

The Arizona Border Study

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Arizona National Human Exposure Assessment Survey (NHEXAS) Study
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Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

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Standard Operating Procedure

SOP-BCO-L-8.0

Title: Operation, Calibration, and Maintenance of the Thermo Jarrell
Ash ICAP 61-975 Plasma AtomComp Emission Spectrometer

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
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Operation, Calibration, and Maintenance of the Thermo Jarrell Ash ICAP 61-975 Plasma AtomComp Emission Spectrometer

1.0 Purpose and Applicability

- 1.1 This standard operating procedure (SOP) details the procedures for the start-up, operation, calibration, shut-down, and maintenance of the Thermo Jarrell Ash ICAP 61-975 Plasma AtomComp Emission Spectrometer.
- 1.2 These procedures will be used for the determination of the trace target metals Al, As, Ba, Cd, Cr, Mn, Ni, Pb, Se, and V in soil, house dust, filter, and surface and dermal wipe sample digestates, prepared as specified in SOP BCO-L-3.0, "Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES Analysis."

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 Post-Digestion Spike (PDS) - 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.
- 2.5 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.
- 2.6 Zero Standard - a solution acidified similarly to the digested samples and other calibration solutions. This solution is not spiked with any analytes, nor digested. It defines the baseline calibration of the instrument.
- 2.7 Initial Calibration Verification (ICV): standard used to determine whether an instrument is calibrated to within a preset limit ($\pm 15\%$).

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

3.0 References

- 3.1 "ICAP 61," Thermo Jarrell Ash Operator's Manual, Thermo Jarrell Ash Publ. No. 125791-01, 1987.
- 3.2 "The Inductively Coupled Argon Plasma Atomcomp," Thermo Jarrell Ash Publ. No. 96-975, 1973.
- 3.3 "ICAP 61 Inductively Coupled Argon Plasma Spectrometer Pre-Installation Guide," Thermo Jarrell Ash Publ. No. G06, January 1987.
- 3.4 "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.
- 3.5 "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.
- 3.6 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.

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, based on the responses obtained by running calibration standards.

5.0 Responsibilities

- 5.1 The sampling and shipping will be performed by University of Arizona personnel, according to SOPs UA-F-8.0 and UA-F-9.0. The extractions 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 preparation 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 ($\mu\text{g/g}$, on a wet basis). 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 Thermo Jarrell Ash ICAP 61-975 Plasma AtomComp.
- 6.1.2 IBM PS-50 computer, or substitute, with Thermo Spec software.
- 6.1.3 RS-232 serial line printer, or substitute.
- 6.1.4 High purity argon, gas or liquid, 99.99% pure.
- 6.1.5 Volumetric flasks, 100 mL, Class A.
- 6.1.6 Eppendorf air displaced adjustable volume pipetters, 5-100 μ L, 100-1,000 μ L, 1,000-5,000 μ L, 5,000-10,000 μ L.

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 NIST traceable/J.T. Baker Concentrated target metals stock solutions, 1,000 and 10,000 $\mu\text{g/mL}$ (or equivalent).
- 6.2.4 ASTM Type II water (ASTM D 1193)

7.0 Procedure

7.1 Start-Up Procedures

- 7.1.1 Turn on the RF power generator breaker switch, and open the argon valve to ca 80 psi. Turn on water for a minimum flow of 0.4 L/min.
- 7.1.2 Start with the mass flow controller.
- 7.1.3 Turn the preset gas flow, coolant, sample, and plasma switches to "ON".

- 7.1.4 Start the peristaltic pump and check that the sample is aspirating correctly at 0.62 mL/min.
- 7.1.5 Turn off the mass flow controller after ca 3 min of purge gas. Turn the RF on, and increase the incident wattage to 0.5 kW. Push the plasma ignition button. If the plasma fails to ignite, turn the RF off immediately in order to keep the glass torch from melting. Repeat steps in Section 7.1.5 until the plasma forms.
- 7.1.6 As soon as the plasma forms, slowly turn the mass flow controller on, and switch off the plasma flow.
- 7.1.7 Boot the ThermoSPEC software.

7.2 Operating and Calibration Procedures

- 7.2.1 Optimize the ICP with a 2 mg/L copper solution in "profile" mode in the operation menu. Refer to Sections 5-7 of the operator's manual (Ref. 3.1).
- 7.2.2 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.
- 7.2.3 The instrument must be calibrated with no fewer than three solutions at different concentration levels that bracket the expected concentration of the metal in the samples.
- 7.2.4 A linear regression performed on the concentration of the calibration solutions versus the signal intensity must give a correlation coefficient greater than 0.995 for the analyst to proceed with the quantification of the samples.
- 7.2.5 Once the calibration curve is established, an initial calibration verification (ICV) solution must be analyzed. The ICV must be prepared 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.
- 7.2.6 Once the operation of the instrument has been verified with the ICV, the analyst may use aqueous standards, matrix-matched standards,

bracketing, or MSA, as deemed necessary, to quantify the samples, field blanks, and method blanks.

7.3 Shut Down Procedures

- 7.3.1 Turn the RF off.
- 7.3.2 Shut the argon gas off at the cylinder.
- 7.3.3 Turn the water off.
- 7.3.4 Turn the peristaltic pump off and release the tension in the tubing.

7.4 Maintenance

- 7.4.1 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.
- 7.4.2 If non-routine maintenance or service is needed, the Project Laboratory Director or Thermo Jarrell Ash will be contacted for further instructions.

7.5 Safety

- 7.5.1 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.
- 7.5.2 Looking directly at the plasma may cause eye damage; always view the plasma through the view port.
- 7.5.3 The RF generator may interfere with pacemakers.

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.

- 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 and must be traceable to NIST, J.T. Baker, or equivalent.
- 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 similarly, 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 $0.5x$.
- 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:

$$RPD = (|C_1 - C_2|) / [(C_1 + C_2)/2]$$

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

- 7.7.6 Percent recovery in a PDS sample is expressed as:

$$\text{Recovery (\%)} = [(C_{spk+sam} - C_{sam}) / C_{spk}] \times 100$$

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

- 7.7.7 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.

7.7.8 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.

7.7.9 Calculation of the metal concentration ($\mu\text{g/g}$) 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 ($\mu\text{g/g}$) in soil or dust; C_{metal} = concentration of metal ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard ($\mu\text{g/mL}$), calculated using a calibration curve; C_{MB} = concentration of the method blank ($\mu\text{g/mL}$), 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-3.0; 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.)

7.7.10 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 ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard ($\mu\text{g/mL}$), calculated using a calibration curve; C_{MB} = concentration of the method blank ($\mu\text{g/mL}$), 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-3.0; 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 greater than 0.995 for the analyst to proceed with the quantification of the samples.
- 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 will be 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. Table 1 lists some interference effects for the recommended wavelengths given in Table 2. The data in Table 1 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 min 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 $\pm 30\%$ is indicated.

7.8.2.3 Estimated method detection limits for the target elements are presented in Table 3.

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 the 1000 mg/L Level*

Analyte	Wave-lengths (nm)	Interferent, (mg/L)								
		Al	Cr	Fe	Ni	Sb	Si	Sn	U	V
Al	308.22						0.0020		0.0044	0.0199
Al	237.21		-0.0022	-0.0084					0.0350	
Ba	493.41									
Cd	226.50			0.0002	-0.0004					
Cr	267.72								0.0025	0.0018
Cr	298.92								0.0560	
Mn	257.61								0.0002	
Ni	231.60			-0.0002		0.0003		0.0001	0.0003	
Ni	341.48								0.0027	
Pb	220.35	-0.0012	-0.0028	0.0002	0.0006				0.0016	
V	292.40		-0.0029						-0.0014	

* Ref. 3.6.

^a These are typical reference values; interference values for this particular instrument have not yet been determined.

Table 2. Suggested Analytical Wavelengths (nm) of Typical Elements for ICP-AES**

Element	Suggested Wavelength (nm)	Estimated Detection Limit (mg/L)	Alternative Wavelength (nm)	Estimated Detection Limit (mg/L)
Al	308.22	0.04	237.32	0.03
As	193.70	0.05	189.04	0.01(a)
Ba	493.41	0.002	455.40	0.001
Cd	214.44	0.002	--	--
Cr	267.72	0.007	205.55	0.006
Pb	217.00	0.09	220.35	0.04
Mn	257.61	0.001	294.92	0.008
Ni	231.60	0.02	221.65	0.01
Se	203.99	0.1	196.03	0.08(a)
V	292.40	0.008	--	--

** Ref. 3.5. The values listed here are typical reference values; interference values for this particular instrument have not yet been determined.

^a Vacuum spectrometer.

Table 3. Estimated ICP-AES Method Detection Limits.*

Element	Suggested Wavelength (nm)	Estimated Method Detection Limit (µg)	Alternative Wavelength (nm)	Estimated Method Detection Limit (µg)
Al	308.22	4,000	237.32	3,000
As	193.70	5,000	--	--
Ba	493.41	200	455.40	100
Cd	214.44	200	--	--
Cr	267.72	700	205.55	600
Pb	217.00	9,000	220.35	4,000
Mn	257.61	100	294.92	800
Ni	231.60	2,000	221.65	1,000
Se	203.99	10,000	--	--
V	292.40	800	--	--

* For soluble target elements in soil, dust, air filter, and surface and dermal wipe samples, extracted according to SOP BCO-L-3.0, "Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES."