Title: HARDNESS BY TITRATION
SM 2340C

Approvals (Signature/Date):

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1.0 SCOPE AND APPLICATION

Method SM 2340C is used to determine hardness by EDTA titration in drinking, surface and saline water, domestic and industrial wastes. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

1.1 Analytes, Matrix(s), and Reporting Limits

These methods can be used to determine hardness in drinking, surface and saline water, domestic and industrial wastes. The reporting limit for Hardness by titration is 4 mg/L

2.0 SUMMARY OF METHOD

Calcium and magnesium ions in the sample are sequestered upon the addition of Ethylene-diamine-tetraacetic acid (EDTA) by forming a chelated soluble complex. The end point of the reaction is detected by means of Erichrome Black T indicator, which has a red color in the presence of calcium and magnesium at a pH of 10.0 ±0.01 and a blue color when the cations are sequestered.

3.0 DEFINITIONS

3.1 Total hardness is defines as the sum of calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

3.2 There are no additional specific definitions associated with this test. See the QAPM and SM2340C for general definitions.

4.0 INTERFERENCES

Some metal ions interfere by causing indistinct endpoints. MgEDTA reduces this interference.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, Labcoat, Nitrile Gloves

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Ammonium chloride	Irritant	None listed	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Supplies

6.1.1 10 mL buret, class A
6.1.2 100 mL glass beakers
6.1.3 50 mL graduated cylinders
6.1.4 Stirbars
6.1.5 Magnetic stirrer
6.1.6 pH strips
6.1.7 5mL pipets

7.0 REAGENTS AND STANDARDS

7.1 Standard

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material.

7.1.1 Hardness WasteWatR standard from ERA (or equivalent), used to prepare LCS

7.2 Reagents

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceabililty must be maintained by the laboratory

7.2.1 Reagent grade water
7.2.2 Buffer solution with MgEDTA, purchased, certified APHA Standard.
7.2.3 Eriochrome Black T
7.2.4 EDTA Titrant 0.01M, purchased, certified traceable to NIST SRM 915
7.2.5 NaCl, reagent grade
7.2.6 Ammonium hydroxide
7.2.7 Ammonium chloride

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding time and the reference that includes preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Polyethylene bottles	100 ml	HNO_3, pH < 2;	Six months	40CFR 136

Notify the Project Manager if the hold time has been exceeded.

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (flag the result accordingly).
- The sample result is > 10x the blank level (flag the result accordingly).

9.1.2 Laboratory Control Sample (LCS).

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within the vendor's specified limits (or ±10% of vendor's certified value if limits are not provided). If the LCS is outside of these limits, re-prepare the whole batch unless:

- The LCS recovery is above the upper limit and samples are ND. Flag sample results accordingly and write an NCM.

9.1.3 Sample Duplicate

- Analyze a sample duplicate with every batch of twenty samples or less. The RPD between the sample and the duplicate must be within ±20 %.
- For drinking water, analyze a sample duplicate with every batch of ten samples or less.

9.1.4 Batch QC for Solid Samples

Prepare a solid matrix MB and LCS in the same manner as solid samples but using Teflon chips or glass beads.

10.0 PROCEDURE

10.1 Reagent and Standard Preparation

10.1.1 Eriochrome Black T Indicator

Weight 0.5g Eriochrome Black T and 100g NaCl. Mix well in a beaker. Store in a tightly stopper plastic bottle.

10.1.2 Buffer Solution (if not purchased)

Dissolve 16.9g NH_4Cl in 143 mL concentrated NH_4OH in a 250mL volumetric flask. Add 1.25g of MgEDTA and bring up to volume with Reagent grade water. Store in a tightly stopper plastic bottle. Shelf life is one month. Discard when 1 or 2 mL added to sample fails to produce a pH of 10.0± 0.1 at end point of titration.

10.1.3 Laboratory Control Sample-LCS

Prepare the LCS by adding to 25 mL Hardness WasteWatR standard from ERA (or equivalent) QC Standard to 25 mL Reagent grade water.

10.2 Preparation of Water Samples

- The sample must be preserved with HNO_3 to a pH<2
- The sample must be at room temperature before analysis. Mix the sample well.
- Measure 25mL of sample with a graduated cylinder. Transfer to a glass beaker. Add 25mL Reagent grade water to the beaker.

10.3 Preparation of Solid Samples

- Weigh 4 ± 0.1 grams of the well mixed sample into a disposable 50 mL centrifuge tube.
- Add 40mL Laboratory Reagent Grade water using a Class A graduated cylinder. All initial and final amounts must be documented.
- Shake samples by hand to ensure water and soil are mixed and then place on an orbital shaker for minimum of 10 minutes. If necessary, centrifuge for 3 – 5 min or until separation of the phases occurs.
- Filter the resultant supernatant water through a 0.2um filter.

10.4 Sample Analysis

- Add a stir bar. Turn on the stir plate and mix well.
- Add 1-2mL buffer solution. Measure pH to ensure it is at 10.0 ±0.1
- Add 1 small scoop of indicator
- Titrate sample slowly with standard EDTA titrant with continuous stirring. At the endpoint the solution is blue.
- NOTE: The titration must be completed within 5 min of buffer addition.
- Record the volume of EDTA titrant used in the logbook.
- If the EDTA used for titration is more than 10mL, use a smaller aliquot of sample and re-analyze the sample. Record the volume of EDTA titrant used in the logbook.
- For waters of low hardness (less than 5 mg/L), take a larger aliquot of sample (50-100 mL), add proportionally larger amount of buffer, inhibitor and indicator and re-analyze the sample. Record the volume of EDTA titrant used in the logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Sample Duplicate RPD} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.3 Concentration

$$\text{Hardness (EDTA) as mg } CaCO_3\text{/L} = \frac{A \times N \times 50000}{\text{mL sample}}$$

where A= mL of EDTA titrant
N= Normality of EDTA titrant

Hardness result may be calculated using the Excel spreadsheet and attach the sheet to the logbook.

11.4 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. For this titrimetric method, an MDL is not applicable as the lowest discernable unit of measure that can be observed (0.1 mL in a 25 ml sample) is defined as the reporting limit (RL) or 4 mg/L.

11.5 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples with an average recovery and RSD within laboratory acceptance limits. An on-going Demonstration of Capability must be documented annually and consists of 4 consecutive passing LCS samples or a passing PT.

11.6 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

12.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Environmental Health and Safety Manual (CW-E-M-001).

13.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

Titrated sample waste. This is generated during the analysis of the sample. The waste is collected in a 5 gallon satellite container. The waste is bulked as base waste.

Sample waste. Non-Hazardous waste is disposed of by pouring the samples water that have been titrated into the sink, measuring the pH and neutralizing the water using soda ash, and then draining the neutralized contents into the sewer system. The soil generated in these tests is collected in the 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid.

Unused standards or reagents. If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).

If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4).

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14.0 REFERENCES / CROSS-REFERENCES

14.1 Method 2340C, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998

15.0 METHOD MODIFICATIONS

Item	Method 2340C	Modification
1.	*2340C – Sec 2.a.2*	*The Laboratory uses purchased Certified APHA Buffer solution with specified Expiration Date. Solution will be discarded when 1 or 2 mL added to sample fails to produce a pH of 10.0± 0.1 at end point of titration.*
2.	*2340C – Sec 2.d*	*The Laboratory uses purchased Certified traceable to NIST EDTA Titrant solution with specified Expiration Date.*

16.0 ATTACHMENTS

16.1 Attachment 1: Analysis Information

16.2 Attachment 2: Logbook

16.3 Attachment 3: Data Review Checklist

17.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

17.1 Revision 4, dated 28 February 2013

- This revision supersedes IR-WET-HARD, revision 3 (10/28/2011)
- Added solid sample preparation procedures
- Revised Data Review Checklist
- Revised Waste Disposal requirements
- Added Method Modifications
- Revised by DC, NB, DD and LH

17.2 Revision 5, dated 07 March 2014

- This revision supersedes IR-WET-HARD, revision 4 (02/28/2013)
- Clarified that there is no MDL for this method
- Removed logbook; data entered directly into LIMS
- Revised data review checklist
- Revised by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	Reporting Limit	Duplicate RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Hardness in Water by Titration (SM2340C)				
Preservation: HNO3				
Container: 500 mL Poly	**Amount Required:** 100 ml		**Hold Time:** 180 days	
Hardness (as CaCO3)	4.0 mg/l	20	90 - 110	

TestAmerica Irvine

Analytical Method Information

Analyte	Reporting Limit	Duplicate RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Hardness in Solid by Titration (SM2340C)				
Preservation: None				
Container: 4 oz jar	**Amount Required:** 10 grams		**Hold Time:** 180 days	
Hardness (as CaCO3)	40.0 mg/l	20	90 - 110	

Attachment 2

Data Review Checklist

HARDNESS DATA REVIEW CHECKLIST
SM 2340C

Method: _____ Analysis Date: _____ 2nd Level Reviewer: _____

Batch: _____ Analyst Initials: _____ Review Date: _____

Item to Review	Analyst	2nd Level	Notes/Specific Criteria
Calibration			
N/A			
Sample Preparation Batch:			
Water samples preserved with sulfuric acid to pH<2			
All samples prepared and analyzed within holding time of six months			
Batch contains no greater than 20 samples			
Method Blank reads < RL			
LCS recovery within limits 90-110%			
SA/DU RPD ≤20%			
Data Documentation:			
All standards used are uniquely identified and are not expired			
EDTA normality and lot number entered into LIMS			
Buffer and indicator lot numbers entered into LIMS			
All flags correctly applied and NCMs written, as required			
Correct sample volume entered into LIMS			
Analysis times accurately entered into LIMS			
All calculation correct (final results, recovery, RPD)			

Hardness_2340C_Check_r2.doc
Rev.: 02/28/2014