United States Environmental Protection Agency

Office of Research and Development

National Human Exposure Assessment Survey (NHEXAS)

Region 5 Study

Quality Systems and Implementation Plan for Human Exposure Assessment

Research Triangle Institute
Research Triangle Park, NC 27079

Cooperative Agreement CR 821902

Standard Operating Procedure **NHX/SOP-300-001**

Title: The Operation of PS Analytical Hydride Generation Atomic Fluorescence Spectrometer (HGAF)

Source: Research Triangle Institute

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

United States Environmental Protection Agency

Office of Research and Development

National Human Exposure Assessment Survey (NHEXAS)

Region 5 Study

Quality Systems and Implementation Plan for Human Exposure Assessment

Research Triangle Institute
Research Triangle Park, NC 27079

Cooperative Agreement CR 821902

Standard Operating Procedure **NHX/SOP-300-001**

Title: The Operation of PS Analytical Hydride Generation Atomic Fluorescence Spectrometer (HGAF)

Source: Research Triangle Institute

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

TITLE: STANDARD OPERATING PROCEDURE FOR THE OPERATION OF PS ANALYTICAL HYDRIDE GENERATION ATOMIC FLUORESCENCE SPECTROMETER (HGAF)

SOURCE: Research Triangle Institute
Post Office Box 12194
Analytical and Chemical Sciences
Research Triangle Park, NC 27709-2194

AUTHOR(s):

R Bernardo Date: 05.31.95

Date:

Date:

APPROVED BY:

Principal Investigator: E Pellizzari Date: 6/2/95

QA Officer: W J Smith Date: 6/12/95

STATUS:

IN PROGRESS: ☐

DRAFT: ☐

FINAL VERSION: ☒

REVISIONS:

No.	Date	No.	Date
0	‡	6	
1		7	
2		8	
3		9	
4		10	
5		11	

‡ Effective date of this version is the date of the last approval signature; revision 0 is the original version.

OPERATION OF PS ANALYTICAL HYDRIDE GENERATION ATOMIC FLUORESCENCE SPECTROMETER (HGAF)

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

Atomic fluorescence is an element specific, highly sensitive atomic spectrometric technique which is often used in trace element analyses. When coupled to hydride generation, the atomic fluorescence technique provides extremely high sensitivity for hydride forming elements.

The hydride generation technique makes use of the property of the hydride forming elements to form covalent, gaseous hydrides which are unstable at elevated temperatures. The formation of hydrides is usually carried out by the addition of a reducing agent, such as sodium borohydride, to an acidified solution of the analyte. Once the hydride is formed, it is passed together with any excess hydrogen gas directly to a miniature flame where the hydride species dissociate to form free atoms. The free atoms that formed are excited by an intense excitation source focused onto the flame and the resultant fluorescence is measured using an interference filter and a photomultiplier tube detection system. The wavelength of the emitted radiation is characteristic of the analyte atoms, thus the fluorescence intensity is directly proportional to the concentration of the analyte.

The PS Analytical hydride generation atomic fluorescence spectrometer (HGAF) consists of a 48-cup, random access autosampler (PSA 20.100), fully automated continuous vapor generator (PSA 10.003) with a Perma Pure dryer tube, an Excalibur detector (PSA 10.033) with a boosted hollow cathode lamp (BHCL) and a solar blind photomultiplier tube (PMT), and a dedicated personal computer (486 DX/33Mhz).

The system has the capability to analyze five different hydride forming elements, As, Sn, Se, Te and Sb. The instrument can be switched from one element to another simply by changing the excitation source.

The purpose of this SOP is to provide the user with general guidelines to operate the PS Analytical hydride generation atomic fluorescence spectrometer (HGAF).

1.1 Sensitivity and Detection Limits

Although the sensitivities are different from element to element, detection limits in parts per trillion levels are typical (Table 1). Sensitivities and detection limits depend on the experimental parameters such as acid and reductant concentration, carrier gas flow rate, reagent and sample flow rates, lamp current (primary and boost) and the gain setting.

1.2 Interferences

Typical matrix interferences that effect atomic fluorescence signals are greatly reduced by a hydride generation technique. The hydride formation step helps in separating the analyte from a great majority of interferences and has an added advantage as a result of the increased transfer efficiency of the element of interest to the measurement cell.

1. Chemical Interferences: Certain elements (transition metals) can interfere with the analyte of interest if present at high concentrations (usually > 10 ppm). These influences can be effectively reduced by using a high HCl concentration.
2. Physical Interferences: Physical interferences are usually associated with malfunction in the reagent/sample/blank delivery systems. Instability of the flame, fluctuations of gas flows and moisture carryover can interfere by suppressing the fluorescence signal. Proper regulation of the gas flows, correct concentration of the reductant, proper flow rates and use of the dryer tube may help in reducing the interferences.

2.0 INSTRUMENT OPERATION AND ANALYTICAL PROCEDURES

2.1 Apparatus and Materials

The instrument components along with the materials required for routine operation are given below:

System Components

- Random access 48-cup autosampler (PSA, 20.100)
- Vapor generator and perma pure dryer tube (PSA, 10.300)
- Excalibur fluorescence detector (PSA, 10.033)
- Boosted HCL (BHCL)
- 33MHz, 486 DX personal computer
- Epson Model MX-100III printer
- Touchstone software

Materials/Reagents

All reagents must be of analytical reagent grade, unless specified.

- Sodium borohydride

- Sodium hydroxide
- Hydrochloric acid (Trace metal grade or better)
- Potassium iodide
- Ascorbic acid
- Oxygen free argon
- Volumetric flasks, beakers
- Elemental reference standards

2.2 Instrument Start-up Procedure

When the computer is turned on, it will prompt either to load the TouchStone software or to exit to DOS.

1. Choose LOAD TOUCHSTONE SOFTWARE and press <enter>.
2. If lamp installation is required, carry out the lamp installation as described in Section 2.6.1 of the Excalibur user manual.
3. The proper orientation of the lamp is described in Section 2.6.2 of the Excalibur user manual.
4. If the lamp is installed and correctly oriented, turn on the power to the detector. Turn the primary and boost current knobs to a minimum and switch on the lamp by pressing the lamp power switch on the front panel.
5. Select the correct primary and boost currents for the analyte selected. Allow the lamp to warm up for about 30 minutes.
6. Select range "100" and fine gain "10" from the front panel of the detector.
7. After the warm up period, check the alignment of the BHCL image over the atom cell chimney and adjust as described in line 11, Section 2.6.2 in Excalibur user manual.
8. Adjust the potentiometer knob inside the detector compartment until the display reads 250 ± 30. Refer to line 14, Section 2.6.2 in Excalibur user manual.
9. Inspect the autosampler probe tubing, peristaltic pump tubing and the reagent delivery tubing for clogging and bends and replace if needed. Refer to Section 5.1 of the vapor generator user manual. Typically, peristaltic pump tubing needs replacement after a full day of operation.
10. Turn on the power to the vapor generator and autosampler.

11. Connect all three (Blank, sample and reagent) peristaltic pump tubings to the pump while the pump is running and pump deionized water for about 10 to 20 minutes.
12. Check all liquid lines for leaks. Measure the flow rates in all three lines. Refer to Sections 3.4 and 3.5 of the vapor generator user manual.
13. Turn the purge gas (Ar) on and set the flow rate to 300 cc/min and set the dryer gas (Ar) flow to 300 L/min.
14. Connect the reagents to appropriate flow lines. Make sure that solutions are flowing and hydrogen is forming in the gas liquid separator.
15. Wait for about five minutes and ignite the flame by pushing the ignite button on the front panel of the detector. Allow the flame to stabilized for about 10 to 15 minutes.
16. Run the instrument performance test as described in Section 2.3 and record the results in the instrument log book. If the minimum performance specifications are not met, manufacturer recommended corrective actions will be taken or a Question Service representative will be consulted to bring the instrument to the specified performance.
17. Select a method from the LIBRARY menu.
18. If the method needs modification, move the cursor to SETTING and select <F4> to edit the method. The method file contains the following information:
    * Method Name
    * Curve fit Type
    * Measurement Mode
    * Range and Fine Gain
    * Auto Zero Function
    * Vapor generation set up times (Delay, rise, analysis and memory times).
    * Carrier gas flow rate
    * Reagents: Blank and reductant

    Choices available for the above settings can be accessed through the cursor keys. Press <ENTER> to confirm a setting. Refer to Section 3.11 of Merlin user manual.

19. Move the cursor to the OPTIONS menu and select the options. Refer to Section 3.2.0 of the Merlin manual.
20. Select the calibration from the main menu and proceed with the calibration as described in Section 3.3.0 of Merlin user manual.
21. Analyze samples against the calibration curve constructed in the previous step. Samples can be run individually or as a batch by using an autosampler program file. Refer to Sections 3.5 and 3.6 of the Merlin user manual.

2.3 Performance Check

The performance of the instrument will be verified prior to any sample analysis. The experimental parameters are set and the performance is evaluated as follows:

1. Vapor Generator
   (i) Flow rates:
   Blank - 7-10 mL/min.
   Reductant - 2-5 mL/min.
   Sample - 7-10 mL/min.
   (ii) Gas flow rates:
   Purge (Ar) - 0.3 L/min.
   Dry (Ar) - 3 L/min.
2. Detector
   (i) Lamp current:
   Primary - 27.5 mA.
   Boost - 35 mA.
   (ii) Potentiometer - 5.5
   (iii) Sensitivity:
   Gain - 100
   Fine - 5.0
   (iv) Integration period - 1/4 sec.

After the Warm Up Period (about 30 min) the Display Should Read 250 ± 30 (Refer to item 8, Section 2.2).

3. Method
   (i) Curve fit - Least square straight line

(ii) Measured by - Peak Height

(iii) PSA Excalibur set up:

Range - 100

Fine - 5.0

Zero - Manual

4. Hydride generator set up

(i) Delay - 10sec.

(ii) Rise - 20 sec.

(iii) Analysis - 0.5 min

(iv) Memory - 20 sec.

(v) Solutions:

* Blank - 25% HCl in 1% KI and 0.05% Ascorbic acid.
* Reductant - 1.3% $NaBH_4$ in 0.1M NaOH.
* Samples - 0.0 (reagent blank) and 1.0 ng/mL as standard solutions in the Blank matrix.

Run a 0.0 and a 1.0 ppb As standard solution in duplicate.

Acceptance criteria are defined as follows:

* After the warm up period the display should read 250 ± 30.
* 1.0 ppb As standard should provide a net signal of 70 ± 20.

If any of the acceptance criteria is not met, necessary corrective actions must be performed to bring the instrument to an acceptable performance before sample analysis. Refer to Table 1 and Section 6.0 of the "Standard Operating Procedure for the Maintenance of PS Analytical Hydride Generation Atomic Fluorescence Spectrometer HGAF", NHX/SOP-300-005.

3.0 CALIBRATION

Calibration of the instrument is required before any sample analysis by either constructing a new calibration curve or re-sloping an existing calibration curve with reference standard(s). Refer to Sections 3.3.0 and 3.4.0 of the Merlin user manual.

4.0 SAMPLE ANALYSIS

Typical sample preparation involves dissolution of the sample in mineral acid, digestion of the sample, if applicable, and a final dilution step. Samples and standards should be matrix matched to the blank whenever possible. Typically 1 to 6 M HCl is used as the blank solution. An appropriate calibration check standard(s) should be analyzed at least every 10 samples in addition to any QC check standard(s) required by the project. Check standard recoveries should be with in 10% of the initial value or the nominal value for the analysis to continue. All valid data must be bracketed by the check standards with accepted performance.

The Touchstone software allows the user to analyze samples either as single samples or by a batch of samples. Refer to Sections 3.5 and 3.6 of the Merlin user manual.

5.0 DATA REPORTING

Hard copies of the method, the autosampler table, and the calibration curve should be included in the project notebook. The original hard copies should be filed with necessary information (project number, date of analysis, etc.) in a specific location (file cabinet number, room number) depending on the project requirement.

Data is stored on the hard drive in the directory C:\TS\RESULTS. Data files and method files should be archived to floppy disks on a regular basis and should be cross referenced to the project notebook. All floppy disks should be labelled appropriately to reflect their contents and stored in a location specified by the project protocols.

All final results are calculated from the raw intensities using Touchstone software or another validated software. Refer to Section 3.3.6 in the Merlin user manual.

6.0 REFERENCES

1. PSA 20.100 Autosampler User Manual, version 1.0, PS Analytical Ltd., U.K., January 1994.
2. PSA 10.003 Hydride/Vapor Generator User Manual, PS Analytical Ltd., U.K.
3. PSA 10.033 Excalibur User Manual, version 2.0, PS Analytical Ltd., U.K., February 1993.
4. PSA Merlin Plus/System Manual, version 1.3, PS Analytical Ltd., U.K., January 1993.
5. Methods of Analysis Handbook, Yorkshire Water Methods of Analysis, U.K., fifth edition, 1988.

TABLE 1. MANUFACTURER REPORTED HGAF DETECTION LIMITS

Element	Instrumental Detection Limit (ng/mL)[a]
As	0.02
Se	0.01
Te	0.05
Sb	0.05

[a] Instrumental detection limit is defined as three times the standard deviation of the calibration blank.