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QUANTITATIVE ANALYSIS OF ELEMENTS IN SEDIMENTS AND SOILS BY X-RAY FLUORESCENCE: A DISCUSSION

Key Words—Sample Homogeneity, Soil Analysis, X-ray Fluorescence.

In a recent issue of this journal, Tuncer *et al.* (1977) described a mathematical treatment of X-ray fluorescence (XRF) data to estimate the elemental composition of soils. The following discussion refers to this paper:

Tuncer *et al.* (1977) compared results obtained by three analytical techniques; however, their methodology for preparing samples for atomic absorption spectrophotometry (AA) indicates that an undisclosed amount of "insoluble residue" was removed from the solution prior to analysis. The soils analyzed by XRF, on the other hand, contained this material as one of their components, with resultant matrix problems. It is not clear as to whether or not this "insoluble residue" contained iron; the reagents employed to digest the soil, namely, a mixture of perchloric acid, phosphoric acid, and nitric acid, will not totally destroy the silicate structure. Hence, some iron could still have been locked up in the residue. The situation can best be resolved by a separate XRF analysis of the residue. In the absence of such information, the data obtained in the XRF analysis should not be compared with those obtained by AA methods. Also, the soils could be totally digested by fusion with lithium metaborate, followed by dissolution in a mild acid. Such a solution would contain all of the chemical components of the original soil, and a comparison of XRF and AA data would then be valid.

Matrix effects due to the addition of an internal standard to the soil need to be examined fully. Sediments and soils follow log-normal size distribution, whereas freshly ground powders, commonly used as internal standards, follow Rossin's law of size distribution (Dapples, 1975). Different size distribution implies different grain-size population. Hence, mixing the two components, namely the laboratory ground standard powder and natural soils, will produce a size distribution different from that of the original soil. The effective penetration depth of XRF depends on the mean particle size of the sample (Jenkins and De Vries, 1967); thus, soil and soil-hematite mixtures will have different X-ray-penetration depths.

Soils contain a large number of elements, and it is not possible to add an internal standard which will contain all the elements of interest. Hence, internal standards have to be separately and individually added for each element, such as SiO_2 for Si and Fe_2O_3 for Fe. Such numerous additions complicate the already complex nature of the soil, and the resultant XRF intensities cannot be easily converted to concentrations using existing equations. Also, a large number of samples with different internal standards must be analyzed, in order to obtain the complete chemical analysis of the single soil sample.

Soils and sediments contain X-ray amorphous materials, such as hydroxides of Fe and Mn and organic matter. XRF intensities measured for soil on one hand, and a mixture of soil and crystalline hematite on the other, are not necessarily comparable. In complex matrices such as soils, "spiking" with hematite for measuring concentrations of Fe is valid only if the concentration/count-rate ratio is linear. Also, addition of a standard for one element may interfere with XRF measurements for another element in the mixture. For instance, the XRF intensity for Fe in an Fe-Ni alloy has been reported to be higher compared to that of pure Fe due to the close spacings of FeKα (1.743 Å) and NiKα (1.659 Å) lines (Jenkins and De Vries, 1967, p. 114). Further, it is difficult to calculate exactly the mass absorption coefficient of the matrix for soil without knowing its chemical composition.

Tuncer *et al.* (1977) used the internal standard technique only for iron determinations. The suitability of the equations developed by them for the analysis of other elements by XRF method remains to be verified experimentally. In conventional XRF techniques for sediments, USGS standards in the form of rock powders are normally used (see, for example, Cann and Winter, 1971). But it has been pointed out by Subramanian and d'Anglejan (1976) that standard rock powder and natural sediments have different textural properties even if care is taken to obtain standards with the same grain-size distribution as that of the sample. The textural difference is due to the presence of binding materials in sediments and soils. Applying a modified thin-film technique, they successfully analyzed small amounts of suspended sediments, using the same sediments as external standards. The use of a similar thin-film technique for soils needs to be explored. A fusion technique for specimen preparation should also be explored for soils and sediments.

In conclusion, the mathematical treatment developed by Tuncer *et al.* (1977) appears to have limited scope in the chemical analysis of soils and sediments due to a number of problems involving matrix effects. Alternate techniques in preparation of standards need to be examined.

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