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CALCIUM CONTENT OF LIME MORTARS FROM 19th CENTURY CHURCH RUINS IN THE PHILIPPINES USING VOLUMETRIC ANALYSIS

(Kandungan Kalsium Mortar Batu Kapur dari Runtuhan Gereja Abad Ke 19 di Filipina Menggunakan Analisis Volumetrik)

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Abstract

A calcium determination method for lime mortars in old church ruins is described. Two volumetric analysis methods were employed: titration using EDTA solution, and with $KMnO_4$ solution. The binder fraction with sieve size (<0.075mm) was used for titration which is abundant in $CaCO_3$ as established by Fourier-Transform Infrared Spectroscopy (FTIR) technique. The mortar sample from Misamis Oriental yields a mean calcium concentration of 59.60% ± 4.64 and 60.48% ± 6.68 for EDTA and $KMnO_4$, respectively, while the Metro Manila mortar sample is 73.54% ± 2.68 for EDTA and 73.33% ± 6.88 for $KMnO_4$. Two tailed *t*-test and *F*-test analysis confirm that there is no statistical difference between EDTA and $KMnO_4$ methods in determining the calcium content. Atomic Absorption Spectroscopy (AAS) technique validated the mean concentration values obtained from each method with less than 6.4% difference. The proposed titration methods are simple, rapid and sufficiently precise, without the use of expensive analytical instruments. This study is a good alternative method to easily determine the amount of calcium in historic lime mortars which is valuable in heritage conservation work and restoration of old structures in the Philippines.

Keywords: lime mortar, titration, Fourier transform infrared spectroscopy, atomic absorption spectroscopy, cultural heritage conservation

Abstrak

Satu kaedah penentuan kalsium untuk mortar batu kapur dalam runtuhan gereja lama telah dibincangkan. Dua kaedah analisis volumetrik telah dibangunkan; pentitratan menggunakan larutan EDTA dan $KMnO_4$. Pecahan mengikut saiz ayak (<0.075mm) telah digunakan untuk pentitratan yang kaya dengan $CaCO_3$ yang telah ditentukan oleh teknik inframerah transformasi Fourier (FTIR). Sampel mortar batu kapur dari Misamis Oriental menghasilkan purata kepekatan kalsium 59.60% ± 4.64 dan 60.48% ± 6.68 untuk masing-masing EDTA dan $KMnO_4$, manakala sampel mortar batu kapur Metro Manila adalah 73.54% ± 2.68 untuk EDTA dan 73.33% ± 6.88 untuk $KMnO_4$. Analisis ujian-t dan ujian-F mengesahkan bahawa tidak ada perbezaan signifikan antara kaedah EDTA dan $KMnO_4$ dalam penentuan kandungan kalsium. Teknik spektroskopi serapan atom (AAS) telah menentusahkan nilai kepekatan yang diambil dari setiap kaedah memberikan perbezaan kurang daripada 6.4%. Kaedah pentitratan yang dicadangkan adalah mudah, cepat dan cukup tepat, tanpa menggunakan instrumen analisis mahal. Kajian ini merupakan alternatif yang baik dengan mudah menentukan kandungan kalsium dalam mortar batu kapur bersejarah yang berharga dalam kerja-kerja pemuliharaan warisan dan pemulihan struktur lama di Filipina.

Kata kunci: mortar kapur, pentitratan, spektroskopi inframerah transformasi Fourier, spektroskopi serapan atom, pemuliharaan warisan budaya

Introduction

The overall amount of calcium is an important parameter for replicating historic lime-based mortars for restoration work. Calcium is the principal chemical element found in binders which is the component of mortars responsible for holding together the different stone and sand aggregates. Binders are essentially composed of lime or $CaCO_3$ produced by burning limestone. In the Philippines, lime can also be obtained from crushed seashells and corals [1]. The temperature and manufacturing process of lime is crucial in determining the mortar's physical properties and mechanical behaviour. Specifically, the crystal arrangement, porosity and the lime's reactivity when water is added (slaking) will be affected [2, 3]. The absence of standard methodologies in lime preparation in the past, as well as the lack of detailed documentation on its manufacture in the Philippines, have produced old lime-based mortars which are non-uniform and varied in chemical compositions relative to its location. Hence, proper scientific investigation to understand conventional lime-making techniques in the past based on calcium content is crucial for proper conservation work of historic structures in the Philippines.

This study describes the amount of calcium in a lime-based historic mortar from church ruins built during the Spanish Colonial Period in the Philippines. The country was under Spanish rule for almost 400 years from 1521 to 1898 and was heavily influenced by Roman Catholic traditions. The church ruin in Misamis Oriental in the southern island of Mindanao was built during the mid-1800's [4] while the one collected from Metro Manila, which is the capital city of the Philippines, was constructed in the early 1800's [5]. These sites were chosen for this study because of their different geographical locations, hence, different raw materials used in its construction. It also represents the unique building-making methods characteristic of the Jesuits (Misamis Oriental) and the Franciscans (Metro Manila) which are major Catholic religious orders during the Spanish Era in the Philippines.

Complexometric titration using ethylenediaminetetraacetic acid (EDTA) and oxidation-reduction (redox) titration with potassium permanganate ($KMnO_4$) were the techniques utilized to quantify the amount of calcium in the historic mortar samples from Misamis Oriental and Metro Manila. The accuracy of these methods was confirmed using atomic absorption spectroscopy (AAS). Statistical analysis (*t*-test and *F*-test) was also employed to determine if both titration methods yield comparable results. EDTA can be completely deprotonated to the anion, $EDTA^{4-}$ in basic solution, to form a 1:1 complex with the calcium ions present in the lime mortar sample as shown in equation (1). Since EDTA is a stronger complexing agent than the indicator, Eriochrome black T (EBT), it will displace the calcium-EBT complex forcing the indicator to return to its original form (blue color) marking the endpoint of the titration.

$$CaCO_3 + EDTA^{4-}_{(aq)} \rightarrow Ca(EDTA)^{2-}_{(aq)} + CO_3^{2-}_{(aq)} \quad (1)$$

The redox reaction between oxalic acid and $KMnO_4$ is another method to detect the amount of calcium in old mortar samples. Calcium was precipitated with oxalate ion and dissolved in dilute acid as represented by equation (2). The liberated oxalic acid was titrated with $KMnO_4$ as shown in equation (3), which is a strong oxidizing agent. Due to the intense color of the permanganate ion, it is already sufficient in detecting the endpoint of the titration. The permanganate ion which forms a Mn^{+7} oxidation state was reduced to manganese ion with an oxidation state of Mn^{+2} while carbon was oxidized from C^{+3} to a C^{+4} oxidation states.

$$CaC_2O_{4(aq)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2C_2O_{4(aq)} \quad (2)$$

$$5H_2C_2O_{4(aq)} + 2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 10CO_{2(g)} + 8H_2O_{(l)} + 2Mn^{2+}_{(aq)} \quad (3)$$

Different complexometric and redox titration methods were applied for limestone [6, 7] using a variety of titrants and colored indicators, such as disodium EGTA, calcon and EBT indicators [8, 9], and azochromotropic acid derivative indicators [10]. Potentiometric titration using calcium sensitive electrodes [11] was also reported in literature, as well as flow-injection analysis [12] and atomic absorption spectroscopy methods [13]. Calcium oxide was determined in lime mortars by titrating with EDTA and methylene blue indicator [14]; however, the sample preparation and analysis are different from this study. In general, none of these reported methods were applied directly on historic lime-based mortars whose chemical properties were influenced by the local manufacturing process.

Materials and Methods

Mortar samples

The lime-based mortar samples were collected from two different sites in the Philippines. One sample was acquired from the southern Mindanao Island at Misamis Oriental in April 2015 and the other was obtained from the northern Luzon Island at Metro Manila, where the capital city of the Philippines is located (Figure 1), in April 2014. Each respective sample was found within the ruins of old Catholic churches built in the 19th century. The sample from Misamis Oriental (8.2g) was gently scraped-off from a coral-stone wall ruin, which is believed to be part of the church's window arch, while the Metro Manila sample (14.7g) was taken from a loose brick fragment wall believed to be a segment of the old church foundation. The mortars used in the analysis were removed from its surrounding materials at an approximate depth of about 0.5 to 1.5 cm from its surface to prevent contamination. Both mortars are made entirely of lime binder which was evident from its powdery texture.

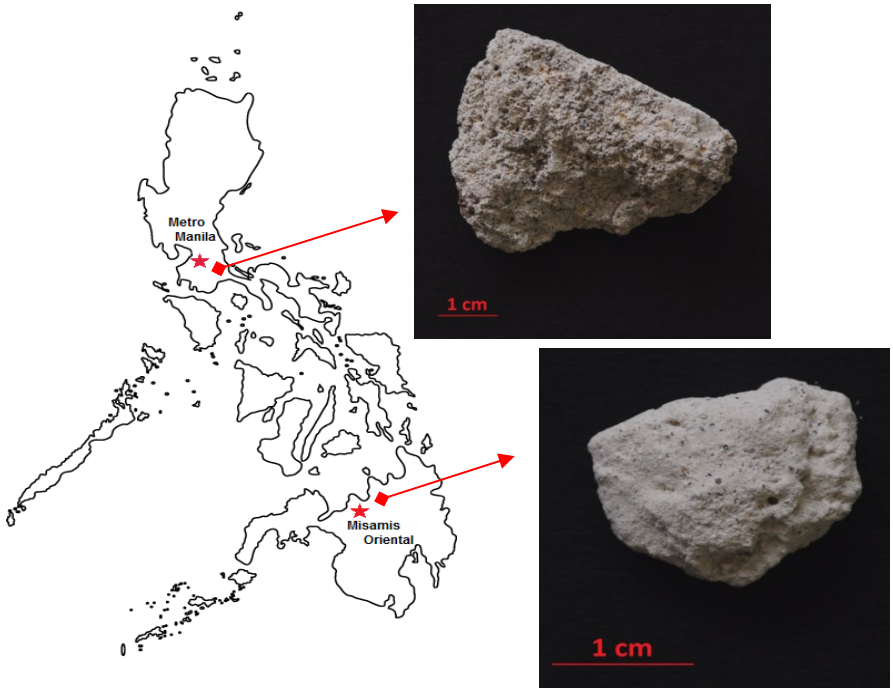

Figure 1. Location map showing the collection site at Misamis Oriental and Metro Manila. Inset photos show the historical lime mortars used for this study

Each mortar samples (between 4.0 to 8.0g) were gently pulverized into small pieces and disaggregated, ensuring that the original texture of the aggregate is not lost in this process. The crushed materials were sieved through sizes of 4.750, 2.360, 1.180, 0.600, 0.425, 0.250, 0.150 and 0.075 mm using a USA Standard Testing Sieve ASTME11 Specification. Fractions smaller than 0.075 mm and retained in the "pan" were also included. Efficient separation of the different fractions was achieved by having the sieves shaken in a mechanical shaker (US Tyler brand) for 5 minutes. The resulting fractions were individually weighed and labelled according to their respective retained sieve size.

Analysis by Fourier transform infrared spectroscopy

For both mortar samples, a small portion of sieved fraction retained in the "pan" (<0.075mm) was mixed, grounded, and pressed together with KBr powder to form a thin and transparent pellet. The ratio of sample relative to the amount of KBr is about 1 to 2%. Pure analytical grade SiO_2 (Sigma-Aldrich) and $CaCO_3$ (Unichem, 98%) were also pelletized with KBr. The IR spectrum was recorded using a Thermo Scientific Nicolet 6700 FT-IR

Spectrophotometer in the finger print region 2400 – 400cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per spectrum [15]. The spectrum was reported as absorbance relative to the wave number.

Titration with EDTA solution: Standardization of EDTA
The EDTA solution was prepared by mixing 2.0g EDTA powder (Himedia, 99.5%), 1.0g of NaOH (Unichem, 96%) and 0.15g of $MgCl_2 \cdot 2H_2O$ (Qualikems, 99%). It was diluted with distilled water in a 1L volumetric flask. All chemical reagents are analytical grade.

Preparation of standard analyte
The analyte was prepared by measuring 0.20g of oven dried (110^{0}C for 24 hours.) analytical grade $CaCO_3$ (Unichem, 98%) in three separate 100 mL beakers. Concentrated analytical grade HCl (Macron) was added drop wise until 6.0 mL. This was followed by the addition of 50.0mL distilled water and boiled in water bath for 5 minutes. The solution was transferred into a 250 mL volumetric flask after cooling and diluted with distilled water.

A 25.0 mL aliquot was pipetted in three individual 250 mL Erlenmeyer flasks and combined with 10.0 mL of ammonium buffer and 5 drops of EBT indicator (Merck). A titration set-up was assembled and the $CaCO_3$ solution in the flask was titrated with EDTA solution in the burette until the first appearance of a persistent clear blue color, marking the endpoint of the titration. The concentration of EDTA was calculated in molarity.

Preparation of unknown analyte
About 0.10 to 0.15g of mortar samples from the sieve size left in the pan (<0.075mm) were dried in an oven for 24 hours at 110 ^{0}C. Drop-wise addition of concentrated HCl was done directly on the sample until dissolution was complete. It was then boiled in 50 mL distilled water, cooled and diluted to the mark with distilled water in a 250 mL volumetric flask. A 25.0 mL aliquot portion was titrated with the standardized EDTA solution until the appearance of a persistent clear blue color with EBT indicator. Three replicate trials were done. The concentration of calcium in the unknown sample was reported in terms of its percentage composition.

Titration with $KMnO_4$ solution: Standardization of $KMnO_4$
The $KMnO_4$ solution was prepared by dissolving 1.58g analytical grade $KMnO_4$ powder (Univar, 99%) in 50.0 mL distilled water and diluted in a 1L volumetric flask.

Preparation of standard analyte
A dried (110 ^{0}C for 2 hours) $Na_2C_2O_4$ (Unichem, 99.8%) measuring about 0.22g was placed in a 500.0 mL beaker and dissolved in 250.0 mL 0.75M H_2SO_4 (Macron). It was heated and maintained at a temperature between 80 – 90 ^{0}C, while being titrated with the prepared $KMnO_4$ solution. The appearance of a persistent pink color marks the end point of the titration. Three trials were done. A blank sample was also prepared by using 0.75M H_2SO_4 and titrated directly with $KMnO_4$. The volume obtained (0.2 mL) was subtracted from the volume of titrant acquired with the sample. The concentration of $KMnO_4$ was calculated and expressed in molarity.

Preparation of unknown analyte
The sieved fractions retained in the "pan" were dried for 3 hours at 120 ^{0}C in an oven and cooled. About 0.25 – 0.30g were obtained for each dried mortar sample and placed in separate 250 mL beakers. To dissolve the solid samples, 20.0 mL drop-wise addition of concentrated analytical grade HCl (Macron) was carefully done. This was followed by mixing 40.0 mL distilled water and stirred for 10 minutes at room temperature (30 ^{0}C) until all carbon dioxide was removed from the solution.

A 20.0 mL aliquot of the digested mortar samples was added with 3 drops of saturated bromine water and gently boiled for 3 minutes. Each sample portion was diluted with 20.0 mL distilled water, boiled and added with 15.0 mL of hot 6% (w/v) $(NH_4)_2C_2O_4$ (Mallinckrodt, 99%) solution. To precipitate the CaC_2O_4, 6M NH_3 (Merck, 25%) solution was added slowly until color changes from an intermediate yellow-orange or pH range from 4.5 – 5.5. The solution was allowed to stand for 20 minutes and filtered. The precipitate was washed several times with 5.0 mL of cold water to induce the formation of more precipitates.

The CaC_2O_4 precipitate from each trial was dissolved in 15.0 mL distilled water and 7.0 mL 3M H_2SO_4 in a beaker. It was heated and maintained at a temperature between 80 – 90 ^{0}C while being titrated with the standardized $KMnO_4$. A blank volume was titrated (0.20 mL) and subtracted from the volume of $KMnO_4$ consumed. The percentage of calcium in the mortar samples was computed.

Calcium determination by atomic absorption spectroscopy

Calibration curves were prepared by diluting a commercially available 1000 ppm analytical standard grade calcium solution (Fluka) to concentrations of 0.10, 0.30, 0.50, 0.80 and 1.0 ppm, respectively, in separate 50 mL volumetric flasks. The concentration range assures that the calibration curve is linear as required by Beer's Law. A chemical suppressant (2.5 mL, 5.0% w/v strontium nitrate, $Sr(NO_3)_2$) were also added to each standard solution before diluting to the mark with distilled water. Absorbance readings were recorded in a Shimadzu AA-6300 Atomic Absorption Spectrophotometer in an air-acetylene gas mixture at a detection wavelength of 423 nm. Three replicate measurements were performed. Distilled water was used as solvent blank during the experiment [16].

For the mortar samples, 0.20 mL aliquot portion from the original 250 mL EDTA digested binder fraction (< 0.075 mm) was added with 0.50 mL of 5.0% $Sr(NO_3)_2$ in separate 100 mL volumetric flasks. The same AAS parameters mentioned in the preparation of the calcium standard curve were followed afterwards.

Results and Discussion

Particle size distribution in mortars

The mechanical separation of different grain sizes in the mortar samples was achieved through sieve analysis. The relative sizes of the particles and their distribution in the mortar are related to their engineering behaviour [17]. Figure 2 shows the relationship between the mesh size and the percentage of particles retained in a specific sieve for both lime mortar samples. Based on the American Society for Testing and Materials (ASTM, 1980) classification system, the sample from Misamis Oriental is generally composed of fine sand aggregates since most of its weight retained in the 0.250 mm and 0.150 mm sieve sizes, respectively. The Metro Manila sample, however, is mainly made up of medium to fine sand aggregates due to more particles distributed within the sieve size range of 0.600 mm to 0.250 mm, respectively. The absence of particles retained in the 4.750 mm sieve size for the Misamis Oriental sample was compensated by a higher percentage amount of binder fraction from the "pan" (<0.075 mm) [18] which is comparable in weight with the 0.150 mm sieve size. This is in contrast with the Metro Manila sample which has a well-represented particle size distribution, hence, a relatively lower percentage of the binder fraction was observed. There was no evidence which may suggest that the aggregates in both mortar samples are calcitic ($CaCO_3$) in nature.

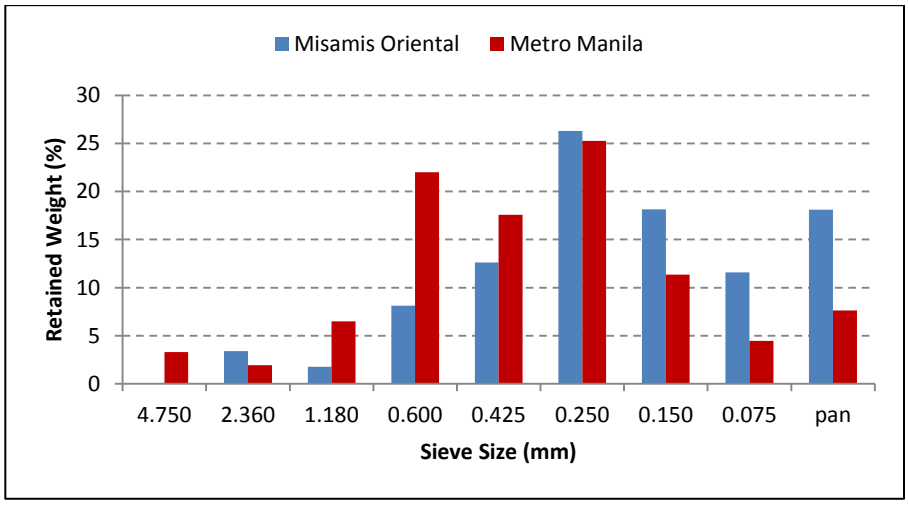

Figure 2. Grain size weight distributions of the mortar samples

To know if the old mortar samples were manufactured with good representations of each particle sizes, a gradation curve was plotted as shown in Figure 3. From this logarithmic plot, the important basic parameters of effective size (D_{10}), uniformity coefficient (C_u) and coefficient of curvature (C_c) were computed. D_{10} is defined as the value for the grain size diameter (D) that passed through the sieve at 10% and was extrapolated on the graph. To compute for C_c and C_u, the values for D_{30} and D_{60}, or 30% and 60% of particles that passed through the sieve, respectively, were also obtained. The results were tabulated in Table 1 for each mortar samples. Since the values for C_c are within the ranges of 1 to 3 and have C_u values that are greater than 4, both Misamis Oriental and Metro Manila samples are considered as well-graded [19].

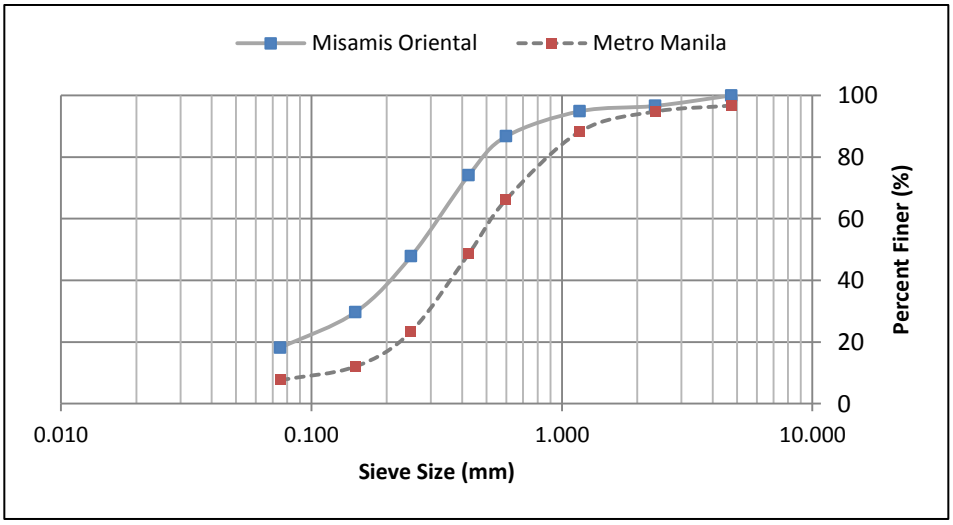

Figure 3. Particle size gradation curve of the mortar samples

Table 1. Soil parameters used for classification of mortar samples

Parameters	Mortar Samples	
	Misamis Oriental	Metro Manila
D_{10}	[a]0.040	0.125
D_{30}	0.150	0.300
D_{60}	0.325	0.525
[b]C_u	8.13	4.20
[c]C_c	1.73	1.37

[a]determined by extrapolation, [b]greater than 4, [c]between 1-3

Binder characterization by Fourier transformation infrared spectroscopy

There are evidences from X-ray diffraction (XRD) studies that peak intensities corresponding to calcite increases relative to the other minerals present in lime mortars as the sieve size decreases [18]. Hence, the finest fraction which was retained in the "pan" (<0.075 mm) is considered to be the binder fraction and concentrated with $CaCO_3$. Figure 4 shows the infrared spectrum of the mortar sample's binder fractions (<0.075) compared with pure calcium carbonate and pure silicon dioxide. These will serve as IR absorption standards for comparing the old lime mortar sample with sand (composed of SiO_2) and lime (mainly contains $CaCO_3$), respectively, which are raw materials in its manufacture. For calcium carbonate, the characteristic IR absorption peaks are the C-O in-plane bending ($\upsilon 4$) at 712 cm^{-1} and C-O out-of-plane bending ($\upsilon 2$) at 876 cm^{-1}. These sharp peaks are suitable in determining the presence of $CaCO_3$ because few compounds absorb strongly at this wavenumber. Furthermore, the broad peak at 1419 cm^{-1} is

attributed to the C-O asymmetric stretching (υ3) of $CaCO_3$. The most intense absorption bands of silicon dioxide are centered at 1082 cm^{-1} assigned to the asymmetric stretching mode of Si-O-Si, 795 cm^{-1} which is the symmetric stretching mode of Si-O-Si and the bending vibrations of Si-O-Si centered at 463 cm^{-1}, respectively [20,21]. Based on the IR spectrum in Figure 4, the binder fractions from both mortar samples have absorption peaks that are very similar with the bands of calcium carbonate. The absence of peaks attributed to silicon dioxide confirms that the binder fraction in the mortar sample is purely $CaCO_3$. Hence, this fraction was targeted for digestion with acid and titrated with EDTA and $KMnO_4$ to determine the calcium content.

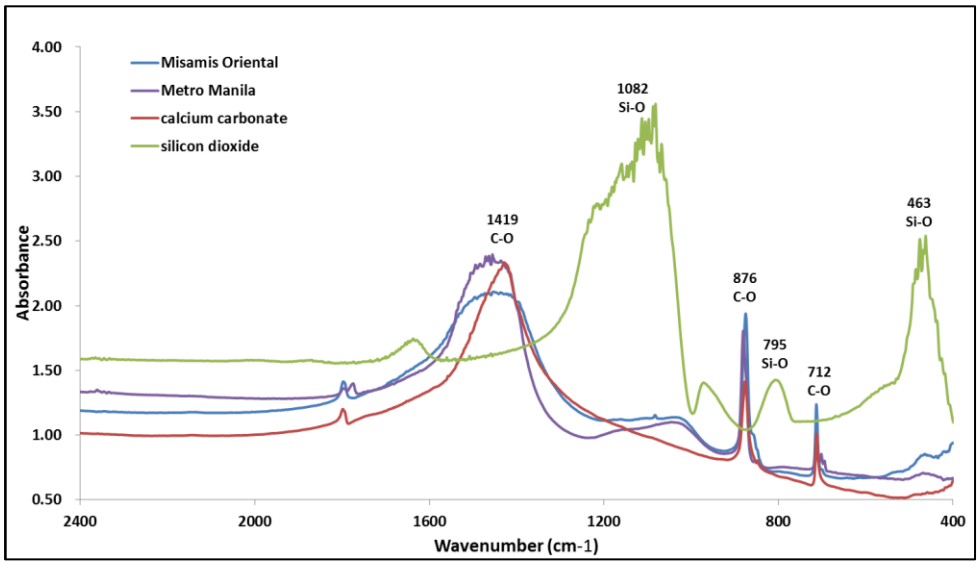

Figure 4. Spectrum of mortar fractions retained in pan (<0.075 mm) taken at finger print region (2400 – 400 cm^{-1})

Analysis of EDTA titration

The mean value obtained from the standardization of EDTA solution using pure analytical grade $CaCO_3$ was 4743 ± 132.9 µM at 95% confidence level. The standard deviation of 1.49 x 10^{-5} indicates that the concentration of each trial run is precise. From this standardized EDTA concentration, mortar samples from Misamis Oriental and Metro Manila were titrated. Results show that calcium content of the binder fraction for Metro Manila sample (73.54%) is higher compared to the Misamis Oriental sample (59.60%), representing a difference of 13.94%. This implies that the lime material used for making mortars were sourced from different locations which is highly possible because the church ruins are geographically apart. Absence of direct trade of raw materials between Metro Manila and Misamis Oriental was also inferred. Moreover, difference in mortar preparation techniques may contribute to this variation. Since the Misamis Oriental church ruin is located on a promontory, probably sea shells or corals may have been used as sources of lime which accounts to the observed difference.

Table 2 shows the important parameters used to determine the percentage of calcium in the Misamis Oriental sample. Binder fractions in mortars are expected to be homogenously mixed [1, 5]. Therefore, a 95% confidence level for the mean calcium content of 59.60% ± 4.64 gives a range of 54.96% to 64.24%. This percentage represents the true amount of calcium in the entire mortar sample obtained from the site. The percentage calcium from each trial is also within the 95% confidence limits. Since the coefficient of variation is 3.14%, which is less than the acceptable percentage of 5%, the values from this titration are considered precise [22].

Table 2. Calcium content of Misamis Oriental sample using EDTA

Mass of Mortar Sample (g)	Trial	Volume of EDTA Consumed (mL)	Concentration of Ca (ppm)	Mass of Ca (g)	% Ca (w/w) in Sample	Mean (w/w) and Standard Deviation
0.1079	1	32.70	248.62	0.06216	57.60	59.60% ± 4.64*
	2	34.80	264.59	0.06615	61.30	(1.87)
	3	34.00	258.50	0.06463	59.89	

* at 95% confidence level

Results from Table 3 shows that the Metro Manila sample has a 95% confidence level for the mean calcium content of 73.54% ± 2.68 or a calcium percentage range of 70.86% to 76.22%. Hence, the actual calcium content for the entire Metro Manila mortar sample obtained from the site should be within this interval range. The individually measured calcium concentration per trial also falls in these confidence limits. The titration of the Metro Manila sample was considered to be more precise than the Misamis Oriental sample based on the smaller confidence interval value which is attributed to random errors brought about by the visual determination of the end point color. The computed coefficient of variation (1.47%) supports this higher precision compared to the Misamis Oriental titration. Samples from both sites yielded mean calcium contents that are statistically consistent with each other suggesting that EDTA titration can be used for old lime mortar samples.

Table 3. Calcium content of Metro Manila sample using EDTA

Mass of Mortar Sample (g)	Trial	Volume of EDTA Consumed (mL)	Concentration of Ca (ppm)	Mass of Ca (g)	% Ca (w/w) in Sample	Mean (w/w) and Standard Deviation
0.1027	1	39.30	298.80	0.07470	72.74	73.54% ± 2.68*
	2	39.50	300.32	0.07508	73.11	(1.08)
	3	40.40	307.16	0.07679	74.77	

* at 95% confidence level

Analysis of $KMnO_4$ titration

The $KMnO_4$ solution was first standardized using sodium oxalate and the mean concentration is 10660 ± 640.5 μM at a 95% confidence level. Precision for the standardization method was considered high due to the small value (2.58×10^{-4}) of the standard deviation. The results of $KMnO_4$ titration on the Misamis Oriental sample shown in Table 4 is consistent with the mean calcium concentration values obtained from EDTA titration and differs only by 1.47 units. However, the confidence limits (± 6.68) and standard deviation equal to 2.69 is higher compared to that of the EDTA titration. This is due to the tedious process of crystallization and in maintaining the temperature during the titration which may introduce random errors in the system. Nevertheless, the measured calcium concentration values per replicate are within the allowable confidence limits and the coefficient of variation (4.45%) is still less than 5%, making the titration process precise.

Table 4. Calcium content of Misamis Oriental sample using $KMnO_4$

Mass of Mortar Sample (g)	Trial	Volume of $KMnO_4$ Consumed (mL)	Mass of Ca (g)	% Ca (w/w) in Sample	Mean (w/w) and Standard Deviation
0.03597	1	20.50	0.02190	60.87	60.48% ± 6.68*
	2	21.20	0.02264	62.95	(2.69)
	3	19.40	0.02072	57.61	

* at 95% confidence level

The same pattern of consistency was also observed for $KMnO_4$ titration of Metro Manila sample shown in Table 5 compared to the results of EDTA titration and differs by 0.286 units. A high confidence limit value (± 6.88) and standard deviation (2.77) were also obtained from the Metro Manila sample supporting the idea that $KMnO_4$ titration method is more prone to random errors. A coefficient of variation of 3.78% and calcium concentration values per replicate, which are within the given confidence limits, make the data obtained precise and reliable.

Table 5. Calcium content of Metro Manila sample using $KMnO_4$

Mass of Mortar Sample (g)	Trial	Volume of $KMnO_4$ Consumed (mL)	Mass of Ca (g)	% Ca (w/w) in Sample	Mean (w/w) and Standard Deviation
0.03423	1	23.80	0.02542	74.26	73.33% ± 6.88*
	2	24.20	0.02585	75.51	(2.77)
	3	22.50	0.02403	70.21	

* at 95% confidence level

Comparison of EDTA and $KMnO_4$ titration methods

Results of the two tailed *t*-test for two independent means performed on the Misamis Oriental mortar samples indicate that at 95% confidence level, the calculated *t* (t_{calc}) is 0.4653 which is less than the critical *t* (t_{table}) value of 2.776 for 4 degrees of freedom. Hence, the null hypothesis (H_0) is accepted and the two titration methods, EDTA and $KMnO_4$, are not significantly different at $p < 0.05$. For the Metro Manila mortar samples, the same *t*-test yielded a t_{calc} value of 0.1242 which is also less than the t_{table} (2.776) for a 95% confidence and 4 degrees of freedom. The null hypothesis is therefore accepted and there is no significant difference between the calcium concentrations resulting from the EDTA and $KMnO_4$ titration [23, 24].

The precision of the two different titration methods was evaluated using the *F*-test. For the Misamis Oriental mortar samples, the computed *F*-value (F_{calc}) is 2.07 and for the Metro Manila sample F_{calc} is equal to 6.58. Since both F_{calc} values did not exceed the tabulated critical value of *F* for a 95% confidence level at two degrees of freedom (19.0), there is statistically no significant difference between the standard deviations of the EDTA and $KMnO_4$ titration methods for both mortar samples [23].

The *t*-test and *F*-test analysis proves that the EDTA and $KMnO_4$ titration methods done in this study will provide the same analytical results and the observed difference are attributed entirely to random errors and not to systematic errors. This shows that both methods are comparable and either method is effective in determining the concentration of calcium on old lime mortar samples.

Atomic absorption spectroscopy analysis of calcium

AAS was used to further validate the results of the titration methods in determining the amount of calcium on the old mortar sample's binder fraction. Table 6 shows that the calcium concentration obtained in the AAS of the Misamis Oriental sample differs by about 1.2 to 2.3 units from the titration methods or a percentage difference of

about less than 3.9%. The Metro Manila sample however differs from the titration method by about 4.3 to 4.8 units which translates to a percentage difference of roughly less than 6.4% from the titration methods. These percentage differences are statistically acceptable considering the comparison is between a classical method and an instrumental method [25].

Table 6. Summary of AAS data for calcium content

Sample Site	Trial	Mass of Sample (g)	Absorbance	% Ca	Mean and Standard Deviation
Misamis Oriental	1	0.1079	0.0538	61.09	58.21% ± 6.31* (2.54)
	2	0.1079	0.0506	57.19	
	3	0.1079	0.0499	56.34	
Metro Manila	1	0.1027	0.0640	77.26	78.11% ± 4.82* (1.94)
	2	0.1027	0.0664	80.33	
	3	0.1027	0.0636	76.74	

* at 95% confidence level

Conclusion

The calcium content of the binder fractions in the historic lime mortar samples were determined quantitatively using EDTA and $KMnO_4$ titration. This serves as a very useful baseline information for future renovation work of historic structures in the Philippines. Lime mortars are not manufactured the same since the two church ruins in this study have no direct relation with each other and are geographically apart. Both EDTA and $KMnO_4$ titration methods yielded comparable results and have high precision based on the statistical tests performed and supported by AAS data in this study. Hence, both titration techniques can be applied for calcium analysis of historic mortars. Furthermore, the approach of analyzing the sieved fractions separately is not common in literature, especially since the analysis of calcium content in this study was focused on the finest fraction (<0.075mm) which makes it unique. This study could be utilized readily for routine analysis of calcium in lime mortars that is simple, reproducible and cost-effective.

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