Comparison and correction of element measurements using XRF core scanning and ICP-AES methods in lacustrine sediments

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Abstract: An integrated analysis has been carried out on core dated by qualitative X-ray fluorescence core scanning combination of quantitative ICP-AES in order to characterize the extent of elements Cd, Cr, Cu, Zn, and Pb in the Lake Toson in the northeastern Tibet Plateau. When combining both the quantitative and qualitative measurements, we observed a significantly positive correlation. Comparing the ratios between element intensities and concentration, we found that the XRF element intensities were related to the amount of water. Using the intensity of Cl as an indicator of water content, the element intensities of Cd, Cr, Cu, Zn, and Pb in the core samples were corrected. The correlation coefficients of each pairs of the two datasets among Cd, Cr, Cu, Zn, and Pb were significantly raised. These data sets with highly correlations were used to produce a transfer function to relate XRF element intensity with element concentration. Calculated element concentrations from the intensities show only minor differences from concentrations obtained by ICP-AES, indicating XRF core scanners are a very useful tool for measuring element concentration in lacustrine sediments.

1. Introduction
A lake is a point of connection between different layers of the earth's surface. It preserves the details of any paleolake and paleoenvironmental conditions. It is therefore important to study the environmental impact made by elements within the sedimentary layer. With the development of the global economy, anthropogenic heavy metal pollution has been found on the Tibetan Plateau (TP) [1-4]. The TP, with its low population density and lack of industrial development, is important to the regional hydrological cycle, as well as to regional and global atmospheric circulations. There has, over recent years, been an increasing number of studies of the rivers, lakes, vegetation, soil and aerosols found on the TP [1, 5, 6]. Due to the TP’s relatively stable sedimentary environment and the relative ease with which, in such a comparatively pristine environment can be identified[7], the deep-water lacustrine sediments of this region are likely to have faithfully recorded, and are also able to serve as a global indicator of the presence of elements within the environment[2, 3, 8, 9]. It is important to understand and identify the sources of the elements found in lacustrine sediments as being either derived from natural or anthropogenic activities so that any contamination of lakes can be better controlled, and their unique environments sustained.
The inductively coupled plasma-atomic emission spectrometry (ICP-AES) method is widely used to analyze the elements of sedimentary samples [10-12]. The advantages of this method are its high sensitivity and precision, and its low interference. Sample preparation is critical and has a direct effect on ICP-AES analysis. In recent years, many scholars have honed the methods involved in the scientific treatment of sediment and soil, achieving remarkable results [13]. X-Ray Fluorescence Core Scanning (XRF core scanning) is characterized by the rapid, non-destructive, continuous testing of elements and the preparation of samples; as a method, it can improve the veracity and accuracy of any analysis, and can thus strengthen any research into the development of lakes and the evolution of their local environments [14, 15]. Many researchers have combined these two approaches to improve the quality of their analysis and reduce the impact of any potential errors within their experiments [16-19]. This paper studies the determination of elements in the sediments of Lake Toson by combining measurements derived from both the qualitative XRF core scanning and quantitative ICP-AES methods. It constitutes not only the first study of Lake Toson’s sediments, but is also the first piece of such research to combine qualitative and quantitative analyses. The shortcomings of the existing analytical methods were overcome and the veracity and accuracy of the analysis appeared improved. The resolution and reliability of the environmental data were greatly.

In this first study of the heavy metal elements of Lake Toson, samples from Core Ts4 were investigated. In particular, we measured the element concentrations in the top sedimentary layer in an attempt to analyze them and to evaluate whether or not they were veracity. A comparison of the analyzed data from both XRF core scanning and ICP-AES measurements aided geochemical and environmental reconstructions. These environmental characteristics provided the basic data required for an overall environmental assessment of the Delingha Basin (DB).

2. Sample and methods

2.1 Study area
Lake Toson (37°04′–37°13′ N, 96°50′–97°03′E) is located in the lowlands of the DB, a closed-drainage basin in the northeastern Qaidam Basin (QB). The QB has an area of 120,000 km², and is thus the largest inland basin on the TP (figure 1). The QB is surrounded by the Kunlun Mountains to the south, the Altyr Mountains to the west and the Qilian Mountains to the north and east. The surface area of Lake Toson is ~145 km², and the lake has a maximum water depth of 25 m. It is fed mainly by the Bayin River, which collects precipitation from its large, mountainous catchment. Water from Lake Hurleg drains into Lake Toson through a ~3 km long river northwest of the lake. Lake Toson is also fed by local groundwater and intermittent river water from the surrounding mountains. Lake Hurleg (37°17′N, 96°54′E) is a freshwater lake mainly fed by the Bayin and Balegen rivers, but also by groundwater from the mountains north of the QB [20].

Figure 1. Sketch maps of the Bayin River catchment and the sampling location in Lake Toson. The extraction site of Core Ts4 is indicated in the inset.
2.2 Sample collection
Core Ts4 was extracted using a gravity corer consisting of an acrylic pipe with a 7 cm inner diameter and a length of 69 cm (figure 1), a sediment catcher and a clear vent. The slow and careful entry of the corer into the sediment allowed us to obtain an undisturbed sedimentary column. The sediments sampled were all from the upper part of Core Ts4, i.e., the upper 19 cm of the sedimentary layer at the interface between the sediment and the water. The core was kept upright and then cut open. Half of the core was scanned for elements using the XRF scanning method, and the other half was measured using extrusion-type piston sample points at 0.5 cm intervals (n=38). Samples were dried to a constant weight.

2.3 Analytical methods
Using an X-ray Fluorescence (XRF) core scanner, chemistry features of sediment core can be measured directly which does not destruct sediment surface nor split sediment cores. This method has been potentially and widely applied to core sediment analysis, but little is known about the effects of sediment physical properties on XRF core scanner measurements. X-ray fluorescence (XRF) core scanning is enable rapid collection of high-resolution chemical data from core profiles. Prior to analysis, the surface of the sediment core section is carefully flattened with a spatula, and covered with a thin Ultralene® foil (4μm thick) to prevent any contamination, oxidation and drying. The depth of surface sediment analyze by XRF core scanning generally does not exceed a few tens of microns. The step of analysis is set up to 10 mm in order to acquire a continuous record of elemental compositions along the sediment cores. The measurement time is 20s for each individual step analysis.

The optimum processes for the pre-treatment of samples for element analysis are vital when conducting analyses using the ICP-AES method, and following detailed experimental work. On the basis of the comprehensive literature available, and combining this with lacustrine sedimentary element data, we were able to determine a suitable digestion system for the sediments of Lake Toson. When analyzing elements, 0.25 g dry samples of Lake Toson sediment were selected; the sediments were subsequently digested by adding a mixture of 5:5:1:1 HNO₃+HCl+HF+HClO₃+H₂O₂ to each sample. The ICP-AES process was then used to analyze the heavy metal content within each sample of the elements Cd, Cr, Cu, Pb and Zn.

3. Dating results
Table 1 shows the ICP-AES analysis of elements within the selected Lake Toson sedimentary core samples (n=38). The mean contents of the elements Cd and Zn in Lake Toson’s sediments are therefore on the high side when compared to the background and standard values; the other elemental contents fall within the background and standard value ranges. The mean concentrations of Cr, Cd, Cu, Zn and Pb in the sedimentary samples were 32.9 mg.kg⁻¹, 2.2 mg.kg⁻¹, 19.5 mg.kg⁻¹, 188.5 mg.kg⁻¹ and 32.3 mg.kg⁻¹, respectively.

XRF core scanning has several advantages, e.g. the need for only simple pre-treatment of samples, the ability to maintain the integrity of each sample during the sampling process, the ability to detect even low concentrations of elements, and the high-resolution quality of any imagery. Analyses of core profiles scanned with XRF core scanners over recent years therefore allowed any changes in the concentrations of each element to be relatively easily mapped and analyzed.

| Heavy metals | Cd  | Cr  | Cu  | Pb  | Zn  |
|--------------|-----|-----|-----|-----|-----|
| Minimum      | 1.97| 27.67| 17.3| 29.35| 175.6|
| Maximum      | 2.44| 38.86| 22.81| 35.7| 198.1|
| Average      | 2.2 | 32.9 | 19.5 | 32.3 | 188.5|

The data derived from the ICP-AES process were correlated with a five-point running mean based on XRF core scanning results. The correlation coefficients ranged from 0.638 to 0.777 (n=38, p<0.001), apart from for the element Zn, whose correlation coefficient was relatively small (r=0.338).
The relative correlation coefficients for Cd, Cr, Cu and Pb assemblages were between 0.6 and 0.7, demonstrating that the results derived from these two different methods are comparable.

During the XRF core scanning process, any measurements will relatively heavily influenced by the energy levels of any X-ray source, as well as by the physical and chemical properties of the sediment etc. XRF core scanning results from studies of marine sediments will necessarily have been affected by the moisture content of the core, as well as the particular core’s carbonate content, particle composition and any changes in the density and porosity of its mineral composition. Of these drawbacks, high water content could be seen as the most negative influence on the accuracy of any results, as a high water content would inevitably reduce the density of any elements scanned using the XRF method. Nonetheless, the accuracy of such XRF scanning can be improved by making scientifically-based water content corrections. The strong chemical activity, and hence density, of the element Cl plays an important part in any sedimentary composition, meaning that this intensity can be used as an alternative indicator of the extent of any changes in moisture content in a sedimentary core. The higher the water content, the higher the Cl density. Measurements resulting from XRF scanning can therefore potentially be calibrated using the elemental intensity of Cl. Out results showed a clear correlation between XRF scanning and ICP-AES data, and that the correlation coefficient between the calculated results for each element and the ICP-AES dataset improved after water/Cl correction. The correlation coefficient ranged from 0.673 to 0.925 (figure 2). It demonstrated that water content exerts a certain influence on element intensity. This is especially true of the element Zn; XRF scanning results showed that water content heavily influenced Zn intensity, with its correlation coefficient increasing from 0.338 to 0.673. The correlation coefficient of the element Pb showed no clear difference after correction, however, demonstrating that, for Pb, water content exerted little impact upon the XRF scanning results.

When looking in detail at the lacustrine sediments extracted from Lake Toson, it became apparent that the XRF scanning strength depended principally on the relative contents of the elements Cd, Cr, Cu, Zn and Pb. This was especially true when employing the element Cl to correct any measurements; following such correction, the linear correlation coefficient between the densities of elements scanned

![Figure 2. Correlations between XRF elemental intensity and ICP-AES elemental concentration (+: non-corrected; ●: water-corrected)](image-url)
using the XRF method and the ICP-AES measurements of Cd, Cr, Cu, Zn and Pb increased. As a consequence, a quantitative conversion method was applied to the XRF-scanned element fluorescence intensity to determine the content of these elements. This quantitative relation between the contents of Cd, Cr, Cu, Zn and Pb (mg/kg) in the trace elements of Lake Toson lacustrine sediments and the element intensities measured by XRF scanning (counts/second) used a linear regression method, as follows: Cd$_{XRF}$=0.019*Cd$_{ICP-AES}$-0.022; Cr$_{XRF}$=0.006*Cr$_{ICP-AES}$-0.041; Cu$_{XRF}$=0.001*Cu$_{ICP-AES}$-0.01; Zn$_{XRF}$=0.004*Zn$_{ICP-AES}$-0.034; Pb$_{XRF}$=0.001*Pb$_{ICP-AES}$-0.013 (figure 3). To calculate any potential change in the contents of the elements Cd, Cr, Cu, Zn and Pb in the sections extracted from Core Ts4, these measurements were compared with the results of the ICP-AES analyses. The relative errors (RE) were 0.46%, 1.07%, 16.2%, 1.07% and 21.35% for Cd, Cr, Cu, Zn and Pb, respectively; the mean relative deviations (MRD) for Cd, Cr, Cu, Zn and Pb were 0.17%, 0.01%, 0.02%, 0.00% and 0.01%, respectively.

![Figure 3](image.png)

**Figure 3.** Comparisons between the chemical concentrations derived from ICP-AES measurements and those calculated using XRF core scanning (the thick, solid line represents the element content as measured by the ICP-AES method; the thin, solid line represents the element content as calculated by the XRF method)

In the sections extracted from Core Ts4, the trends and ranges exhibited by element contents appeared close to those found when statistical regression was applied to the ICP-AES results. This was especially true when looking at the accuracy of such ranges in element content. This combined methodology can therefore go some way to satisfying the need for an accurate, high-resolution analysis of both the paleoclimate and the paleoenvironment.

4. Conclusion

When comparing this method with qualitative XRF core scanning analysis, it became clear that the results gained using these two different analytical methods were significantly comparable, especially when water content correction techniques were applied to the XRF scanning results. Correlation analysis of the two datasets, one compiled from Cl-calibrated XRF scanning results, and another from ICP-AES measurements, indicated that the two datasets correlate fairly well. This would suggest that interference of any water content in core samples needs to be calibrated. This indicated that, combined with the ICP-AES method, the XRF method can be a useful tool for establishing the contents of Cd, Cr, Cu, Zn and Pb in sediments.
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