METHOD FOR PROJECT NO. 100-005-2

DETERMINATION OF TOTAL ELEMENTAL ARSENIC, WATER SOLUBLE BROMIDE, AND SOIL MOISTURE CONTENT IN SOIL TREATED WITH ARSENIC ACID.

Effective Date: November 21, 1988

THIS METHOD CONSISTS OF 3 PROCEDURES FOR THE ANALYSIS OF SOILS TREATED WITH ARSENIC ACID. THE FIRST PROCEDURE IS FOR THE DETERMINATION OF TOTAL ELEMENTAL ARSENIC VIA ZEEMAN EFFECT GFAA. THE SAMPLES WILL BE DIGESTED AND THE DIGESTATE DILUTED AS NECESSARY AND ANALYZED.

THE SECOND PROCEDURE IS FOR THE DETERMINATION OF WATER SOLUBLE BROMIDE VIA MEASUREMENT WITH AN ION-SPECIFIC ELECTRODE. SAMPLES WILL BE DILUTED AS NECESSARY AND ANALYZED.

THE FINAL PROCEDURE IS FOR THE DETERMINATION OF WATER CONTENT OF SOIL VIA MEASUREMENT OF THE LOSS OF MASS DUE TO DESICCATION BY OVEN DRYING.

I. Special Reagents

A. All reagents shall be ACS reagent grade or better. Water shall be ASTM Type I or better.

B. $HClO_4$; Fisher Scientific; lot no. 872469 and H_2SO_4; Mallinckrodt AR Select; lot no. 5557 KARJ.

C. NaBr (granular); Fisher Scientific; lot no. 884333.

D. Bromide Ion Strength Adjustor; Fisher Scientific; lot no. 73471.

E. 1000ppm Arsenic standard; American Scientific; lot no. 5149.

F. Preparation of Special Reagents.

1. 0.5% HNO_3: Pipet 10.0mL concentrated HNO_3 into a 2000mL volumetric flask containing ca. 500mL Type I water. Dilute to volume with Type I water.

2. Nickel Matrix Modifier: Weigh ca. 7.92g $Ni(NO_3)_2 \cdot 6H_2O$ into a tared 200mL volumetric flask and dilute to volume with Type I water. This is approximately 8000ppm Ni.

3. 100ppm Arsenic Spiking Solution: Pipet 10mL 1000ppm arsenic standard into a 100mL volumetric flask and dilute to volume with Type I water. Transfer solution to a polyethylene bottle for storage.

4. 100ppm Arsenic (as Arsenic Acid) Spiking Solution: Weigh out 0.0251g 75% arsenic acid desiccant L^{10} into a 100mL volumetric flask and dilute to volume with Type I water. Store in a polyethylene bottle.

5. 10ppm Arsenic Stock Solution: Pipet 1.0mL 1000ppm As standard into a 100mL volumetric flask and dilute to volume with Type I water.

6. 1:1 v/v $HClO_4$:H_2SO_4: Using a graduated cylinder dispense 500mL sulfuric and 500mL perchloric acids (concentrated) to a large Ehrlenmeyer flask and mix thoroughly.

7. 1000ppm NaBr standard: weigh out 1.30g granular NaBr into a tared 1000mL volumetric flask and dilute to volume with Type I water.

8. 100ppm NaBr spiking solution: Using an adjustable pipet dispense 10.0mL 1000ppm NaBr standard into a 100mL volumetric flask and dilute to volume with Type I water.

II. Equipment

A. All volumetric glassware shall be NBS class A.

B. Equipment Used.

1. Perkin Elmer Zeeman 3030 Atomic Absorption Spectrophotometer equipped with a Perkin Elmer HGA-600 Graphite Furnace and Perkin Elmer AS-60 Autosampler or equivalent.

2. Perkin Elmer and/or Westinghouse Arsenic Electrodeless Discharge lamp with appropriate power supply or equivalent.

3. Labconco Rapid-Digestor 25 equipped with a fume removal system.

4. Balance, Mettler, model PK 300.

5. Constant Temperature Oven, American Scientific, model DN81, or equivalent.

6. Dynacrush Soil Grinder model 5K121AA, or equivalent.

7. Microprocessor Ionalyzer, Orion Research, model 901, or equivalent.

8. Bromide Ion Selective Electrode, Fisher Scientific, or equivalent.

9. Orbit Shaker, Labline, model 3590, or equivalent.

III. Methodology for Total Arsenic Determination.

A. Grinding of soil samples for digestion.

1. Samples shall be kept frozen prior to grinding and may be ground frozen.

2. For each replicate plot, 7 soil cores will be composited for each sampling depth.

3. All control samples shall be ground first starting at the lowest depth and proceeding to the shallowest depth. All treated samples shall

be ground next in the same manner.

4. The soil grinder shall be flushed with sand following the grinding of each depth.

5. Once samples are ground they shall be placed in labeled buckets and put back into freezer storage until digestion begins.

B. Sample Preparation for Total Arsenic Analysis.(field and validation samples)

1. Weigh out 5.0g (+/- 0.05g)soil into a tared digestor tube.

2. Fortify spike samples as indicated in section E below.

3. Using a repeater pipet add 10mL 1:1v/v $HClO_4$:H_2SO_4 to each sample.

4. Place samples on Rapid Digestor 25 and set digestor temperature to ca. 200-225°C.

5. After ca. one hour raise the digestor temperature to 300-350°C and allow digestion to proceed until sample is dry. Remove samples and allow to cool.

6. Dilute cooled sample by rinsing the digestor tube repeatedly with 0.5% HNO_3 and transferring the rinse to a 500mL volumetric flask. Bring solution to volume with 0.5% HNO_3 and mix well. Transfer an aliquot to a polyethylene bottle for storage.

C. Sample Prepartion for Total Arsenic Analysis. (freezer stability)

1. Weigh out 5.0g sample into a tared polyethylene vial.

2. Fortify spike samples as indicated in E below.

3. All method spikes are fortified at the time of sample preparation. All QC spikes are fortified at the time of analysis. See section III. D.2 of protocol BR-88-05-2 for storage times.

4. Follow instructions in steps III. B.3-6 at time of analysis.

I. Sample Preparation for Total Arsenic Analysis. (water samples)

1. Using a class A volumetric pipet, dispense 1.0mL concentrated HNO_3 into a 200mL volumetric flask and dilute to volume with water sample to be analyzed. This provides a 0.5% HNO_3 matrix. Transfer an aliquot to a polyethylene vial for storage until analysis.

J. Dilution and Spiking Procedures for Total Arsenic Analysis.

1. For validation samples use the 100ppm arsenic (as arsenic acid) spiking solution. Fortify spike samples in the following manner.

   a. 5ppm As spike: Using an adjustable pipet spike soil with 0.25mL 100ppm As spiking solution and allow to air dry.

   b. 10ppm As spike: Using a class A volumetric pipet add 0.50mL 100ppm As spiking solution to soil and allow to air dry.

   c 25ppm As spike: Using an adjustable pipet spike soil with 1.25mL 100ppm As spiking solution.

2. For field samples use 100ppm As spiking solution. Fortify spike samples in the following manner.
   a. 10ppm As spike: Using a volumetric pipet, spike soil with 0.5mL 100ppm As spiking solution and allow to air dry.

   b. 25ppm As spike: Using an adjustable pipet spike soil with 1.25mL 100ppm As spiking solution and allow to air dry.

   c. 50ppm As spike: Using class A volumetric pipets spike soil with 2.50mL 100ppm As spiking solution and allow to air dry.

3. For freezer stability samples use 100ppm As as arsenic acid) spiking solution.

   a. 25ppm As spike: Using an adjustable pipet spike soil with 1.25mL 100ppm As spiking solution and allow to air dry.

F. GFAA Analysis.

1. Total arsenic analysis shall be performed on a Perkin Elmer Zeeman 30/30 Atomic Absorption Spectrophotometer equipped with a Perkin Elmer HGA-600 Graphite Furnace and AS-60 Autosampler using pyrocoated tubes and L'vov graphite platforms.

2. Calibration shall be performed using the method of standard additions. Standards shall be prepared in the following manner.

a. 20ppb As standard: Using an adjustable pipet dispense 0.20mL 10ppm As stock solution into a 100mL volumetric flask and dilute to volume with 0.5% HNO_3. Store in a polyethylene bottle.

b. 50ppb As standard: Using a class A volumetric pipet dispense 0.5mL 10ppm As stock solution into a 100mL volumetric flask and dilute to volume with 0.5% HNO_3. Store in a polyethylene.

c. Blank: 0.5% HNO_3 will be used as a blank.

3. Instrumental and Analytical Conditions.

a. Pipet exactly 1.0mL sample, standard, or blank into an autosampler vial and add 0.10mL nickel matrix modifier. Mix solution well.

b. Instrumental conditions presented in appendix A.

c. Absorption line wavelength may be at 193.7nm or 197.3nm as necessary for lamp stability. 193.7 nm is preferred.

IV. Methodology for Water Soluble Bromide Analysis.

A. Sample Preparation

1. Samples obtained from the same soil shipped total arsenic analysis.

2. Weigh out ca. 10g (+/- 0.1g) thawed soil tared wide-mouth polyethylene bottle.

3. Fortify spike samples as indicated in sec:

4. Using a graduated cylinder add 100mL Type I water to each sample.

5. Place samples on Labline orbit shaker set at 350RPM for 30 minutes.

B. Spiking Procedure

1. For validation, field samples, and freezer stability samples, Prepare 10g spike samples in the following manner.

   a. 0.5ppm bromide spike: Using an adjustable pipet, spike soil with 50uL 100ppm NaBr and allow to air dry.

   b. 1.0ppm bromide spike: Using an adjustable pipet, spike soil with 0.1mL 100ppm NaBr and allow to air dry.

   c. 5.0ppm bromide spike: Using a class A volumetric pipet, spike soil with 0.5mL 100ppm NaBr and allow to air dry.

   d. 10.0ppm bromide spike: Using a class A volumetric pipet, spike soil with 1.0mL 100ppm NaBr and allow to air dry.

   e. 25ppm bromide spike: Using an adjustable pipet, spike soil with 0.250mL 1000ppm NaBr and allow to air dry.

C. Analysis

1. Analysis will be performed using an Orion Research Microprocessor Ionalyzer and a Fisher Scientific Bromide Ion Selective Electrode.

2. Calibration will be performed using a blank consisting of Type I water and a 5ppm bromide standard prepared by pipeting 1.0mL 1000ppm NaBr into a 200mL volumetric flask and and diluting to volume with Type I water.

3. Transfer samples to 250mL beakers for analysis.

4. Place a sample to be analyzed on a magnetic stirrer and place reference electrode and bromide electrode into sample solution. Allow reading to stabilize and record.

V. Methodology for Soil Moisture Determination.

A. Combine 20g samples from the 0-8, 8-15, 15-30, and 30-60cm depth strata. Divide the resulting 80g aggregate approximately in half so that two samples of about 40g remain.

B. Record the weight of an aluminum weigh boat.

C. Place first sample in weigh boat and record weight. Repeat for second sample.

D. Place samples in American Scientific Constant Temperature Oven set at 110°C for 24 hours.

E. Remove samples from oven, weigh, and record weights.

VI. Calculations

A. Effective dilution volume is the volume to which the sample would have been diluted had the dilution been carried out in a single step.

B. Total Arsenic Calculations.

1. Total ug As (analytical) =

$$\frac{\text{ppb As (analytical) X effective diln. vol. (mL)}}{\text{1000ng/ug}}$$

2. As concentration (analytical ppm) (ug/g) =

$$\frac{\text{total ug As (analytical)}}{\text{sample wt. (g)}}$$

3. Spike percent recovery =

$$\frac{\text{(ug As spike-(spike wt.(g)X(ug As control/control wt(g)))}}{\text{spike level (ug)}} \text{X100}$$

4. Actual As concentration (ppm)(corrected for dry wt.)=

$$\frac{\text{total ug As (analytical)}}{\text{sample wt. (g) X (1-sample moisture)}}$$

C. Water Soluble Bromide Calculations.

1. total ug bromide =

bromide conc.(analytical ppm)(ug/mL) X dilution vol. (mL)

2. Bromide concentration (analytical ppm)(ug/g) =

$$\frac{\text{total ug bromide}}{\text{sample wt. (g)}}$$

3. spike percent recovery =

$$\frac{\text{(ug bromide spike)}-\text{(spike wt.(g)X(ug control/control wt.(g))))}}{\text{spike level (ug)}}$$

4. bromide concentration (ppm)(corrected for dry wt.)

$$\frac{\text{total analytical ug bromide}}{\text{sample wt(g)X(1-sample moisture)}}$$

D. sample moisture =

$$\frac{\text{fresh wt.(g) - dry wt. (g)}}{\text{fresh wt. (g) - container wt. (g)}}$$

Analytical Method
Appendix A

PROGRAMMING MODE INSTRUMENT USER METH # 05 - AS DATE: 88/12/1

ELEMENT: AS WAVELENGTH (NM): 193.7 SLIT (NM): 0.7
PYRO COATED TUBE WITH PLATFORM - MAX POWER HEATING - GAS STOP - MATPIX MOD.
PRETREAT TEMP: 1300 ATOMIZE TEMP: 2300 CHAPACT. MASS (PG) 17.0

1. TECHNIQUE: ZEEMAN
2. LAMP CURRENT (MA): 0
3. SIGNAL PROCESSING: PEAK AREA
4. CALIBRATION: METHOD OF ADDITION
5. TIME (SECONDS): 3.0
6. READ DELAY (SECONDS): 1.0
7. SCREEN FORMAT: 1.0 GRAPHICS
8. PRINTER: MAIN SUPPL
9. RECORDER SIGNAL: 0.2 CONT ABS
10. RECORDER EXP: 1000
11. STATISTICS: 3 AVG. & SD & CV
12. NOMINAL WEIGHT 1.0
13. ROLLOVER(ABS): 1.300
14. BG SCALE: 1.0

15. S1: 20
16. S2: 50.0
17. S3:
18. S4:
19. S5:
20. S6:
21. S7:
22. S8:
23. PSLP:

TIME: 09:5

PROGRAMMING MODE HGA 600 USER METH # 05 - AS DATE: 88/12/

ELEMENT: AS WAVELENGTH (NM): 193.7 SLIT (NM): 0.7
PYRO COATED TUBE WITH PLATFORM - MAX POWER HEATING - GAS STOP - MATRIX MOD.
PRETREAT TEMP: 1300 ATOMIZE TEMP: 2300 CHAPACT. MASS (PG) 17.0

STEP NUMBER	FURNACE TEMPERATURE	TIME RAMP	TIME HOLD	INTERNAL GASFLOW	READ	RECORDE
1	150	5	55	300	-	-
2	1300	5	25	300	-	-
3	20	1	14	300	-	-
4	2500	0	5	0	•	-
5	2600	1	5	300	-	-
6	20	1	10	300	-	-
7	----	1	--	300	-	-
8	----	1	--	300	-	-
9	----	1	--	300	-	-

TIME: 09:5

PROGRAMMING MODE AUTOSAMPLER USER METH # 05 - AS DATE: 89/12/19
METHOD OF ADDITION :STANDARD

SOLUTIONS	LOCATION	VOLUME	BLANK VOLUME
BLANK	01		10
ADDITION 1	02	10	--
ADDITION 2	03	10	--
ADDITION 3	--	20	--
ADDITION 4	--	20	--
ADDITION 5	--	20	--
ADDITION 6	--	20	--
ADDITION 7	--	20	--
ADDITION 8	--	20	--
RESLOPE	--	20	--
MATRIX MODIFIER 1	--	05	--
MATRIX MODIFIER 2	--	10	--
SAMPLE 04 TO 14 WITH MODIFIER - + -		10	10
SAMPLE -- TO -- WITH MODIFIER - + -		10	--

RECAL LOCATIONS: -- : -- : -- : -- : --
PROTOCOL: STANDARD/PREMIXED

NUMBER OF INJECTIONS:

TIME: 19:55