Chemical Characterization of a Tower in Monterubiaglio, Umbria (Italy) Utilizing Portable X-Ray Fluorescence Spectrometry

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Objective
The mortar on two faces of a stone masonry tower in Monterubiaglio, Umbria was analyzed using portable X-ray fluorescence spectrometry (pXRF). From an autopsy of the building the lower part is of Roman technique and the upper is of medieval engineering (Figures 1 & 2). The objective of this research was to:

• Determine whether mortar identified as visually different also differed chemically
• Assuming chemical differences did exist, determine the specific elements that did differ between the two mortars
• Compare the tower mortar to that found at the excavation site (Coriglia)

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Instrumentation & Procedure
A Bruker AXS Tracer III-SD (Kenneswick, WA) pXRF was used for analyses.

• Rh target X-ray tube excitation source; 40 kV excitation, 21 μA tube current
• Green Filter composed of 0.006 in Cu, 0.001 in Ti, and 0.12 in Al, were used for all analyses
• Signal was collected for 120 seconds for each analysis in triplicate at each location on the tower.
• Smooth, flat sample locations were used for the analyses.
• The chosen sample locations were cleaned with a brush, marked, and digitally photographed; GPS coordinates were recorded (Figures 3 & 4).
• Data were collected for cement reference materials throughout mortar analyses to assure quality control. The reference materials were: SRM 1881a Portland Cement and SRM 1886a Portland Cement (National Institute of Standards and Technology, Gaithersburg, MD).

Background
The samples explored in this research were located on a town square tower in Monterubiaglio near Orvieto, Italy. The tower was part of the castle that was in the possession of the Monaldeschi della Cervara family from 809 until 1698. The records indicate that the base of the tower was in good shape in 809 and was recognized as an old Roman tower of unspecified date. No documented repairs have been made to areas pertaining to the study. The most extensive repair of the tower was reported in 1299 when Cardinal Theodoric ordered the building of a defensive wall into the base of the tower. He also expanded the piazza at the base (fundo la torre de Monterubiallo) which would indicate work on the substructure of the tower below its Roman phase. The tower and castle were then passed to the current family whose archives are confidential. The next major event in its history was during World War II when the castle was bombed by the Allies. There was substantial damage, but the lower sections remained completely intact. These documentation assure that the Roman portion of the tower was preserved and could be analyzed for composition and then compared to the other sections and the excavation site.

Results & Discussion
The 2-dimensional scores plot (Figure 5) shows:

• The Roman mortars on the two different walls are in one cluster showing they are similar in chemical composition.
• The Medieval mortars on the two different walls are in one cluster showing they are similar in chemical composition.
• The Roman mortar and Medieval mortar are in separate clusters showing they are different in chemical composition.

The loadings plot (Figure 6) was used to determine which elements explained the variance for each PC.

PC 1: Sr & Rb  PC 2: Fe  PC 3: Ca

Two-way analysis of variance (ANOVA) with replicates was performed on peak areas (Ca, Cu, Fe, Mn, Pb, Rb, Sr, Zn, and Zr) for the lower and upper:

• Statistically significant difference at 95% confidence
• F_{\text{crit}} = 7.13, F_{\text{calc}} = 3.85, for 32 degrees of freedom

Figure 7 is the overlay of the Roman and Medieval mortar spectra.

• Roman mortar has a significantly higher signal for Ca.
• Medieval mortar has a slightly higher signal for Fe, Sr and Rb.
• Calcium is the major component of mortar in various forms such as calcite, dolomite, and gypsum. The lower calcium signal for the Medieval mortar indicates that non-calcium containing materials are used in higher amounts in the this mortar, possibly as filler.

Figure 8 shows pXRF spectra collected for wall mortars at the Coriglia excavation site. Instrument conditions were identical to those for the tower mortars analyses.

• Mortars from trench C are of similar compositions.
• The Roman Tower mortar is not similar to the Trench C mortars.
• Roman Tower mortar and Trench B mortar.

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