Calibration of XRF core scanners for quantitative geochemical logging of sediment cores: Theory and application

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ABSTRACT

On-line analysis of split sediment cores by XRF core scanners has become increasingly popular in the past decade, because it allows nondestructive extraction of near-continuous records of element intensities from sediment cores with a minimum of analytical effort. A disadvantage of XRF core scanning relative to conventional geochemical analysis is the problematic conversion of core-scanner output to element concentrations. The main reason for this long-standing problem is the poorly constrained measurement geometry, attributable to inhomogeneity of the specimens (e.g. variable water content and grain-size distribution), irregularities of the split core surface, and in some setups, spatial variations in thickness of an adhesive pore-water film which forms directly below a protective foil covering the core surface.

We propose a log-ratio calibration model for XRF core scanners, derived from a combination of XRF-spectrometry theory, principles of compositional data analysis, and empirical evidence. The log-ratio calibration model provides accurate and precise predictions of sediment composition (element concentrations) from XRF core-scanner output with a limited number of parameters, namely $2(D-1)$, where D equals the number of chemical elements whose concentrations are to be estimated. The model can accommodate the inherent non-linearity of the relation between (relative) intensities and concentrations, which is apparent from the fact that it provides unbiased estimates.

An immediate corollary of our results is that log-ratios of element intensities, which are related to log-ratios of element abundances by a simple linear transformation, provide the most easily interpretable signals of relative changes in chemical composition. Consistent use of log-ratios of element intensities or concentrations should minimise the risk of drawing erroneous conclusions from geochemical proxies.

The relative standard deviation (precision) of predicted element concentrations in core GeoB7920 is less than 2%. Stochastic simulations indicate that this level of precision can be attained with 40 randomly selected calibration specimens. Improved control over input errors and development of robust goodness-of-fit statistics allows XRF core scanning to be developed into a rigorous quantitative measurement technology. The log-ratio calibration equation derived in this study may be adapted to inter-laboratory and inter-instrument calibration as well.

1. Introduction

X-ray fluorescence (XRF) is a well-established analytical technique for estimating the composition of rocks and sediments (Ramsey et al., 1995; Jenkins, 1999; De Vries and Vrebos, 2002). The principle of XRF analysis is based on excitation of electrons by incident X-radiation. Ejection of electrons from inner atomic shells creates vacancies which are filled by electrons falling back from the outer shells, whereby surplus energy is emitted as a pulse of secondary X-radiation. Emitted fluorescence energy and wavelength spectra are characteristic for

atoms of specific elements, which permits estimation of their relative abundances. Progress in XRF instrumentation has opened the way to in-situ and on-line measurement of geological materials, in the field as well as aboard ship (Jansen et al., 1998; Wien et al., 2005; Ge et al., 2005). As a result of these advancements, on-line analysis of soft sediment cores by XRF core scanners has become increasing popular during the past decade (Rothwell and Rack, 2006). Since the introduction of the first prototype XRF core scanner by the Netherlands Institute of Sea Research (NIOZ) in 1988 (Jansen et al., 1998), more than fifty scientific publications have appeared in which use is made of core-scanning techniques to support interpretations of palaeo-environmental records from soft-sediment cores (e.g. Arz et al., 1998, 2001, 2003; Norris and Röhl, 1999; Behling et al., 2000; Labeyrie, 2000; Peterson et al., 2000; Röhl et al., 2000; Haug et al., 2001, 2003; MacLeod et al., 2001; Pälike et al., 2001; Andres et al.,

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2003; Grützner et al., 2003; Lamy et al., 2001, 2004; Jaccard et al., 2005). Technical descriptions of the various XRF core scanners in current use are given by Jansen et al. (1998), Croudace et al. (2006), Haschke et al. (2002), Haschke (2006), and Richter et al. (2006).

The major advantage of XRF core scanning over conventional geochemical analysis of discrete specimens is that element intensities are obtained directly at the surface of a split sediment core. In addition, the spatial resolution of XRF core-scanning devices is much higher than that of conventional destructive methods, and allows the extraction of near-continuous records of element intensities from sediment cores. However, conversion of element intensities measured by XRF core scanners to element concentrations, essential for quantitative applications involving mass-balance and flux calculations, is perceived as problematic. Therefore, results obtained by XRF core scanning are usually presented in the form of count rates (expressed as counts per unit time per unit area), or as ratios of counts, count rates, or intensities of elements (Richter et al., 2006; Rothwell et al., 2006; Thomson et al., 2006). Attempts to convert XRF core scanner output to element or oxide concentrations by means of linear regression have been only moderately successful (Jansen et al., 1998; Jaccard et al., 2005; Croudace et al., 2006; Kido et al., 2006; Böning et al., 2007; Tjallingii et al., 2007). Cross-plots of intensity and concentration tend to show considerable scatter and bias, reflecting non-linearity due to element interactions, effects of specimen inhomogeneity, variable water content, and a general lack of control on measurement geometry. In view of these problems, XRF core-scanner data are widely regarded as semi-quantitative only (Croudace et al., 2006; Richter et al., 2006; Rothwell and Rack, 2006).

The many advantages of XRF core scanning over conventional destructive techniques indicate that this tool has great potential for palaeo-environmental research (Calvert and Pedersen, 2007). However, full realisation of this potential requires a universally applicable, robust procedure for converting core-scanner output to quantitative measures of sediment composition with associated measures of uncertainty. In this study, we propose a new model to solve the long-standing problem of XRF-core-scanner calibration based on a combination of XRF-spectrometry theory, empirical evidence, and principles of compositional data analysis. We give a few examples of model application, and evaluate the predictive capabilities of the new model by means of stochastic simulation. We close with some recommendations for processing of core-scanner output in relation to common objectives of geoscientific application, and outline possible avenues of further research.

2. Calibration in conventional XRF analysis

In conventional quantitative XRF analysis under well-constrained laboratory conditions, conversion of the net intensity of an element to a weight proportion is provided by the following general equation (Jenkins, 1999; De Vries and Vrebos, 2002):

$$W_{ij}=K_jI_{ij}M_{ij}S_i \tag{1}$$

where W_{ij} represents the concentration (weight proportion) of element j in specimen i. K_j represents a device-specific calibration constant for element j (the sensitivity or detection efficiency). I_{ij} represents the net intensity of element j in specimen i, obtained by preprocessing of the raw spectrum by background subtraction, sum-peak and escape-peak correction, deconvolution and peak integration. M_{ij} is the matrix effect which corrects for scattering, absorption and enhancement effects on I_{ij} caused by the presence of other elements in the specimen. Note that for a series of specimens covering a range of compositions, the matrix effect is a non-linear function of the concentrations (or intensities) of the full range of elements present. S_i is the specimen effect which captures the measurement geometry and specimen homogeneity relative to the standard configuration.

Equation (1) is pseudo-dimensionless, because W_{ij} is expressed in units of concentration such as element (or oxide) weight proportions (or percentages), which implies that the variables on the right-hand side can have different units as well. The matrix effect M_{ij} is also defined in terms of concentration units, whereas I_{ij} is commonly expressed in terms of counts per unit time (per unit area). If K_j is interpreted as a device-specific constant, which describes the sensitivity of the measurement device under standard conditions, it should be expressed in dimensionless terms (i.e., as concentration units divided by concentration units). Units of S_i then equate to the inverse of units of I_{ij}, which is appropriate given the fact that S_i describes the departure from standard measurement conditions.

Under laboratory conditions, K_j and S_i are fixed, and W_{ij} is estimated from I_{ij}, with a correction factor given by M_{ij}. The matrix effect is commonly expressed as a function of the concentrations of the other elements present in the specimen under consideration, although formulations in terms of intensities are also available. Various methods for estimating M_{ij} have been proposed, most of which are based on a combination of theory and empirical evidence (calibration specimens). Under ideal conditions, entirely theoretical methods for estimating M_{ij} (so-called fundamental parameter methods) may be utilized to predict net intensities based on known specimen compositions. Fundamental parameter methods are commonly implemented in the form of physically-based non-linear optimisation techniques, in which intensities calculated from an initial guess of a specimen's composition are compared to measured intensities, and the estimated composition of the sample is iteratively adjusted so as to minimise some measure of discrepancy between predicted and measured intensities (Jenkins 1999; De Vries and Vrebos, 2002).

The XRF micro-core-scanners described by Croudace et al. (2006) and Haschke (2006) are capable of adjusting the position of the detector to accommodate variations of core-surface elevation. This approach minimizes variations in measurement geometry (S_i) and maximizes the signal-to-noise ratio. However, the degree of control on measurement geometry is proportional to spatial resolution, because larger irradiated areas have a higher probability of being perceived as inhomogeneous in terms of surface elevation. The sediment volume sampled by XRF core scanners is very small relative to sample volumes used in conventional destructive chemical analysis, especially when they operate at maximum spatial resolution. The spot size of the excitation beam employed in high-resolution sediment characterization can be as small as 20 μm (Croudace et al., 2006; Haschke, 2006). Because sampled volume is inversely proportional to spatial resolution, contributions of small-scale inhomogeneity within the core will increase with decreasing sampling interval and spot size. As a result of this, the probability that a sample faithfully mirrors the properties of the target population also decreases with sampling interval and spot size. In practice, the signal-to-noise ratio depends on the degree of inhomogeneity of the core (surface elevation, grain size, water content) relative to the sampling interval of the core scan. The highest resolution which may be considered meaningful in sediment characterization should be well above the size of the largest grains present in a given core interval. The trade-off between these two limitations of XRF core-scanning devices implies that quantitative on-line XRF analysis will be most successful if the ratio of characteristic grain size to characteristic wavelength of variations in core-surface elevation is as small as possible. Cores consisting of clayey or silty sediments, which match the grain size of homogeneous powder specimens used in conventional XRF analysis (Potts, 1987), are therefore most amenable to XRF scanning. An example of core-scanner measurements collected under such favourable conditions was published by Haug et al. (2001, 2003), who presented high-resolution XRF scanning data of cores consisting of very fine-grained, laterally homogeneous, laminated deposits.

The fundamental problem in on-line XRF core scanning is that S_i is very poorly constrained, owing to inhomogeneity of the specimens