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Portable X-ray Fluorescence (PXRF) Spectrometry of Soils: Method Limitations

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X-ray fluorescence spectroscopy (XRF) is a non-destructive analytical technique used for qualitative and quantitative determinations of elemental composition [1]. XRF technology has existed since the 1950's and has a long history in the geological sciences. Several forensic applications have also been documented [2]. Originally XRF analysis was performed using laboratory-based machines that required sample homogenization and the creation of pressed power pellets or fusion of the sample in a glass matrix. Technical advances have led to the development of field portable units (PXRF) with detection limits in the part per million (ppm) range that can be used on unmodified samples. With current technology, the elemental signature of dry samples ($\geq K$ in air and $\geq Na$ under vacuum) can be rapidly (<5 minutes for bulk composition) and non-destructively measured. This greatly increases the flexibility and utility of XRF analysis, however, this also greatly increases the potential for misuse of the technology. Manufacturers often sell the units as 'point and shoot', which mischaracterizes the technology and has led to poorly structured analytical studies and the publication of flawed data.

A typical PXRF system uses an x-ray tube as an excitation source to irradiate samples. The incident x-rays interact with the atomic structure of the sample causing some electrons to eject from their inner orbital shells, leaving vacancies that are filled by outer shell electrons that release energy in order to fall into new ground states. The fluorescent x-ray energy released is equal to the specific difference in energy between two quantum states of the electron. Since each element has a characteristic arrangement of electrons, the x-rays released by such transitions are also unique, allowing for elemental identification. Quantification, however, requires application of a suitable processing technique and all quantification methods have baseline assumptions about the sample being analysed. For accurate quantification, samples must be homogeneous, uniform, very well sorted, and have flat, smooth surfaces to ensure the correct beam geometry. They must be large enough to interact with the entire incident beam and 'infinitely thick' (i.e. incident x-rays do not go through the sample into a substrate or into the air). Finally, the sample should be dry because water dramatically attenuates x-rays. For example, studies involving *in situ* measurements [3] show that for every 1% increase in soil moisture there was a 1.15 to 1.75% decrease in measured analyte concentration.

Clearly forensic soil samples will often deviate from the ideal, thus it is vital to ensure appropriate selection of instrument parameters to maximize data quality, while at the same time recognizing and acknowledging the limitations of the method. In the literature, PXRF analysis of soils and trace evidence samples has been reported using data collected *in situ* against the ground surface (sometimes without even the ground-cover having been removed), collected across stratified cross-sections, and quite often, collected while the soil is contained in a plastic storage bag. The last case is of particular interest because plastic and Mylar coverings also attenuate x-rays, especially impacting quantification of light elements. If a soil sample is analysed in a 4 mil polyethylene storage bag, no aluminium will be observed because its characteristic radiation will be completely attenuated by the bag [4]. Likewise, silicon and phosphorous are also highly attenuated, by 96 and 90% respectively. No amount of post-processing and statistical analysis will make up for inappropriately chosen conditions and analysis parameters. Such

misunderstandings of technique can potentially lead to errors in casework, as when an *in situ* sample was initially excluded incorrectly when compared to reference samples that were housed in plastic bags due to the differences in light element ratios.

References:

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