Arikaree Environmental Laboratory
Revision 1
Date: April 30, 2020

Atomic Absorption Spectroscopy

Calcium/Magnesium/Potassium/Sodium/Manganese/Lithium/Total Iron

TITLE: EPA 7000B

ANALYTES: Ca, Mg, K, Na, Mn, Li, Total Fe

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1) Applicable Matrices

a) This method is applicable to ground, surface, and waste waters**.**

b) The method is applicable in the range from 0 to 10.0 mg/L Calcium, and Total Iron, 0 to 2.0 mg/L Magnesium, Potassium, Sodium, and Lithium, and 0 to 1.0 mg/L for Manganese.

2) Scope and Application

a) Samples are analyzed using a Perkin-Elmer AAnalyst 200.

3) Interferences

a) Any element emitting light at the same wavelength of the target element will cause interference. Wavelengths are chosen to minimize or eliminate this interference.

4) Equipment and Supplies

a) Analytical balance capable with 0.0001g sensitivity.

b) Top loading balance with 0.01g sensitivity.

c) Adjustable Pipets capable of precisely dispensing1.0-10.0mL and 0.1-1.0mL

d) Pipet tips appropriate for each pipet

e) Class A volumetric flasks and pipets for reagent and standard preparation.

f) Perkin-Elmer AAnalyst 200 Atomic Absorption Spectrometer

g) Water purifier for preparation of ASTM Type I water (Ultrapure).

h) 15mL centrifuge tubes

i) 50mL centrifuge tubes

j) Breathing grade compressed air

k) Analysis grade acetylene (cont'd on page 2)

l) Trace metal grade Nitric Acid

5) Reagents and Standards

1,000ppm Ca, Mg, K, Na, Mn, Li, Fe Stock Standards

1) Use purchased, certified 1,000ppm stock standards.

0.5% Lanthanum Chloride Solution

1) In a 1,000mL volumetric flask, add about 250mL of ultrapure water, then quantitatively transfer 13.37g of Lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$). Using a magnetic stir bar, stir the flask contents until the crystals are dissolved. Using a stir bar retriever, pull stir bar out of the solution and rinse the stir bar with ultrapure water, then fully remove stir bar from flask. Fill flask to 1,000mL mark with ultrapure water. Replace cap and invert to mix. Store in a clean 1L Nalgene. Refrigerate.

Matrix Spike Solution

1) In a 100mL class A volumetric flask, using calibrated adjustable pipets, dilute 9.0mL of 1,000mg/L Ca stock standard, and 1.8mL each of 1,000mg/L Mg, K, and Na stock standards. Dilute to the 100mL mark on the flask. Replace stopper and invert several times to mix. Store in a clean 125mL Nalgene. Refrigerate.

6) Sample Collection, Preservation, Shipment, and Storage

a) Collect and filter samples in acid washed, plastic bottles. Sample shall be filtered using a 0.45μm membrane filter.

7) Quality Control

a) Calibrate the AA before each analytical run. Analyze Instrument Performance Check (IPC)/ from a second source standard every analytical run. Calibration r-value is required to be > 0.995, if not re-calibrate.

b) Run an initial calibration verification blank (ICVB) at the beginning of each run and then once every 10 samples. ICVB must be <LOD. If not, re-analyze, if still out of control qualify data. Subsequent blanks (CCVB) must be <LOD, or less than 10% of the measured concentration in the samples from the adjacent set.

c) Analyze an Initial Calibration Verification Standard (ICVS) at the beginning of each run and Continuing Calibration Verification Standard (CCVS) with every 10 samples. Standard must be within 10% of known value. If not, reanalyze. If still out of control, recalibrate.

d) A duplicate and matrix spike must be analyzed every 10 samples (10%). Prepare a spiked sample by pipetting 0.1mL of Matrix Spike Solution (see matrix spike solution in section 5) into empty IC sample tube. Pipet 8.9mL of sample into the same tube, along with 1.0mL of 0.5% LaCl. Cap and invert tube carefully to mix.

8) Calibration

a) Prepare cation calibration standards as listed below. Use only clean class A volumetric pipets or calibrated adjustable pipets and class A volumetric flasks. Dilute using ultrapure water. Store in clean Nalgene plastic bottles.

Standard	mg/L Ca/Mg/K/Na/Li/Mn	mL 1,000ppm Ca/Mg/K/Na/Li/Mn Standard	Total volume
1	10.0/2.0/2.0/2.0/2.0/1.0	10.0/2.0/2.0/2.0/2.0/1.0	1000mL
2	5.0/1.0/1.0/1.0/1.0/0.5	5.0/1.0/1.0/1.0/1.0/0.5	1000mL
3	2.0/0.5/0.5/0.5/0.5/0.2	2.0/0.5/0.5/0.5/0.5/0.2	1000mL
4	1.0/0.2/0.2/0.2/0.2/0.1	50.0mL of Cal Std 1	500mL
5	0.5/0.1/0.1/0.1/0.1/0.05	50.0mL of Cal Std 2	500mL
6	0.2/0.05/0.05/0.05/0.05/0.02	50.0mL of Cal Std 3	500mL
7	0.1/0.02/0.02/0.02/0.02/0.01	50.0mL of Cal Std 4	500mL
8	0.05/0.01/0.01/0.01/0.01/0.005	50.0mL of Cal Std 5	500mL

b) Prepare Total Iron calibration standards as listed below. Use only clean class A volumetric pipets or calibrated adjustable pipets and class A volumetric flasks. Dilute using ultrapure water. Store in clean Nalgene plastic bottles.

Standard	mg/L Fe	mL 1,000ppm Fe Standard	Total volume
1	10.0	10.0	1000mL
2	5.0	5.0	1000mL
3	2.0	2.0	1000mL
4	1.0	50.0mL of Cal Std 1	500mL
5	0.5	50.0mL of Cal Std 2	500mL
6	0.2	50.0mL of Cal Std 3	500mL
7	0.1	50.0mL of Cal Std 4	500mL
8	0.05	50.0mL of Cal Std 5	500mL

9) Procedure for AAnalyst 200 Set-up and Operation

Sample Set-up Procedure

1) Using the master data sheets in the lab office, prepare a list of samples needing analysis. Take LaCl spike solution out of the fridge to warm.

2) Using the prepared list, round up all of the samples for analysis. These samples should be unpreserved and filtered.

3) Bring the samples in the lab. Find a clear benchtop and organize the samples in ascending order based on their LabID#. (Procedure cont'd on page 4)

4) Print an AA benchsheet from the "Arikaree Share" folder. Fill the benchsheet with the Lab ID#'s of the samples in ascending order. Remember to include one duplicate and matrix spike for every 10 samples.

5) Obtain new clean 15mL centrifuge tubes. Going through the benchsheet, label each tube with a Lab ID#. Prepare 2 tubes for each sample (for reruns and duplicates). Place each tube in order back in the Styrofoam rack. Also, prepare tubes for the samples listed as matrix spikes.

6) Calibrate pipets for 0.1mL, 9.0mL, and 1.0mL.

7) Remove the caps from the centrifuge tubes. Pipet 1.0mL of 0.5% LaCl solution into each tube. Keep track of your progress to be sure each tube receives LaCl and no tubes receive a double.

8) Once all of the tubes have LaCl, the samples can be pipetted into the tubes. Pipet 9.0mL of sample into each tube, changing pipet tips for each sample. Don't pipet sample into the matrix spike tubes yet.

9) After all of the sample tubes are filled, recap the tubes and invert them to mix. This can be done by placing a hand on top of the tubes in the rack and inverting the tubes multiple times.

10) Calibrate a pipet for 8.9mL.

11) Prepare the matrix spike samples by pipetting 0.1mL of matrix spike solution into each tube. Pipet 8.9mL of sample into the corresponding tubes. Cap the tubes and invert to mix.

Instrument Set-up Procedure

1) Take the calibration standards out of the fridge to warm to room temp.

2) Make sure the hollow cathode lamp needed to analyze the element you need is installed. If not, locate the required lamp (in the furthest left drawers in the drawer second from the bottom. Wearing gloves, carefully remove one of the lamps from the carousel and place it in its correct box. Do not touch the glass part of the lamp. Put the lamp box into the lamp drawer and close the drawer. Carefully remove the needed lamp from its box and insert the lamp in the vacated position on the instrument. Make sure the electrodes line up and the lamp should slide into place.

3) Turn on AAanlyst 200 by switching the power toggle switch on the lower right-hand side of the instrument. Allow the instrument to go through its start-up procedures.

4) Once the instrument is fully booted, on the touch-screen, tap the "Lamp" tab, then tap the "Element" field. Select the element of interest then tap "OK." Tap the "Setup Instrument" button next to the "Element" field. The instrument will automatically set up the lamp with the saved parameters. Allow lamp to warm-up for at least 15 min.

5) Carry samples and benchsheet over to instrument. (Procedure cont'd on page 5)

6) Open the AA folder on the AA laptop. Open a template for the analyte needed (excel file). Go to “Save As” and save the template as a new spreadsheet using the following naming structure: Atomic symbolYYMMDD (i.e. Na200511). Save it in the corresponding element folder in the AA folder.

7) Record the sample numbers in the excel spreadsheet as they are listed on the benchsheet. Save the file.

8) Look over the instrument and be sure the torch and nebulizer are installed correctly. Maintenance should be performed with instrument completely off. See instrument manual for maintenance procedures. Do not perform maintenance unless instructed by the manager to do so.

9) Open the valves on the acetylene and breathing air tanks. Note the amount of pressure in both tanks. Don’t allow the pressure of the acetylene tank to go below 85lbs. Change tanks before this happens.

10) In the flame tab in the instrument touch screen, check over the flame parameters to be sure everything is correct. Touch the oxidant tab and make sure the flame type is set for air-acetylene.

11) Place the sample tube in a bottle full of ultrapure water. This is the rinse water.

12) Ignite the flame by touching the “Flame On/Off” switch. Sometimes the ignitor swings too far. This can be remedied by using a combination wrench to stop its swing.

13) Allow the flame to burn for about 5 minutes to allow everything to heat up.

14) If the torch needs to be aligned or instrument optimized, see the alignment procedure in the instrument manual. Optimization should not need to be done. The lab manager shall perform both of these tasks.

15) The first standard to run is the blank. Touch the “Analyze” tab. Shake the Blank solution. Remove the cap and place the sample tube into the blank solution. Touch the “Analyze Blank” button on the touch screen. Allow the instrument to read the sample. When the green progress bar is full, the instrument is now zeroed. Remove the sample line from the blank and replace it in the water.

16) Continue with the calibration, analyzing the standards like you did the blank except touch the analyze sample button or step on the black pedal to start analyzing the sample. After standard is analyzed, remove the sample tube from the standard and replace it in the water, and record the average absorbance in the correct cell in the spreadsheet. Repeat this for each standard until calibration is complete.

17) Apply the calibration curve to the rest of the spreadsheet by changing the equation in the concentration cells for the samples.

18) Run a blank, 2 check standards, and a second source QC standard after calibration. The blank must be below the Limit of Detection (LOD) and the check standards and QC standard must be within 10% of their known values. (Procedure cont’d on page 6)

19) If the initial checks pass, continue to analyzing samples, running a blank and check standards every 10 samples to verify the calibration is still valid. The instrument may need to be re-zeroed with the blank periodically. End the run with a blank and check standards as well.

20) If a sample is over range (higher than the highest standard in the calibration), it will need to be diluted. Calculate what dilution factor is needed to bring the sample within the calibrated range. Using the prepared sample and blank, prepare the dilution. An example of a dilution is as follows: Calcium range is 0-10mg/L. Sample is ~30mg/L. 30mg/L divided by 5 is 6mg/L which is in the calibrated range, therefore a 1:5 dilution will be sufficient. To prepare 10mL of sample at a 1:5 dilution, take 10mL/5=2mL. 2mL of sample with 8mL of blank = 10mL of a 1:5 diluted sample.

21) Clean the nebulizer and torch by placing the sample tube into a 10% HCl solution for a minute. Return the tube to the rinse water after cleaning and allow to rinse for 5 minutes.

22) Remove sample tube from water and allow to draw air.

23) Extinguish the flame by touching the “Flame On/Off” switch in the flame tab (touchscreen).

24) Close the valves on the gas tanks.

25) Touch the “Bleed Gases” button in the flame tab. This will evacuate the gas lines.

26) Allow the gases to completely evacuate, then turn off the AA by flipping the power switch below the lamps.

27) On the AA laptop, save the finished run. Transfer the run spreadsheet to a thumb drive to be printed in the office.

28) Print the run spreadsheet. Staple the run sheet to the back of the benchsheet.

29) If samples are not to be analyzed further that day, place them in the fridge, along with standards. In fact, put everything away from set-up and analysis and clean the bench tops.

30) Record the QC data in the AA QC data spreadsheet in the Arikaree Share folder.

31) Record the results on the master data sheets. Use proper significant figures and write legibly!

32) Three-hole punch the benchsheet and place in AA binder if samples don’t require further AA analysis. Otherwise, place benchsheet by AA for further analysis.

10) Corrective Action for Out-of-Control Data

a) Any CCV blank that exceeds the LOD, the analyst must inspect the concentration of the previous sample. If the blank is greater than 10% of the previous sample, reanalyze the blank immediately following the CCVS. No samples can be run until the blank meets requirements.

b) CCV and LCS standards must fall within 10% of true value (90%-110% Recovery). If not re-mix and re-analyze, if still out of range re-calibrate.

11) Contingencies for Handling Out-of-Control Data

a) Samples that fail the CCVB or ICVS will have to be reanalyzed or qualified back to the last sample that the quality control met the above conditions.

12) Waste Management

a) All waste must be collected and disposed of according to CU EHS policies.

13) References

a) U.S. EPA. 2007. “Method 7000B: Flame Atomic Absorption Spectrophotometry.” Revision 2.