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ORIGINAL ARTICLE

Determination of $CaCO_3$ and SiO_2 content in the binders of historic lime mortars

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Abstract The binders of historic mortars composed of small grain sized silica (SiO_2) and carbonated lime ($CaCO_3$) are considered as the main part that give hydraulic character and high strength to the mortar. In this study, FTIR, SEM–EDS, LIBS and XRD spectroscopy were used to find out the weight ratios of $CaCO_3$ to SiO_2 in the binders of historic lime mortars. For this purpose, a series of pure calcium carbonate and silica mixture were prepared in ten combinations in varying ratios from 0.5 to 5. Calibration curve was prepared for each analysis by plotting the peak area or intensity ratios of $CaCO_3$ to SiO_2 versus the weight ratios of $CaCO_3$ to SiO_2. A good linear correlation coefficient was obtained for each analysis respectively. The analyses were then tested on the binder of the Roman mortar samples. The results indicated that FTIR, SEM–EDS and LIBS spectroscopy are convenient tools to determine the weight ratios of $CaCO_3$ to SiO_2 in the binders of mortars. But XRD spectroscopy is not convenient for quantitative analysis of binders due to the presence of varied amounts of amorphous or poor crystalline silica in their compositions.

Keywords Historic mortar · Binder · Calcite · Silica · FTIR · SEM–EDS · LIBS · XRD

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1 Introduction

Lime mortars have been widely used from the Roman period until the invention of modern cement by the start of the Industrial Revolution around 1800 [1].

They are manufactured using lime as binder and aggregates as filling materials. They can be classified as non-hydraulic and hydraulic [15]. Non-hydraulic ones are produced by using lime with inert aggregates and harden by the evaporation and carbonation of lime due to the carbon dioxide in the air. Hydraulic ones can be produced either by using hydraulic lime with inert aggregates or lime with pozzolanic aggregates [15]. Pozzolanic aggregates are composed of amorphous silicates which react with lime in the presence of water at ambient temperatures and form insoluble calcium silicate hydrates [15]. Hydraulic lime mortars harden by carbonation of lime and the reaction between lime and pozzolanic aggregates or the formation of hydraulic phases in the presence of water [15].

Pozzolanic aggregates can be classified as natural pozzolans and artificial pozzolans [15]. Natural pozzolans are generally of volcanic origin such as

volcanic ashes, tuffs, pumice etc. [9]. The first known example of mortars produced by using lime and natural pozzolans was the waterside building in the harbour of Puteoli in Campania [22]. Natural pozzolans were widely used in many Roman structures such as Pantheon, Colleseum, Tournai Cathedral, Domitilla catacombs, Serapis Temple and in the construction of many buildings at different cities [2, 8, 10, 16, 25]. Artificial pozzolans are ceramic materials like crushed bricks and tiles. They are produced by heating natural clays between 450 and 800°C [13]. They were mostly used in the mortars of cisterns, aqueducts, bridges and bath buildings [6, 19, 20, 26].

The high silica content, the small grain size and the high specific surface area enhance the reactivity of pozzolans with lime and provide high strength to the mortars [7, 21]. Hence, fine mortar matrices (<63 μm) composed of small grain sized silica and carbonated lime called as "binder" was considered as the main part that gave high strength to mortars [3, 17].

Mineralogical compositions of binders constituted of many studies to define the mortar characteristics [3, 4, 20]. Mineralogical compositions of binders were determined by X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR) analyses [18]. XRD is suitable for identification of minerals in crystalline structure. Amorphous substances and organic additives can not be detected by XRD. However, FTIR can be used for the identification of amorphous minerals and organic additives, and also for their quantification.

Scanning electron microscope (SEM) is used for determination of microstructural properties of binders. It is also used for determination of chemical compositions if it is equipped with X-ray energy dispersive system (EDS).

X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) are more precise methods than SEM–EDS for determination of chemical compositions of binders. But these analyses need experience, complex sample preparation, and takes long time [24]. Moreover, binder analyses do not require the use of very sensitive analysis due to their non-homogeneous characteristics.

Laser induced breakdown spectroscopy (LIBS) [23], has emerged in the last two decades as an elemental analysis technique for the determination of chemical composition of the various cultural heritage objects [11]. LIBS, with its ability to make multielement and on-line analysis, offers several advantages over commonly employed atomic spectrometric techniques.

In this study, a relatively fast and easy method for the quantitative determination of $CaCO_3$ and SiO_2 content in binder compositions is proposed by using FTIR, LIBS, SEM–EDS and XRD analyses.

2 Experimental

2.1 Preparation of standard $CaCO_3$ and SiO_2 mixtures

In this study, a series of standard mixtures of $CaCO_3$ (*Carlo Erba 327059*) and SiO_2 (*Sigma-Aldrich S5631*) were prepared in ten combinations of varying weight ratios from 0.5 to 5.0, to generate calibration curves for FTIR, SEM–EDS, XRD and LIBS analysis. These ratios are nearly equivalent to $CaCO_3/SiO_2$ ratios that are usually found within the compositions of the binders of the historic mortars [14, 19, 20]. The samples were prepared by gently mixing the stoichiometric proportions of two components in an agate mortar.

2.2 Preparation of Roman mortar samples

The methods proposed by FTIR, LIBS, SEM–EDS, XRD analysis were applied on eight mortar samples collected from Roman buildings in Nysa and Aigai archaeological sites (Turkey). First phase of the study was to investigate the microstructural characteristics of the binders by SEM analysis on fractured samples surfaces. For the XRD, FTIR, SEM–EDS and LIBS analyses, mortar matrices which are free from coarse grained aggregates were gently ground into powder form and then sieved to obtain a less than 1/16 mm-diameter fraction [19, 20]. XRD, SEM–EDS, FTIR and LIBS analysis were then carried out for the prepared binder samples to find out the weight ratios of $CaCO_3$ to SiO_2 by using calibration equations obtained from standard mixtures analyses.

2.3 FTIR analysis

For FTIR analysis, a few milligram of standard mixtures and the powdered binders of the Roman

mortar samples were dispersed in about 80 mg of spectral grade potassium bromide (KBr) and pressed into pellets by about 10 tons/cm^2 pressure. Spectral measurements were carried out on a Spectrum BX II FTIR spectrometer (Perkin Elmer) that was operated in the absorbance mode. Spectra were normally acquired with the use of 4 cm^{-1} resolution yielding IR traces over the range of 400–4,000 cm^{-1}. All data were corrected for pure KBr spectrum. Three measurements were taken for each sample. The average of the three measurements was used for preparing the calibration curve.

The area of the absorbance peaks of $CaCO_3$ at 1,432 cm^{-1} and SiO_2 at 1,100 cm^{-1} were used to plot calibration curves against their standard weight ratios.

2.4 SEM–EDS analysis

SEM–EDS analyses were carried out on pellets prepared by pressing powder samples under 10 tons/cm^2 pressures. Philips XL 30S FEG SEM coupled with X-Ray EDS was used. Analyses were carried out on three different 0.63 mm^2 areas of the pellets. The average of the three results was used for preparing the calibration curve and the calculations of the weight ratios of $CaCO_3$ to SiO_2 in the binders of the mortar samples.

2.5 LIBS analysis

The elemental compositions of the standard mixtures and the binders of the mortars samples were determined by LIBS. For this analysis, pressed powder pellets were used. LIBS analyses were performed by measuring the spectral line intensities of the neutral calcium and silicon emitted from the plasma produced by a Q-switched Nd:YAG laser. Each data is produced from the addition of ten consecutive single laser pulses. Plasma emission was detected by an echelle type spectrograph (200–850 nm spectral range) equipped with an ICCD detector.

2.6 XRD analysis

XRD patterns of the standard mixtures and the powdered binders of the Roman mortars were obtained by using a Philips X-Pert Pro X-ray Diffractometer. The instrument was operated with CuKα radiation with Ni filter adjusted to 40 kV and 40 mA in the range of 2–60° with a scan speed of 1.6° per minute. The Rietveld method was used to quantify the $CaCO_3$ and SiO_2 content in the standard mixtures and in the binders of the mortar samples by using X'Pert High Score Plus analysis software. The weight ratios of $CaCO_3$ to SiO_2 found by Rietveld method were used to generate a calibration curve.

3 Results and discussions

3.1 FTIR, SEM–EDS, LIBS and XRD analysis of standard mixtures of $CaCO_3$ and SiO_2

FTIR, SEM–EDS, LIBS and XRD analysis of standard mixtures were carried out and the calibration curves were generated. Details of each analysis are given below.

3.1.1 FTIR analysis

FTIR spectra of standard mixtures showed the characteristics of $CaCO_3$ and SiO_2 bands. The main $CaCO_3$ bands at 1,432 cm^{-1} (C–O stretching), 876 and 712 cm^{-1} (C–O bending) and SiO_2 bands at 1,100 cm^{-1} (Si–O stretching) and 470 cm^{-1} (Si–O bending) were indicated (Fig. 1). The FTIR spectrum of the $CaCO_3$ and SiO_2 mixtures demonstrated that there is no interference between the bands of the two components. Hence, in the preparation of calibration curves, stretching bands of $CaCO_3$ and SiO_2 were used. The weak bands of bending vibrations of $CaCO_3$ and SiO_2 were not used due to low sensitivity values when compared to the bands of the stretching ones. As it is seen in Fig. 2, calibration curve showed the linear relationship with good correlation coefficient. The error bars shown on the graph were obtained from the standard deviation of three replicate FTIR measurements and the error in terms of the relative standard deviation (RSD) of measurements were calculated to be around 8%.

3.1.2 SEM–EDS analysis

The chemical compositions of the standard mixtures were determined by SEM–EDS analysis and the weight ratios of $CaCO_3$ and SiO_2 were used in the preparation of the calibration curve. Calibration curve showed the linear relationship with good correlation

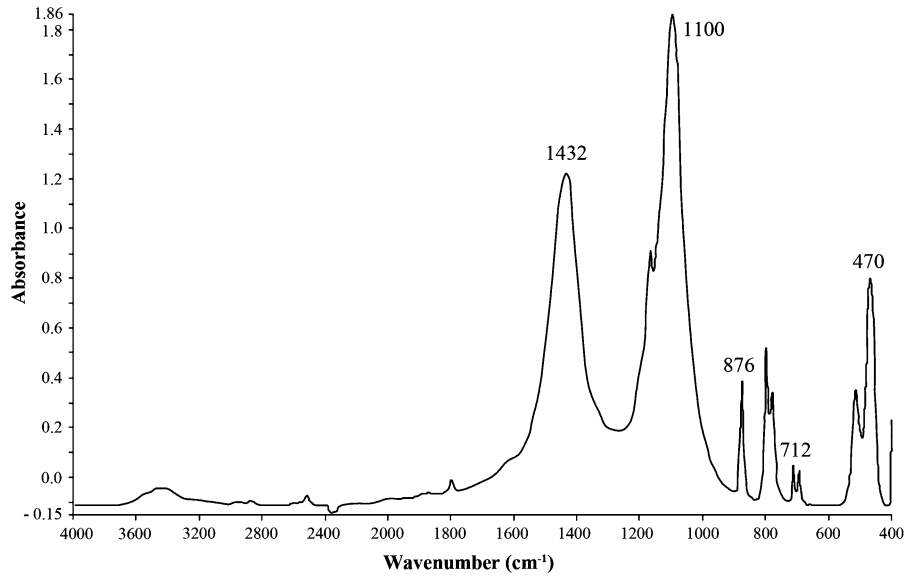

Fig. 1 FTIR spectra of a standard mixture ($CaCO_3$/SiO_2: 1/1)

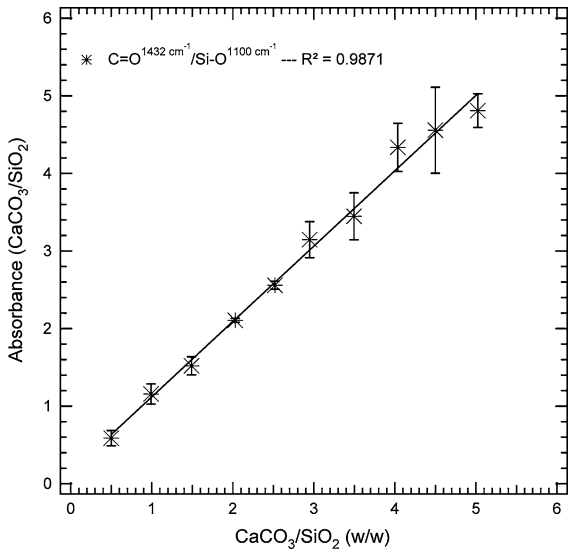

Fig. 2 Calibration curve for FTIR analysis results of standard mixtures

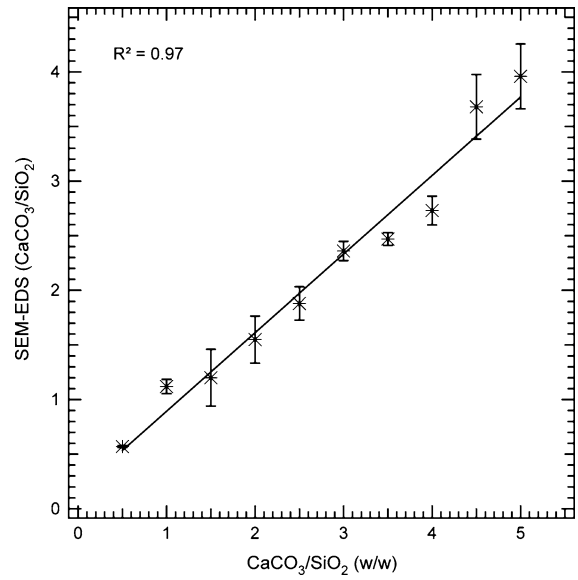

Fig. 3 Calibration curve for SEM–EDS analysis results of standard mixtures

coefficient (Fig. 3). The error bars shown on the graph were obtained from the standard deviations of the measurements, and the average error (RSD) was estimated to be around 7.7%.

3.1.3 LIBS analysis

The LIBS spectra of standard mixtures of $CaCO_3$ and SiO_2 showed neutral Ca(I) at 504.2, 534.9, 714.8 and 720.2 nm and neutral Si(I) at 288.15 nm (Fig. 4). They were used to generate calibration curves against their weight ratios. The calibration graphs present linear relationships in signal intensities versus Ca/Si weight ratios with good correlation coefficients (Fig. 5). However, Ca(I) line emission at 504.16 nm presents higher sensitivity compared to other Ca(I) emissions at 714.8 and 720.2 nm due to the higher spectral sensitivity of the spectrograph at that wavelength. The error bars shown in the graph were

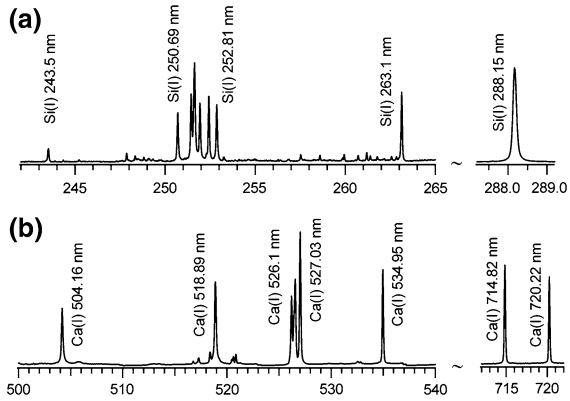

Fig. 4 LIBS spectra of a standard mixture ($CaCO_3/SiO_2$: 1/1)

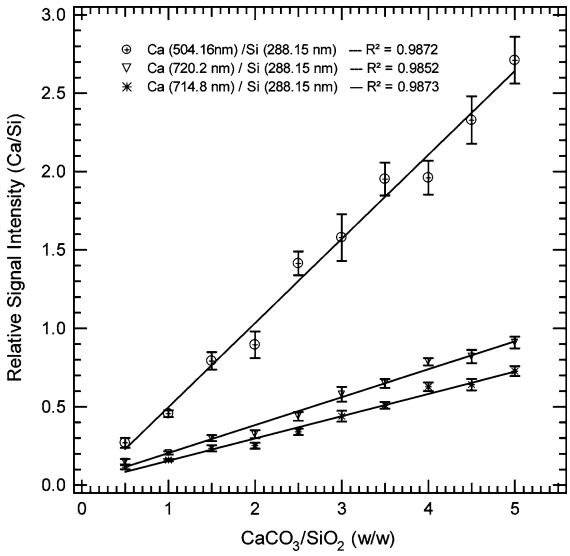

Fig. 5 Calibration curve for LIBS analysis results of standard mixtures

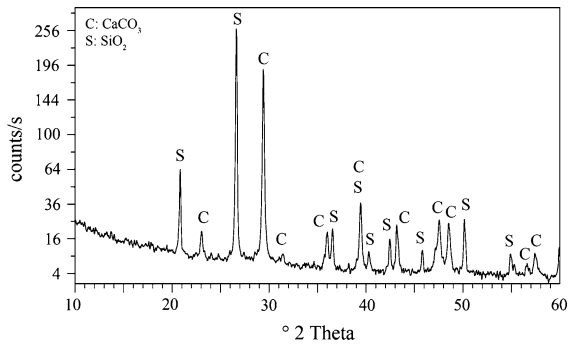

Fig. 6 XRD pattern of a standard mixture ($CaCO_3/SiO_2$: 1/1)

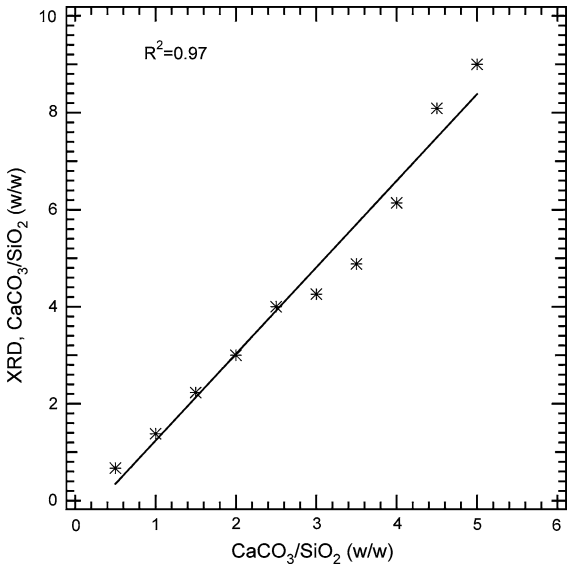

Fig. 7 Calibration curve for XRD analysis results of standard mixtures

obtained from the standard deviation of ten sequential LIBS measurements, and the error was estimated to be around 10%.

3.1.4 XRD analysis

In the XRD patterns of the standard samples, the main $CaCO_3$ peaks at 2θ of 22.9°, 29.3°, 39.3°, 43.1°, 47.4° and SiO_2 peaks at 2θ of 22.9°, 29.3°, 39.3°, 43.1°, 47.4° were indicated (Fig. 6). The $CaCO_3$ and SiO_2 peaks were then analyzed using X'Pert High Score Plus analysis software to found weight percent of $CaCO_3$ and SiO_2 in the mixtures by Rietveld method. The weight percent of $CaCO_3$ and SiO_2 were used to generate a calibration curve against their standard concentration ratios (Fig. 7). As it is seen in Fig. 7, calibration curve showed the linear relationship with good correlation coefficient. The observed errors ranged between 7 and 10%.

3.2 Determination of $CaCO_3/SiO_2$ ratio in the binders of Roman mortar samples by FTIR, SEM–EDS, LIBS and XRD analysis

The binders of the mortars collected from Roman buildings were mainly composed of $CaCO_3$ and SiO_2. They are hard, fine grained and compact due to strong adherence between silica and lime.

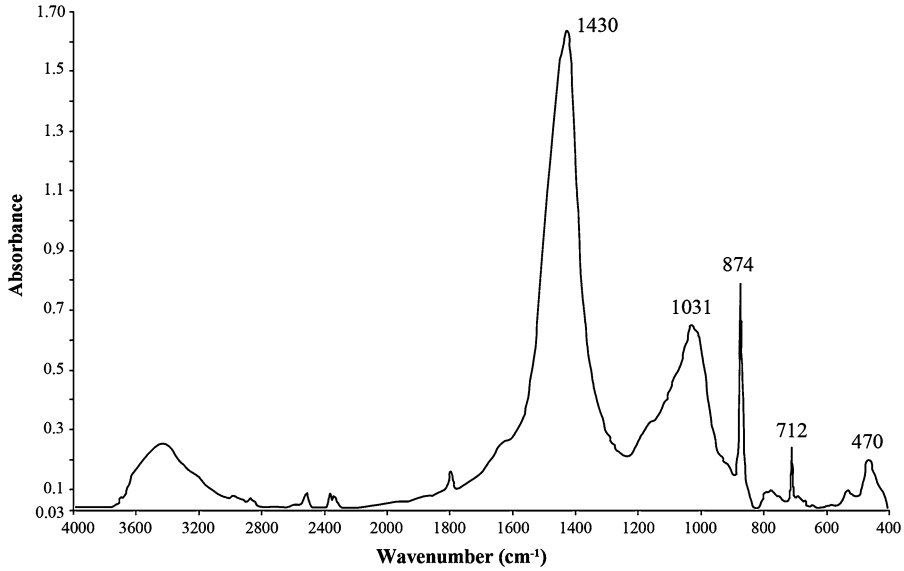

Fig. 8 FTIR spectrum of a Roman binder sample (N2)

3.2.1 *FTIR analysis*

The FTIR spectrum of the binders showed the bands of stretching and bending vibrations of $CaCO_3$ ($\sim$1430, 874 and 712 cm^{-1}) and SiO_2 ($\sim$1,031 and $\sim$470 cm^{-1}) (Fig. 8). The areas of absorption of $CaCO_3$ (1,430 cm^{-1}) and SiO_2 (1,031 cm^{-1}) were used in the determination of weight ratios of $CaCO_3$ to SiO_2 by using the line equation of FTIR analysis (Fig. 2). The results indicated that the $CaCO_3/SiO_2$ ratio was between 0.5 and 2.2 in the binders of the mortars compositions (Table 1).

Table 1 $CaCO_3/SiO_2$ ratio in the binders of Roman mortar samples by FT-IR, SEM–EDS, XRD and LIBS analysis

Sample	Definition	$CaCO_3/SiO_2$			
		FTIR	SEM–EDS	LIBS	XRD
A1	Stage building of theatre (Aigai)	1.9	1.9	2.2	0.7
A2	Vomitorium of theatre (Aigai)	0.6	0.6	0.7	6.0
A3	Terrace wall of agora (Aigai)	1.2	1.3	1.5	20.5
A4	Stadium, terrace wall (Aigai)	1.3	1.6	1.0	18.4
N1	Library, wall (Nysa)	0.6	0.5	0.7	1.8
N2	Building, vault (Nysa)	2.2	2.2	1.6	3.5
N3	Bath, arch (Nysa)	0.6	0.8	0.8	1.8
N4	Bath, arch (Nysa)	0.5	0.6	0.6	1.7

Table 2 Elemental compositions of binders of Roman mortars

Sample	Na_2O	K_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
A1	1.6 ± 0.2	1.7 ± 0.1	42.5 ± 1.8	2.2 ± 0.1	40.4 ± 1.2	9.4 ± 0.1	1.7 ± 0.4	0.6 ± 0.2
A2	2.2 ± 0.6	2.0 ± 0.2	19.7 ± 0.7	4.4 ± 0.7	56.9 ± 1.1	12.4 ± 0.7	2.1 ± 0.2	0.4 ± 0.3
A3	1.9 ± 0.1	2.2 ± 0.3	32.6 ± 0.6	2.5 ± 0.4	46.5 ± 0.8	11.7 ± 0.4	2.1 ± 0.4	0.5 ± 0.1
A4	1.2 ± 0.0	2.4 ± 0.1	39.1 ± 0.6	3.2 ± 0.3	42.4 ± 0.7	9.0 ± 0.3	2.4 ± 0.4	0.4 ± 0.0
N1	2.2 ± 0.2	2.3 ± 0.3	15.7 ± 1.4	3.5 ± 0.3	55.2 ± 0.7	18.3 ± 0.6	1.8 ± 0.1	1.1 ± 0.2
N2	2.2 ± 0.6	1.9 ± 0.1	41.5 ± 4.9	4.6 ± 1.0	33.9 ± 2.9	12.1 ± 1.1	3.3 ± 1.4	0.5 ± 0.5
N3	1.9 ± 0.2	2.8 ± 0.2	22.4 ± 0.3	3.7 ± 0.3	51.0 ± 1.4	13.2 ± 0.3	4.1 ± 1.4	0.9 ± 0.9
N4	2.1 ± 0.3	2.0 ± 0.2	18.1 ± 1.9	3.7 ± 0.5	54.4 ± 2.3	15.3 ± 1.1	3.0 ± 1.8	1.6 ± 0.5

3.2.2 SEM–EDS analysis

The elemental compositions of the binders expressed as the percent oxide were determined by SEM–EDS analysis. The results indicated that binders contain high amounts of CaO and SiO_2 and low amounts of Al_2O_3 and Fe_2O_3 (Table 2). The percent CaO and SiO_2 were used in the determination of weight ratios of $CaCO_3$ to SiO_2 by using the line equation of SEM–EDS analysis (Fig. 3). The results indicated that the $CaCO_3/SiO_2$ ratio was between 0.5 and 2.2 in the binders of the mortars compositions (Table 1).

3.2.3 LIBS analysis

LIBS spectrum of the binders showed the strong Ca and Si lines together with weak Mg and Al lines. A full and detailed spectra of the sample (N2) is shown in Fig. 9. The line intensities of Ca observed at 504.16 nm and Si at 288.15 nm were used in the

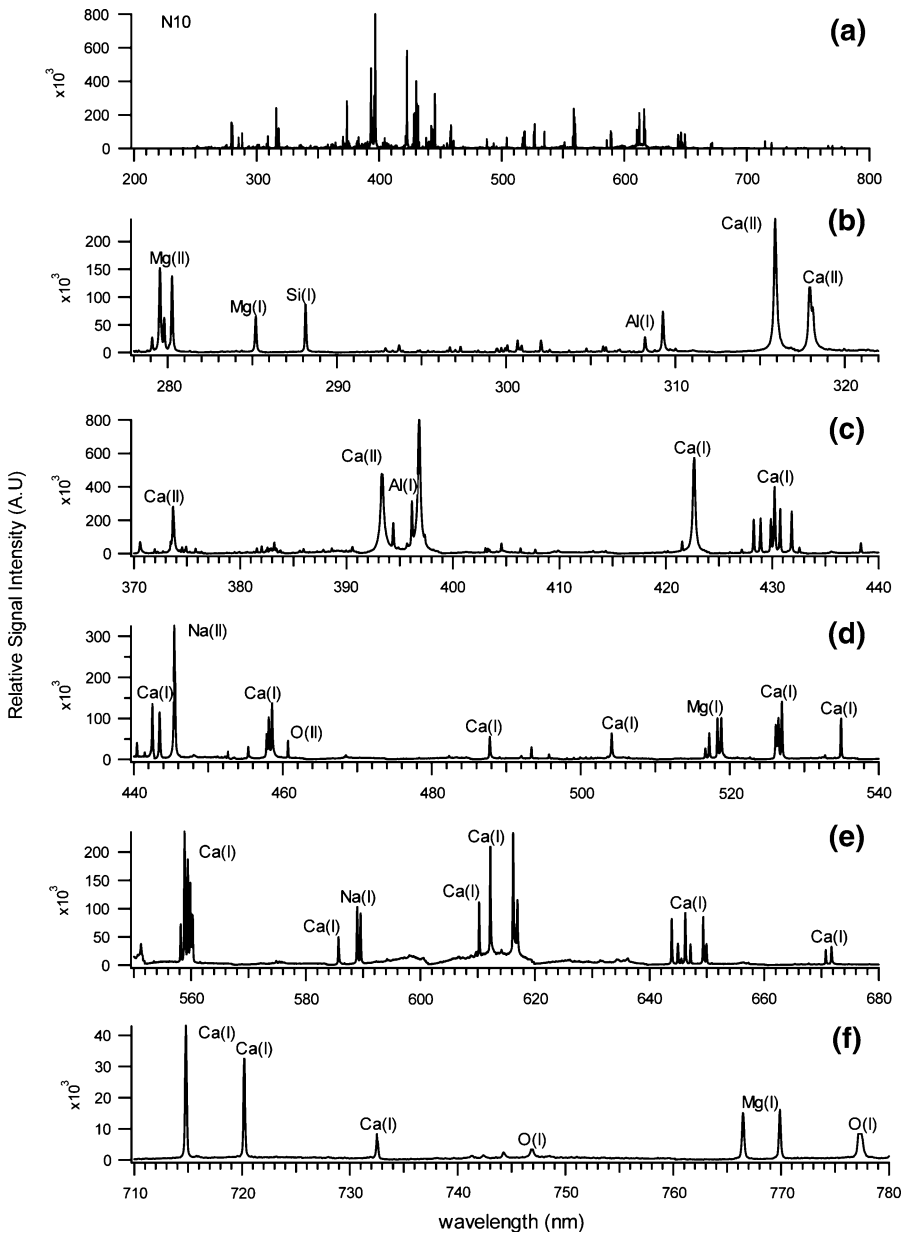

Fig. 9 LIBS spectrums of a Roman binder sample (N2)

determination of the weight ratios of $CaCO_3$ to SiO_2 in the binders of the mortars by using the line equation of LIBS analysis (Fig. 5). The results showed that the $CaCO_3/SiO_2$ ratio was between 0.6 and 2.2 in the binders of the mortars compositions (Table 1).

3.2.4 XRD analysis

XRD patterns of the binders of the mortars indicated that they were mainly composed of $CaCO_3$ and SiO_2 (Fig. 10). Their patterns were analyzed by Rietveld method and their weight ratios were determined by using the line equation of standard mixtures of $CaCO_3$ and SiO_2 (Fig. 7). XRD analysis did not show consistent results with the ones found by FTIR, SEM–EDS and LIBS analysis (Table 1). This can be explained due to the existence of various amounts of amorphous or poor crystalline silica in their composition which cannot be detected by XRD analysis.

3.3 Comparison of the methods

The methods proposed in this study gave satisfactory results in the determination of weight ratios of $CaCO_3$ to SiO_2 for standard mixtures. The analysis results of Roman binders indicated that these analyses can also be used to evaluate the weight ratios of $CaCO_3$ to SiO_2 for historic lime mortar binders except for XRD analysis due to the existence of amorphous or poor crystalline silica in the binder. As it seen in Fig. 11, the results obtained by FTIR, SEM–EDS and LIBS appear to be in good agreement. However, there are some factors that influence the analysis. Particle size, polymorphism and orientation are the main factors that affect the quantitative IR analysis. The effects of

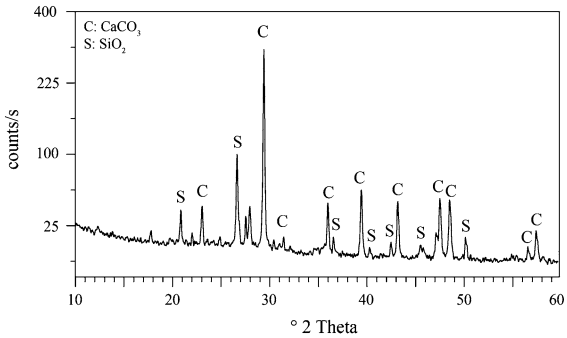

Fig. 10 XRD spectrum of a Roman binder sample (N2)

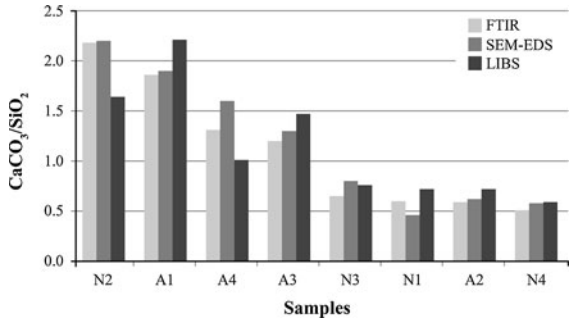

Fig. 11 Weight ratios of $CaCO_3/SiO_2$ obtained by FTIR, SEM–EDS, LIBS methods in binders of Roman mortars

polymorphism and orientation are negligible for the analysis of inorganic substances [5]. Particle size of the sample is also significant, but it can be eliminated by well grinding processes.

In the quantitative analysis of the substances by SEM–EDS and LIBS analysis, the samples must be in small analytic volume and homogeneous on the microscopic scale [12]. Hence, in the quantification of carbonated lime and silica content in the historic mortars, the samples must be well ground and homogenized.

4 Conclusions

In this study convenience of FTIR, SEM–EDS, LIBS and XRD analysis for the determination of weight ratios of $CaCO_3$ to SiO_2 in the binder parts of historic lime mortars was investigated. The results showed that the FTIR, SEM–EDS and LIBS analysis can be safely used to determine the lime and fine silica content in the binder of historic lime mortars. But, XRD analysis can not be used for historic mortars due to the varied amounts of amorphous or poor crystalline silica in their compositions.

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