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Effect of pH, sulfate and sodium on the EDTA titration of calcium

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Abstract

The ethylenediaminetetraacetic acid (EDTA) titration method limits the measurement of calcium concentration to 50 mg/l in water. However, various acids and salt solutions are used in the investigation of the durability of concrete, and the adaptability of the EDTA titration method to determine the calcium in these solutions must be investigated. Hence, the purpose of this study was to investigate the interfering effects of hydrochloric acid, sulfuric acid, sodium chloride and sodium sulfate on measuring the calcium in the aqueous leaching solutions using the EDTA titration method. The calcium standard solutions were prepared using $CaCl_2$ with initial pH from -0.8 to 7 and calcium concentration up to 160 mg/l. Sulfuric acid and hydrochloric acid were used to prepare calcium solutions with lower pH. Salt solutions with 3% NaCl and 3% Na_2SO_4 were used to evaluate the interfering effects of salt elements such as sulfate and sodium on the EDTA titration. Results indicated that the EDTA titration method was reliable in measuring the calcium up to 160 mg/l, the maximum concentration investigated in this study, in hydrochloric acid with pH higher than zero and 3% sodium chloride solution. Sulfuric acid with pH higher than zero and 3% sodium sulfate solutions showed 3% to 4% less calcium in the solutions. Acid solutions with pH less than zero showed interference with calcium measurement.

Keywords: Calcium; Ethylenediaminetetraacetic acid (EDTA); Sulfate; Titration; pH

1. Introduction

Concrete structures, including buried structures, in wastewater systems and industrial facilities are exposed to various chemical environments; hence the durability of concrete under various chemical solutions, especially in acidic and salt solutions are of interest [6–8,10,12,13]. Concrete can be attacked by acids and sulfates to varying degrees, and quantifying the level and rate of deterioration is considered a challenge [3,6,8]. Portland cement has about 64% lime (CaO) and deterioration results in leaching of calcium from various hydrated cement products such as hydrosilicates, hydroaluminates and hydroferrites. This results in concrete losing its strength and integrity [6,8]. Hence, dissolved calcium in the leaching solutions can provide important information on the extent of concrete deterioration. Wang and Vipulanandan [14] have measured calcium concentration in the pore fluid during the initial period of hydration of cement in their lead stabilization study and found that calcium concentration increased with lead addition. Macias et al. [8] studied the behavior of cement matrices in acid media and its influence on metal immobilization. They measured the flexural strength to determine the loss of mechanical properties and concluded that flexural strength measurement was inadequate to estimate the cement degradation under acid attack. It was stated that calcium content could be a good parameter to evaluate the degree of corrosion [8]. Mainguy et al. [9] developed a model for calcium leaching in cementitious materials to predict the long-term evolution of concrete used for waste disposals in aggressive conditions. It was observed that constantly renewed water was one of the aggressive agents that affected the chemistry of concrete [9]. Hence, some of these observations by other authors indicate that quantifying the calcium in the solution is important and measuring the calcium can be the first step in monitoring the concrete deterioration. There are a few methods available for measuring the calcium in solution. Using the ion-selective electrode (ISE) is one method that is currently adopted but the interference of other factors such as pH, sulfate and

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other cations are not known. The calcium ISE has an operating pH range of 3 to 10. Using the electrode at other pH values will adversely affect the membrane. Hydrogen ion interferes with measurements of very low levels of calcium. Although ISE is rapid, titration methods are about 10 times more accurate than the ISE measurement (literature from Cole-Parmer Instrument).

Atomic absorption spectroscopy can be used to measure the calcium concentration in aqueous solutions [1]. Practically, the titration method is the one that assures accuracy and easiness of measuring calcium in the solution. Ethylenediaminetetraacetic acid (EDTA) forms a very stable, water-soluble chelation complex with Ca^{2+} in the ratio of 1:1 [11]. Organic dyes are used as indicators, which also complex with these ions, resulting in a change of the color of the dye. In the case of murexide, used as an indicator in calcium titration, changes from pink (complexed) to purple (uncomplexed) occur. It derives its stability in part from calcium being connected to the EDTA by six bonds. In order to make the EDTA titration method of measuring calcium more practical and versatile, the effects of several variables such as pH, sulfate, salts, and the sample size should be determined and quantified.

1.1. Standard methods

ASTM and AWWA have test methods where EDTA is used to determine the concentration of calcium.

1.1.1. ASTM methods

ASTM has several methods where EDTA is directly or indirectly used to measure metal concentrations in acid and alcohol solutions. The test methods are summarized in Table 1 [2]. Most of the methods are for paint driers and use the indirect method to measure the cations in the solutions (Table 1). In these methods, excess EDTA standard solution is used to complex the metals and then the excess EDTA is determined by titrating with another solution in the presence of an indicator. Direct titration with EDTA was used only for water to determine the concentrations of calcium and magnesium. The repeatability of these methods varied from 0.5% to 1.42%. The effectiveness of the EDTA titration method to determine the calcium in low pH and sulfate solutions are not documented in the literature.

1.1.2. AWWA methods

The presence of calcium in water supplies can range from zero to several hundred milligrams per liter depending on the source and treatment of water. Calcium contributes to the total hardness of water. The atomic absorption method and inductively coupled plasma method are accurate means of determining calcium [1]. The EDTA method (Method 3500-Ca D) gives good results for control and routine applications. It is not recommended for calcium concentration greater than 50 mg/l because of interferences with the EDTA method using the indicators [1]. According to this test method, the following concentrations of ions cause no interference with the determination of calcium concentration: Cu^{2+}, 2 mg/l; Fe^{2+}, 20 mg/l; Fe^{3+}, 20 mg/l; Mn^{2+}, 10 mg/l; Zn^{2+}, 5 mg/l; Pb^{2+}, 5 mg/l; Al^{3+}, 5 mg/l; and Sn^{4+}, 5 mg/l. However, orthophosphate precipitates calcium and strontium and barium gives a positive interference. In addition, alkalinity in excess of 300 mg/l may cause an indistinct endpoint in high-calcium water [1].

2. Objective

Current EDTA titration method limits the calcium measurements to a maximum concentration of 50 mg/l in water. Since various chemical solutions are used in studying the durability of concrete, it is important to evaluate the interference of pH, sulfates and sodium on the calcium measurement using the EDTA method. The specific objectives of this study are (1) to investigate the effects of pH, sulfates and salts on the calcium measurement, (2) to

Table 1
Summary of ASTM methods using EDTA titration

Standard	Material	Element	Method	Indicator	pH testing	Repeatability (%)
D 2373	Paint drier	Cobalt	Indirect	PAN[a]	Constant	0.05
D 2374	Paint drier	Lead	Indirect	PAN[a]	Constant	0.10
D 2375	Paint drier	Manganese	Indirect	Eriochrome Black-T	Not specified	0.05
D 2613	Paint drier	Calcium, zinc	Indirect	Eriochrome Black-T	Not specified	0.05
D 3804	Paint drier	Iron	Indirect	Eriochrome Black-T	Not specified	0.8
D 3969	Paint drier	Zirconium	Indirect	Xylenol orange	Constant	1.42
D 3988	Paint drier	Vanadium	Indirect	Eriochrome Black-T	Adjust	0.08
D 3989	Paint drier	Rare-earth metals	Indirect	Xylenol orange	5.0	1.25
D 511	Water	Calcium	Direct	Ammonium purpurate,	12–13	Not reported
		Magnesium	Direct	Eriochrome Black-T, fluorescein methylene iminodiacetic	10	
Remark	Mainly used with paint drier	Used for metals	Direct method for water only	Several indicators are used	pH higher than 5	0.05–1.42

[a] PAN: 1(2-pyridylazo)-2-naphthol.

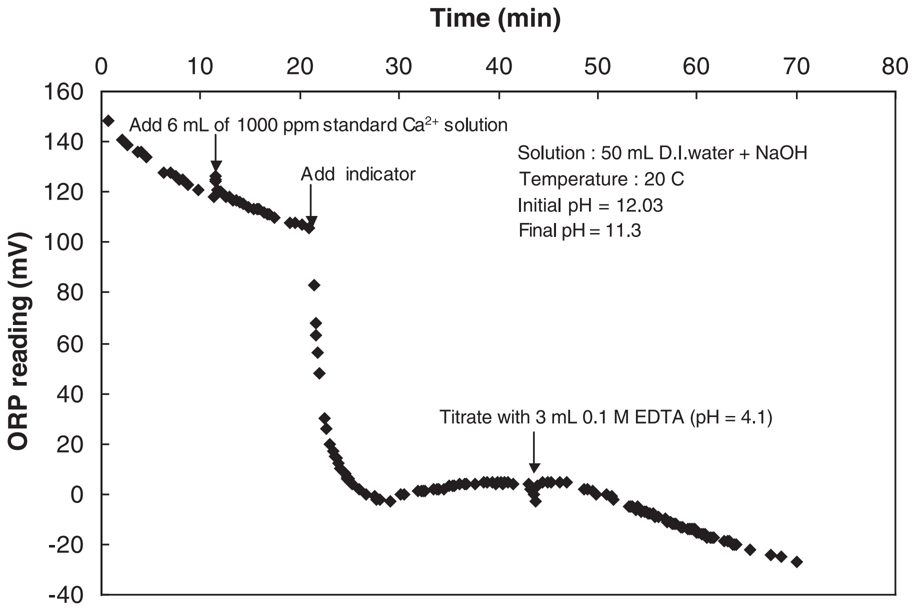

Fig. 1. Typical change in ORP during EDTA titration.

investigate the repeatability of measurements at higher calcium concentrations, and (3) to determine the effect of sample size on the calcium measurement.

3. Materials and testing program

3.1. Materials

Reagent-grade chemicals were used in all tests. Concentrated sulfuric acid and hydrochloric acid were used to prepare acidic calcium solutions in the pH range of -0.8 to 7. The pHs of the solutions for titration were adjusted using 1 N sodium hydroxide (NaOH) solution. For the salt solutions, 3% NaCl and 3% Na_2SO_4 solutions were used. Deionized water was used in preparing all the solutions. Murexide (ammonium purpurate) was used as the indicator for detecting the calcium endpoint [1]. This indicator changes color from pink to purple at the endpoint. In order to facilitate the endpoint recognition by color comparison, a blank containing 2.0 ml NaOH solution, 0.2 g solid indicator mixture, and sufficient standard EDTA titrant (0.05 to 0.10 ml) was used. Standard EDTA titrant (0.01 M) was prepared as described in the EDTA total-hardness method

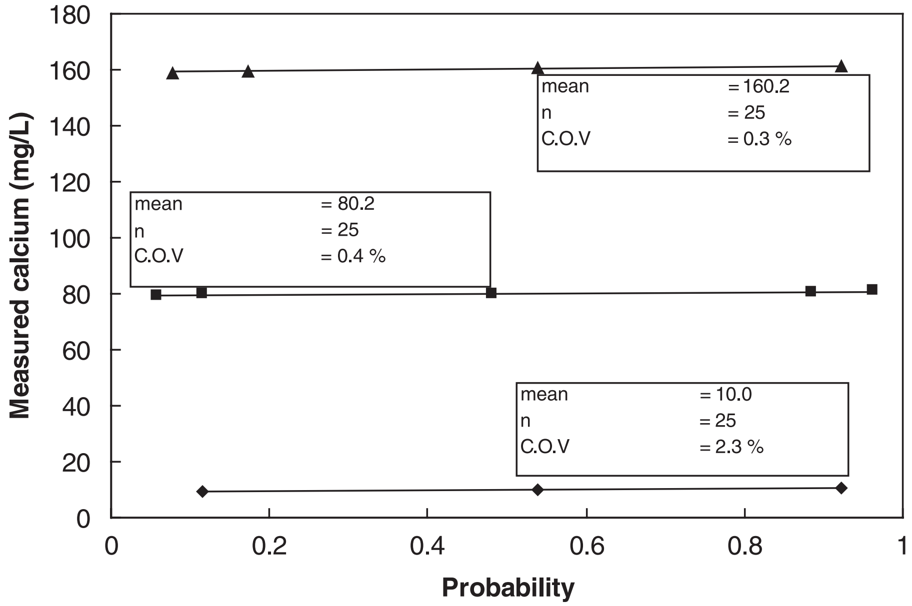

Fig. 2. Repeatability of EDTA titration at various calcium concentrations.

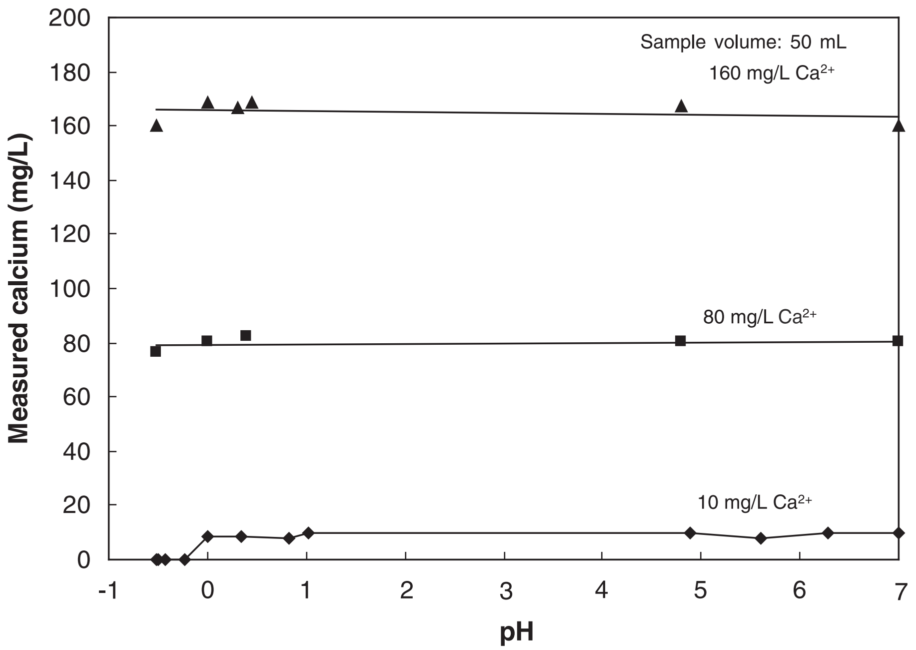

Fig. 3. Effect of hydrochloric acid on the calcium measurement.

[1]. Standard EDTA titrant, 0.01 M, is equivalent to 400.8 μg Ca/1.00 ml.

3.2. Test program

All tests were performed at room temperature (23 ± 2 °C). Calcium solution sample at a volume of 50 ml was used in the interference studies. In order to investigate the effect of sample size on calcium measurement, 1- to 40-ml samples were also used. Before each titration, 5 M NaOH solution was added to increase the pH to between 12 and 13, then 0.1 to 0.2 g of indicator was added to the solution and mixed thoroughly by swirling. EDTA solution was added slowly from a burette, with continuous stirring using a Teflon-coated magnetic stirrer, until the proper endpoint. The endpoint was checked by further adding one to two drops of titrant in excess to make certain that there was no further color change in the solution. The EDTA was measured accurately to 0.5 ml using the burette. More details on the testing procedures are summarized in the CIGMAT Standard CH 1-99 [4].

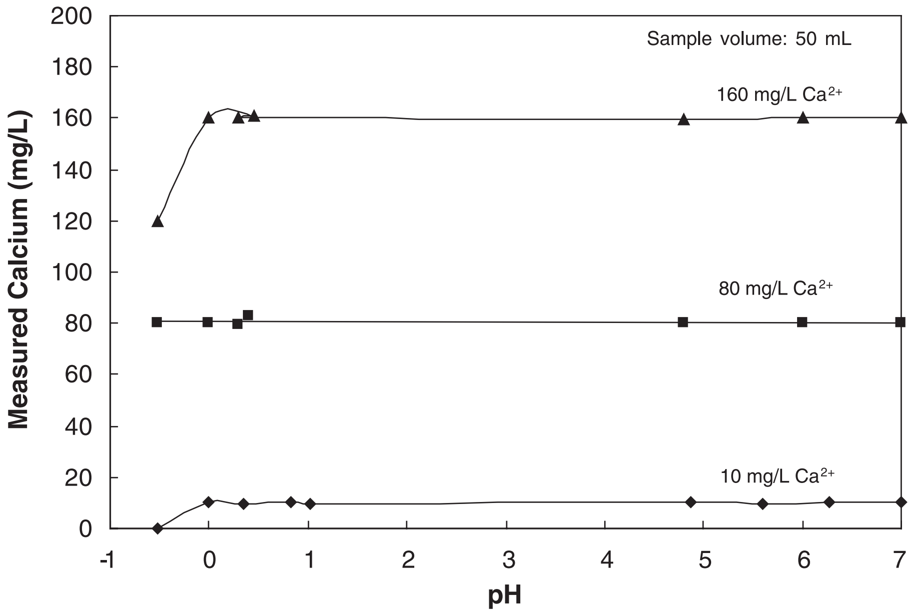

Fig. 4. Effect of sulfuric acid on the calcium measurement.

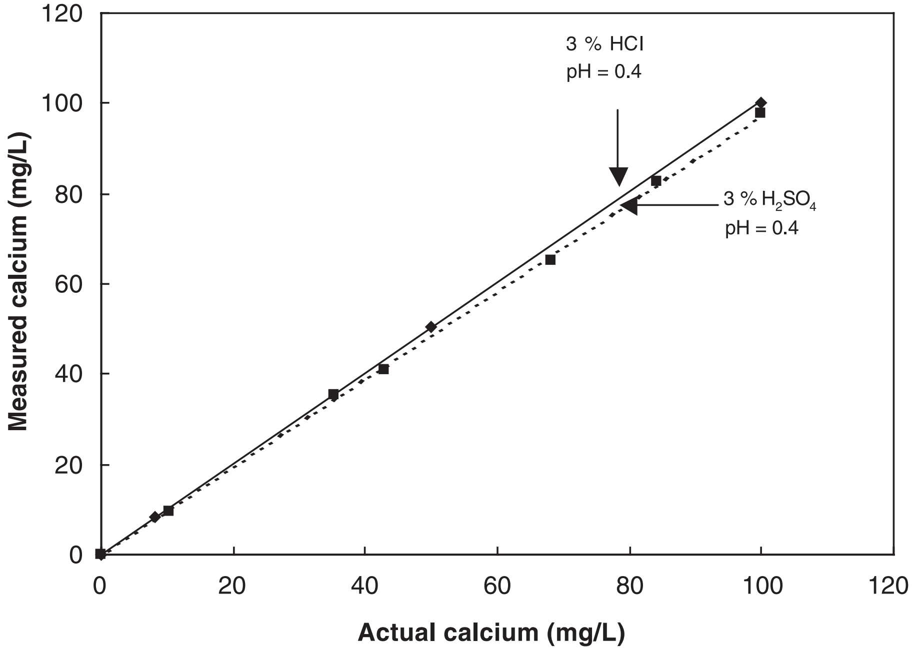

Fig. 5. Acid and sulfate on EDTA (V = 50 ml).

Using the following equation, the amount of Ca^{2+} ions in the solution was calculated [1].

$$\text{mg Ca/l} = \text{EDTA (ml)} \times 400.8\ (\mu g\ \text{Ca}/1.00\ \text{ml}) / \text{volume of solution (ml)} \qquad (1)$$

4. Results and discussion

In order to better understand the titration procedure, the oxygen reduction potential (ORP) of the calcium solution was monitored and the results are reported in Fig. 1. The ORP represents the availability of electrons in the solution, and negative ORP represents excess electrons and reduced environment in the solution. The addition of murexide indicator reduced the ORP of the solution rapidly and the EDTA addition had only a small change in the ORP. In addition, at the endpoint of titration no noticeable change in the ORP was observed. Hence, ORP cannot be used to detect the endpoint during the titration. In Fig. 2, the repeatability test results are presented for 10, 80 and 160 mg/l concentrations of calcium. Based on 25 titration tests at each calcium concentration, the distribution of the data was

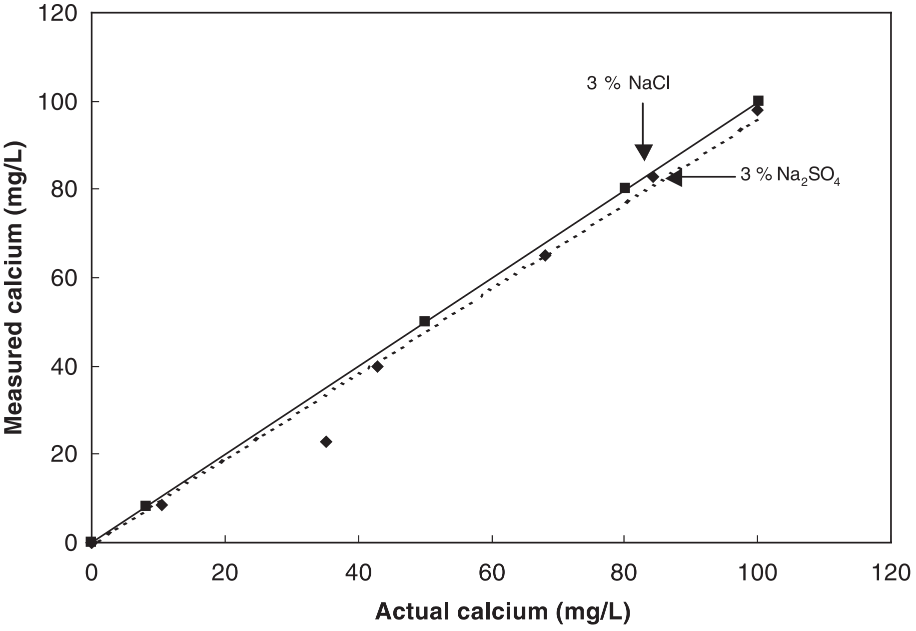

Fig. 6. Salts and sulfate on EDTA (V = 50 ml).

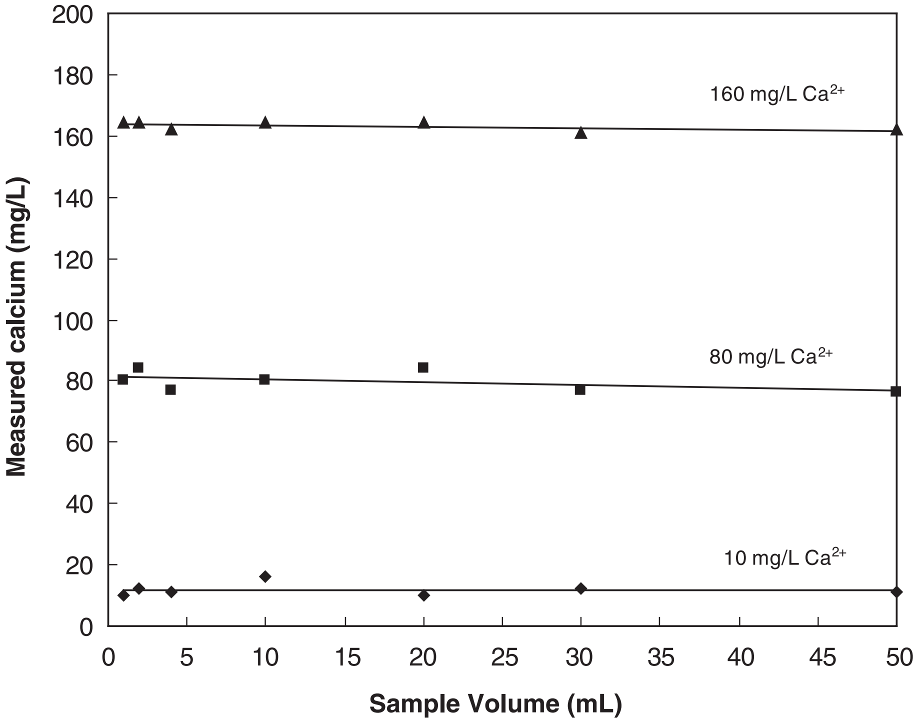

Fig. 7. Typical sample size versus calcium measurement in various solutions investigated (pH>0).

uniform with the coefficient of variations (COV) of 2.2%, 0.4% and 0.3% for 10, 80 and 160 mg/l calcium solutions, respectively. Hence, the EDTA method can be used to measure calcium concentration higher than 50 mg/l.

The effect of hydrochloric acid and pH on the calcium measurement are shown in Fig. 3. Test results indicated that for the calcium concentrations investigated EDTA could be used to measure Ca^{2+} in the pH range of 0 to 7. Further lowering the pH [30% HCl solution with $pH = -0.8$ (measured value)] interfered with the calcium measurement and in some cases calcium was not detected or no color change was observed during titration. At lower pH, the high concentration of hydrogen ion interfered with the indicator or EDTA or both, causing error in the calcium measurement. The results with sulfuric acid and three concentrations of calcium is shown in Fig. 4. In Fig.

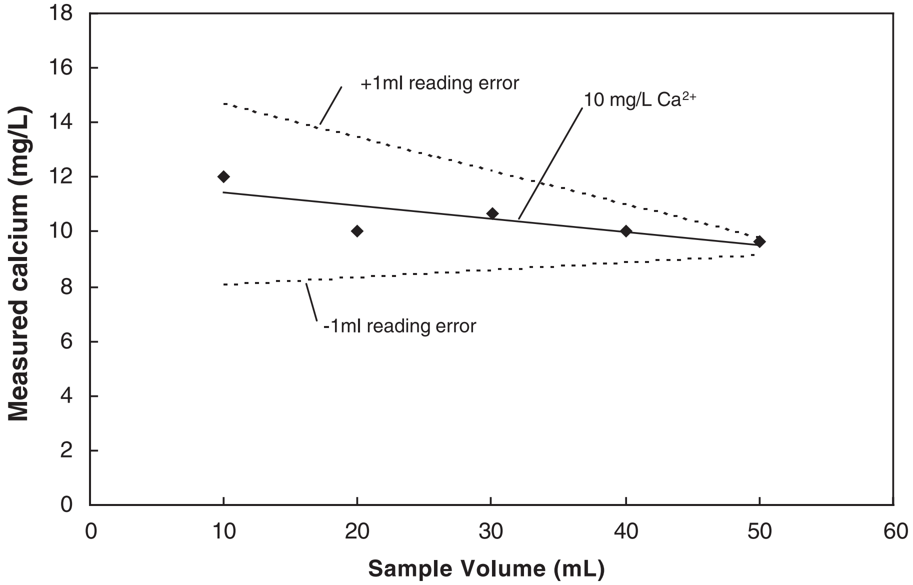

Fig. 8. Sample size and possible error in calcium measurement.

5 the actual and measured calcium in the presence of 3% HCl and 3% H_2SO_4 are compared. The 3% HCl showed no interference with the calcium measurement while the 3% H_2SO_4 showed slight interference with about 3% less measured calcium.

The effect of 3% salt solutions is shown in Fig. 6. No interference was observed in the measurement of calcium with 3% NaCl solution. Slight interference was observed with the 3% Na_2SO_4 solution where 4% less calcium was measured. In the case of sulfate solutions, when the $[Ca^{2+}][SO_4]$ ionic product is greater than the solubility product (K_{sp}) of $CaSO_4$, the calcium ions would be precipitated and hence can result in interference with the measurements [5].

AWWA Standard suggests using a volume of 50 ml to perform the EDTA test. In some practical situations, only a small volume of sample will be available; hence, the use of smaller sample volume was investigated. Sample volume from 1 to 50 ml was used in this study to investigate the effect sample size. As shown in Fig. 7, the results confirm that the sample size did not affect the calcium measurement. However, care should be taken when small volume of sample is used for calcium measurement. The error in measuring the volume of EDTA can cause a larger error with smaller samples as shown in Fig. 8, where ± 1 ml error in EDTA measurement is compared to the correct measurement. By measuring the titrating EDTA volume more accurately, the error with smaller sample volume can be reduced.

5. Conclusions

Based on the experimental results and analysis, the following observations are presented.

1. The EDTA titration method can be used to measure the calcium concentrations up to 160 ppm in the pH range of 0 to 7. The ORP of the solution cannot be used to determine the endpoint of titration.
2. The hydrochloric acid in the pH range of 0 to 7 and 3% NaCl solutions did not affect the calcium measurement. Sulfuric acid and 3% Na_2SO_4 showed slight interference. This method cannot be used with solutions where the initial pH is less than zero.
3. A sample volume of 50 ml had the minimum error but a sample volume of 1 ml can be used to determine the calcium concentration. With smaller sample size, greater errors in calcium measurement is possible.

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