Using field-portable X-ray fluorescence spectrometry to identify the origin of Linqing brick: Considering for impact factors, assessing reliability and providing scientific advices

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Abstract

Linqing brick is very famous in Chinese history. In 2008, "The manufacturing process of Linqing brick" was selected as the intangible cultural heritage list in China. Now in China, how to identify the origin of Linqing brick is an important issue in archeology and architectural history research. It can be used to verify some assumptions about the history of heritage buildings which cannot be solved only by historical documents. It can also be used to study the history of Linqing brick. Field portable X-ray fluorescence spectrometry (FPXRF) can quickly and non-destructively determine the main elements and concentrations of Linqing brick in situ. It may be significant for identifying the origin of Linqing brick. But FPXRF could be affected by many factors and it can only measure the element concentrations of surface. Which method we use can provide the most reliable data is an important issue. The aim of this study was to verify the reliability of FPXRF and to systematically evaluate different influential factors on measurement precision and accuracy, which can help with scientific advice for its use. We set up four experiments to determine the influential factors and assess reliability by cross validation using ICP-OES. Finally, we ensured that the FPXRF was reliable and determined the scientific advice required to use it to measure the main elements and concentrations of Linqing brick.

1. Introduction

Linqing brick is very famous in Chinese history. The main halls and city walls of the Forbidden City, which is the Imperial Palace of the Ming and Qing dynasties, were mainly built with Linqing brick. In the meantime, there are many other architectural heritages mainly built by Linqing brick in China, such as the Temple of Heaven, Ming Tombs, East Qing Tombs and Western Qing Tombs. In 2008, "The manufacturing process of Linqing brick" was selected as the intangible cultural heritage list in China.
Now in China, how to identify the origin of Linqing brick is an important issue in archeology and architectural history research. A small number of Linqing bricks have inscriptions which contain the origin information. Accurately measuring the main elemental concentrations of Linqing brick with inscriptions may be significant for identifying the origin of Linqing brick. Using the elemental information we measured, related inscriptions and mathematical methods can form a set of formulas between origin and elemental information. The formulas can help to identify the origin of most ancient bricks without inscriptions on the cultural heritage buildings. It can be used to verify some assumptions about the history of heritage buildings which cannot be solved only by historical documents. In the meantime, it can also be used to study the history of Linqing brick.

How to quickly and accurately measure the main element concentrations of bricks is an important issue. Currently, in China, the main methods to measure the element concentrations of bricks are laboratory methods such as ICP-OES, ICP-MS, ICP-AES and AAS. If we use traditional methods to make measurements, the bricks must be taken back to the laboratory first and all of these methods are destructive methods. Traditional methods cannot be used for measurements in situ and it is very difficult to perform a large number of sample measurements because they are expensive and complex. For the bricks located in ancient buildings, traditional methods are no longer applicable. In the meantime, bricks located in ancient buildings are of great research value. Using field portable X-ray fluorescence spectrometry (FPXRF), the main element concentrations of bricks can be measured rapidly and it is non-destructive to ancient buildings. Element concentrations can be determined in situ.

FPXRF has already been used in archaeological field. Some scholars have used information of elements to make archaeological lithic sourcing studies [1-5]. Some scholars have been
focused on verifying the reliability of using FPXRF in archaeology [6-10]. Except for that, FPXRF has also been used with other instruments to study diseases of heritage building materials such as bricks and stone masonries [11-16]. We want to use FPXRF to measure the main element concentrations of Linqing brick so that we can use the information of elements to identify the origin of Linqing brick. But FPXRF could be affected by many factors and it can only measure the element concentrations of surface. Which method we use can provide the most reliable data is an important issue. Shackley once encouraged archeologists using FPXRF to take the time to establish a rigorous and consistent analytical protocol through systematic experimentation [17].

In our study, we set up four experiments to assess different influential factors on measurement precision and accuracy when we measured. The reliability was assessed by cross validation using ICP-OES. Finally, we ensured that FPXRF is a reliable technology and determined scientific advice for using it to measure the main element concentrations of Linqing brick.

2. Material And Methods

2.1 The instrument we used

2.1.1 Instrument model

The instrument model was a Niton XL2-960 GOLDD XRF Analyzer. This instrument was equipped with an Ag anode operating at a maximum of 45 kV and 100 uA. The spot size of the emitted X-Ray beam is 8 mm. It could provide a standard analytical range of up to 30 elements from Mg to U.

2.1.2 Theory

The mechanism for X-ray fluorescence of an atom is illustrated in Fig. 2. An inner shell
vacancy is created (by an incident X-ray photon or other phenomena) leaving an electron hole in the inner shell. An outer shell electron falls to fill the inner shell vacancy as the atom relaxes to the ground state. This process gives off photons with energy in the X-ray region of the electromagnetic spectrum, which is equivalent to the energy difference between the two shells [18]. Different photon wavelengths come from different atoms. Therefore, analysis of the wavelengths provides qualitative identification of the element. Then the calibration curve in the instrument can convert the intensity of the photons of the measured elements into the element concentrations.

2.2 Sample and elements we studied

The samples were five Linqing bricks (shown in Table 1 and Fig. 3). For experiment 1 and experiment 2, we used brick 4. For experiment 3, all of the bricks were used. The main elements in our research were Fe, Ca, K, Al, and Si, and their concentrations were higher than 1% (five highest content elements of brick). However, to determine whether FPXRF can be used to measure all the elements of the brick according to evaluation of the measurement precision of each measurement time, the elements we studied in experiment 1 are the 11 highest content elements of bricks whose concentrations were higher than 0.1% (Fe, Ca, K, Al, Si, Ba, Zr, Mn, Mg, Ti, and Cl). The elements we studied in experiment 2 and experiment 3 were the main elements of our research (Fe, Ca, K, Al, and Si).

| Brick   | Inscription information                  | Years  |
|---------|-----------------------------------------|--------|
| Brick1  | Manufactured by Kai Wang in A.D.1645     | A.D.1645 |
| Brick2  | Manufactured by Shougui Guo in A.D.1676  | A.D.1676 |
| Brick3  | Manufactured by Hui Li in A.D.1539       | A.D.1539 |
| Brick4  | Manufactured by Bao Wang in A.D.1549     | A.D.1549 |
| Brick5  | Manufactured by □□ in A.D.1602 (Manufacturer’s name cannot be distinguished) | A.D.1602 |

2.3 Experiment 1: Considering the effect of measurement time on
measurements

To establish the effect of measurement time on precision, brick 4 was measured five times at one point for 60, 90, 120, 150, 180, 210, and 240 s. We measured that point after polishing with a sickle. The relative standard deviation (RSD) for each element at each measurement time was used to determine the effect of measurement times on measurement precision. The US EPA criteria were used to evaluate precision (Table 2).

| Data quality level       | Statistical requirement                                                                 |
|--------------------------|----------------------------------------------------------------------------------------|
| Definitive Q3            | $R^2 = 0.85-1$. Relative standard deviation (RSD) ≤ 10%. Inferential statistics (test for gradient of line $= 1$ and y-intercept $= 0$) must indicate the two data sets are statistically similar (at the 95% confidence level), i.e. relationship $y = x$ accepted. |
| Quantitative screening Q2| $R^2 = 0.70-1$. Relative standard deviation (RSD) < 20%. Inferential statistics indicate the two data sets are statistically different; i.e. relationship $y = mx$ or $y = mx + c$ accepted. |
| Qualitative screening Q1 | $R^2 = \text{less than } 0.70$. Relative standard deviation (RSD) > 20%. Inferential statistics indicate two data sets are statistically different. |

2.4 Experiment 2: Considering the effect of rain on the day of measurement

To establish the effect of rain, we do the following experiments to verify it. Before brick 4 was washed by rain, we take measurements for it. Then we put it in the rain. When the rain was finished, we measured it with FPXRF. We polished the point with a sickle before we begun the measurement stages (before rain and 0 s after rain).

We took measurements under 10 conditions: before rain, 0 s after rain, 1 hour after rain, 2 hours after rain, 3 hours after rain, 5 hours after rain, 7 hours after rain, 9 hours after rain, and 12 hours after rain. Brick 4 was measured five times at one point in each condition for 60 s. The mean concentrations calculated from these five replicates were used for further analysis. The rainfall was 11.2 mm (1 day). The average temperature was 24.3 °C (1 day), and the average humidity was 69.2% (1 day).
2.5 Experiment 3: Considering the effect of surface conditions of the brick on measurements. Providing a surface treatment method and verifying its reliability

To establish the effect of surface conditions on accuracy, as well as propose a method to reduce the error and verify its reliability, we set up two experiments.

2.5.1 Experiment 3 – 1: The uniformity of the element distribution on the brick surface: Comparison of direct measurement vs. measurement after polishing with a sickle

This experiment showed the effect of surface conditions on accuracy, and showed how the error rate will be reduced after polishing with a sickle.

We identified three points on the surface to measure for each brick. The points on each brick were measured under two surface conditions: first, direct measurement (DM); then, measurement after polishing by (MPS). Each point was measured three times for 60 s. The mean concentrations by three replicates were used for further analysis. The uniformity of the element distributions on the brick surfaces was evaluated by the RSD for each element of each brick under two surface conditions using the US EPA criteria (Table 2).

2.5.2 Experiment 3 – 2: The concentration difference between the brick surface and brick interior

This experiment showed the effect of surface conditions on accuracy and verified the reliability of MPS.

For the five bricks that were measured, we cut three fresh sections for each brick. Each section was measured three times for 60 s. The mean concentrations by three replicates were used for further analysis. The elemental concentrations of the three fresh sections were used to compare with the elemental concentrations of the previous surface points
polished by the sickles, which were measured in experiment 3 − 1. The RSD for each element of each brick was used to evaluate the concentration differences between the brick surface and interior using the US EPA criteria (Table 2).

2.6 Cross-validation procedure by ICP-OES

We cut up the five bricks into small pieces and then ground the brick sample into a fine powder less than 150 μm. Then the total microwave digestion was used to digest the sample. 500 mg of sample was placed in a PTFE reactor with 4 mL of HNO₃ (70%), 1 mL of H₂O₂ (20%) and 2 mL of HF (40%). When the foam caused by decomposition of organic matter disappeared, the container was capped and heated in accordance with a three-stage digestion procedure using a microwave digestion instrument called Solutions MD (Beijing Ying'an Meicheng Scientific Instrument company). The heating process included a first step of three minutes to reach 150 °C, a second step of 5 minutes at 180 °C and a third step of 5 minutes to reach 200 °C. After microwave digestion, it was heated in the acid-driven processor. Finally, the digest was transferred into a 50 mL flask and brought to volume with MilliQ water. Subsequently, the diluted digest was analyzed using a PerkinElmer ICP-OES Optima 8300. We performed two measurements for each brick. The mean concentrations calculated from these two replicates were used for further analysis.

3. Results And Discussion

3.1 Evaluating the effect of measurement time on measurements

Measurement time is important for the accuracy of the data we obtained. If we used the wrong measurement time, the element concentration of each measurement would be very different even if the same point is measured. Using PCA to analyze data of element information is a very practical method in archaeology. But if we used the wrong measurement time, the difference between the element information could not be due to
the origin, but due to the instrument itself. At this time, when we use PCA or other methods to analyze the data, there will be a large error due to the measurement accuracy. So it is essential to choose the right measurement time for each element.

Some previous studies have shown that increasing the measurement time can achieve higher precision with lower values of RSD [19, 20]. However, RSD does not decrease linearly with measurement time and extended analysis may not result in tangible improvements in precision [21]. In the meantime, some studies found that the precision and reliability of FPXRF data does not improve significantly at measurement time greater than 180 s [8].

Some studies have suggested that a suitable compromise between measurement time and precision is 120 s [19]. While others have used shorter measurement times such as 45 s [22] and 60 s [20].

Our study showed that optimal measurement time is strongly dependent on the investigated element. The RSD for the 11 elements (Fe, Ca, K, Al, Si, Ba, Zr, Mn, Mg, Ti, and Cl) with different measurement times in the brick and the effect of measurement time is shown in Fig. 4. For the elements Fe, Ca, K, Al, and Si, which are the main research objects of the study, the RSD was lower than 5% for every measurement time. For the elements Ba, Zr, and Mn, the RSD was lower than 10% for every measurement time, which still achieved a Q3 quality level. We therefore suggest choosing 60 s as the measurement time for the elements Fe, Ca, K, Al, Si, Ba, Zr, and Mn. However, for the element Mg, the RSD was 64.93% when the measurement time was 60 s, which was Q1 level by the US EPA, meaning that the two datasets were statistically different. The RSD obviously decreased from 64.93% for 60 s to 11.42% for 180 s. When measurement time is greater than 180 s, the data precision does not improve significantly by increasing the measurement time. This rule also applies to element Ti. For element Cl, the RSD values fluctuated over a wide
range. The values were sometimes larger than 30% and sometimes smaller than 5%, which had no relationship with measurement time. Therefore, using a Niton XL2-960 GOLDD XRF Analyzer to measure the elements Cl in Linqing brick is inappropriate.

Our suggestions for element measurement times are shown in Table 3.

### Table 3
Suggestions for element measurement times.

| Element | Fe | Ca | K | Al | Si | Ba | Zr | Mn | Mg | Ti |
|---------|----|----|---|----|----|----|----|----|----|----|
| Measure time | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 60 s | 180 s | 180 |

In general, to get a single precise measurement time is inappropriate. Different elements need different measurement times. It is essential to conduct preliminary tests on the elements with specific samples to determine appropriate measurement times, which can help meet the precision requirements of the survey data.

### 3.2 Evaluating the effect of rain on measurements

If the brick is washed by rain, the photoelectric absorption and scattering will increase, which may increase baseline values (noise) and lower emission peaks (signal), leading to higher limits of detection and reductions in the apparent concentration [21]. It has a great influence on the accuracy of measurements with FPXRF.

Our study showed that, except for K, other elements are greatly influenced by rain, and it took long time for the concentrations of these elements to return to the concentrations before rain. After the influence of rain, the variety of concentrations of each element, and their contrast with the concentration before being washed, is shown in Fig. 5. In this case, it takes about 7 hours to return to the concentration value before the rain (Rainfall: 11.2 mm, Average temperature: 24.3 °C, Average humidity: 69.2%).

It is difficult to correct the effect of rain because it requires laboratory analysis of unaffected bricks with a similar matrix as with bricks affected by rain on the ancient buildings to determine appropriate correction factors. It is a complicated procedure and is
not possible with portable testing in situ. We therefore suggest it is very important to measure on a sunny day without rain for the previous three days. In the meantime, if conditions permit, it is better to choose measuring bricks in the inside rooms of ancient buildings. The rainy days have less impact on bricks inside the building.

If rain arrives before measurements, measurements must stop. When the rain is over, preliminary tests should be conducted on the brick affected by the rain and a comparison should be made with the concentration value before rain to ensure reliable and accurate data is obtained.

3.3 Evaluating the effect of surface conditions of the brick on measurements, providing a surface treatment method and verifying reliability

The bricks on the exterior wall of ancient buildings have been exposed to the external environment for hundreds of years and are affected by many factors, such as acid rain, humidity [23], dry and wet depositions [24–26], freeze-thaw cycles [27], infiltrations by aqueous solutions [28]. These sources of deterioration, can promote efflorescence formation, loss of material and crystalline bloom, etc, especially for brick surface [15]. Such factors can greatly influence the surface of the brick. In the meantime, we can only measure the brick surface when FPXRF is used for in situ measurements. Therefore, to improve the precision and accuracy of the measurements, an applicable surface treatment method is needed to ensure that we can use the data we measured to represent the element concentration of the entire brick.

3.3.1 Evaluating the uniformity of element distributions on brick surfaces: Comparison of DM vs. MPS
The results are shown in Table 4 to Table 8. We can clearly see that for element Fe, the data quality for both DM and MPS is good. The RSD of both DM and MPS are lower than 10% (Table 4). For element Ca, except for brick 4, the DM could not reach sufficient data precision. The reason is the concentration differences of three points of the bricks were very large, which leads to poor precision and high values of RSD (Table 5). The uniformity of element distributions can increase by MPS. It was obvious that the RSD value decreased from 21.50–1.93% for brick 2 and from DM to MPS for element Ca (Table 5). This phenomenon is also applicable for element Ca of brick 3, element K of brick 2, element Al of brick 5, and element Si of brick 2 (Table 5 to Table 8). This is shown more intuitively in Fig. 6, which reveals the comparison of the concentration differences between the three points under conditions DM and MPS for those whose RSD was larger than 10% for DM, but was smaller than 10% for MPS. It demonstrates the MPS can improve precision by increasing the uniformity of the element distributions on brick surfaces. For element K, Al, and Si, except for the situation mentioned above, whose precision is increased by MPS, other data quality for each brick and method was good, whose RSD is smaller than 10% (Table 6 to Table 8). Therefore, measuring elements of bricks using MPS to treat the surface of the brick can increase the uniformity of the element distributions of brick surfaces and obtain more reliable data. The case situations are for the element Ca of brick 1 and brick 5 (Table 5). Even using MPS to treat the surface, the precision cannot improve significantly. For brick 1 the RSD of MPS is 12.83% (Table 5). For brick 5, the RSD of MPS is 28.64% (Table 5). This is shown more intuitively in Fig. 7, which demonstrates MPS cannot improve the data precision for element Ca of brick 1 and brick 5. We selected three more points from brick 1 and brick 5 and measured them with FPXRF (each point was measured 3 times). The concentration contrast between six points of brick 1 and six points of brick 5 for element Ca is shown in Fig. 8. We can clearly see that for brick 1 and brick
5, the element concentration differences in element Ca between each point of the surface was very large.

|       | Brick 1 | Brick 2 | Brick 3 | Brick 4 | Brick 5 |
|-------|---------|---------|---------|---------|---------|
| Point 1 | 3.31    | 2.95    | 2.80    | 3.69    | 2.65    |
| Point 2 | 3.34    | 2.83    | 2.72    | 3.49    | 2.89    |
| DM     | 3.65    | 2.68    | 2.82    | 3.91    | 2.78    |
| RSD    | 5.17    | 4.29    | 2.37    | 4.93    | 3.97    |
| Point 1 | 3.60    | 3.68    | 2.91    | 4.18    | 2.91    |
| Point 2 | 3.61    | 3.47    | 2.85    | 4.09    | 2.70    |
| MPS    | 3.99    | 3.49    | 2.91    | 4.07    | 2.97    |
| RSD    | 5.25    | 3.09    | 1.46    | 1.75    | 4.36    |

Table 4. Data of element Fe measured by DM and MPS for 5 bricks.

|       | Brick 1 | Brick 2 | Brick 3 | Brick 4 | Brick 5 |
|-------|---------|---------|---------|---------|---------|
| Point 1 | 4.15    | 3.84    | 4.40    | 5.18    | 6.37    |
| Point 2 | 3.57    | 6.32    | 3.44    | 5.75    | 3.61    |
| DM     | 4.96    | 4.92    | 3.96    | 4.82    | 3.74    |
| RSD    | 14.73   | 21.50   | 10.60   | 7.81    | 29.74   |
| Point 1 | 4.63    | 3.64    | 3.18    | 5.48    | 5.28    |
| Point 2 | 4.35    | 3.70    | 3.29    | 5.67    | 3.98    |
| MPS    | 5.71    | 3.71    | 3.30    | 5.59    | 3.23    |
| RSD    | 12.83   | 1.93    | 2.14    | 3.19    | 28.64   |

Table 5. Data of element Ca measured by DM and MPS for 5 bricks.

|       | Brick 1 | Brick 2 | Brick 3 | Brick 4 | Brick 5 |
|-------|---------|---------|---------|---------|---------|
| Point 1 | 2.72    | 2.68    | 4.50    | 2.34    | 4.27    |
| Point 2 | 3.09    | 2.15    | 4.47    | 2.24    | 4.94    |
| DM     | 2.97    | 2.18    | 4.31    | 2.49    | 4.41    |
| RSD    | 7.41    | 11.24   | 2.20    | 5.14    | 7.00    |
| Point 1 | 2.43    | 2.09    | 5.06    | 2.01    | 4.83    |
| Point 2 | 2.93    | 2.18    | 5.01    | 1.94    | 4.30    |
| MPS    | 2.73    | 2.13    | 4.91    | 1.92    | 3.19    |
| RSD    | 8.34    | 3.09    | 1.48    | 3.16    | 8.59    |

Table 6. Data of element K measured by DM and MPS for 5 bricks.

|       | Brick 1 | Brick 2 | Brick 3 | Brick 4 | Brick 5 |
|-------|---------|---------|---------|---------|---------|
| Point 1 | 5.11    | 4.86    | 5.19    | 6.01    | 4.38    |
| Point 2 | 5.37    | 4.36    | 5.31    | 6.00    | 5.59    |
| DM     | 5.66    | 5.10    | 5.45    | 6.89    | 5.37    |
| RSD    | 8.81    | 7.24    | 5.10    | 7.65    | 11.54   |
| Point 1 | 5.49    | 5.82    | 5.75    | 6.90    | 5.35    |
| Point 2 | 5.27    | 5.59    | 5.12    | 6.49    | 5.21    |
| MPS    | 5.83    | 5.94    | 5.13    | 6.93    | 5.46    |
| RSD    | 4.85    | 5.23    | 6.26    | 5.77    | 3.43    |

Table 7. Data of element Al measured by DM and MPS for 5 bricks.
Table 8. Data of element Si measured by DM and MPS for 5 bricks.

Note 1: The bricks were measured three times at each point under two surface conditions. The point concentrations shown in Table 4 to Table 8 are the mean concentrations calculated from these three replicates. The RSD shown are calculated from 9 concentration values for three points (total 9 concentration values: 3 points and each point was measured 3 times). The US EPA criteria were used to evaluate precision (Table 2).

Note 2: The bricks were measured three times at each point under two surface conditions. The point concentrations shown for Fig. 6 and Fig. 7 are the mean concentrations calculated from these three replicates. The US EPA criteria is used to evaluate precision (Table 2).

For this phenomenon, crystalline bloom must be a very large influencing factor. The moisture in the foundation soil can move up along the pores of the bricks due to the capillary suction. Due to wind blowing, light, and other factors, the moisture will evaporate into the atmosphere, while the soluble salt cannot be evaporated, which led to stay on the surface of the brick. Crystalline bloom can greatly influence the elements we studied in experiment 3 of brick surfaces, especially for element K and Ca. For element Fe, Al, and Si, crystalline bloom has less of an impact on them.

To ensure accuracy of the measurements, at least three points of each brick must be selected for measurement. Each point was measured three times and the mean concentration by three replicates was used as the concentration value of this point. The
mean concentration of the three points represents the elemental concentration of the brick. If there is a point with an abnormal concentration value, then three more points should be selected for measurement to ensure whether that point is an abnormal point. If it is an abnormal point, it should be discarded. If the concentration difference of the element between each point of brick surface is too large, then that brick should be discarded and not measured for this element. Each point must be polished by a sickle before measurement, which can improve accuracy of measurement.

3.3.2 Evaluate the concentration differences between brick surfaces and interiors

To verify the reliability of MPS, only looking at the uniformity of the surface is not enough. For phenomenon such as efflorescence, loss of material and crystalline bloom, the concentration differences between surface element concentrations and internal element concentrations of brick must be larger than that of new brick. In the meantime, we can only measure the brick surface of an exterior wall when we use FPXRF to do the in situ measurements. Therefore it is very important to analyze the concentration differences between the surfaces and interiors of ancient brick.

The result is shown in Fig. 9.

We can clearly see that the size concentration differences between surface (point 1 to point 3) and interior (section 1 to section 3) is dependent on both the brick and elements.

(1) **For brick:**

For brick 2 and brick 4, the concentration differences for all elements were small, with a RSD smaller <10%.

For brick 1, the uniformity of the element distributions on the brick surface was not good for element Ca. Therefore, the element Ca was not considered in experiment 3-2 for brick
1. For element Fe, Al, and Si, the concentration differences were small (RSD: Fe: 4.11%; Al: 6.91%; Si: 1.48%). For element K, the concentration difference was large (RSD: K: 18.85%).

For brick 3, the concentration difference for element Si was small (RSD: Si: 5.55%). For elements Fe, Ca, K, and Al, the concentration differences were small (RSD: Fe: 14.84%; Ca: 23.19%; K: 43.32%; Al: 10.58%).

For brick 5, the element Ca was not considered in experiment 3-2 for the same reason as for brick 1. For elements Al and Si, the concentration differences were small (RSD: Al: 9.29%; Si: 5.71%). For elements Fe and K, the concentration differences were large (RSD: Fe: 12.10%; K: 44.42%).

It can be seen that, for the same element, the RSDs for brick 2 and brick 4 was much smaller than for brick 1, brick 3, and brick 5. For some elements, even if the RSDs were all less than 10%, the RSDs for brick 2 and brick 4 were lower than for other bricks.

(2) For elements:

We can clearly see that the RSDs for elements Fe, Al, and Si were much smaller than for elements Ca and K, which means the concentration differences between the exterior and interior for elements Fe, Al, and Si were smaller. The reason for this phenomenon is mentioned in 3.3.1. The elements Ca and K are greatly affected by crystalline bloom, while the elements Fe, Al, and Si are less affected by crystalline bloom.

Except for crystalline bloom, some other factors will also influence the brick surface. For example, acid rain will lead to loss of material, Ca, K, and Al on the brick surface. Even if the differences of element concentrations are not as large as that of Ca and K, the RSDs of Fe for brick 3 and brick 5 as well as of Al for brick 3 were larger than 10%.

For this phenomenon, we chose a brick located on a higher position of the wall. Compared to the bricks close to the ground, the capillary suction of the wall in a higher position is
much smaller [29]. Therefore, the crystalline bloom in the high position will be lighter, which will have less impact on K and Ca.

In the meantime, if conditions permit, it is better to choose the bricks in a room of an ancient building to measure.

3.4 Correlation and linear regression analysis

In a previous study, many FPXRF analysis methods for each field were used in cross validation to assess reliability of the instrument by analysis of samples using an alternative laboratory technique such as ICP-OES, AAS, ICP-MS and ICP-AES.

For example, some researchers have used ICP-OES to perform cross validation [19, 30, 31]. In 2009, Radu assessed the reliability of FPXRF by AAS [22], whereas some other scholars also used ICP-MS [21, 31–34] and ICP-AES [35–37] to conduct comparison with FPXRF.

In our study, we used ICP-OES to carry out cross validation of elements Fe, Ca, K, Al, and Si. XRF analysis targets all atoms within the critical penetration depth, regardless of mineral structure. Aqua-regia hot-plate dissolution prior to ICP-OES/MS analyses have been shown in some cases to result in reduced recovery of elements when compared to microwave extraction protocols incorporating hydrofluoric acid to break down silicate phases [8]. Therefore, we used total microwave acid digestion, which is suitable for organic rich and silicate containing media with proven recoveries approaching 100% to ensure maximum comparability between FPXRF and ICP data.

In our study, to verify the reliability of FPXRF results, data comparison and correlation regression analysis was employed between the concentration values measured by ICP-OES with the values measured by FPXRF. The US EPA quality criteria for FPXRF data is shown in Table 2. If the coefficient of determination (R²) of linear regression analysis between FPXRF and the validation method is greater than 0.7, a Q2 quality level will be achieved.
To achieve a Q3 quality level, $R^2$ must be greater than 0.85.

The results are shown in Fig. 10.

For elements Fe and K, the coefficient of determination was satisfactory ($R^2 = 0.95$ for Fe; $R^2 = 0.95$ for K). The coefficient of determination was larger than 0.85, which means a Q3 quality level was achieved. In the meantime, the concentration values measured by FPXRF and ICP-OES were very close for element Fe. But for element K, the concentration values measured by FPXRF and ICP-OES were statistically different.

For elements Al and Si, Q2 quality level was achieved. ($R^2 = 0.77$ for Al; $R^2 = 0.71$ for Si).

In the meantime, the concentration values measured by FPXRF and ICP-OES were also statistically different. For element K, Al and Si, this indicates a measurement bias for all 5 bricks, and there is similarity between the biases.

For element Ca, the concentration values measured by FPXRF and ICP-OES were significantly different. The bias for each brick was erratic. Therefore, the reliability of FPXRF for element Ca was not satisfactory.

For elements K, Al and Si, we used the value of ICP-OES to correct the value of the FPXRF measurements. The equations used for correction are:

$$Sample_{corr} = \frac{Sample_{meas} - c}{m}$$

$Sample_{corr}$ is the corrected concentration of the measured sample; $Sample_{meas}$ is the raw concentration of the measured sample; $c$ and $m$ are the intercept and slope of the linear model from XRF and ICP-OES results, respectively.

The correction results are shown in Table 9, Table 10 and Table 11. After correction, the values were very similar to the values measured by ICP-OES. When we use FPXRF to measure the elements in situ for K, Al and Si, a few bricks should be chosen that have the
same matrix as the aimed bricks in situ. A few bricks should be chosen to perform a preliminary experiment to build up a correlation regression analysis between FPXRF and ICP-OES, which can provide cross validation correction for the values that were measured in situ.

| Brick | Mean concentration by ICP-OES (n=2) | Mean concentration by FPXRF (n=9, sections, each section 3 times) | FPXRF concentration corrected by cross validation |
|-------|------------------------------------|---------------------------------------------------------------|--------------------------------------------------|
| 1     | 1.78%                              | 1.95%                                                         | 1.85%                                            |
| 2     | 2.61%                              | 2.12%                                                         | 2.50%                                            |
| 3     | 2.75%                              | 2.21%                                                         | 2.85%                                            |
| 4     | 2.15%                              | 2.01%                                                         | 2.08%                                            |
| 5     | 2.27%                              | 2.05%                                                         | 2.23%                                            |

Table 9. The correction for element K by cross validation.

| Brick | Mean concentration by ICP-OES (n=2) | Mean concentration by FPXRF (n=9, sections, each section 3 times) | FPXRF concentration corrected by cross validation |
|-------|------------------------------------|---------------------------------------------------------------|--------------------------------------------------|
| 1     | 5.62%                              | 6.19%                                                         | 5.77%                                            |
| 2     | 5.38%                              | 6.05%                                                         | 5.59%                                            |
| 3     | 6.23%                              | 6.34%                                                         | 5.97%                                            |
| 4     | 6.87%                              | 7.32%                                                         | 7.28%                                            |
| 5     | 6.27%                              | 6.31%                                                         | 5.93%                                            |

Table 10. The correction for element Al by cross validation.

| Brick | Mean concentration by ICP-OES (n=2) | Mean concentration by FPXRF (n=9, sections, each section 3 times) | FPXRF concentration corrected by cross validation |
|-------|------------------------------------|---------------------------------------------------------------|--------------------------------------------------|
| 1     | 24.21%                             | 26.18%                                                        | 23.36%                                           |
| 2     | 23.92%                             | 27.09%                                                        | 24.20%                                           |
| 3     | 24.63%                             | 28.22%                                                        | 25.25%                                           |
| 4     | 23.31%                             | 26.23%                                                        | 23.41%                                           |
| 5     | 25.63%                             | 28.56%                                                        | 25.56%                                           |

Table 11. The correction for element Si by cross validation.

4. Conclusion

We can conclude that the FPXRF is a reliable instrument to measure the main elements in situ, except for element Ca. For the complex conditions of bricks in situ and the characteristics of FPXRF, the scientific method is necessary. Our scientific suggestions to use FPXRF for in situ measurements are concluded as: (1) For measurement times, our suggestions are shown in Table 3. However, a suitable measurement time must depend on
the aim elements and samples. Preliminary tests for the aim elements to determine appropriate measurement times must be done to ensure the precision of measurements; (2) Choosing a sunny day, where there was no rain in the previous three days, is important. If the rain begins during measurements, it is essential to stop measuring and make comparisons of the concentrations measured after the rain and before the rain to ensure measurement accuracy; (3) For the surface conditions of bricks, at least three points should be selected for measurements and a sickle should be used to polish the point. If the surface is not uniform for some elements, the brick should be discarded for those elements. To avoid the influence of factors such as crystalline bloom and acid rain, the brick located in a higher position of the wall should be chosen. If conditions permit, it is better to choose bricks in a room of the ancient building; (4) For elements K, Al and Si, a few bricks should be used in a preliminary experiment that will allow a correlation regression analysis between F PXRF and ICP-OES(or other reliable laboratory methods), which can provide cross validation corrections for the values measured in situ.

Declarations

Availability of data and materials

All data generated during this study are included within the article.

Competing interests

The author declares that they have no competing interests.

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Authors’ contributions

All the authors contributed to the current work. ZXC and LZ planned and conducted the experiments and collected the data. ZXC and LZ performed the analyses and write the article. JLX assisted in experiment 3-1. FH supervised the entire process and provided constructive advice. All authors read and approved the final manuscript.

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Figures

Figure 1

The Forbidden City (left) and the Temple of Heaven (right) constructed by Linqing bricks.
Figure 2

Mechanism for field portable X-ray fluorescence.

Figure 3

The measured bricks. From left to right are brick 1-5.
Figure 4

Relationship between measurement time and RSD on precision for Fe, Ca, K, Al, Si, Ba, Zr, Mn, Mg, Ti, and Cl. The US EPA criteria were used to evaluate the precision (Table 2). Each brick was measured 5 times for each measurement time. The RSD shown are calculated from these five replicates.
Figure 5

Variety of concentrations of each element, and their contrast with the concentrations before being washed. The bricks were measured five times in each time condition. The concentrations shown are the mean concentrations calculated from five replicates.
Figure 6

Comparison of the concentration difference between the three points when using DM and MPS.
Comparison of the concentration difference between the three points when using DM and MPS.

The concentration contrast between six points of brick 1 and six points of brick 5 for element Ca. The bricks were measured three times at each point. The point concentrations shown are the mean concentrations calculated from these three replicates.
Figure 9

Comparison of the concentrations of element Fe, Ca, K, Al and Si from three points and three fresh sections (from brick 1-5). The US EPA criteria were used to evaluate precision (Table 2). Because the concentration differences for element Ca between each point of the brick surface for brick 1 and brick 5 were too large,
brick 1 and brick 5 were not used to compare the concentrations of element Ca between the brick surface and brick interior. The bricks were measured three times at each point and each section. The point and section concentrations shown are the mean concentrations calculated from these three replicates. The RSD shown are calculated from 6 concentration values for each point and each section of bricks.
Concentration comparisons between FPXRF and ICP-OES for element Fe, Ca, K, Al and Si. The correlation regression analysis for FPXRF data and ICP-OES concentrations for element Fe, K, Al and Si. The US EPA criteria were used to evaluate precision (Table 2). The solid red line is a fitted linear regression, the dashed black line is 1:1, the dashed blue line represents the 95% confidence limit. The concentration for ICP-OES was the mean concentration calculated by two replicates and the concentration for FPXRF was the mean concentration calculated by three sections, which was obtained in experiment 3-2.
