

DEPARTMENT OF ENVIRONMENTAL QUALITY

WATER DIVISION


MEMORANDUM

P. O. Box 10009

Richmond, VA 23240-0009

**SUBJECT: OWRM Program Guidance Memorandum No. 94-012
Calcium Carbonate Equivalence (CCE) Testing Requirement**

TO: Regional Directors

FROM: Larry G. Lawson, P.E. 
Director, Office of Water Resources Management

DATE: October 20, 1994

**COPIES: Bob Burnley, James Adams, Martin Ferguson, Regional Office
Permit Managers, Ron Gregory, OWRM Permit Staff**

The purpose of this memo is to correct the confusion resulting from the CCE and Alkalinity reporting requirements in VPA Permit Application Forms C and D, and in a few recently issued VPA permits.

Detailed background information is provided through the attached memo from Lily Choi to Dale Phillips dated September 23, 1994.

In order to resolve the aforementioned issues, the following recommendations are provided:

- 1. VPA Form C and Form D.** CCE as a separate parameter should be eliminated (by simply marking through it) from the waste characterization list for sludge analysis. Alkalinity will continue to be required as a screening parameter and will retain the footnote requiring CCE testing for sludges containing more than 10% lime (dry weight). CCE testing should be run by following the methodology in Attachment A.
- 2. VPA Permit.** CCE monitoring, per attachment A, should not be required routinely in the permit unless review of the application indicates that the sludge is expected to contain a lime content of 10% (dry weight) or more.

**DEPARTMENT OF ENVIRONMENTAL QUALITY
WATER DIVISION
OFFICE OF WATER RESOURCES MANAGEMENT**

MEMORANDUM

P. O. Box 10009

Richmond, VA 23240-0009

SUBJECT: Calcium Carbonate Equivalence (CCE) Testing Requirement

TO: Dale Phillips

FROM: Lily Choi *ll*

DATE: September 23, 1994

COPIES: Martin Ferguson, Fred Holt, Richard Ayers

The purpose of this memo is to address the confusion resulting from the CCE and Alkalinity reporting requirements in VPA Permit Application Forms C and D, and in a few recently issued VPA permits.

Some laboratories do not distinguish between the methods in Attachment A (CCE) and Attachment B (Alkalinity) and may report identical results for both parameters.

However, the titration end point for alkalinity can be as low as pH 4.5. The titration end point for the CCE testing can be as high as pH 8.3 in accordance with the indicator titrimetric method which is commonly used by the commercial labs. Obviously, the reported results will be dramatically different.

CCE represents a "true" acid-neutralizing capacity when agricultural liming is of concern. Besides the fact that natural soil in Virginia is already in an acidic condition, an acidic soil environment is generally expected when nitrogen enriched sludge is land applied. This is due to the release of hydrogen ions through nitrification. Therefore, liming is part of soil amendment procedures.

It should be recognized that, generally, the CCE testing methodology is only reliable for materials containing significant amounts of lime (>10% CaCO₃), such as lime treated sludges (mainly sewage sludge). Negative values may be reported if the test is run for low or zero lime materials (such as aerobically digested sludge or water treatment coagulation sludge). For example, two water treatment plant sludges have been required to run CCE per their permit requirements and negative values have been reported. Both sludges exhibit low alkalinity values (0.1% and 2.3% CaCO₃ respectively).

Alkalinity measurements are often used in the interpretation and control of water and wastewater treatment processes. Alkalinity testing results do not provide much meaning for land application of sludges. However, it continues to be a valid screening parameter to detect those sludges that may contain a high lime content, and subsequently to assess the maximum allowable sludge loading based on its lime content. This is especially critical for coastal plains soil where micronutrient deficiencies could occur due to overloading, or high pH conditions. The liming effect of a proposed sludge should be assessed by reviewing the CCE testing results, coupled with the exhibited pH values and the treatment processes employed.

Attachment A

**OFFICIAL
METHODS OF ANALYSIS**

OF THE

**ASSOCIATION OF OFFICIAL
ANALYTICAL CHEMISTS**

EDITED BY KENNETH HELRICH

FIFTEENTH EDITION, 1990

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2200 WILSON BOULEVARD
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1. Agricultural Liming Materials

Frank J. Johnson, Associate Chapter Editor
National Fertilizer Development Center, Tennessee Valley Authority

924.01 Sampling of Liming Materials Procedure

(Caution: See safety note on calcium oxide.)

Take sample representative of lot or shipment. Avoid disproportionate amt of surface or any modified or damaged zone.

(a) *Burnt or lump lime, in bulk.*—Collect composite sample of ≥ 10 shovelfuls/car, with proportionate amts from smaller lots, taking each shovelful from different part of lot or shipment. Immediately crush to pass 5 cm (2") diam. circular opening, mix thoroly and rapidly, reduce composite to ca 2 kg (5 lb) sample by riffing or quartering, and place in labeled, dry, air-tight container.

(b) *Hydrated lime and ground burnt lime, in bags.*—Select 10 bags from different parts of each lot or shipment of ≤ 20 tons and 1 addnl bag for each addnl 5 tons. Use sampling tube to withdraw top to bottom core from each bag selected. Combine cores, mix thoroly and rapidly, reduce composite to ca 1 kg (2 lb) by riffing or quartering, and place in dry, air-tight container.

(c) *Ground limestone and ground marl, in bags.*—Proceed as in (b).

(d) *Ground limestone, ground burnt lime, ground marl, and slag, in bulk.*—Use slotted sampling tube to withdraw samples to full sampler depth from 10 points in lot or shipment. Proceed as in (b), beginning "Combine cores,"

Refs.: JAOAC 7, 252(1924); 48, 95(1965).

CAS-1317-65-3 (limestone)

924.02 Mechanical Analysis of Liming Materials Procedure

(Caution: See safety note on calcium oxide.)

If entire sample is not to be dried, obtain lesser portions by riffing or quartering. Dry at 110° to const wt and cool to room temp.

Obtain 90–150 g dry sample by riffing or quartering. Break any agglomerates formed during drying by rolling dry sample with hard rubber roller on hard rubber mat, wet sieving, or by equally effective means that does not result in crushing the limestone.

Wet sieving.—Place 100 g sample on No. 200 sieve and wash with moderate stream of tap H₂O at max. gage pressure of 0.28 kg/sq cm (4 lb/sq in.) until H₂O passing sieve is clear, with care to avoid loss of sample by splashing. Dry material remaining on sieve at 105° and transfer to No. 100 sieve in series with No. 200 sieve of same diam. and depth. Shake 8 min in mech. shaker. (If wet sieving is used to break agglomerates, do wet sieving on sieve having smallest opening to be used in final testing. After drying, transfer to sieves to be used in final testing. If only 1 sieve is to be used, do not transfer.) Quant. transfer weighed sample to 8" diam. std sieve or set of sieves (e.g., Nos. 10, 20, 40, 60, 80, and 100 or other appropriate combination).

Sieve by lateral and vertical motion accompanied by jarring action. Continue ≥ 5 min or until addnl 3 min of sieving time fails to change results of any sieve fraction by 0.5% of total sample wt. Do not overload any sieve when assaying closely sized materials.

Dct. wt of each sieve fraction and report as % of total sample wt.

Refs.: JAOAC 7, 252(1924); 55, 539(1972); 48, 95(1965); 52, 322(1969).

924.03 Liming Materials Preparation of Sample Procedure

Reduce dried sample, 924.02, to amt sufficient for analysis and grind ≥ 225 g (0.5 lb) reduced sample in mortar, ball mill, or other mech. app. to pass No. 60 sieve. Mix thoroly, and store in air-tight container.

Refs.: JAOAC 7, 252(1924); 48, 95(1965).

955.01 Neutralizing Value for Liming Materials Final Action

(Uncorrected for sulfide content)

A. Reagents

(a) *Sodium hydroxide std soln.*—0.25N. Prep. and stdze as in 936.16.

(b) *Hydrochloric acid std soln.*—0.5N. Stdze against (a), using phthln.

B. Indicator Titrimetric Method

Place 0.5 g burnt or hydrated lime (1 g ground limestone or ground marl), prepd as in 924.03, in 250 mL erlenmeyer; add 50 mL HCl std soln and boil gently 5 min. Cool, and tit. excess acid with NaOH std soln, using phthln. For burnt and hydrated lime, report as % CaO; for limestone and marl, report as % CaCO₃ equivalence.

$$\begin{aligned} \% \text{ CaCO}_3 \text{ equivalence of sample} &= 2.5 \times (\text{mL HCl} - \text{mL NaOH}/2) \\ \% \text{ CaO equivalence} &= 2.8 \times (\text{mL HCl} - \text{mL NaOH}/2) \end{aligned}$$

C. Potentiometric Titration Method

(Applicable to liming materials contg large amt of Fe⁺² or coloring matter, but not to silicate materials)

Proceed as in 955.01B thru "Cool. . . ." Transfer to 250 mL beaker and insert glass and calomel electrodes of pH meter, buret contg 0.25N NaOH, and mech. stirrer. Stir at moderate speed to avoid splash. Deliver NaOH rapidly to pH 5, then dropwise until soln attains pH 7 and remains const 1 min while stirring. (If end point is passed, add, from 1 mL Mohr pipet, just enough 0.5N HCl to bring pH to <7, and back-tit. slowly to pH 7.) Add mL of excess acid, if used, to initial 50

increments of 0.02N sulfuric acid (H₂SO₄) (Section 2320B.3c) to reduce pH to 4 or less. Remove electrodes. Add 5 drops 30% H₂O₂ and boil for 2 to 5 min. Cool to room temperature and titrate with standard alkali to pH 8.3 according to the procedure of 4d.

b. *Color change:* Select sample size and normality of titrant according to criteria of ¶ 1e. Adjust sample to room temperature, if necessary, and with a pipet discharge sample into an erlenmeyer flask, while keeping pipet tip near flask bottom. If free residual chlorine is present add 0.05 mL (1 drop) 0.1M Na₂S₂O₃ solution, or destroy with ultraviolet radiation. Add 0.2 mL (5 drops) indicator solution and titrate over a white surface to a persistent color change characteristic of the equivalence point. Commercial indicator solutions or solids designated for the appropriate pH range (3.7 or 8.3) may be used. Check color at end point by adding the same concentration of indicator used with sample to a buffer solution at the designated pH.

c. *Potentiometric titration curve:*

1) Rinse electrodes and titration vessel with distilled water and drain. Select sample size and normality of titrant according to the criteria of ¶ 1e. Adjust sample to room temperature, if necessary, and with a pipet discharge sample while keeping pipet tip near the titration vessel bottom.

2) Measure sample pH. Add standard alkali in increments of 0.5 mL or less, such that a change of less than 0.2 pH units occurs per increment. After each addition, mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record pH when a constant reading is obtained. Continue adding titrant and measure pH until pH 9 is reached. Construct the titration curve by plotting observed pH values versus cumulative milliliters titrant added. A smooth curve showing one or more inflections should be obtained. A ragged or erratic curve may indicate that equilibrium was not reached between successive alkali additions. Determine acidity relative to a particular pH from the curve.

d. *Potentiometric titration to pH 3.7 or 8.3:* Prepare sample and titration assembly as specified in ¶ 4c1). Titrate to preselected end-point pH (¶ 1d) without recording intermediate pH values. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached before making the next addition.

5. Calculation

$$\text{Acidity, as mg CaCO}_3/\text{L} = \frac{[(A \times B) - (C \times D)] \times 50 (000)}{\text{mL sample}}$$

where:

- A = mL NaOH titrant used,
- B = normality of NaOH,
- C = mL H₂SO₄ used (¶ 4a), and
- D = normality of H₂SO₄.

Report pH of the end point used, as follows: "The acidity to pH _____ = _____ mg CaCO₃/L." If a negative value is obtained, determine the alkalinity according to Section 2320.

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

Forty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 20 mg CaCO₃/L. Titration according to the procedure of ¶ 4d gave a standard deviation of 1.8 mg CaCO₃/L, with negligible bias. Five laboratories analyzed two samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of ¶s 4b and 4d. The mean acidity of one sample (to pH 3.7) was 487 mg CaCO₃/L, with a standard deviation of 11 mg/L. The bromphenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L, with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater, with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

7. Bibliography

- WINTER, J.A. & M.R. MIDGETT. 1969. FWPCA Method Study I. Mineral and Physical Analyses. Federal Water Pollution Control Admin., Washington, D.C.
- BROWN, E., M.W. SKOUGSTAD & M.J. FISHMAN. 1970. Methods for collection and analysis of water samples for dissolved minerals and gases. Chapter A1 in Book 5, Techniques of Water-Resources Investigations of United States Geological Survey. U.S. Geological Survey, Washington, D.C.
- SNOEYINK, V.L. & D. JENKINS. 1980. Water Chemistry. John Wiley & Sons, New York, N.Y.

2320 ALKALINITY*

2320 A. Introduction

1. Discussion

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary

significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface

* Approved by Standard Methods Committee, 1991.

waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly

operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate (CaCO_3)/L.¹

2. Reference

1. POHLAND, F.G. & D.E. BLOODGOOD. 1963. Laboratory studies on mesophilic and thermophilic anaerobic sludge digestion. *J. Water Pollut. Control Fed.* 35:11.

2320 B. Titration Method

1. General Discussion

a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 2310B.1a.

For samples of low alkalinity (less than 20 mg CaCO_3 /L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.^{1,2}

b. End points: When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams CaCO_3 per liter. "Phenolphthalein alkalinity" is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or

metacresol purple may be used for alkalinity titration to pH 8.3. Bromocresol green or a mixed bromocresol green-methyl red indicator may be used for pH 4.5.

c. Interferences: Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. Selection of procedure: Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ 1b. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg CaCO_3 /L only if it has been determined by the low-alkalinity method of ¶ 4d.

Construct a titration curve for standardization of reagents.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

e. Sample size: See Section 2310B.1e for selection of size sample to be titrated and normality of titrant, substituting 0.02N or 0.1N sulfuric (H_2SO_4) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02N H_2SO_4 from a 10-mL buret.

f. Sampling and storage: See Section 2310B.1f.

2. Apparatus

See Section 2310B.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05N: Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

b. Standard sulfuric acid or hydrochloric acid, 0.1N: Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents (see inside front cover). Standardize against 40.00 mL 0.05N Na_2CO_3 solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently

TABLE 2320:I END-POINT pH VALUES

Test Condition	End Point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, mg CaCO_3 /L:		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where:

- A = g Na_2CO_3 weighed into 1-L flask.
- B = mL Na_2CO_3 solution taken for titration, and
- C = mL acid used.

Use measured normality in calculations or adjust to 0.1000N: 1 mL 0.1000N solution = 5.00 mg CaCO_3 .

c. *Standard sulfuric acid or hydrochloric acid, 0.02N:* Dilute 200.00 mL 0.1000N standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05N Na_2CO_3 according to the procedure of ¶ 3b; 1 mL = 1.00 mg CaCO_3 .

d. *Bromcresol green indicator solution, pH 4.5 indicator:* Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. *Mixed bromcresol green-methyl red indicator solution:*³ Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. *Metacresol purple indicator solution, pH 8.3 indicator:* Dissolve 100 mg metacresol purple in 100 mL water.

g. *Phenolphthalein solution, alcoholic, pH 8.3 indicator.*

h. *Sodium thiosulfate, 0.1N:* See Section 2310B.3i.

4. Procedure

a. *Color change:* See Section 2310B.4b.

b. *Potentiometric titration curve:* Follow the procedure for determining acidity (Section 2310B.4c), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. *Potentiometric titration to preselected pH:* Determine the appropriate end-point pH according to ¶ 1b. Prepare sample and titration assembly (Section 2310B.4c). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. *Potentiometric titration of low alkalinity:* For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ 4c, above, using a 10-mL microburet and 0.02N standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations

a. *Potentiometric titration to end-point pH:*

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times N \times 50,000}{\text{mL sample}}$$

where:

- A = mL standard acid used and
- N = normality of standard acid

or

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times t \times 1000}{\text{mL sample}}$$

where:

- t = titer of standard acid, mg CaCO_3 /mL.

Report pH of end point used as follows: "The alkalinity to pH _____ = _____ mg CaCO_3 /L" and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. *Potentiometric titration of low alkalinity:*

Total alkalinity, mg CaCO_3 /L

$$= \frac{(2B - C) \times N \times 50,000}{\text{mL sample}}$$

where:

- B = mL titrant to first recorded pH.
- C = total mL titrant to reach pH 0.3 unit lower, and
- N = normality of acid.

c. *Calculation of alkalinity relationships:* The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity. These relationships may be calculated by the following scheme, where P is phenolphthalein alkalinity and T is total alkalinity (¶ 1b):

Select the smaller value of P or (T - P). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance (T - 2P) is bicarbonate. When the smaller value is (T - P), the balance (2P - T) is hydroxide. All results are expressed as CaCO_3 . The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when $P \approx 1/2 T$ has been proposed.⁴)

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO₂). Accurately measure pH, calculate OH^- concentration as milligrams CaCO_3 per liter, and calculate concentrations of CO_3^{2-} and HCO_3^- as milligrams CaCO_3 per liter from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
 - 1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
 - 2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
 - 3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
 - 3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
 - 3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
 - 3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
 - 4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ± 2° C.
 - 4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
 - 4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
 - 4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
 - 5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ± 0.2 g (to nearest mg) Na₂CO₃ (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

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Issued 1971
Editorial revision 1978

- 5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter

B = ml Na_2CO_3 solution

C = ml acid used to inflection point

- 5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05 N Na_2CO_3 solution as above.

6. Procedure

6.1 Sample size

- 6.1.1 Use a sufficiently large volume of titrant (> 20 ml in a 50 ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.
- 6.1.2 For < 1000 mg $CaCO_3$ /l use 0.02 N titrant
- 6.1.3 For > 1000 mg $CaCO_3$ /l use 0.1 N titrant
- 6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

- 6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask
- 6.2.2 Measure pH of sample
- 6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.
- 6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

- 6.3.1 For alkalinity of < 20 mg/l titrate 100–200 ml as above (6.2) using a 10 ml microburet and 0.02 N acid solution (5.3).
- 6.3.2 Stop titration at pH in range of 4.3–4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7. Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A \times N \times 50,000}{\text{ml of sample}}$$

where:

A = ml standard acid

N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l CaCO}_3 = \frac{(2B - C) \times N \times 50,000}{\text{ml of sample}}$$

where:

B = ml titrant to first recorded pH

C = total ml titrant to reach pH 0.3 units lower

N = normality of acid

8. Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

<u>Increment as Alkalinity mg/liter, CaCO₃</u>	<u>Precision as Standard Deviation mg/liter, CaCO₃</u>	<u>Bias, %</u>	<u>Accuracy as Bias, mg/l, CaCO₃</u>
8	1.27	+ 10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg CaCO₃/l, the standard deviation was ±3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).

VIRGINIA POLLUTION ABATEMENT PERMIT APPLICATION

FORM D

MUNICIPAL WASTE

PART D

PART D-V SLUDGE CHARACTERIZATION FORM

1. Facility Name: _____
2. Source or Generator: _____
3. Type of Treatment: _____
4. Sludge Treatment Classification: _____
5. Provide at least one analysis for each parameter. Upon review, additional analyses may be required by DEQ.

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<u>Parameter</u>	<u>Sludge</u>	
Percent Solids	_____	%
Volatile Solids	_____	%
pH	_____	S.U.
Alkalinity as CaCO ₃ *	_____	mg/kg
Calcium Carbonate Equivalence	_____	%
Nitrogen, (Nitrate)	_____	mg/l
Nitrogen, (Ammonium)	_____	mg/kg
Nitrogen, (Total Kjeldahl)	_____	mg/kg
Phosphorus, (Total)	_____	mg/kg
Potassium, (Total)	_____	mg/kg
Lead	_____	mg/kg
Cadmium	_____	mg/kg
Copper	_____	mg/kg
Nickel	_____	mg/kg
Zinc	_____	mg/kg
Arsenic	_____	mg/kg
Boron	_____	mg/kg
Chromium	_____	mg/kg
Mercury	_____	mg/kg
Aluminum	_____	mg/kg
Chlorides	_____	mg/kg
Manganese	_____	mg/kg
Calcium	_____	mg/kg
Sulfates	_____	mg/kg
Molybdenum	_____	mg/kg
PCBs	_____	mg/kg

* Lime treated sludges (10% or more lime by dry weight should be analyzed for percent CaCO₃).

6. Provide at least one analysis of any other pollutants which you believe may be present in the sludge. Upon review, additional analyses may be required by DEQ.

4. Waste Characterization

a. Wastewater - Provide at least one analysis for each parameter. Upon review, additional analyses may be required by DEQ.

<u>Parameter</u>	<u>Concentration</u>	
Flow to treatment	_____	MGD
Flow to storage	_____	MGD
Vol. to treatment	_____	MG
Vol. to storage	_____	MG
Vol. Land applied	_____	MG/year
BOD	_____	mg/l
COD	_____	mg/l
TOC	_____	mg/l
TSS	_____	mg/l
Percent Solids	_____	%
pH	_____	S.U.
Alkalinity as CaCO ₃	_____	mg/l
Nitrogen, (Nitrate)	_____	mg/l
Nitrogen, (Ammonium)	_____	mg/l
Nitrogen, (Total Kjeldahl)	_____	mg/l
Phosphorus, (Total)	_____	mg/l
Potassium, (Total)	_____	mg/l
Sodium	_____	mg/l

b. Sludge - Provide at least one analysis for each parameter. Upon review, additional analyses may be required by DEQ.

<u>Parameter</u>	<u>Concentration*</u>	
Percent Solids	_____	%
Volatile Solids	_____	%
pH	_____	S.U.
Alkalinity as CaCO ₃ **	_____	mg/kg
Calcium Carbonate Equivalence	_____	mg/kg
Nitrogen (Nitrate)	_____	%
Nitrogen (Ammonium)	_____	mg/kg
Nitrogen (Total Kjeldahl)	_____	mg/kg
Phosphorous (Total)	_____	mg/kg
Potassium (Total)	_____	mg/kg
Lead	_____	mg/kg
Cadmium	_____	mg/kg
Copper	_____	mg/kg
Nickel	_____	mg/kg
Zinc	_____	mg/kg

* Unless otherwise noted, report results on dry weight basis.

** Lime treated sludges (10% or more lime by dry weight should be analyzed for percent CaCO₃).