards into 100-mL volumetric flasks.

7.3.3 Record the concentration for each element from each calibration standard in the method file. Refer to the operator's manual for complete details.

7.3.4 Use the computer keyboard to switch to the calibration sequence. Each calibration standard is displayed automatically in order of increasing concentration.

7.3.5 Manually aspirate each calibration standard and respond to the computer prompts. The computer automatically performs a linear regression using the concentrations of the calibration standards and the corresponding signal responses. Hard copy printouts of all of the data are produced by the computer.

7.3.6 Once the calibration curve has been established, switch to the analysis screen. The sample identification code is entered directly via the computer keyboard and any diluted samples are also identified.

7.3.7 An initial calibration verification (ICV) solution must be analyzed. The ICV must be prepared independently from stock(s) other than those used to prepare the calibration solutions. The percent recovery of the ICV solution must be within 85 - 115% for the analyst to proceed with the quantification of the samples.

7.3.8 Once the operation of the instrument has been verified with the ICV, the analyst may proceed with the analysis of samples, which are arranged in groups of five, ten, or twenty, depending on the level of difficulty expected with the sample set.

7.3.9 Manually aspirate each sample. The computer will process each sample and print out hard copy summaries of wavelength and concentration for

each target element in each sample. Quality control samples should be run after the analysis of every 10 to 20 samples.

7.4 Shut Down Procedures

7.4.1 Push the "RF OFF" button.

7.4.2 Turn the water valve off.

7.4.3 Turn the GP45 argon flow off.

7.4.4 Turn the mass flow controller and peristaltic pump off.

7.4.5 Exit from JY-70 program, and turn the computer off.

7.4.6 Turn the breaker switch on the RF generator to the "OFF" position.

7.4.7 For instructions on shutting the system down for extended periods, refer to Section V of the operator's manual (ref. 3.1).

7.5 Maintenance

7.5.1 If the samples form deposits on the torch, remove the torch and clean by soaking in aqua regia. Organic deposits can be removed by placing torch in a muffle furnace at 600°C for ca 30 min.

7.5.2 If non-routine maintenance or service is needed, the Project Laboratory Director or manufacturer will be contacted for further instructions.

7.6 General Considerations

7.6.1 ICP-AES provides simultaneous multielement capability of emission while, in many cases, retaining the detection limits of the graphite furnace.

7.6.2 The specific spectral lines employed for the determination of each target element must be reported with the raw data.

7.6.3 All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). All reported analyte data must have been obtained within the linear range of the respective analyte emission line. If any analyte concentration results in the linear range of the spectral line

being exceeded, the sample must be diluted with Type II ASTM water acidified such that the acid content and strength match that of the calibration solutions.

7.6.4 Laboratory glassware to be used in preparing metals solutions must be cleaned according to SOP BCO-L-10.0. Stock solutions to be used for preparing instrument or method calibration standards may be purchased from an outside vendor.

7.6.5 Pipette guns used to prepare calibration solutions must be calibrated according to SOP BCO-L-9.0.

7.7 Calculations

7.7.1 The initial calibration curve is expressed as:

$$y = mx + b$$

where y = signal intensity of the response; x = concentration of the target analyte in the calibration solution; m = slope of the linear regression; and b = intercept.

7.7.2 Once the regression is performed (through the use of a calculator or computer program), the concentration of the target analyte x is found from:

$$x = (y - b) / m$$

7.7.3 Bracketing is expressed similiarly, with only a two-point calibration curve. However, the standard concentrations must bracket the unknown's concentration tightly. If the unknown has a concentration of x, then the upper standard concentration must be no greater than $2x$, and the lower standard concentration must be no less than than $0.5x$.

7.7.4 For MSA, take three identical volumes from a sample. Spike the first portion with a volume of Zero Standard less than 2% of the volume of the sample. Designate this as the zero spike. Spike the second portion with the same volume of a solution containing a known amount of the target element. Designate this as the 50% spike. Spike the third portion with the same volume of a solution containing twice the known amount of the target element used for the second portion. Designate this as the 100% spike. All spike solutions must be acidified to the same acid content and

concentration as the sample being analyzed. Measure the signal intensities of the solutions (duplicate injections, which will be averaged, for the zero spike only). Consider the concentration of the zero spike to be zero, and perform a linear regression on the signal intensity of the response (y-axis) versus the metal concentrations of the spiked solutions (x-axis):

$$y = m'x + b'$$

where y = signal intensity of the response; x = metal concentrations of the spiked solutions; m' = slope of the linear regression; and b' = intercept.

The metal concentration in the sample C_{sam} is expressed as:

$$C_{sam} = |b'|$$

7.7.5 The RPD between duplicate injections from the same sample is expressed as:

$$RPD\ (\%) = [(|C_1 - C_2|) / \{(C_1 + C_2)/2\}]*100$$

where C_1 = concentration of target element in injection 1; C_2 = concentration of target element in injection 2.

7.7.6 Percent recovery for an LPF sample is expressed as:

$$\text{Recovery}\ (\%) = \left[\frac{(C_{spk+samp})(V_{spk} + V_{samp}) - (C_{samp}.V_{samp})}{C_{spk}.V_{spk}}\right].100$$

where $C_{spk+sam}$ = concentration of target element in the spiked sample;
V_{spk} = volume of the spike aliquot; V_{samp} = volume of the sample;
C_{samp} = concentration of the target element in the spike aliquot;
C_{spk} = concentration of the target element in the spike aliquot.

7.7.7 Percent recovery for an LSF sample is expressed as:

$$\text{Recovery}\ (\%) = \left[\frac{\{(C_{spk+samp})(V_{spk} + V_{samp})/W_{spk+samp}\} - (C_{samp}.V_{samp})}{C_{spk}.V_{spk}}\right].100$$

where $C_{spk+sam}$ = concentration of target element in the spiked sample;
$V_{spk+samp}$ = volume of the spiked sample; $W_{spk+samp}$ = weight of the spiked

sample; C_{samp} = concentration of the target element in the sample; V_{samp} = volume of the sample; C_{spk} = concentration of the target element in the spike aliquot; V_{spk} = volume of the spike aliquot.

7.7.8 Percent recovery of the ICV and/or CCV is expressed as:

$$\text{Recovery}(\%) = [(C_{meas} - C_{zs})/C_{known}] \times 100$$

where C_{meas} = concentration of the target analyte measured for ICV or CCV; C_{zs} = concentration of the target analyte in the zero standard; C_{known} = known concentration of the target analyte in the ICV or CCV.

7.7.9 MDL is expressed as:

$$MDL = 3 \times SD_{MB}$$

where SD_{MB} = standard deviation of the measured concentrations of the method blank for that analytical set.

7.7.10 Calculation of the metal concentration (µg/g) for soil and dust is expressed as:

$$C_{S/D} = [(C_{Metal} - C_{ZS}) - (C_{MB} - C_{ZS})] \times [V_1 / (W \times P)] \times (V_2 / V_3)$$

where $C_{S/D}$ = concentration of metal (µg/g) in soil or dust; C_{metal} = concentration of metal (µg/mL), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard (µg/mL), calculated using a calibration curve; C_{MB} = concentration of the method blank (µg/mL), calculated using a calibration curve, bracketing, or MSA; V_1 = volume (mL) of the digestate after the sample preparation procedure (100 mL), as described in SOP BCO-L-3.1; W = wet weight of soil; P = percent solids of soil sample, expressed as a decimal, as calculated in SOP BCO-G-2.0. (For dust samples, it is assumed that $P = 1$); V_2 = (valid only if sample is diluted further), final volume of diluted digestate; V_3 = (valid only if sample is diluted further), volume of the aliquot taken from the digestate. (NOTE: the measurement units of V_2 and V_3 must be the same.)

7.7.11 Calculation of metal concentration (µg) for filter or wipe samples is expressed as:

$$C_{F/W} = [(C_{Metal} - C_{ZS}) - (C_{MB} - C_{ZS})] \times V_1 \times (V_2 / V_3)$$

where $C_{F/W}$ = concentration of metal (µg) in filter or wipe sample; C_{metal} = concentration of metal (µg/mL), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard (µg/mL), calculated using a calibration curve; C_{MB} = concentration of the method blank (µg/mL), calculated using a calibration curve, bracketing, or MSA; V_1 = volume (mL) of the digestate after the sample preparation procedure (100 mL), as described in SOP BCO-L-3.1; V_2 = (valid only if sample is diluted further), final volume of diluted digestate; V_3 = (valid only if sample is diluted further), volume of the aliquot taken from the digestate. (NOTE: the measurement units of V_2 and V_3 must be the same.)

7.8 Quality Control

7.8.1 Controls, Blanks, and Duplicates

7.8.1.1 The correlation coefficient for the initial calibration curve must be equal to or greater than 0.995 for the analyst to proceed with the quantification of the samples. When two or more elements are being determined, the analyst can proceed if one or more of the elements has a correlation coefficient of 0.995 or greater. Any element with a correlation coefficient less than 0.995 must be re-analyzed. Subsequent quantifications of any element must be documented and related back to the original quantification.

7.8.1.2 The percent recovery of the ICV must be within 15% of the true value (85-115%) for the analyst to proceed with the quantification of the samples.

7.8.1.3 If the analyst is using aqueous or matrix-matched standards to quantify samples, a continuing calibration verification solution (CCV) must be analyzed at a rate of no less than one every 15 samples. The percent recovery of the CCV must be within 15% of its true value (85 - 115%) for the analyst to continue quantifying samples. The CCV solution must also be at a concentration level commensurate with the response levels evidenced by the samples being analyzed.

7.8.1.4 PDS samples will be analyzed at a rate of no less than one every fifteen samples to determine possible chemical interferences in the samples. PDS recoveries must be between 85 - 115% for the analyst to continue quantifying the samples without using MSA, or diluting the matrix in order to alleviate chemical interferences.

7.8.1.5 If the analyst is using MSA to quantify samples, the unspiked sample solution requires two replicate injections, which are averaged, the two spiked sample solutions require only one apiece. The correlation coefficient for the linear regression of the added analyte versus measured signal intensity must be > 0.995 for the analyst to report results using MSA. If the correlation coefficient is <0.995, the MSA must be repeated until a correlation coefficient of > 0.995 is achieved.

7.8.1.6 All ICP-AES sample measurements require a minimum of two replicate injections. All exposure times must be the same for all analyses. The average of each set of injections shall be used for sample reporting. All injections must be reported in the raw data. When the concentration of a sample is greater than five times the MDL, the RPD between duplicate injections of the same sample must be less than 50%; otherwise the injections must be repeated.

7.8.1.7 Zero standards and method blanks will be analyzed no less than three times each for each analytical run; and sample results will be corrected accordingly.

7.8.1.8 The MDL will be calculated from the method blank results. Sample results below the MDL will be marked "<MDL".

7.8.1.9 Spectral interferences are germane to this technique. Spectral interferences can be corrected for by (1) the use of calculated interelement corrections in the form of factors, or first- or second-order equations that describe the interference function (on-peak correction), (2) the use of measurement of background shift on either side, or both sides of the analyte line (off-peak correction), and/or (3) the use of wavelength scans (for each of the target element wavelengths) for each of the samples, simultaneously plotted with a calibration blank scan and a calibration standard scan. The data in Table 1, which lists some interference effects, are intended for use only as a rudimentary guide for indicating potential spectral interferences.

7.8.1.10 Chemical interferences may be controlled by adjusting the sample matrix through dilution or matrix matching, or by

mathematical correction using the method of standard additions (MSA).

7.8.1.11 Physical interferences may be minimized by the use of a peristaltic pump to introduce the acid extracts into the nebulizer, and adequate rinsing (one minute or more) between sample analyses, using a wash solution of ten percent nitric (or hydrochloric) acid, and the use of humidified argon or a nebulizer tip washer, as necessary.

7.8.2 Precision, Bias, and Detection Limits

7.8.2.1 Precision and bias are largely dependent upon the precision and bias of the digestion and the analytical procedure for each target compound, and the precision and bias of the sampling process.

7.8.2.2 When the errors involving the determination of digestion efficiency and analysis are combined, a relative precision of ±30% is indicated.

7.8.2.3 Estimated method detection limits for the target elements are presented in Table 2.

8.0 Records

8.1 Computer data files containing the raw data, and any data workup will be archived on floppy disks.

8.2 Hard copies of raw data and any data workup will be kept in study folders marked with the name of the computer file containing the raw data and the analysis date.

8.3 Routine and/or non-routine maintenance will be recorded in the instrument maintenance log with the date, signature/initials of the person responsible.

8.4 Records of pipette gun calibration will be recorded in the pipette gun record book.

8.5 Electrical resistivity (megohms-cm, 25 °C) of all Type II water stations will be recorded with daily use in the deionized water stations log books.

8.6 Records of glassware acid bath maintenance will be recorded in the acid bath record book.

Table 1. Analyte Concentration Equivalents Arising from Interferents at 1,000 mg/L Level*

		Interferent, (mg/L)[a]									
Analyte	**Wave-lengths (nm)**	**Cr**	**Cu**	**Fe**	**Ni**	**Sb**	**Si**	**Sn**	**U**	**V**	**Zn**
Ba	493.41										
Cd	226.50			0.0002	-0.0004						
Cr	267.72								0.0025	0.0018	
Cr	298.92								0.0560		
Cu	324.75										
Pb	220.35	-0.0028		0.0002	0.0006				0.0016		
Mn	257.61								0.0002		
Ni	231.60			-0.0002		0.0003		0.0001	0.0003		
Ni	341.48								0.0027		
V	292.40	-0.0029							-0.0014		
Zn	213.86		0.0034	0.0001	0.0038						

* Ref. 3.5.

[a] Typical reference values; actual values for this instrument not yet determined.

Table 2. Analytical Wavelengths and Estimated ICP-AES Method Detection Limits.*

Element	Suggested Wavelength (nm)	Estimated Method Detection Limit (µg/L)
As	193.70	53
Ba	493.41	2
Cd	214.44	4
Cr	267.72	7
Cu	324.75	6
Pb	217.00	42
Mn	257.61	30
Ni	231.60	15
Se	203.99	75
V	292.40	8
Zn	213.86	2

* For soluble elements in soil/dust, air filter, and surface/ dermal wipe samples, extracted by SOP BCO-L-3.1.