Challenges in rapid soil quality assessment and opportunities presented by multivariate chemometric energy dispersive X-ray fluorescence and scattering spectroscopy

M.I. Kaniu *, K.H. Angeyo

Department of Physics, University of Nairobi, P.O. Box 30197, 00100 Nairobi, Kenya

ABSTRACT

There is, especially in precision agriculture, an increasing demand world over for affordable sensors for in situ (field deployable) soil quality assessment (SQA) applicable at an ecological scale due to the interplay between soil quality and environmental degradation. Although spectrometric (particularly optical) techniques offer the opportunity to meet this demand due to their high analytical versatility, their utility in rapid SQA is limited by the complexity of the soil matrix, and the interpretation of the resulting spectra and (usually) multivariate quality assurance (i.e. SQA) data. In this paper, we examine the utility of spectrometric techniques for soil analysis and critique their applicability to rapid SQA; in particular, we appraise their potential for development towards intelligent portable SQA systems for in situ application. We then evaluate in this perspective the applicability of a new method we have recently developed namely chemometrics energy dispersive X-ray fluorescence and scattering spectrometry (EDXRFS) for SQA, emphasizing its potential for realizing rapid intelligent sensor architecture for in situ SQA. We conclude that a point of care soil sensor that infers soil properties, and intelligently modulates precision agriculture may be realized by integrating the EDXRFS spectroscopy method to a portable XRF spectrometer.

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1. Introduction: SQA and measurement techniques

Agricultural practice and development of precision agriculture in most parts of the developing world are undermined by the lack of knowledge in, and appropriate technology for, soil quality assessment (SQA) which demands simple, affordable and rapid but accurate soil quality sensing technologies (Adamchuk et al., 2004). The importance of soil quality is however not limited to agricultural practices, but extends to environmental quality, human and animal health, and food safety (Karlen et al., 2003). SQA is normally conducted by evaluating basic soil quality indicators (SQIs) otherwise known as the minimum data set (MDS) defined for a particular region (or ecological zone) (Doran et al., 1996). In this paper, we focus on soil fertility by evaluating organic carbon (OC) content, bio-available macro- and micro-nutrients, as well as low atomic number (Z) elements as SQIs.

Hardly is there a method that can simultaneously furnish, with speed, reliability and accuracy most of the above nominated SQIs.

The complex nature of soil as a matrix, especially its compositional variability, high organic and inorganic mineral matters imposes serious difficulties in the quantitative analyses of soils utilizing existing conventional techniques. Soil is composed mostly of low Z (<11) elements, refractories (which are not easy to digest), and is inhomogeneous. Conventional methods for soil testing are normally wet chemistry-based and involve collecting a large number of soil samples from the field, performing the necessary sample preparation and ultimately conducting laboratory analyses.

Examples of these analytical methods include the 'Mehlich' method (Mehlich, 1978) for determining macronutrients including phosphorous (P), magnesium (Mg), sodium (Na); the Walkley–Black procedure for OC and organic matter (OM) analysis; dry combustion for total carbon (C) analysis (Nelson and Sommers, 1996), and the 'Kjeldahl after Bremner' method (Bremner and Mulvaney, 1982) for determining total nitrogen (N). Among the analytical spectroscopic methods, atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) techniques are preferable and thus are routinely used for elemental analysis of soils. Although these methods may be accurate, they involve tedious sample preparations, are expensive and prone to inaccuracies due to the possibility of contamination from the chemical reagents used for sample digestion (Jones, 2001). Moreover, digestion often involves heating which may lead to weight loss of inorganic soil constituents and overestimation of soil organic matter (SOM) (Cambardella et al., 2001). Utility of these methods to SQA is limited to elemental

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Table 1
Characteristics of soil samples studied.

	Soil type/agro-ecological zone	Soil properties
Artificial soils		
[1]Laboratory simulate	Kaolinite, <10 μm	Kaolinite mixed with simulated compositions of Fe, Cu, Zn, NO_3^-, SO_4^{2-} and $H_2PO_4^-$
[2]IAEA soil-7	Cambisol, <71 μm	Reference material for measurement of trace elements
[3]IAEA SL-1	Lake sediment, <0.1 mm	Reference material for measurement of trace and minor elements
Field soils		
Kitale block-A	Red ferrosol, lower highland	Obtained from an intensively cultivated area
Kitale block-D	Red ferrosol, lower highland	Obtained from a furrow non-cultivated area
Katumani	Red ferrosol, semi-arid (tropical)	Obtained from a furrow non-cultivated area

[1] Kaniu et al. (2011).
[2] Pszonicki et al. (2000).
[3] Campbell et al. (1999).

analysis and as a result, they are not easily used to capture the spatial and temporal changes of soil properties.

1.1. Novel spectroscopic approaches for SQA

Nonetheless, spectroscopic techniques have the best potential to assess various SQIs simultaneously and offer the potential to be applied in situ, thus providing for spatial and temporal SQAs (Shepherd and Walsh, 2002; Vohland et al., 2009). These techniques have inherent high sensitivity, accuracy, speed and versatility for a wide range of soil types. Notable are those based on visible and near infra-red (vis–NIR) diffuse reflectance (Stenberg et al., 2010), X-ray fluorescence (XRF) (Cesareo, 1999), and laser induced breakdown spectroscopy (LIBS) (Martin et al., 2003). For instance, the vis–NIR reflectance spectrum has been adopted in the measurement of key soil properties i.e. moisture component, SOM, total C and OC, pH, cation exchange capacity (CEC) and total N (Kuang et al., 2012). LIBS is based on atomic emission spectroscopy and is mainly applied in the determination of metal ion soil constituents, N and total C (Gehl and Rice, 2007). XRF is mainly applied for the assessment of major and minor soil nutrients, trace elements and heavy metals (Dos Anjos et al., 2000). However, the utility of these techniques is limited by a number of factors among them: weak spectral signals for low trace and light element analysis, spectra overlaps, noise, complexity of the spectra and interpretation of the resulting soil quality (SQ) data which is normally multivariate.

XRF spectroscopy is based on the principle of irradiation of a specimen with X- or gamma rays from a source i.e. accelerator, radioactive isotope, X-ray tube or synchrotron which results in the excitation of inner electrons of the atom and subsequent transitions by the outer shell electrons to the ionized level. The elements present in the specimen emit characteristic fluorescent X-ray radiation with discrete energies. This process is governed by the quantum mechanical selection rules, and interaction of X-rays with matter is dominated by two mechanisms namely the photoelectric effect and X-ray scattering (West et al., 2010). Emergent instrumentation technologies have led to the development of portable XRF (PXRF) (Hou et al., 2004) which provides viable and effective analytical approaches to meet on-site analysis needs for SQA. However, accuracy challenges have been cited due to the uncertainty caused by soil morphology and matrix effects (Kalnicky and Singhvi, 2001).

We recently developed the energy dispersive X-ray fluorescence and scattering spectroscopy (EDXRFS) method for characterization of complex materials (Angeyo et al., 2012a, 2012b; Kaniu et al., 2011, 2012a). The method, which is based on extending the capabilities of conventional XRF analysis exploits, in addition to weak isotope source X-ray fluorescence, scatter peaks measured directly from test matrices to develop multivariate analytical models for quality assurance (QA) problems. The EDXRFS method enabled, for the first time, an XRF technique for determination of low Z elements and anions in materials. This was realized as the full spectrum (i.e. both fluorescence and scatter, henceforth referred to as EDXRFS spectra) carries various explicit and implicit signatures related to the chemical and physical properties of the

material, so multivariate chemometrics may be exploited for the trace quantitative and exploratory analyses of these signatures.

2. Chemometrics in analytical spectroscopy

Chemometric techniques are capable of overcoming most of the challenges associated with analytical spectroscopy as they have the ability to extract important features (e.g. underlying soil properties) from complex (spectral) data sets and hence can be developed in conjunction with spectrometric methods (Mark and Workman, 2010) to perform rapid and stable SQA. Chemometrics is most popular in experimental design and in the application of multivariate analysis to complex data matrices (such as soil spectra which are combinations of diverse SQIs). The greatest potential of chemometrics as utilized in XRF analysis is being demonstrated in the fields of curve fitting (spectra deconvolution), multivariate calibration and pattern recognition (Luo, 2006). For example, using chemometrics it is possible to estimate a range of soil properties such as bioavailable soil nutrients directly from the XRF spectra; an explicit evaluation of the spectrum is not required (Kaniu et al., 2012a).

One of the main advantages of chemometrics is the representation and reduction of extensive multivariate data into fewer dimensions (i.e. the data matrix is divided factorially and projected on a lower dimensional space) and the depiction of the information in a graphical interface (Brereton, 2003). Other advantages gained in utilizing chemometrics in analytical spectroscopy include the ability to model and reduce spectral noise and to handle spectral interferences and outliers i.e. correction of matrix effects, and to achieve multivariate calibration for rapid quantitation especially at trace levels.

Typical problems related to SQA that can be successfully handled by multivariate chemometric techniques in conjunction with spectroscopy include the following.

(i) Determination of the concentration of compounds e.g. nitrate content in soil by EDXRFS and mid-IR spectroscopy (Kaniu, 2011; Linker et al., 2005).

(ii) Classification of soil in terms of origin and soil type by XRF and mid-IR spectroscopy (Custo et al., 2002; Linker et al., 2005).

(iii) Prediction of soil chemical composition and contamination by EDXRFS, vis–NIR and LIBS (Kaniu et al., 2012b; Kemper and Sommer, 2002; Martin et al., 2003; Zornoza et al., 2006).

(iv) Development of quantitative structure activity relationship (QSAR) in for example soil ecotoxicology by IR and ultra-violet (UV) spectroscopy (Posthumus and Slooff, 2001).

(v) Remediation process monitoring of contaminated soils by vis–NIR, ICP and mass spectrometry (MS) (Kemper and Sommer, 2002; Stanimirova et al., 2006; Vogt et al., 1987).

(vi) Discrimination of soil types for intelligence and forensics by IR spectroscopy (Baron et al., 2011).

These capabilities make chemometrics attractive for analysis and evaluation of SQA utilizing EDXRFS spectra in the following way.