National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 821560

Standard Operating Procedure **SOP-BCO-L-5.1**

Title: Operation Calibration and Maintenance of the Perkin-Elmer 5100 PC Atomic Absorption Spectrometer

Source: The University of Arizona

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

Operation, Calibration, and Maintenance of the Perkin-Elmer 5100 PC Atomic Absorption Spectrometer

1.0 Purpose and Applicability

1.1 This standard operating procedure (SOP) outlines the start-up, calibration, operation, and maintenance procedures for the Perkin-Elmer 5100 PC Atomic Absorption Spectrophotometer (PE 5100).

1.2 These procedures are used for the determination of the target trace metal As 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 (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) - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess the sample analyte concentration.

2.4 Post-Digestion Spike (PDS) - a known amount of a given element spiked into an already digested solution. The volume of the spiking solution must not exceed 10% 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 duplicate samples, 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.

2.7 Initial Calibration Verification (ICV) - standard used to determine whether an instrument is calibrated to within established control limits of ±15%.

2.8 Continuous Calibration Verification (CCV) - analytical standard run every 10 to 20 samples, or as needed, to verify continued instrument calibration with respect to established control limit of ±15%.

3.0 References

3.1 "Model 5100 PC Atomic Absorption Spectrometer," Perkin-Elmer Hardware Guide, PE No. 0993-8699, January 1992.

3.2 "Recommended Analytical Conditions and General Information for Flow Injection Mercury/Hydride Analyses Using the Perkin-Elmer FIAS – 100/400," Perkin-Elmer Publication, PE No. TSAA-10C.

3.3 "Factors Affecting Hydride Generation Using Flow Injection," Perkin-Elmer Publication, PE No. TSAA-17.

3.4 "Standard Specification for Reagent Water," Standard D 1193, American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 11.01, 11.03, 1991.

4.0 Discussion

4.1 This method describes the general procedures to be used for the analysis of arsenic using hydride generation atomic absorption spectrometry (hydride AAS). The method specifically utilizes a Perkin-Elmer Model 5100PC Atomic Absorption Spectrometer equipped with a heating mantle and a Perkin-Elmer Model FIAS 400 Flow Injection System.

4.2 A representative aliquot of standard or sample is loaded into a sample loop by the pump of the flow injection system (FIAS). The valve of the FIAS switches to the inject position and the aliquot is injected into the mixing block where the arsenic is reduced to the hydride by sodium borohydrate. The arsenic hydride is swept into a heated quartz cell where the As absorbs radiation of the characteristic wavelength of As passing through the cell. The amount of absorption is related to the concentration by a calibration curve constructed from the instrument response to calibration standards.

4.3 Flow injection hydride generation atomic absorption (FI-Hydride AAS) is largely free of any chemical interferences, matrix interferences and background interferences. The analyte is separated from the matrix through formation of the hydride, and only the hydride along with an inert gas is present in the quartz cell.

5.0 Responsibilities

5.1 Sampling and shipping will be performed in Arizona by University of Arizona personnel, according to SOPs UA-F-8.1 and UA-F-9.1. Extractions and analyses will be carried out in the Atmospheric Science and Applied Technology Department at Battelle.

5.2 Samples will be logged in at 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 and analysis.

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

5.4 The analyst is responsible for calculating zero standard and method blank corrected target metals concentrations 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 Perkin-Elmer Model 5100 PC atomic absorption spectrophotometer.

6.1.2 Perkin-Elmer 3300/5100 PC 486 computer.

6.1.3 Perkin-Elmer AS91 autosampler.

6.1.4 Perkin-Elmer Model FIAS 400 flow injection system.

6.1.5 Perkin-Elmer EDL power supply.

6.1.6 Quartz cell with heating mantle.

6.1.7 High purity argon gas.

6.1.8 RS-232 dot matrix printer, or substitute.

6.1.9 Automatic air displaced adjustable volume pipetters, 10-100 µL, 100-1000 µL, 1-10 mL.

6.1.10 Target element EDL.

6.1.11 Six 100-mL Volumetric Class A Flask, used to prepare calibration standards.

6.2 Reagents

6.2.1 Concentrated nitric acid (HNO_3), trace metals grade or equivalent.

6.2.2 Concentrated hydrochloric acid (HCl), trace metals grade or equivalent.

6.2.3 Concentrated (1,000 and 10,000 µg/mL) premixed and commercially-available single element target metal stock standards, traceable to NIST, J.T. Baker, or equivalent.

6.2.4 Sodium borohydrate ($NaBH_4$), reagent grade.

6.2.5 Sodium hydroxide (NaOH), reagent grade.

6.2.6 Potassium iodide (KI), reagent grade.

6.2.7 Ascorbic acid, reagent grade.

6.2.8 ASTM Type II water (ASTM D 1193).

7.0 Procedure

7.1 Safety

7.1.1 Personnel will not operate any AAS unit until the manufacturer's instruction manual has been read and understood. Additionally, all personnel must follow safety requirements pertaining to the handling, storage, and use of compressed gases.

7.1.2 Analysts are cautioned by the manufacturer of the EDL lamps to not look directly into them for extended periods of time.

7.1.3 Instrument exhaust gases contain the products of the hydride system including metal vapor from the sample, which are definite personnel hazards. Therefore, instrument exhaust gases shall be mechanically vented from the laboratory.

7.1.4 Refer to the Operator's Manuals for more details.

7.2 Preparation of Reagents

7.2.1 Pre-reducing agent - 5% KI (w/v)/5% ascorbic acid (w/v). Weigh 50 g of KI and transfer to a 1000 mL volumetric flask. Weigh 50 g ascorbic acid and transfer to the same volumetric flask. Dilute to volume with ASTM Type II water.

7.2.2 Reducing agent - 0.2% $NaBH_4$/0.05% NaOH. Weigh 4 g of NaBH4 and transfer to 2 L volumetric flask. Dilute part way with ASTM Type II water. Add 1g of NaOH pellets. Finish diluting solution to appropriate volume, 2 L. Transfer solution to 2 L polypropylene or polyethylene bottle.

7.2.3 Carrier - 10% HCl. Fill 2 L volumetric flask halfway with ASTM Type II water. Add 200 mL of concentrated trace metal grade HCl. Finish adding the ASTM Type II water.

7.2.4 Preparation of Arsenic Working Stock Standard – In a 100 mL volumetric flask prepare a 10 mg/L stock standard by diluting 1 mL of a 1000 mg/L certified arsenic standard with ASTM Type II water and enough concentrated trace metal grade HNO_3 to make the final solution 2% HNO_3.

7.2.5 Preparation of Arsenic Calibration Standards - Calibration standards can be prepared from the stock standard by pipetting the appropriate amount

(see table below) of stock certified standard into a 100 mL volumetric flask and diluting to volume with ASTM Type II water.

Concentration	Stock Standard (μL)
0	0
2.5	25
5	50
15	150
25	250

Pipet 10 mL of the respective standards into 50 mL polypropylene sample tubes. Add 10 mL of pre-reducing agent and 10 mL or concentrated HCl. Add 20 mL of ASTM Type II water to each calibration standard. Let calibration standards react for at least 45 minutes before using.

7.3 Preparation of Samples

Pipet 3 mL of sample into 15 mL polypropylene sample tubes. Pipet 3 mL of the pre-reducing agent and 3 mL of concentrated HCl into each sample tube. Add 6 mL of ASTM Type II water to each sample tube. Let samples react for at least 45 minutes before analysis.

For soil samples pipet only 1 mL of sample and 8 mL of ASTM Type II water.

7.4 Instrument Start-Up

7.4.1 Insert the arsenic electrodeless discharge lamp (EDL) in the turret of the spectrometer. Connect the arsenic EDL to the power supply and turn the power supply ON. Rotate the power setting knob to the warm-up position indicated by the dot. The EDL should be allowed to warm up for 1 hour before use.

7.4.2 Connect all the tubing of the FIAS as indicated in Figure 1. Replace the peristaltic pump tubing each day of use.

7.4.3 Turn on the gas and be sure that the outlet pressure is set correctly: argon (kPa, 40-50 psig).

7.4.4 Turn the computer ON and wait for it to request the password. Type the password into the computer and press return. From the Windows Presentation Manager, select the Benchmate icon in the Accessories group menu. Double click on the Benchmate icon to launch the Benchmate software.

7.4.5 Turn ON the FIAS system and AAS spectrometer. Once these instruments are ON, select the FIAS-MHS icon in the Benchmate main window. Also select the type of file system and manual operation. Pull down the File menu and select Open. In the dialog window, select the ASHYD method.

7.4.6 Click on the WINDOWS title. A drop-down menu will appear. Click on ALIGN LAMPS. The Align Lamps window will appear. If the lamp parameters have not already been supplied by the system, fill in the parameters for the lamps.

7.4.7 Click on the lamp number to designate the turret position of the lamp to be aligned. The message "Instrument is busy. Please wait" appears while the system rotates the turret to the position shown by the highlighted lamp number and sets the current, wavelength, and slit for the lamp. Wait until the message disappears. Once the lamp has been set up, the AA bar graph appears on the screen.

7.4.8 Monitor the AA bar graph while adjusting the horizontal and vertical alignment screws. Slide the lamp back and forth until the bar graph reaches a maximum. If the bar graph goes off scale, click on the AGC/AIC button in the window to bring it back on scale.

7.4.9 Click anywhere in the CONTINUOUS GRAPHICS window to activate it. Turn the horizontal adjustment knob so that the heating mantle and quartz cell are approximately centered in the light beam. The absorbance value in the CONTINUOUS GRAPHICS window will decrease to a minimum value.

7.4.10 Using the vertical adjustment knob, raise and lower the heating mantle and quartz cell until the quartz cell is centered vertically in the light beam. This is indicated by a minimum in the absorbance displayed in the CONTINUOUS GRAPHICS window

7.4.11 Using the rotation adjustment knob rotate the heating mantle and quartz cell clockwise or counterclockwise until a minimum absorbance is indicated in the CONTINUOUS GRAPHICS window display.

7.4.12 In the FIAS control window, turn ON the cell and allow it to warm-up for at least 30 minutes.

7.4.13 In the FIAS control window, turn ON pump one and pump two. Make sure the valve position is in the FILL position. With the CONTINUOUS

GRAPHICS window active, aspirate a blank solution by placing the free end of the sample probe into the blank solution. Allow the solution to aspirate for several seconds, and press the AUTOZERO function key (F3). The signal immediately drops to the baseline if it is not already there.

7.5 Setting Up the Autosampler

7.5.1 From the BENCHTOP, click on the ID/WEIGHT PARAMETER. The ID/Weight Parameter window allows one to build an ID/weight file containing information that the system needs to run samples.

7.5.2 Enter the name of the person preparing the ID/weight file (up to 15 characters).

7.5.3 Record the volume of sample solution prepared.

7.5.4 Enter the Nominal Weight. The Nominal Weight specifies the target weight when samples are weighed. This entry is required *only if* corrections are being made to weight/volume measurements to compensate for weight variations among samples.

7.5.5 Designate the units to be used for the nominal weight and individual sample weight values. This entry is required *only if* the final sample concentrations are being reported in weight/weight units.

7.5.6 Designate the units to be used for the sample volume. This entry must be completed *only if* the final sample concentrations are being reported in weight/weight units.

7.5.7 Enter the sample identification code (any combination of letters and numbers, up to fifteen characters). Each ID code must correspond to its position in the autosampler.

7.5.8 Enter the dilution ratio. This field indicates the ratio between the amount of original sample solution and the final volume to which it is diluted. This entry must be completed *only if* the dilution varies among the samples. If no value is entered, a dilution of 1.0X is assumed.

7.5.9 From the File menu choose either to save the ID/Weight Parameter file or leave it as an active file.

7.6 Making a Determination

7.6.1 From the BENCHTOP, double-click on the AUTO layout on the right side of the screen. Since there is already an active file, the layout appears automatically. Wait while the system sets up, during which the message "Instrument is busy. Please Wait." is displayed.

7.6.2 Click on the full box in the AS-90/91 Control window to display all available parameters, then click on PROB UP/DOWN in the AS-90/91 Control window to raise the autosampler probe, if it is not already in the "UP" position.

7.6.3 Load the tray with samples arranged in groups of ten to twenty, followed by a CCV and blank in the autosampler.

7.6.4 Double-click the ID/WEIGHT FILE. Select the sample list file and click OK.

7.6.5 Select the SAMPLES TO RUN entry. Click on the LISTED IN ID/ WEIGHT FILE. The arrow in the check box switches to indicate that automatic selection of the samples to be run is being used.

7.6.6 Highlight the PRINTER ON/OFF icon if the results are to be printed.

7.6.7 To begin the analysis, choose CALIBRATE. The blank, standard 1, standard 2, standard 3, and the total number of standards are processed in order. The system prints the results as they are generated and displays them in the Display Data window. The analysis is complete when the READ button is no longer highlighted. The Display Data window shows the absorbance and concentration of the sample.

7.6.8 Once the calibration has been completed, the calibration curve is reviewed by the analyst as part of the standard data analysis routine. To display the calibration curve, click anywhere on the Display Calibration window to make it active.

7.6.9 Click on the FULL BOX in the upper right corner of the Display Calibration window. The Display Calibration window appears in full size, showing both the curve for the standards just run, the correlation coefficient, and slope. If the correlation coefficient is less than or equal to 0.995, recalibrate the instrument. If the correlation coefficient is greater than 0.995, proceed to Step 7.6.10.

7.6.10 Click on the AS-90/91 Control window. Click RUN SAMPLES in the AS-90/91 Control window. The system will analyze all samples identified in the ID/WEIGHT PARAMETER file in order of input.

7.6.11 Once the calibration curve has been established, an initial calibration verification (ICV) solution must be analyzed. The ICV must not be prepared from dilutions of the same stock standards used to prepare the calibration standards. An independent set of diluted stock standards must be used to prepare the ICV.

7.7 Maintenance

7.7.1 The quartz cell must be cleaned in a hydrofluoric acid bath periodically followed by deionized water prior to each days' analyses. The nebulizer system must be cleaned by aspirating deionized water for 5 min at the end of the days' analyses.

7.7.2 The EDL and/or HCL must be removed and stored upon completion of the days' analyses.

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

7.8 General Considerations

7.8.1 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.

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

7.8.3 All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibration linear range, re-analysis of that analyte(s) is required after the appropriate dilution. All sample dilutions shall be made with deionized water (ASTM Type II) appropriately acidified to maintain acid content and strength.

7.9 Calculations

7.9.1 The RPD between duplicate samples is expressed as:

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

where C_1 = concentration of target element in sample 1;
C_2 = concentration of target element in the duplicate sample.

7.9.2 Percent recovery in 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 spiked sample; C_{sam} = concentration of target element in the sample; C_{spk} = concentration of the target element spike.

7.9.3 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.

7.9.4 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.

7.9.5 The metal concentration (µg/g) for soil and dust is calculated from:

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

where $C_{S/D}$ = concentration of metal (µg/g) in soil or dust; C_{MB}= concentration of the method blank; C_{ZS}= concentration of the zero standard; D = dry weight of the sample; V_1= volume (mL) of the digestate after sample preparation; V_2= final volume of diluted digestate (valid only if sample is diluted); V_3= volume of the aliquot taken from the digestate. (NOTE: the units of V_2 and V_3 must be the same.)

7.9.6 The metal concentration (µg/sample) in a filter or wipe sample is calculated from:

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

where $C_{F/W}$ = concentration of metal (µg) in filter or wipe sample; C_{Metal} = concentration of metal (µg/mL); C_{ZS}= concentration of the zero standard; C_{MB} = concentration of the method blank; V_1 = volume (mL) of the digestate after the sample preparation; V_2 = final volume of diluted digestate (valid only if sample is diluted); V_3 = volume of the aliquot taken from the digestate. (NOTE: the units of V_2 and V_3 must be the same.)

7.10 Quality Control

7.10.1 The correlation coefficient for the initial calibration curve must be greater than 0.995 for the analyst to proceed with the quantification of samples.

7.10.2 The percent recovery of the ICV must be within ± 15% of the true value for the analyst to proceed with the quantification of samples.

7.10.3 The continuing calibration verification solution (CCV) must be analyzed at a rate of no less than once for every 15 samples analyzed. The percent recovery must be within ± 15% of the true value for the analyst to proceed with the quantification of samples.

7.10.4 Zero standards will be analyzed no less than tree times for each analytical run. Method blanks will be prepared in triplicate and analyzed for each analytical run. Sample results will be corrected accordingly.

7.10.5 The MDL will be calculated from the method blank results obtained for that analytical run date and reported for that day's analytical data set. Sample results below the MDL will be marked "<MDL."

7.10.6 The estimated method detection limit for the target element, arsenic, is 0.2 µg/L

8.0 Records

8.1 Computer files containing raw data and any data workup will be archived on floppy disk.

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

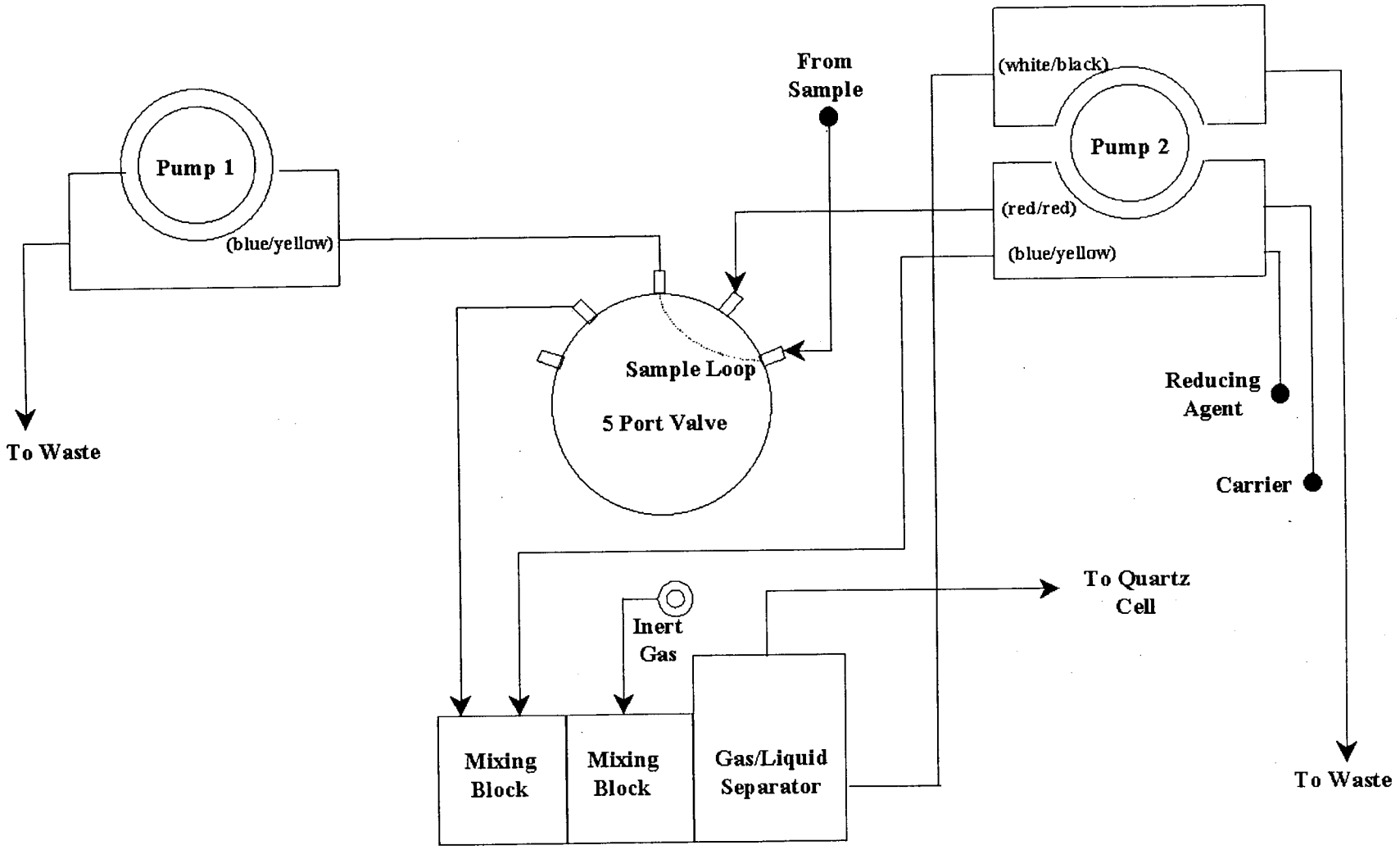
8.3 Both routine and non-routine maintenance will be recorded in the instrument maintenance logbook. A separate logbook established for this study will record instrument setup information for a give analytical run.

8.4 Records of pipette calibrations will be kept in the pipette calibration logbook.

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 logbooks.

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

Figure 1


From Sample
(white/black)
Pump 2
(red/red)
(blue/yellow)
Pump 1
(blue/yellow)
To Waste
Sample Loop
5 Port Valve
Reducing Agent
Carrier
To Quartz Cell
Inert Gas
Mixing Block
Mixing Block
Gas/Liquid Separator
To Waste