Georgia Department of Natural Resources
Environmental Protection Division Laboratory

Effective Date:06/11/2021
SOP 2-019 Rev.1
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Hardness Calculated by Standard Methods 2340 B. Analysis by Inductively Coupled Plasma-Atomic Emission Spectroscopy

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1 Scope and Application

Standard Methods 2340 B. is a calculation method for hardness by the analysis of calcium and magnesium concentration in ground water and surface water by EPA Method 200.7 by ICP-AES. Samples analyzed by this method must be acceptable for analysis by direct aspiration in to the ICP. This method is used to analyze the following metals:

Metal	CAS No.
Calcium	7440-70-2
Magnesium	7439-95-4

1.2 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of an optical ICP. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

3 Interferences

3.1 Method interferences may be caused by background emission, stray light from the line emission from high concentration elements, spectral overlap from another analyte, or unresolved overlap of molecular band spectra.

3.1.1 Subtracting the background adjacent to the analytical wavelength peak compensates for stray light and background emission. This is automatically performed by the instrument software for every analytical scan. Background correction locations are chosen to be free of off-line spectral interference or reflect the same change in the background intensity as does the analytical peak.

3.1.2 Spectral overlaps are compensated for by the use of interelement correction factors

(IECs). IECs are determined by analyzing potential interfering elements individually at 500 ppm concentrations and monitoring the apparent concentrations (both positive and negative) of all other elements. The correction equations and coefficients are determined by the instrument software and are automatically applied for every analytical scan.

3.1.3 Physical interferences are effects associated with the sample nebulization and transport such as changes in viscosity and surface tension. Physical interferences are corrected by using a peristaltic pump for sample delivery and maintenance to keep the sample introduction system clean.

3.1.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally these interferences are not a major concern with ICP spectroscopy, but are minimized by matrix matching the standard matrix to the sample matrix and by acid digesting all samples. The presence of chemical interferences is monitored for by the use of matrix spikes and matrix spike duplicates.

3.1.5 Memory interferences occur when elements from a previous sample contribute to the signal measured in a new sample. Memory effects usually arise from a dirty sample introduction system and are minimized by proper instrument maintenance. Memory interferences are detected by analyzing a blank after a sample with an analyte concentration exceeding the linear dynamic range and by periodic analysis of the continuing calibration blank (CCB).

4 Safety

Refer to Laboratory Chemical Hygiene Plan

5 Apparatus and Equipment

5.1 Computer controlled ICP spectrometer with background correction.
5.2 Peristaltic pump for sample delivery.
5.3 Computer controlled autosampler.
5.4 High purity Argon gas supply at 50 PSI.

6. Reagents and Standards

All reagents and standards must be logged into the standard log notebook; the container must be labeled with the standard number, expiration date, name, and initials of the person who prepared the solution.

6.1 1000 mg/kg Yttrium solution for the "bullet" test.
6.2 1% (v/v) nitric acid, reagent grade, as running buffer for water samples and the calibration blank.
6.3 18MΩ water.
6.4 Calibration standards (described in section 8).
6.5 Initial Calibration Verification standard (ICV) (described in section 8).
6.6 Continuing Calibration Check standard (CCC) (described in section 8).

7 Sample Collection

Water samples and liquid waste samples for metal analysis are collected in a 500 ml narrow mouth plastic (HDPE) bottle. Samples are preserved with sufficient HNO_3 to lower the pH below 2. One bottle is required for each sample. Analysis must be performed within 6 months after preservation.

8 Calibration

8.1 Calibration Standards: The ICP-OES is calibrated daily prior to analysis. The calibration curve consists of at least two calibration standards.

8.2 Calibration Verification: The calibration is verified by analyzing the initial calibration verification (ICV) standard.

8.3 Continuing calibration check (CCC): After analysis of the ICV, after every ten samples, and at the end of an analytical sequence a continuing calibration check (CCC) and continuing calibration blank (CCB) are analyzed.

8.4 An interference check sample is analyzed prior to analyzing any samples. The Interference Check Standard (INT-AB) concentrations are as follows:

Table 8.4 Interference Check Standard concentrations.

Element	**Liquids Concentration (mg/L)**
Calcium	500
Magnesium	500

9 Quality Control - Refer to Table 13.1 for reporting limits (PQLs), Table 13.2 for Quality Control Acceptance Criteria, and Table 13.3 for Quality Control Procedures associated with this method.

10 Procedure

10.1 All water samples must have the pH checked a minimum of 18 hours after preservation. If the pH is <2, the sample is poured for analysis by direct aspiration. If the sample pH >2, add sufficient 1:1 nitric acid to adjust the pH <2.

10.2 Start the instrument and run for at least 45 minutes to warm up the instrument.

10.3 Profile the instrument.

10.4 Calibrate the instrument by using at least the low standard then the high standard.

10.5 Analyze the ICV.

10.6 Analyze the CCC. A CCC and CCB must be analyzed at the start of each batch, after every ten samples in a batch, and as the last samples analyzed in a batch. The CCC and CCB do not count towards the sample total in a batch.

10.7 Determine the instrument detection limits (IDLs).

10.7.1 Change the number of repetitions from 3 to 10.

10.7.2 Aspirate the running matrix and analyze for 10 repetitions.

10.7.3 Calculate the IDL for each element by multiplying the standard deviation (SDev) by 3.

10.7.4 Change the number of repetitions back to 3.

10.8 Analyze the instrument detection limit standard.

10.9 Analyze the interference check standard INT-AB.

10.10 Analyze the matrix blank.

10.11 Analyze the LCS and LCSD.

10.12 Begin analyzing samples.

10.12.1 A matrix spike must be analyzed for every ten samples in a batch.

10.12.2 A matrix spike duplicate must be analyzed for every ten samples in a batch.

11 Calculations

11.1 Evaluation of the Linearity of the Initial Calibration
Correlation coefficient of 0.995 is required for EPA 200.7.

11.2 Sample Calcium and Magnesium Concentration

Liquid Sample Concentration for
Calcium and Magnesium:

Concentration = CD_f

Where C = concentration from instrument
D_f = dilution factor

$$D_f = \frac{D}{S}$$

Where D = dilution volume in liters.
S = Sample aliquot volume in liters.

11.3 Hardness Calculation Using Calcium and Magnesium Concentration from 11.2

Hardness Calculation as mg Equivalent $CaCO_3$/L:

$$= 2.497[\text{Ca, mg/L}] + 4.118[\text{Mg, mg/L}]$$

Aqueous sample results are expressed in mg equivalent $CaCO_3$/L

12 References

12.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (*SW-846)*;* U.S. EPA Office of Research and Development: Cincinnati, OH, 1988, Revision 2, 1995.
12.2 *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. 1998.

13 Practical Quantitation Limits (PQLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 13.1 Reporting Limits for EPA 200.7 and SM2340 B.

Method	Analyte	Matrix (Water, Water Quality Metals)	
		RL	Unit
EPA 200.7	Calcium	0.15	mg/L
EPA 200.7	Magnesium	0.15	mg/L
SM 2340 B.	Hardness	1.0	Mg Equivalent $CaCO_3$/L

Table 13.2 Acceptance Criteria for EPA Method 200.7

Method	Analyte	Accuracy Water (%R)	Precision Water (RPD)
200.7	Calcium	85-115	≤ 15
	Magnesium	85-115	≤ 15

Table 13.3 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Calcium, Magnesium	Analyst Initial Demonstration.	Once per analyst	Average of 4 LCS recoveries between 85-115%. Recovery of unknown sample	Recalculate results, correct problem, then rerun the initial demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration	Every 6 Months	Average of 4 LCS recoveries between 85%-115%, mb<RL, Unknown or PE.	Correct the problem.	
		MDL study.	Once every 12 months.	All analyte MDLs must be <RL	Correct the problem.	
		Analysis of PE sample.	Once every 12 months	All analyte results acceptable per the auditing agency.	Correct the problem	
		Initial Calibration. Minimum of 2 standards.	Daily initial calibration prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct the problem and recalibrate	

Table 13.3 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Calcium, Magnesium,	Interference Check Sample (SIC).	Daily after calibration.	Spiked element recoveries between 80% and 120% the absolute value of the true value, other element concentrations must be below the reporting imit.	Correct the problem, calculate new interelement correction factors and recalibrate.	
		MDL Check	Daily after calibration.	All analyte recoveries between 50-150%.	Correct the problem and recalibrate.	
		IDL Calculation	Daily after calibration.	All analyte IDLs < RL.	Correct the problem, recalibrate.	
		Initial Calibration Verification (ICV)	Daily after calibration.	All analyte recoveries between 95% and 105% of true value.	Correct the problem and recalibrate.	
		Continuing Calibration Blank (CCB).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	All analyte concentrations <RL.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	If unable to re-analyze, flag with a “B”.
		Continuing Calibration Check (CCC).	Daily after calibration, after every 10 samples, and at end of analysis sequence.	Initial analyte recoveries between 95% and 105%, subsequent analyte recoveries between 90% and 110%	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCC.	
		Instrument detection limit standard.	Daily after calibration but before analyzing samples.	All analyte recoveries between 50% and 150% of the true value.	Rerun once, if still out of control, correct problem, recalibrate, and reanalyze the samples.	
		Laboratory Control Sample (LCS).	Once per batch.	All analyte recoveries between 85% and 115%.	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a “J”.
		Laboratory Control Sample Duplicate (LCSD).	Once per batch.	≤ 15 RPD.	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to reanalyze, flag with a “J”.
		Matrix Blank.	Once per batch.	All analyte concentrations must <RL.	Correct the problem, redigest, and reanalyze all samples in the batch.	If unable to reanalyze, flag with a “B”.
		Matrix Spike.	Every 10 samples.	All analyte recoveries between 70% and 130%.	If recovery outside QC limits but CCC, CCB, ICV, and LCSD are acceptable, matrix effect is suspected.	Inform data user that data is suspect due to matrix effect.

Table 13.3 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Calcium, Magnesium,	Matrix Spike Duplicate.	Every 10 samples.	≤15 RPD.		Inform data user that data is suspect due to matrix effect.