Trace Analysis: Soils

Malcolm S. Cresser

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By Malcolm S. Cresser

Department of Plant and Soil Science, University of Aberdeen,
Old Aberdeen AB9 2UE, U.K.

Determinations of constituents present in soils and soil solutions at trace concentrations are conducted primarily because of interest in soil as a medium for plant growth or because of its influence upon the solute chemistry of fresh waters and ground waters. Interest may arise from concern over potential toxicity effects or over adverse effects of deficiency of trace nutrient elements essential to soil or freshwater biota.

In the above context, total amounts of elements present in soil are generally of less interest than water-soluble or labile, plant available forms (Marr & Cresser 1983). Rhizosphere soil may be more relevant than bulk soil in assessing plant availability. Over recent decades, optimal chemical extractants (such as EDTA or DTPA for Zn and Cu) have been selected which reflect plant availability of trace elements in terms of high correlations between plant tissue and soil extract concentrations. Occasionally full speciation is conducted. M. S. Cresser & E. El-Sayad (unpublished results), for example, have measured water-soluble, exchangeable and organically bound trace elements, and those in carbonate and amorphorus and crystalline iron and manganese oxides, and residual sand, silt and clay minerals. Such detailed analysis is valuable in elucidation of soil pedogenesis (El-Sayad *et al.* 1988).

No single, low-cost technique is applicable to all the elements of interest at the concentrations normally found, especially in deficiency studies. Flame AAS is useful for Mn, Fe and Zn and sometimes for Cu. For Cd, Co, Cr, Ni and Pb, however, preconcentration is invariably needed (Cresser 1983), or furnace AAS may be used, with a matrix modifier and preferably a L'vov platform. ICPAES provides adequate sensitivity for several, but not all, trace elements (Cresser *et al.* 1990). The more recently introduced ICPMS has great potential, but cost is a limitation. For Hg, cold vapour AFS is suitable, and hydride generation AAS is used for As and Se.

Ion chromatography is invariably used for measuring Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} in soil solutions, but sometimes NO_2^-, NO_3^- and PO_4^{3-} are determined by manual or automated (segmented flow or flow injection) colorimetric analysis. Boron is best determined fluorimetrically at very low concentration. Microprocessor-controlled dispenser–diluters are excellent for low-cost, high-sample-throughput colorimetric or fluorimetric analysis.

In deficiency studies and speciation studies, contamination, including impurities in reagents, may become a major limitation in some working environments.

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Optimization in trace atomic spectroscopy

By Les Ebdon and Michael Foulkes

Plymouth Analytical Chemistry Research Unit, Department of Environmental Sciences, Polytechnic South West, Drake Circus, Plymouth PL4 8AA, U.K.

Optimization of analytical instrumentation enables realization of potential and the valid comparisons of techniques, hence the interest in rigorous, mathematically based, optimization procedures. One of the most effective procedures is variable step-size simplex. Using a simple algorithm, sets of initial operating parameters can be tested and instrumental response evaluated. The worst response is rejected and a new set evaluated, thus in a logical manner the optimal conditions are identified. Particular benefits are speed, computer compatibility, relative freedom from false optima and the irrelevance of prior assumptions or knowledge about response surfaces.

The development of inductively coupled plasma atomic emission spectrometry (ICPAES) was controversial as the interdependent operating variables made optimization difficult. Simplex-based procedures have therefore been extensively used to optimize ICPAES for signal-to-background ratios, multielement determinations and to minimize interferences from easily ionized elements. In the analysis of solids by nebulizing suspensions of powders into plasmas (slurry atomization), the aim is to achieve calibration using aqueous standards. Simplex procedures have been used to achieve equivalent analyte response from slurries and aqueous solutions. The compatibility of simplex algorithms with computers offers the potential for microprocessor-controlled optimization of analytical instruments. Work in this area has been pioneered at Plymouth for ICP spectrometry.

Optimization of direct current plasma AES is also facile. Examples of successful optimizations include for signal-to-background ratio; for slurry atomization; and hydride generation. The latter may include the optimization of the chemistry of the hydride generation parameters along with the instrumental parameters, this is particularly valuable for lead.

Inductively coupled plasma mass spectrometry (ICPMS) is a new technique which offers excellent detection limits but uses complex instrumentation. Simplex optimization is being used to develop methodology and instrumentation, e.g. a recent comparison of low-flow and conventional torches for ICPMS showed the latter offered superior sensitivity and freedom from polyatomic interferences.

Optimization offers a powerful tool to enhance trace analysis.