DOCUMENT RESUME

ED 152 583 SE 024 149

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TITLE Calcium Analysis. Training Module 5.225.2.77.
SPONS AGENCY Department of Labor, Washington, D.C.; Iowa State Dept. of Environmental Quality, Des Moines.
PUB DATE Sep 77
NOTE 26p.; For related documents, see SE 024 138-165; Transparency masters marginally legible

EDRS PRICE MF-$0.83 HC-$2.06 Plus Postage.
DESCRIPTORS Chemical Analysis; *Chemistry; *Instructional Materials; *Laboratory Techniques; *Post Secondary Education; Secondary Education; *Teaching Guides; Units of Study
IDENTIFIERS *Calcium; *Water Treatment

ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor fasiliar with the titrimetric method for determining calcium concentrations in water. Included are objectives, an instructor guide, student handouts, and transparency masters. A videotape is also available from the author. This module considers the chemistry and principles of the determination, preparation of reagents, titration of the sample and calculation and interpretation of results. (Author/RH)

CALCIUM ANALYSIS

Training Module 5.225.2.77

Prepared for the

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by

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The publication of these training materials was financially aided through a contract between the Iowa Department of Environmental Quality and the Office of Planning and Programming, using funds available under the Comprehensive Employment and Training Act of 1973. However, the opinions expressed herein do not necessarily reflect the position or policy of the U. S. Department of Labor, and no official endorsement by the U. S. Department of Labor should be inferred.

September, 1977

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 2 hours	Topic: Summary

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Determine the concentration of calcium in a water sample by the EDTA titrimetric method.
2. List possible interfering ions which may affect the results of the determination.

Instructional Aids:

Transparencies Cal-Ca3

Softening videotape

Instructional Approach:

Lecture, discussion, lab practice, videotape viewing.

References:

1. "Standard Methods for the Examination of Water and Wastewater," 14th Edition pp. 185, 196, 189-191.

Class Assignments:

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.25 hours	Topic: Chemistry of Calcium in Water

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Describe sources of calcium in water supplies.
2. Write a chemical reaction between calcium and EDTA.
3. Describe how Mg can be removed from a water sample so that it will not interfer with the calcium analysis.

Instructional Aids:

Transparency Cal- Reaction of calcium with EDTA.

Instructional Approach:

Lecture/discussion

References:

Standard Methods, p. 185, 186, 189.

Class Assignments:

Module No: Ca	Topic: Chemistry of calcium in water

Instructor Notes:	Instructor Outline:
	1. Calcium, a metal, exists in water and in compounds as the Ca^{2+} ion. It is a major contributor to water hardness. From water passage through Ca containing minerals: a. lime stone $CaCO_3$ b. dolomite $CaCO_3 \cdot MgCO_3$ c. gypsum $CaSO_4 \cdot 2H_2O$ d. gypsiferous shale
Transparency Ca-1 Ca-EDTA reaction	2. $Ca^{2+} + (EDTA)^{4-} \rightarrow (Ca(EDTA))^{2-}$
	3. Magnesium is largely removed by precipitation as $Mg(OH)_2$ at high pH.

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.25 hours	Topic: Principles of Calcium Determination

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Describe the EDTA - calcium analysis briefly.
2. Explain how the calcium analysis is similar to and different from the determination of total hardness.

Instructional Aids:

Softening videotape.

Instructional Approach:

Videotape viewing/discussion.

References:

Standard Methods, p. 189-191, 200-206.

Class Assignments:

Module No: Ca	Topic: Principles of Ca Determination

Instructor Notes:	Instructor Outline:
Softening video tape	1. Show first half of video tape. 2. Answer any questions concerning the video tape.

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.25 hours	Topic: Safety

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Locate the following in the laboratory and demonstrate proper use: emergency shower, fire extinguisher, eye wash, first aid kit.
2. Select and use safety glasses, lab coats or apron and gloves in the appropriate situation.
3. Describe any hazards associated with the calcium determination.

Instructional Aids:

Handout of safety rules for the laboratory.

Instructional Approach:

Lecture, demonstration.

References:

Basic laboratory skills module

Class Assignments:

Read Safety rules

Module No: Ca	Topic: Safety
Instructor Notes:	Instructor Outline:

1. Show the location of the various pieces of safety equipment.

2. Safety glasses should be worn when adjusting pH and during titration.

3. The corrosive nature of NaOH should be pointed out.

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Preparation of Reagents

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Prepare the following reagents for the determination: 1 NaOH, Murexide indicator or Eriochrom Blue Black R indicator.
2. Calculate the concentration in μgCa/ ml equivalent of the standard EDTA solution standardized in units of M or mg $CaCO_3$/l equivalent.

Instructional Aids:

Transparency Ca2 - calculation of equivalent concentrations.

Instructional Approach:

Laboratory practice

References:

Standard Methods, pp. 189, 190.

Class Assignments:

Module No: Ca	Topic: Preparation of REagents

Instructor Notes:	Instructor Outline:
1.a. 1N NaOH: 40g/liter b. 0.2g indicator ground with 100g NaCl c. 0.2 g indicator g ground with 100g NaCl Transparency Ca-2 calculations	1. Reagents may be prepared in groups or be prepared before-hand. a. 1 N NaOH b. murexide indicator or c. Eriochrom Blue Black R 2. Calculation: mg(Ca)/l equivalent=0.4 X (Mg/l) mg(Ca)/l equivalent=$\frac{CaCO_3 \text{ equivalent}}{.04 \text{ X M(EDTA)}}$

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.5 hours	Topic: Titration of sample

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Properly prepare a water sample for titration.
2. Properly titrate the prepared sample to the end point and record the appropriate data.

Instructional Aids:

Instructional Approach:

Laboratory practice

References:

Standard Methods p.190.

Class Assignments:

Module No: Ca	Topic: Titration of Sample
Instructor Notes:	Instructor Outline;

1. Prepare sample by:
   a. 50 ml sample plus 50 ml H_2O
   b. Add 2.0 ml NaOH
   c. Check pH

2. Titration:
   a. titrate rapidly
   b. color changes
      i. Murexide pink-purple
      ii. Eriochrome Blue-Black R red-blue

Module No:	Module Title: Calcium Analysis
	Submodule Title:
Approx. Time: 0.25 hours	Topic: Calculation and Interpretation of results

Instructional Objective:

Upon completion of this module the participant should be able to:

1. Calculate the concentration in a water sample as mg/l Ca or as mg/l $CaCO_3$ (calcium hardness).
2. List several possible sources of interference which may affect the result.

Instructional Aids:

Transparency Ca3-Interferences in the calcium determination.

Instructional Approach:

Lecture/discussion

References:

Standard Methods pp. 189, 190.

Class Assignments:

Module No: Ca	Topic:

Instructor Notes:	Instructor Outline:
Transparency Ca-3 Interferences	1. Calculation: $mg/l\ (Ca) = \frac{ml\ (EDTA)}{ml\ sample} \times mg/l\ equivalent\ Ca$ $mg/l\ (CaCO_3) = \frac{ml\ (EDTA)}{ml\ sample} \times mg/l\ equivalent\ CaCO_3$ 2. Interferences: a. $CaCO_3$ precipitation correct with HCl b. organics - digestion c. high alkalinity - neutralize with HCl, boil

Exam Questions

Calcium Analysis
Chemistry of Calcium in water

1. Which of the following mineral does not contribute to dissolved calcium in water?
   a. limestone
   b. gypsum
   c. dolomite
   d. quartz

2. _____ molecule(s) of EDTA react(s) with one calcium ion to form one complex ion.

3. Magnesium can be removed as an interference in the calcium determination by:
   a. adding cyanide ion
   b. lowering the pH
   c. raising the pH to 12
   d. chlorination

Principles of Calcium Determination

4. Does calcium combine with EDTA before or after magnesium?

5. The titrimetric determination of calcium and the titrimetric determination of hardness are essentially the same except:
   a. a different indicator is used
   b. a different titrant is used
   c. a spectrophotometer is used in one case and not the other
   d. one requires very specialized equipment

Safety

6. Where can one go in the laboratory to find a band aid if one's finger is cut by glass tubing?

7. What can be worn to prevent acid holes in a new shirt worn to the laboratory?

8. Which of the following reagents used in the calcium determination would you consider most hazardous?
   a. EDTA titrant
   b. Sodium hydroxide solution
   c. Indicator mixture

Preparation of Reagents

9. How many grams of NaOH are required to prepare a one liter solution which is 1.0 N?
   a. 500 g
   b. 0.01 g
   c. 40 g
   d. 1 g

10. A solution of EDTA is equivalent to 1 mg $CaCO_3$ per ml. What is its calcium equivalence in micrograms per ml?

Titration of Sample

11. Prior to titration, which of the following should be done to the sample?
    a. add 50 ml EDTA solution
    b. add 2.0 ml sodium hydroxide solution
    c. add 5.0 ml $CaCO_3$
    d. extract the solution with chloroform

12. The Eriochrome Blue-Black R indicator changes from red to _____ at end point.

Calculation and Interpretation of Results

13. It takes 25 ml of an EDTA solution in which the mg/l Ca equivalent is 400.8 to titrate a 50 ml water sample. What is the concentration in mg/l Ca of this sample?

14. How can organic interferences to the calcium determination be over come?

CALCIUM ANALYSIS

EQUIPMENT AND SUPPLIES LIST

1. sodium hydroxide pellets, NaOH
2. 1 ℓ volumetric flask
3. 2000 ml beaker
4. hot plate
5. distilled water
6. 1000 ml graduated cylinder
7. 1 ℓ polyethylene bottle
8. eriochrom blue black R indicator.
9. sodium chloride
10. mortar and pestle
11. 100 ml wide mouth sample bottle
12. disodium ethylenediaminetetraacetate
13. analytical balance
14. calcium carbonate
15. 500 ml erlynmeyer flask
16. funnel
17. hydrochloric acid, concentrated
18. bunsen burner
19. ring stand and ring
20. methyl red indicator
21. concentrated ammonium hydroxide
22. 2 - 50 ml buret
23. 5 - 125 ml erlynmeyer flask
24. 25 - ml pipet

Calcium Analysis

Laboratory Procedure

I. Preparation of Reagents and Standards

A. Obtain the equipment, supplies, and chemicals listed in the "equipment" handout.

B. Prepare the following solutions

1. 1.0 N NaOH Sodium Hydroxide: Add 40 g sodium hydroxyde pellets to a 1l volumetric flask. Boil 1500 ml distilled water for five minutes; allow to cool covered. Add 750 ml of the cooled water to the flask. Mix to dissolve the NaOH, allow to cool. Dilute to the mark with distilled water. Mix. Transfer to a labeled polyethylene bottle.
2. Indicator. Add 0.2 g Eriochrome Blue Black R indicator and 100 g sodium chloride (NaCl) to a mortar. Mix and grind with a pestle. Transfer to a stoppered, labeled bottle.
3. EDTA titrant. Weigh 3.723 g disodium ethylenediaminetetra-acetate dihydrate ($Na_2H_2C_{10}H_{12}O_8N_2$-$2H_2O$) or ($Na_2EDTA$) on an analytical balance and transfer to a 1l volumetric flask. Add 500 ml distilled water, swirl to dissolve. Dilute to the mark with distilled water. Mix and transfer to a labeled polyethylene bottle.

C. Prepare the following standard solution:

Weigh 1.000g anhydrous, primary standard grade calcium carbonate ($CaCO_3$) on an analytical balance and record the exact mass. Quantitatively transfer the $CaCO_3$ to a 500 ml erlynmeyer flask. Place a funnel on the neck of the flask and add 6M hydrochloric acid, HCl (prepared by mixing equal parts concentrated HCl and distilled water) a little at a time until bubbling has ceased and all the $CaCO_3$ has dissolved. Add 200 ml distilled water and boil with a bunsen burner for five minutes. Cool. Add 2 drops methyl red indicator. Mix. If the solution is yellow, add 6M HCl dropwise until orange. If the solution is red, add 3M NH_3 (ammonia). [prepare by dissolving 200 ml concentrated ammonia in distilled water to make a 1 liter solution] dropwise until orange. Transfer the solution to a 1 liter volumetric flask. Dilute to the mark with distilled water. The concentration of the solution in mg /ml $CaCO_3$ is numerically equal to the mass in gram $CaCO_3$ added.

The concentration of Ca in mg/ml is 0.4008 times the concentration of $CaCO_3$.

II. Titration

A. Titration of standard

Fill a 50 ml buret with EDTA solution. Fill another buret with standard Ca solution. Record the initial readings of each buret. Add 25 ml Ca solution to a 125 ml elynmeyer flask. Add 25 ml distilled water. Add 2.0 ml NaOH solution. Stir to mix. Add 0.2g of indicator. Add EDTA titrant slowly with swirling in white light until the solution turns from red to blue (end-point). Record the final values of both burets. Repeat the titration twice. Record results on data sheet. Volume of each solution used is equal to the difference between final and initial buret readings. The $CaCO_3$ equivalence of the EDTA solution is equal to the grams $CaCO_3$ weighed times and $CaCO_3$ solution used divided by ml EDTA solution. Average the three values, call this value B.

B. Sample titration

Pipet three 25 ml well-mixed samples aliquots into three 125 ml erlynmeyer flasks. Add and mix 25 ml distilled water. Add 2.0 ml NaOH and 0.2g indicator. Titrate in triplicate with EDTA solution as in "A" above. Record initial and final buret readings.

III. Calculation and Evaluation of Results.

A. The volume of solution used in each case will be equal to the final minus the initial buret reading. The average volume from the three titrations will be the volume used in calculation. Call this value "A". The calcium hardness (as mgl 1 $CaCO_3$) is calculated from the following formula:

$$C = \text{Calcium hardness (as } CaCO_3) = \frac{AxBx1000}{25}$$

The calcium concentration is C times 0.4008.

B. Comment on possible errors, distinctness of end-point and source of sample.

Calcium Analysis

Data Sheet Sample number _____

Preparation of standard $CaCO_3$

mass of container plus $CaCO_3$ _____ g

mass of container - _____ g

(d) mass of $CaCO_3$ _____ g

concentration $CaCO_3$ standard _____ mg/ml

Standardization of EDTA solution

		I	II	III
	final caburet	____ ml	____ ml	____ ml
	initial caburet	- ____ ml	- ____ ml	- ____ ml
(e)	ml Ca used	____ ml	____ ml	____ ml
	f inal EDTA buret	____ ml	____ ml	____ ml
	initial EDTA buret	- ____ ml	- ____ ml	- ____ ml
(f)	ml EDTA used	____ ml	____ ml	____ ml
	EDTA equivalance ($CaCO_3$) = $\frac{d \times e}{5}$	____ mg/ml	____ mg/ml	____ mg/ml

B. average EDTA equivalence _____ mg/ml $CaCO_3$

$$= \frac{(I + II + III)}{3}$$

Sample titration

	I	II	III
final EDTA buret	____ ml	____ ml	____ ml
initial EDTA buret	- ____ ml	- ____ ml	- ____ ml
ml EDTA used	____ ml	____ ml	____ ml

A = Average EDTA volume _____ ml = $\frac{(I + II + III)}{3}$

C = calcium hardness (as $CaCO_3$) = _____ mg/l

$$C = \frac{A \times B \times 1000}{25}$$

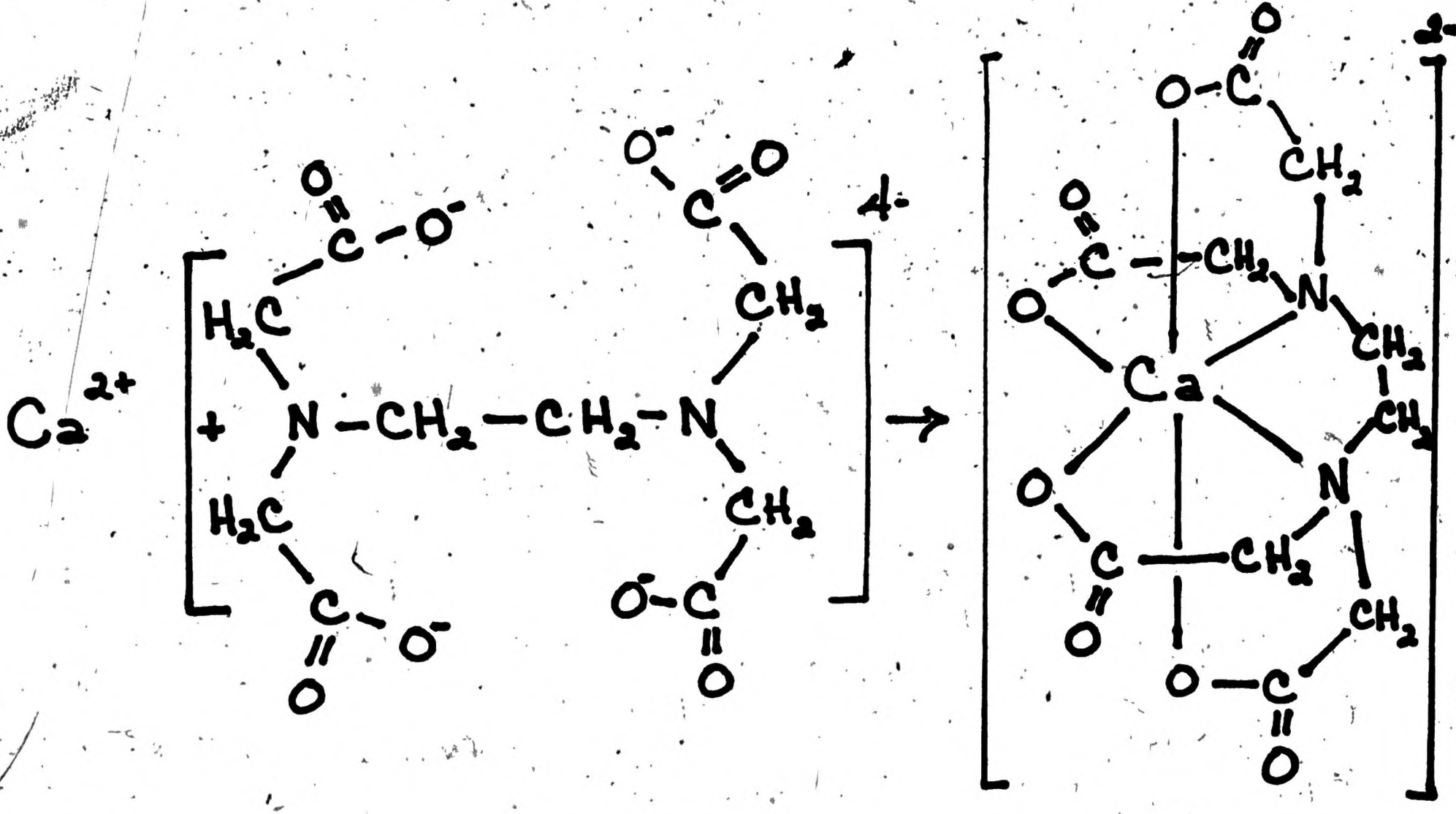
Calcium concentration = C x 0.4008 = _____ mg/l

Comments:

Comments: (con't)

Analyst _____ **Date** _____

Transparency CA 1
Calcium — EDTA Reaction



TRANSPARENCY CA2

Calculation of Equivalent Concentrations

To convert from mg per ml $CaCO_3$ equivalent to mg/l Ca equivalent;
Multiply by 400.8

To convert from mg per ml $CaCO_3$ equivalent to mg/l $CaCO_3$;
Multiply by 1000

To convert from Molar to mg Ca per ml;
Multiply by 0.4.

TRANSPARENCY CA3

Interferences in the Calcium Determination

Interference	Correction
$CaCO_3$ precipitation	Add HCL, boil.
Organics	Digestion
High Alkalinity	Neutralize with HCl, Boil
Magnesium	Precipitate as $Mg(OH)_2$ at high pH