ISSN: 1410-8917
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 21 (3) (2018): 131–138

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Assessing the Composition of 19th Century Lime Mortars from a Mission Chapel in the Former Hacienda de San Isidro de Mariquina Philippines

Jan-Michael C. Cayme [a*], Renz Matthew L. Aurellano [b], Carmen Luisa P. Cabral [b], Gellyn Ann R. Alonzo [c], Aniano N. Asor, Jr. [a]

a Chemistry Department, College of Science, De La Salle University, 2401 Taft Avenue, Manila, 1004, Philippines.
b Philippine Science High School, Main Campus, Agham Road, Diliman, Quezon City, 1101, Philippines.
c Philippine Science High School, Ilocos Region Campus, Poblacion East, San Ildefonso, Ilocos Sur, 2728, Philippines.

* Corresponding author: jm_cayme@yahoo.com

https://doi.org/10.14710/jksa.21.3.131-138

Article Info

Article history:
Received: 10 June 2018
Revised: 28 July 2018
Accepted: 30 July 2018
Online: 3 August 2018

Keywords:
lime mortar; Fourier Transform Infrared Spectroscopy; EDTA titration; Philippines

Abstract

This paper presents the results of a chemical study on lime mortars manufactured during the Spanish Colonial Period in the Philippines. Lime mortar samples, MRK-01 and MRK-02, were obtained from the facade of a historical mission chapel in Marikina City. The nature of the aggregate and binder components in these mortar samples were determined by performing sieve analysis and classified to be poorly graded with uniform gradation. An aggregate to binder ratio of approximately 1:1 was computed based on the solubility of the individual sieved fractions in hydrochloric acid. The silicate character of the aggregate was confirmed by the absorbance peaks attributed to silicon dioxide (SiO_2) in the Fourier Transform Infrared Spectroscopy (FTIR). Natural river sand was used as aggregates in both mortar samples which is apparent from the particle shapes of the sieved fractions. There was also no evidence of sea shells, broken potteries, brick fragments and bulk unburned limestone used as aggregates in any of the mortar samples tested. The binder portion is mainly calcitic or calcium carbonate ($CaCO_3$) based on the FTIR spectra and was shown to be removed by hydrochloric acid digestion. Titration method using ethylenediaminetetraacetic acid (EDTA) was employed to determine the amount of calcium in the acid soluble fractions. The percentage of calcium for MRK-01 ranges from about 1.0% to 9.5%, while MRK-02 ranges from about 2.3% to 16.8%, respectively. These percentages indicate that MRK-02 was manufactured with more lime binder compared to MRK-01. From this study, a simple method of understanding the composition of old lime mortars in the Philippines was established, which is useful for general heritage conservation work.

1. Introduction

The *Hacienda de San Isidro de Mariquina* was acquired by the Jesuits from the Augustinians in 1630. These Catholic religious orders were among the pioneering missionary orders that evangelized the Philippines during the Spanish Colonial Period (1521-1898) [1, 2]. A mission village was originally established within the boundaries of the *Hacienda*. A chapel made of light materials was built along the bank of a river and the missionaries called it *Jesus de la Peña* [3]. Eventually, the chapel's structure was replaced with stronger materials made of adobe stones.

The present-day structure of the chapel is heavily reconstructed. The chapel's southern wall was completely demolished to give way for a parish office and priest's quarters, while the western wall was replaced with modern concrete. Based on archival photos and the local parish commemorative marker mounted on the facade, these modifications were made during the reconstruction of 1988. Only the chapel's facade and the

northern wall section with its prominent buttresses remain relatively intact. Since historical records on the chapel's construction is inconclusive and non-existent, the relative construction period was based on physical and architectural characteristics. These includes the adobe stone layering techniques, physical characteristics of the construction materials and the architectural design of the structure's intact portion (facade and buttresses). All of these characteristics point to a period within the latter part of the Spanish rule in the Philippines [4, 5].

Lime mortars are responsible for holding the stone or brick materials together in old construction methods. Another application of mortars is its use as a plaster or "*palitada*" which serves as a thin outer covering over stones or bricks preventing the damaging effects of the surrounding environment [4]. Both mortar applications were investigated in this study. Generally, old lime mortars in the Philippines are made by mixing together sand, lime or "*apog*" and water. According to historical texts, organic compounds like eggs, sugar (molasses), plant extracts and animal fats were occasionally added to the mortar mixture to improve its binding capabilities [4]. Mortars are physically composed of an aggregate and binder part. The sand is considered as the aggregate and the lime is the binder. Aggregates can also include other solid components added in the mortar like crushed sea shells, broken potteries and brick fragments.

Scientific studies reported in literature for lime mortars in the Philippines are very scarce. Some of these studies are the chemical characterization of mortars from church ruins in Manila and Misamis Oriental [6, 7], determination of albumin additives [8] and X-ray fluorescence (XRF) studies of different Philippine National Cultural Churches [9]. The lack of scientific data has prompted modern day conservators and restorers in the Philippines to resort to incompatible construction materials as a quick remedy for lime mortar repairs. Hence, this practice greatly alters the historical accuracy and significance of heritage buildings [10].

In this study, both physical and chemical techniques for identifying lime mortar composition was presented. The physical methods were necessary to prepare the mortar samples for chemical analysis. The sample mortars were sieved to separate the aggregate and binder fractions. The physical characteristics of these fractions were described and the mixing ratio was determined by acid digestion. The chemical techniques include spectroscopy, specifically Fourier Transform Infrared Spectroscopy (FTIR), and titration analysis. FTIR was used to establish the general mineral and chemical composition of the mortar samples [6, 7]. Since calcium is the major component of binders in lime mortars, knowing its concentration is very important in duplicating the amount of binders in mortars. Titration was employed to determine the amount of calcium using ethylenediaminetetraacetic acid (EDTA) as titrant [7, 11]. All this information is important for assessing the compatibility of replacement materials for future conservation work.

2. Materials and Methods

Collection of mortar samples

The mortar samples were acquired in December 2016 at the facade wall of the historical mission chapel of *Jesus de la Peña* in Marikina City, Metro Manila, Philippines (Figure 1). This is one of the most intact portions of the old chapel. Two representative samples were collected from the main entrance door of the old facade (Figure 2). Sample MRK-01 with a total mass of 18.76 g was scraped-off in-between two adobe stones from the right side column of the door arch. Another sample, MRK-02 with a total mass of 10.56 g is a plaster-like mortar material (*palitada*) removed from the lintel located above the door arch. Very minimal sample amounts were removed from the facade to protect the historical value of the structure. To prevent contamination from surrounding materials, the center portion of the mortar samples were used for the analyses described in this paper [6].

Figure 1. Location of Marikina City in Metro Manila and the facade of the chapel of *Jesus de la Peña* in the former *Hacienda de San Isidro de Mariquina* where the samples were taken

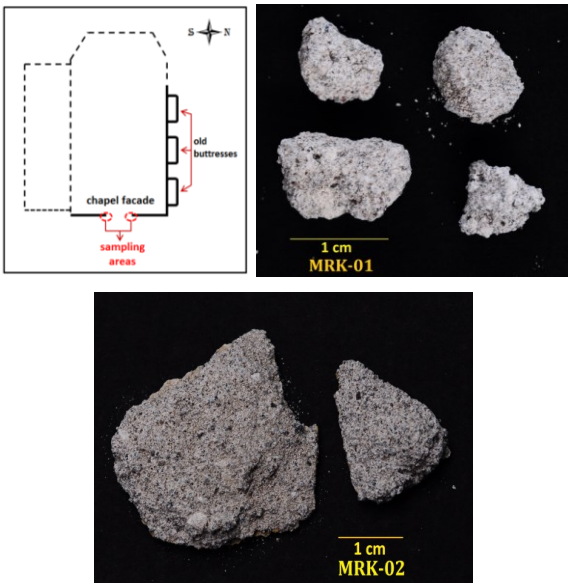


Figure 2. General floor plan of the chapel showing the sampling sites and the intact portion of the structure in solid lines. The lime mortar samples used in this study: MRK-01 and MRK-02.

A portion of the original total mass of samples, 13.17 g for MRK-01 and 6.28 g for MRK-02 were pulverized gently into small pieces using mortar and pestle. The pressure exerted during pulverization was just enough to dislodge the aggregates (sand and stone) with the binder (lime) part. Each sample was subjected individually through sieve analysis by putting the crushed materials on a USA Standard Testing Sieve ASTME11 Specification with sizes of 4.75, 2.36, 1.18, 0.600, 0.425, 0.250, 0.150 and 0.075 mm, respectively. The whole set-up was shaken using a mechanical shaker (US Tyler brand) for 5 min to ensure good separation within the different fractions. The fraction retained in the "pan", which has a sieve size smaller than 0.075mm, was also included in the analysis. All the sieved fractions obtained from Samples MRK-01 and MRK-02 were individually weighed and subjected to acid digestion, FTIR analysis and titration with EDTA.

Digestion with acid solution

Before digesting the sieved fractions with HCl, it was placed in separate 100 mL Erlenmeyer flasks and heated at 110°C for 24 hours in an oven to drive out the absorbed water moisture. Each fraction was then soaked with 4 mL distilled water and 30 mL 2M analytical grade HCl (Macron) solutions, followed by stirring for 5 minutes in room temperature (30 °C). After this stirring period, the mixtures were heated on a hot plate until boiling. It was filtered using a fluted filter paper to separate the residue (aggregates) and the filtrate (binder and other acid soluble components). The filtrate was transferred into separate 100 mL volumetric flasks and diluted to the mark with distilled water. This will serve as the sample stock solution for the titration with EDTA analysis. The residue was oven dried (110°C), weighed and analyzed by FTIR [6, 7].

Analysis by Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was done for the bulk mortar samples and the residue (aggregate) left after the acid digestion. The spectra were recoded using a Thermo Scientific Nicolet 6700 FT-IR Spectrophotometer in the mid-infrared region (4000-400 cm^{-1}) at 16 scans per spectrum. Each sample were prepared by grounding a small amount of the mortar and residue and pressed into a thin, translucent film using the KBr pellet method. A sample-KBr powder ratio of approximately 1:3 for each sample was observed. The spectrum was reported in absorbance relative to wave number readings and was compared to pure analytical grade $CaCO_3$ (Unichem, 98.0 %) and SiO_2 (Sigma-Aldrich).

Titration with ethylenediaminetetraacetic acid (EDTA)

The filtrate obtained after digestion was titrated with EDTA to determine the amount of calcium in the acid soluble fractions. EDTA solution (4 L) was prepared by dissolving 4 g EDTA powder (Himedia, 99.5 %), 2 g NaOH (Unichem, 96.0 %) and 0.2 g $MgCl_2 \cdot 2H_2O$ (Qualikems, 99.0 %). Analytical grade chemical reagents were used throughout the preparation.

Standardization of the EDTA solution was determined by dropwise addition to a known standard solution of pure $CaCO_3$ until a faint blue color was produced. About 4-5 drops of Eriochrome Black T (Merck) was used as the colored indicator. The $CaCO_3$ standard solution was made by dissolving 0.2 g of pure analytical grade $CaCO_3$ (Unichem, 98.0 %) in 6 mL of concentrated analytical grade HCl (Macron) and afterwards added with 50 mL distilled water. The mixture was transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. A 10 mL mixture of ammonium buffer was used throughout the titration. Three trials were done. After knowing the exact concentration of EDTA, the acid soluble fractions obtained from the digested sample fractions were titrated using the same procedure described [7].

3. Results and Discussion

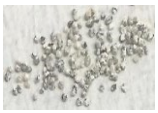
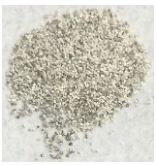
Nature of the aggregate

Examining the mortar samples macroscopically revealed that both contain lime binder and not made of modern concrete. This is due to the powdery texture of the sample observed as opposed to concrete which has a more rigid texture. MRK-02, which is classified as a plaster or "*palitada*", is hardly detached and less powdery compared to MRK-01. The aggregates for both samples are mainly sand and there is no visible evidence of sea shells or broken bricks mixed with the mortars. MRK-01 is whiter in color than MRK-02, since the latter being a plaster, is more exposed to the atmosphere.

To further examine the nature of the aggregates, a sieve analysis was performed. This will provide information on the distribution of aggregates in the old mortar samples according to particle size [6]. The size of each aggregate, particularly its surface area and texture, has a direct effect on how the lime binder attaches itself

on the mortar and influences the compressive strength of the material. Table 1 shows the typical particle shapes obtained from the different sieved fractions of MRK-01 and MRK-02.

Table 1. Representative photo and aggregate descriptions of the different sieved sized fractions

Sieve Size (mm)	MRK-01	Physical description/ particle shape	MRK-02	Physical description/ particle shape
4.160	--	--	--	--
2.360		Rounded to subrounded		Subrounded
1.180		Rounded to subrounded		Subrounded
0.600		Subrounded; subangular to angular		Subrounded; subangular to angular
0.425		Rounded to subrounded; subangular		Rounded to subrounded; subangular
0.250		Rounded to subrounded; subangular		Rounded to subrounded; subangular
0.150		Well rounded to rounded		Well rounded to rounded
0.075		Powedry texture; well-rounded		Powdery texture; well-rounded
<0.075 (pan)		Powdery texture		Powdery texture

Generally, most fractions have predominantly rounded to subrounded particle shapes which are typical for natural river sand that is continually exposed to flowing water. This is possible because the old chapel is located only a few meters from the Marikina River. Mixtures of a few angular to subangular particle shapes were also observed from the medium to fine sand fractions (0.600 mm to 0.250 mm). The extremely fine fractions (0.150 mm to <0.075 mm) were considered as having a well-rounded shape to a powdery texture [12]. The fraction retained in the pan (<0.075 mm) are mainly attributed to the binder fraction [13]. It was also confirmed that crushed shells or bulk unprocessed limestone are not present in any of the sieved fractions in both samples. Hence, digesting the entire sample with HCl can be safely done and will yield a more accurate binder to aggregate ratio for each mortar sample. No aggregate was retained on the sieve size at 4.160 mm for both samples based on the classification of the American Society for Testing and Materials (ASTM, 1980).

MRK-01 and MRK-02 have aggregates that are composed of medium (0.600 and 0.425 mm) to fine (0.250 mm) sized sand particles as seen in Figure 3. The absence of aggregates for grain sizes in 4.750 mm suggests that the mortar samples are both non-load bearing. This observation is consistent with the sampling locations of the mortars wherein both are not supporting any major wall column. A weight difference of about 50-55% on the coarse sand particles (2.360 mm) was also observed between the mortar samples. Since MRK-02 is a plaster, a thin layer of coarse aggregates has to be used to achieve a smooth consistency as compared to the grain requirements of MRK-01. Even with this difference, the binder which is part of the sieve sizes 0.075 mm and less, have weight distributions that are almost similar in both mortar samples.

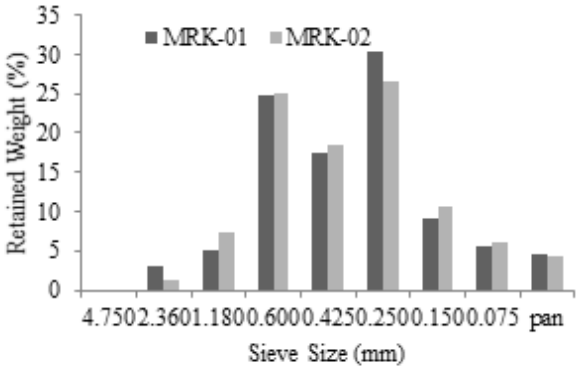


Figure 3. Weight distributions of the mortar samples.

Figure 4 is a gradation curve represented by a logarithmic plot showing the relationship of the equivalent particle size relative to the cumulative percentage of aggregates that passed through a certain mesh size. The curve plots for both mortar samples are distributed similarly which implies that the manufacturing methods, time of manufacture, and raw materials (aggregates and binder) used are almost the same. Moreover, shape parameters identified as coefficient of curvature (C_c) and coefficient of uniformity (C_u) were computed based on 10% (D_{10}), 30% (D_{30}) and 60% (D_{60}) of the grain diameters (D) passing by weight [12]. The value for C_c and C_u are 1.313 and 3.467, respectively, for both mortar samples which denote that MRK-01 and MRK-02 are classified as poorly graded with uniform gradation. This means that majority of the particles in the mortar have the same size or lacking in certain sizes. Hence, creating mortars that have large void spaces and decreasing the contact points between particles, making it more permeable [12]. This shows that

modern day cement mixture is not a compatible material for restoration work on this chapel since it has very small void spaces and generally not permeable.

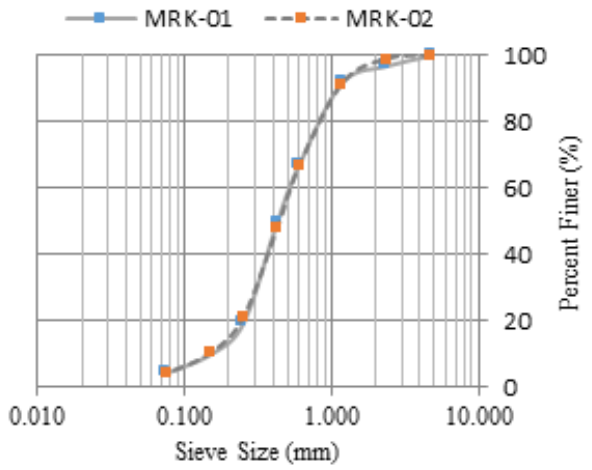


Figure 4. Gradation curve of the mortar samples

Nature of the binder

Binders in mortars are mainly composed of lime or calcium carbonate ($CaCO_3$) which is soluble in strong acids. Based on the physical description of the sieved aggregates in Table 1, sources of $CaCO_3$ like sea shells or bulk unprocessed limestone is not present in both mortar samples therefore it was digested directly with HCl. Digesting the sieved fractions individually is a more accurate method compared to digesting the bulk mortar. From this method, the percentage of acid soluble fraction can be traced within the different fractions. Since the bulk mortar was grinded gently, some of the binder components are still attached to the surface of the aggregates. Therefore, variations in the percentage dissolved were observed. Table 2 lists the percentage of binder dissolved in 2M HCl. For MRK-01, 55.73% dissolved in the acid and it can be inferred that 44.27% were the insoluble fraction which forms most of the aggregates. Furthermore, for MRK-02, 57.76% was acid soluble or the binder fraction, while the aggregate fraction is 42.24%. Getting the ratio of these percentages will yield approximately a 1:1 ratio of the aggregate and binder in both mortar samples. It is important to note that not all acid soluble components in mortars are attributed to $CaCO_3$. There are also other chemical elements in the mortar that are soluble like iron and magnesium but are present in small amounts. The sieve fractions retained in the pan (<0.075 mm) which is supposedly composed mainly of $CaCO_3$ has only about 15-22% by mass dissolved in the acid. This can be explained by looking at the type of soil usually found in the Marikina area which is abundant in smectite-type clays having high amounts of silicon and aluminum [14]. Since these clays are powdery and would be retained in the pan, it is possible that clay soil may have been added during the manufacturing of mortar and may have mixed with the lime binder.

Table 2. Percentage of binder dissolved in HCl solution

Sieve Size (mm)	MRK-01			MRK-02		
	Dry mass before digestion (g)	Dry mass after digestion (g)	Percentage dissolved in 2M HCl	Dry mass before digestion (g)	Dry mass after digestion (g)	Percentage dissolved in 2M HCl
4.160	--	--	--	--	--	--
2.360	0.4110	0.2962	72.07%	0.0764	0.0221	28.93%
1.180	0.6633	0.3818	57.56%	0.4626	0.2976	64.33%
0.600	3.2566	1.9537	59.99%	1.5674	1.0299	65.71%
0.425	2.2845	1.1978	52.43%	1.1658	0.7592	65.12%
0.250	4.0018	2.5027	62.54%	1.6710	1.0759	64.39%
0.150	1.2142	0.5589	46.03%	0.6747	0.3282	48.64%
0.075	0.7489	0.3194	42.65%	0.3862	0.0712	18.44%
<0.075	0.5871	0.1272	21.67%	0.2743	0.0422	15.38%
Total	**13.1674**	**7.3377**	**55.73%**	**6.2784**	**3.6263**	**57.76%**

Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR spectrum in the mid-IR region (4000 to 400 cm^{-1}) of the bulk samples of MRK-01 and MRK-02 were compared to pure $CaCO_3$ and SiO_2 as shown in Figure 5. This comparison was done because binders are generally lime or $CaCO_3$ while SiO_2 represents the silicates found on aggregates in mortars. All spectra for pure $CaCO_3$ and SiO_2 were referenced from a previous publication of our group [7]. MRK-01 exhibited a broad peak centered at 1420 cm^{-1} and two sharp absorption peaks at 877 cm^{-1} and 714 cm^{-1}, respectively. These are characteristic peaks of $CaCO_3$ and sufficient in identifiying the presence of lime in the mortar samples. Specifically, the broad peak at 1420 cm^{-1} is assigned to the C-O assymmetric stretching ($\upsilon 3$) mode in $CaCO_3$, the sharp peaks at 877 cm^{-1} and 714 cm^{-1} are the out-of-plane bending ($\upsilon 2$) and in-plane bending ($\upsilon 4$) modes of C-O in $CaCO_3$, repectively [[6, 7, 15-17]. The same characteristic peaks are also evident on MRK-02, thus confirming the presence of lime or $CaCO_3$.

For the aggregates represented by SiO_2, the Si-O-Si bond will absorb infrared radiation forming absorption peaks centered at 1080 cm^{-1} (assymmetric stretching mode), 793 cm^{-1} (symmetric strectching mode) and 464 cm^{-1} (bending vibrations), respectively [6, 7, 15-17]. The same charcteristic peaks are seen on MRK-01 and MRK-02. This confrms the silicate nature of the mortar samples.

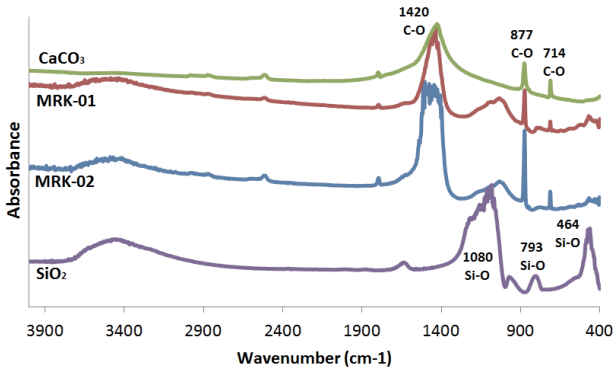


Figure 5. FTIR spectrum of MRK-01 and MRK-02 bulk samples with pure $CaCO_3$ and SiO_2.

After digestion with 12M HCl, the FTIR spectrum of all the aggregates were obtained and again compared to $CaCO_3$ and SiO_2. Figure 6 shows that nothing was left of the $CaCO_3$ (lime) in each sieved fractions, thus implying that the digestion with acid is effective in removing all the binder from the aggregates. Absorption peaks centered at 1080 cm^{-1}, 793 cm^{-1} and 464 cm^{-1} for the SiO_2 were still retained [6, 7, 15-17]. The same observation was seen on MRK-02 in Figure 7. Therefore the binder to aggregate ratio of 1:1 obtained from the acid digestion is accurate.

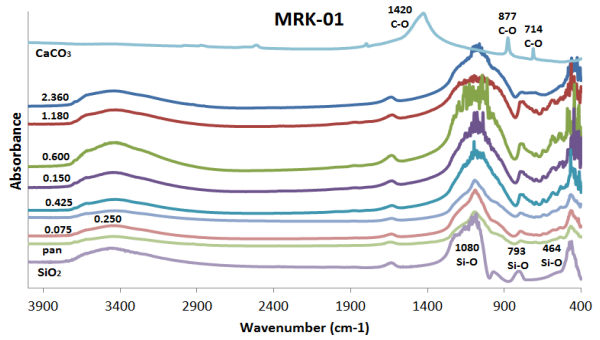


Figure 6. FTIR data of sieve fractions of MRK-01 after digestion with 12M HCl

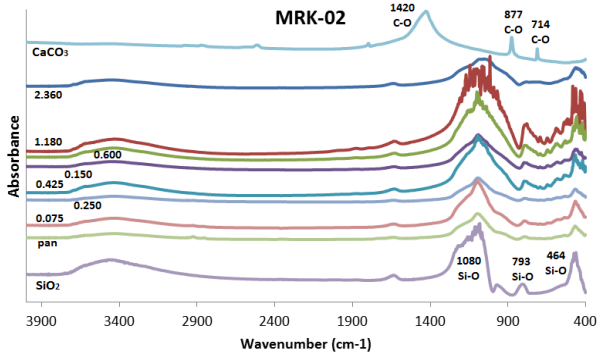


Figure 7. FTIR data of sieved fractions of MRK-02 after digestion with 12M HCl

Titration with EDTA

The titrant (EDTA) was standardized first with an analytical grade $CaCO_3$ and has a mean concentration of 0.004103 ± 0.001322 M. All three trials are within the range of the 95% confidence interval limit. A standard deviation value of 5.322 X 10^{-4} indicates that the concentration obtained per trial run is precise. This was followed by titrating the individual sieved fractions of MRK-01 and MRK-02 with the standardized EDTA solution.

Results show that the mean amount of calcium in MRK-01 (Table 3) ranges from about 1.0 to 9.5%, while MRK-02 ranges from about 2.3 to 16.8% (Table 4).

Table 3. Calcium content of MRK-01 sieved fractions using EDTA

Sieve Size (mm)	Mass of Mortar Sample (g)	Trial	Volume of EDTA Consumed (mL)	Mass of Ca (g)	% Ca (w/w) in sample	Mean (w/w) and Standard Deviation
4.160	-	-	-	-	-	-
2.360	0.4110	1	23.30	0.01533	3.729	3.884 ± 0.3982* (0.1603)
		2	24.20	0.01592	3.873	
		3	25.30	0.01664	4.049	
1.180	0.6633	1	23.20	0.01526	2.301	2.350 ± 0.5162* (0.2078)
		2	21.90	0.01441	2.172	
		3	26.00	0.01710	2.579	
0.600	3.257	1	52.00	0.03421	1.050	1.103 ± 0.1157* (0.04659)
		2	56.40	0.03710	1.139	
		3	55.40	0.03644	1.119	
0.425	2.285	1	33.20	0.02184	0.9560	1.035 ± 0.1707* (0.06871)
		2	37.60	0.02473	1.083	
		3	37.00	0.02434	1.065	
0.250	4.002	1	64.00	0.04210	1.052	1.090 ± 0.08501* (0.03422)
		2	68.00	0.04473	1.118	
		3	67.00	0.04408	1.101	
0.150	1.214	1	61.10	0.04019	3.310	3.240 ± 0.1899* (0.07643)
		2	58.30	0.03835	3.159	
		3	60.00	0.03947	3.251	
0.075	0.7489	1	76.10	0.05006	6.685	6.913 ± 0.4914* (0.1978)
		2	80.0	0.05263	7.027	
		3	80.0	0.05263	7.027	
< 0.075	0.5871	1	85.00	0.05592	9.524	9.293 ± 0.5348* (0.2153)
		2	82.60	0.05434	9.255	
		3	81.20	0.05342	9.098	

* at 95% confidence interval

It can be noted that not all chemical elements dissolved in the acid are calcium containing compounds. The aggregates can also have acid soluble elements like iron and magnesium [6]. MRK-02 in general has a higher percentage of calcium as compare to MRK-01. This implies that more lime material was added to MRK-02 which is reasonable because of its function as a "*palitada*" or plaster and was usually made with more binder than aggregates. For both samples, the mean amount of calcium is highest in the pan (< 0.075 mm) which is consistent with the reported literature [13]. The presence of the mineral calcite, which is the most stable form of $CaCO_3$, is usually greater in lime mortars having sieve sizes at 0.075 mm and lower (< 0.075 mm) in the ASTM classification. It was also observed that for the coarse and medium grain size ASTM classification, the percentage of calcium ranges only from 1.0% to about

4.0% for both samples. These were attributed to the minute lime particles that were not completely detached from the surface of the aggregates during the grinding and sieving steps. All trials made per sieve fraction were within the 95% confidence interval limit and the standard deviations indicate that the data obtained are precise as shown in Tables 3 and 4.

Table 4. Calcium content of MRK-02 sieved fractions using EDTA

Sieve Size (mm)	Mass of Mortar Sample (g)	Trial	Volume of EDTA Consumed (mL)	Mass of Ca (g)	% Ca (w/w) in sample	Mean (w/w) and Standard Deviation
4.160	-	-	-	-	-	-
2.360	0.07640	1	3.10	0.002039	2.669	2.497 ± 0.4280* (0.1722)
		2	2.70	0.001776	2.325	
		3	2.90	0.001908	2.497	
1.180	0.4626	1	15.30	0.01006	2.176	2.996 ± 2.031* (0.8177)
		2	26.80	0.01763	3.811	
		3	21.10	0.01388	3.001	
0.600	1.5674	1	67.00	0.04408	2.812	2.839 ± 0.08900* (0.03570)
		2	67.30	0.04427	2.825	
		3	68.60	0.04513	2.879	
0.425	1.1658	1	59.40	0.03908	3.352	3.403 ± 0.1830* (0.07379)
		2	59.70	0.03927	3.369	
		3	61.80	0.04065	3.487	
0.250	1.6710	1	71.40	0.04697	2.811	2.762 ± 0.1610* (0.06473)
		2	68.30	0.04493	2.689	
		3	70.80	0.04657	2.787	
0.150	0.6747	1	64.90	0.04269	6.328	6.490 ± 0.5220* (0.2101)
		2	65.80	0.04329	6.416	
		3	69.00	0.04539	6.728	
0.075	0.3862	1	63.20	0.04158	10.77	10.95 ± 0.4660* (0.1876)
		2	65.40	0.04302	11.14	
		3	64.20	0.04223	10.94	
< 0.075	0.2743	1	68.80	0.04526	16.50	16.79 ± 0.7150* (0.2878)
		2	70.00	0.04605	16.79	
		3	71.20	0.04684	17.08	

* at 95% confidence interval

4. Conclusion

The methods described in this paper provide a simple means of analyzing the components of historical lime mortar samples and its manufacturing method. The type of aggregates, amount of binder (calcium) and the mixing ratio, are important information for proper heritage conservation work. Employing sieve analysis to understand the behavior of the individual particles in relation to its chemical composition is an effective approach to give a more accurate description of the aggregates and binder fractions. From this analysis, it was proven that the aggregate to binder ratio for both mortar samples is approximately 1:1 which is an important parameter for proper conservation work. The size distribution of aggregates for both mortar samples were not selected properly due to its poorly graded classification. The amount of binder which is based on the amount of calcium is different for both samples. MRK-02 has a more concentrated calcium binder with fewer aggregates compared to MRK-01. This is due to its intended use on the chapel's structure; MRK-01 is a mortar found in between adobe stones while MRK-02 is a thin "*palitada*" mortar.

5. Acknowledgements

The authors would like to express their sincere gratitude to Mr. Christopher de Asis, custodian of the Chapel of *Jesus de la Peña* for allowing the authors to collect the mortar samples used for this study. This research was part of the 2017 Science Immersion Program of the De La Salle University, Manila and Philippine Science High School (PSHS) System. The generous support of the Chemistry Department of the De La Salle University, Manila, is highly appreciated. This study will not be possible without the helpful insights and assistance of the following persons: Dr. Glenn Alea, Dr. Jaime Raul Janairo, Mr. Michael Ajero, Mr. Irving Chiong, and Dr. Maria Carmen Tan.

6. References

[1] J. V. Z. Torres, Ciudad Murada: A Walk Through Historic Intramuros, Jointly published by Intramuros Administration and Vibal Publishing House, 2005.

[2] B. Lalana, P.G. Galende and L. Arboleda, La Casa de Dios: The Legacy of Filipino-Hispanic Churches in the Philippines, Ortigas Foundation, 2010.

[3] Luciano P. R. Santiago, The Last Hacendera: Doña Teresa de la Paz, 1841-1890, Philippine Studies, 46, 3, (1998) 340-360

[4] Ateneo Art Gallery, Zero in: Skin, Surface, Essence, Ateneo Art Gallery, 2003.

[5] Pedro G. Galende, Philippine Church Façades, San Agustin Museum, 2007.

[6] Jan-Michael C. Cayme and Aniano N. Jr. Asor, Characterization of Historica Lime Mortar from the Spanish Colonial Period in the Philippines, *Conservation Science in Cultural Heritage*, 16, (2017) 33-57 http://doi.org/10.6092/issn.1973-9494/7164

[7] Jan-Michael C. Cayme and Aniano N. Jr Asor, Calcium Content of Lime Mortars from 19th Century Church Ruins in The Philippines Using Volumetric Analysis, *Malaysian Journal of Analytical Sciences*, 21, 5, (2017) 1080-1090 https://doi.org/10.17576/mjas-2017-2105-10

[8] M.S. Eusebio, Did Our Church Builders Use Egg Whites as Mortar Ingredients? The Biomolecular Reason Behind Collecting Mortars from Historical Sites, (2009).

[9] L. Z. L. Montilla, Material and Property Characterization of Eight Heritage Churches Declared as National Cultural Treasures, *Journal of Philippine Local History and Heritage*, 1, 2, (2015) 25-29

[10] National Comission for Culture and the Arts, Balangkas: a resource book on the care of built heritage in the Philippines, National Commission for Culture and the Arts, the Committee on Monuments and Sites, 2007.

[11] Douglas A. Skoog, F. James Holler, Donald M. West and Stanley R. Crouch, Fundamentals of Analytical Chemistry, 9 ed., Cengage Learning, 2014.

[12] Robert D. Holtz and William D. Kovacs, An introduction to geotechnical engineering, Prentice-Hall, 1981.

[13] J. Miranda, A. P. Carvalho and J. Pires, Assessment of The Binder in Historical Mortars by Various Techniques, *Archaeometry*, 54, 2, (2012) 267-277 http://doi.org/10.1111/j.1475-4754.2011.00627.x

[14] Edna Patricia Mendoza, Sandra Catane, Chelo Pascua and Mark Albert Zarco, Geological and geotechnical characteristics of Metro Manila volcanic soils and their suitability for landfill soil liner, *Geophysical Research Abstracts*, 12, (2010)

[15] Jan-Michael C. Cayme, Aniano Asor, Jr. N., Maveen Kim Alexis T. Alano and Eric T. Miranda, Chemical Characterization of Historical Brickwork of the Church Convento in Pagsanjan, Laguna, *Kimika*, 27, 1, (2016) 30-41 https://doi.org/10.26534/kimika.v27i1.29-40

[16] Paul A Schroeder, Infrared spectroscopy in clay science, CMS workshop lectures, (2002).

[17] Michele R. Derrick, Dusan Stulik and James M. Landry, Infrared Spectroscopy in Conservation Science, Getty Conservation Institute, 2000.