A COMPARATIVE STUDY OF LABORATORY MORTAR CHEMICAL ANALYSIS METHODS

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ABSTRACT
Determination of the chemical composition of hardened masonry mortars is a common challenge presented to material laboratories. Often the existing mortar formulation is desired in order to determine an appropriate mortar composition for conservation work. The use of portland cement in both historic and modern mortars can complicate the determination of mortar binder components in the laboratory. Although an ASTM standard for mortar analysis exists (ASTM C1324) [1], this standard involves the use of dangerous chemicals and can be expensive to perform.

This paper describes alternative mortar chemical analysis methods, including a literature review of historic and modern mortar analysis methods. The results of a limited survey of United States laboratories describe the current state of practice for mortar chemical analysis. Both the availability and cost of various methods are evaluated. A comparison of various methods for analysis of hardened mortar samples is provided. Methods included are the ASTM C1324 method, historical methods introduced by Cliver [2] and Jedrzejewska [3], and a modern method introduced by Middendorf [4]. Mortar samples were prepared in the laboratory with known proportions of sand, portland cement, and lime, and tested using one of the described methods. Our conclusions regarding the most appropriate test methods to determine hardened mortar chemical composition for the purposes of conservation are provided.

KEYWORDS: mortar analysis, portland cement, lime, aggregate, chemical characterization, test methods

INTRODUCTION
The formulation of existing hardened mortars is often needed for conservation work. Laboratory analysis can provide a detailed description of mortar composition and aggregate gradation to provide appropriate proportions for repointing and rebuilding mortar. Acid digestion of mortars containing portland cement is often not sufficient to determine the proportions of binder components. Other laboratory methods are available, such as petrography as well as other types of chemical analyses to identify parameters such as air content, microstructure, and the various mineral and chemical compositions of hardened mortar. In some cases, this comprehensive level of detail may not be required, and such testing is often quite costly. In masonry repair and conservation work, a contractor or building owner may only wish to know which type of mortar matches most closely with that of the original construction. A simplified mortar analysis technique may provide the desired information at reduced expense, given that the accuracy produced by the method is acceptable.

An examination of past and present mortar analysis methods was conducted through a literature review and a limited laboratory survey. A review of test methods for mortar characterization is presented as a comparison of techniques that have been used and the various attributes studied to identify masonry mortar components. A limited survey was conducted of United States laboratories which offer chemical mortar analysis services in order to determine the current state of practice in regard to mortar characterization. The survey asked which method or procedure was used by the laboratory, the cost of the analysis, and timeframe for completion, if available.

One of the mortar characterization methods reviewed was verified for accuracy by testing several hardened mortar samples of known component proportions. The results determined by the analysis procedure were compared to actual proportions to determine if the method could effectively characterize existing mortar samples by type.

REVIEW OF TEST METHODS

Test methods for mortar characterization including ASTM C1324 as well as alternatives and other historical methods were reviewed to compare the mortar qualities relevant to mortar characterization and techniques used to examine such properties.

It is important to note that mortar may meet the property specification (compressive strength, water retention, and air content) requirements of a mortar type without meeting the proportion requirements of the same mortar type specified in ASTM C270. However, this distinction is not critical when the objective of the test is to determine a suitable mortar material for repairs.

ASTM C1324 provides procedures for both petrographic and chemical analysis of hardened mortar. Both analyses are required to characterize mortar samples under this standard [1]. The petrographic examination follows the practice of ASTM C856, which involves microscopy and may also include X-ray diffraction. Aggregate and paste components are examined separately and paste components can be identified which may include hydrated or unhydrated portland cement, hydration products, lime, and other minerals such as from admixtures. Air content is estimated visually and characteristics of voids are determined to identify air-entrainment. Any additional information resulting from the petrographic analysis such as textural characteristics would be furnished as well. The chemical analysis described in the test method contains sub-procedures which depend on the results of the petrographic analysis, but the method generally utilizes acid digestion of a crushed mortar sample followed by filtration to separate the insoluble aggregate from the soluble mortar paste. A series of evaporation, acid digestion, and boiling is carried out, followed by high-temperature ignition to identify soluble silica resulting from cement hydration. The loss on ignition sub-procedure measures the mass loss at 110°C, 550°C, and 950°C identifies free water, chemically combined water, and carbonates, respectively. The identification and quantities of mortar paste and aggregate components is used to determine mortar type.

Limitations of ASTM 1324 include difficulty interpreting mortars containing masonry cement, mortar cement, fly ash and other materials [5]. A note within the standard also cautions that historic mortars may contain non-resolvable constituents. Entrained air detected within the mortar sample during petrography may help identify masonry cement, however masonry and mortar cements often consist of blends of other materials such as portland or other cements, lime, and other materials, therefore identification of a specific mortar type is not practical. The presence of fly ash in the mortar mix will increase the soluble silica obtained from the analysis, and thus overestimate the portland cement content [5]. The benefit of ASTM C1324 is that the petrographic analysis may produce useful information that the chemical analysis portion cannot.

The method introduced by Cliver [2] was intended as a relatively simple, low cost method that could be conducted on multiple samples to find distinguishing characteristics between them. Gravimetric techniques are used to determine soluble, sand, and fine residue portions of the mortar mix. Similar to other methods, acid digestion is used to determine the soluble and insoluble portions. After being separated from the sand and filtered, the color of the fine residue is used to determine the binder type. Cliver found that clays produced a red to tan residue, and portland cement medium to dark gray. Based on the information given about the binder from the residue color, the binder proportions were then indicated by the amount of residue. Cliver assumed that portland cement binders contained between 60% and 65% lime, and high percentages of clay indicated natural cement binders. A second acid digestion is performed on an additional crushed mortar sample to identify calcium and carbonation from the lime component in the mortar mix. This portion of the test is not intended to match lime for new mortar, but rather to compare various samples. Cliver noted the importance of prior knowledge of the mortar to supplement the experimental results in the identification of components.

The method described by Jedrzejewska [3] was developed as a result of many buildings being destroyed by World War II and was not intended to determine components and proportions but rather to compare and date many samples. The simplified, inexpensive procedure uses volumetric analysis of carbon dioxide content to identify three basic values resulting from mortar components: carbonates, sand, and solubles. Acid digestion is performed on a sample, and the carbon dioxide gas released during the digestion process is collected in a special apparatus to measure its volume. The sand is assumed to be insoluble in acid and therefore the sand component comprises the undigested portion. The carbonates measured from the carbon dioxide collected and sand are expressed as portions of the total mortar volume, while the soluble portion is assumed to make up the remainder. For specific mortar classification, Jedrzejewska noted the importance of additional visual analysis, microscopic examination, archeological records, and careful sample collection.

Middendorf, et al. [4] reported a chemical method which is recommended in conjunction with mineralogical and petrographic analysis for a complete analysis of a historic mortar. Several sub-procedures are listed that are to be followed as appropriate based on the results of the mineralogical and petrographic study, whether the binder is suspected to be lime-based or cement-based, and whether or not the aggregates are expected to be acid soluble. An acid digestion procedure is prescribed for mortars containing acid-insoluble aggregates, however, if calcareous aggregates are detected by prior examination this method will not produce reliable results. A mechanical separation method is recommended for mortars containing acid-soluble aggregates in which the sample is crushed and sieved, thus separating the binder-rich portion from the aggregate-rich portion. Cement content in the binder is determined by identifying soluble silica resulting from cement hydration within the residue. The aggregate is assumed not to contribute any soluble silica to the residue. The soluble silica present in the residue is determined by further digestion and filtration of the residue, followed by high temperature ignition. Several sub-procedures are prescribed for identification of further components such as iron, aluminum, calcium, and others, based on the results of the petrographic examination.

A study conducted by Stewart and Moore [6] found that the Jedrzejewska method produced accurate results for cement and lime mortars, as well as containing pozzolanic and roman cements. The procedure correctly measured the carbonates, sand, and solubles resulting from each mortar, although the method does not identify mortar or binder by type. The same study found that the Cliver method incorrectly identified portland cement components in lime mortars containing clay and pozzolanic materials due to the color produced by the residue.

LABORATORY SURVEY

A limited survey of United States laboratories was conducted to determine the state of practice of mortar identification, as well as identify costs and approximate completion timeframe, if available. A summary of these survey results is presented in Table 1.

Table 1. Summary of Laboratory Survey Results.

	Test Performed	Cost (2011 $ US)	Timeframe
Laboratory A	ASTM C1324 Chemical Only	$1,250	2 Weeks
Laboratory B	ASTM C1324 Petrography Only	$1,250	2 Weeks
Laboratory C	ASTM C1324 Petrography Only	$750	-
Laboratory D	ASTM C1324	$2,300	-
Laboratory E	ASTM C1324	$1,500	3 to 4 Weeks
Laboratory F	ASTM C1324 Petrography Only	$1,150	-
Laboratory G	ASTM C1324	$1,250	-
Laboratory H	ASTM C1324	$1,500	8-10 Business Days
Laboratory I	Middendorf Method	$550	1-2 Weeks
Laboratory J	ASTM C1324	$2,500	2 Weeks
Laboratory K	ASTM C1324	$1,300	1 Week
Laboratory L	ASTM C1324	$2,100	3 to 4 Weeks
Laboratory M	ASTM C1324 Including Custom Mortar for Use	$1,495	-

The vast majority of laboratories surveyed which perform mortar analysis use the ASTM C1324 method or at least the chemical or petrographic portion of the procedure. The insoluble residue and soluble silica sub-procedure of the method described by Middendorf was the only other method in use by the laboratories surveyed which identifies binder component proportions.

Among those laboratories surveyed, costs to perform the ASTM C1324 procedure varied by up to 100%. The costs associated with performing only the chemical or petrographic analysis portion of ASTM C1324 were lower. Expectedly, the costs associated with the less complex analysis methods were significantly lower among the laboratories surveyed. The cost associated with performing the sub-procedures of the Middendorf method is significantly lower than the ASTM C1324 procedure.

TEST METHOD VERIFICATION

Chemical analysis using an adaptation of the insoluble residue and soluble silica sub-procedure adapted from the Middendorf method was carried out on 7 lab-prepared mortar samples with known component proportions as shown in Table 2. Testing was intended to determine if this method is sufficiently accurate to provide repair mix formulation data for hardened mortar material.

Table 2. Component Proportions by Mortar Type.

Standard Mortar Type	Volumetric Proportions		
	Portland Cement	Lime	Sand
Cement-Sand	1	0	3
M	3	1	12
S	2	1	9
N	1	1	6
O	1	2	9
K	1	3	10
Lime-Sand	0	1	3

Crushed and dried mortar samples were digested using a Hydrochloric acid solution to dissolve the binder. The sand content was obtained from the undigested aggregate, while further chemical analysis was performed on the dissolved binder solution. Subsequent digestion and high temperature ignition yielded the amount of soluble silica in each sample, used to calculate the content of portland cement present. Lime was assumed to make up the remainder of binder content. The quality of the results obtained from an acid digestion of mortar is dependent on the nature of the aggregate present in the mortar. The presence of calcareous aggregates or impurities in the mortar can cause misleading results. The samples used in this study, therefore, only contained silica sand aggregate.

The component proportions obtained from chemical analysis were compared to those used to make each type of mortar using ASTM C1324 material densities, listed in Table 3, to calculate weight percentages. The results of chemical analysis for each type of mortar compared with the known proportions used to make the samples are shown in Table 4. The comparison of analytical results to the actual material proportions used in each mortar mix are presented in Figure 1 and Figure 2 for aggregate content and binder content, respectively.

Table 3. ASTM C1324 Material Densities of Mortar Components.

Material	ASTM Material Density kg/m^3 (lb/ft^3)
Portland Cement	1510 (94)
Lime	640 (40)
Sand	1280 (80)

Table 4. Results of Chemical Analysis Compared to Actual Component Proportions.

Mortar Type	Portland Cement Content			Lime Content			Sand Content		
	Actual (%)	By Analysis (%)	Error (%)	Actual (%)	By Analysis (%)	Error (%)	Actual (%)	By Analysis (%)	Error (%)
Cement	28.1%	29.0%	0.9%	0%	0%	0.0%	71.9%	72.3%	0.4%
M	22.0%	18.6%	-3.4%	3.1%	7.9%	4.8%	74.9%	73.5%	-1.4%
S	19.8%	17.1%	-2.7%	4.2%	6.0%	1.7%	75.9%	76.9%	1.0%
N	15.3%	11.4%	-3.9%	6.5%	10.3%	3.8%	78.2%	78.3%	0.1%
O	10.5%	8.1%	-2.4%	8.9%	11.7%	2.8%	80.5%	80.2%	-0.3%
K	9.3%	6.7%	-2.6%	11.8%	14.8%	3.0%	78.9%	78.5%	-0.4%
Lime	0%	0.5%	0.5%	14.3%	13.5%	-0.8%	85.7%	86.0%	0.3%

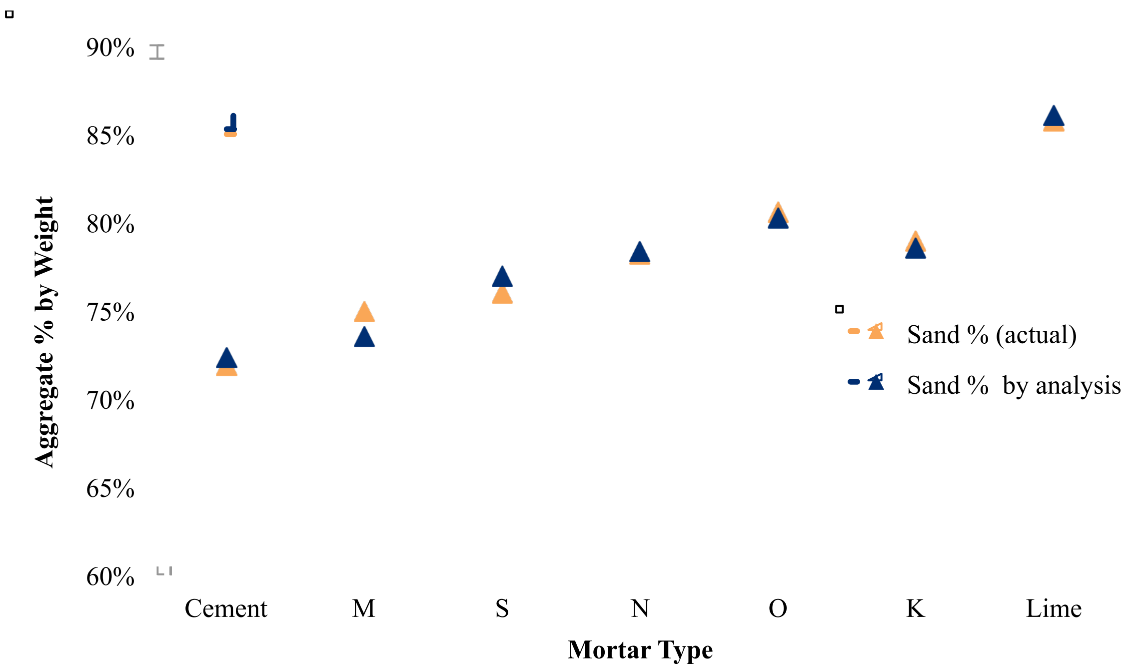

Figure 1. Sand Content Compared to Analysis Result by Mortar Type.

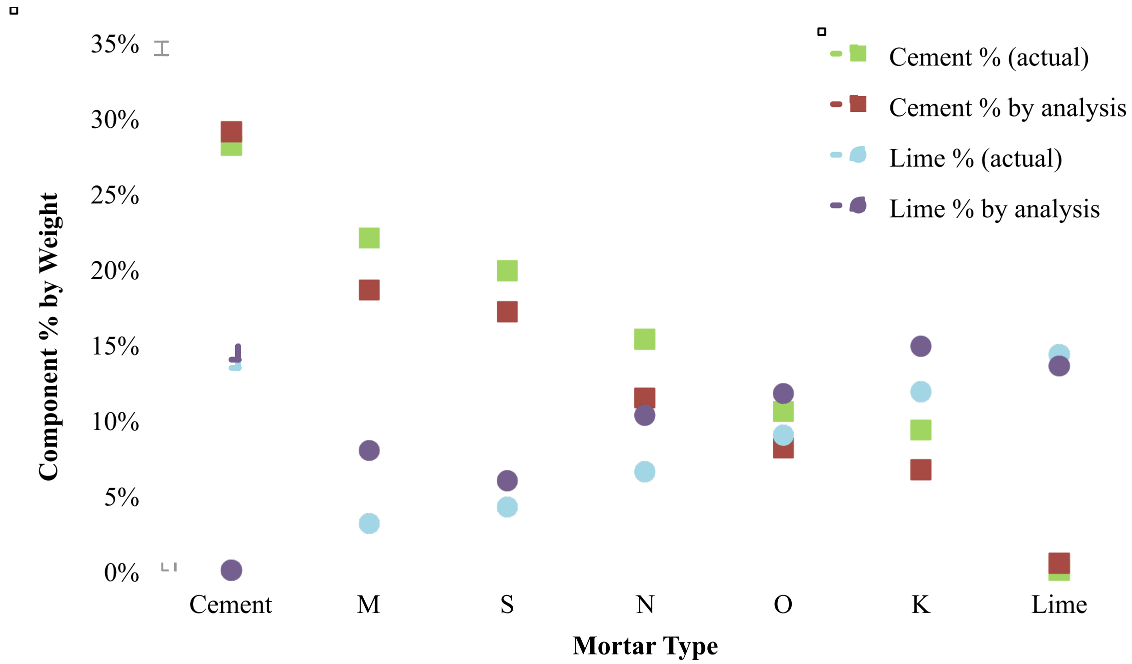

Figure 2. Binder Component Content Compared to Analysis Result by Mortar Type.

Laboratory trials with mortars of known proportions have shown that this method is capable of accurately predicting mortar portland cement content within 0.5% to 4%, lime content within 0 to 5%, and sand content within 0 to 1%. Furthermore, correction factors developed as a result of these trials can be applied to increase the accuracy of the results. The Middendorf method can be effectively used to characterize existing mortars by proportion and type for silica sand mortars. In conjunction with sieve analysis and further ongoing development to account for the effects of other cement types such as masonry cements, as well as admixtures and pozzolans, this relatively inexpensive method may be used to recommend repair mortars for existing and historic masonry structures.

CONCLUSIONS

A review of historical and modern mortar analysis methods showed that despite the existence of several methods to determine the components of masonry mortars, variability of materials and workmanship in masonry construction causes complications when interpreting results. The method used for sampling, the existence of previous repairs, and supplemental materials used in mortar mixes will all affect analysis results. Additionally, each analysis method reviewed contained some inherent limitations to its accuracy or applicability. All analysis methods recommended the use of supplemental information from other types of examination such as petrography, and as much historical knowledge as possible about the masonry construction to successfully characterize mortars. A single chemical analysis technique, especially acid digestion, cannot be applied in every case, but is useful under the right circumstances, such as when the aggregate is acid-insoluble. Petrographic examination is nearly always recommended to accompany chemical analysis of mortar samples.

A limited survey of US laboratories found that ASTM C1324 or either the chemical or petrographic analysis portions of ASTM C1324 were the most commonly used methods for mortar characterization.

Accurate results were obtained for a set of mortar samples with known proportions using the less expensive and less dangerous insoluble residue and soluble silica sub-procedures of the Middendorf method. However, one chemical analysis method should not be applied to all situations. Knowledge of local sand materials, geography, building history, as well as the ultimate goal and use of the results should be carefully considered when selecting a test method and interpreting results.

The recently developed ASTM C1713, "Standard Specification for Mortars for Repair of Historic Masonry" [7] allows repair mortars for historic masonry to be specified by proportions or by properties. The standard specification also allows for the use of various types of binder materials, allowing more flexibility in repair mortars than given by ASTM C270. The inception of this standard allows a wider range of compatible materials for use to match existing mortars based on the results of analysis. The result may be an increase in the need for identification of chemical and mineralogical components, as well as place more emphasis on matching the properties of existing mortars such as strength, air content, and vapor permeability.

REFERENCES

1. ASTM Standard C1324, (2010) "Standard Test Method for Examination and Analysis of Hardened Masonry Mortar" ASTM International, West Conshohocken, PA, DOI: 10.1520/C1324-10.
2. Cliver, B. (1974) "Tests for the Analysis of Mortar Samples" Bulletin of the Association for Preservation Technology, Vol.6, No. 1, pp. 68-73.
3. Jedrzejewska, H. (1960) "Old Mortars in Poland: A New Method of Investigation" Studies in Conservation, Vol. 5, No. 4, pp. 132-138.
4. Middendorf, B., Hughes, J.J., Callebaut, K., Baronio, G. and Papayanni, I. (2004) "Chemical Characterization of Historic Mortars" Characterisation of Old Mortars with Respect to their Repair - Final Report of RILEM TC 167-COM.
5. Powers, L., Coleman, A., and Papas, S. (2007) "A Discussion of the Benefits and Problems of ASTM C 1324 for Analyzing Hardened Masonry Mortars" Journal of ASTM International, Vol. 4, No. 2.
6. Stewart, J. and Moore, J. (1982) "Chemical Techniques of Historic Mortar Analysis" Bulletin of the Association for Preservation Technology, Vol. 14, No. 1, pp. 11-16.
7. ASTM Standard C1713, (2012) "Standard Specification for Mortars for the Repair of Historic Masonry" ASTM International, West Conshohocken, PA, DOI: 10.1520/C1713-12.