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## SIMULTANEOUS MULTIELEMENT ANALYSIS OF CLAYS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY USING SUSPENSION ASPIRATION

**Key Words**—Aspiration, Chemical analysis, Emission spectroscopy, Glacial till, Inductively coupled Ar plasma, Plasma, Soil.

### INTRODUCTION

A variety of techniques, such as colorimetry, atomic absorption spectroscopy, electron microbeam analysis, X-ray fluorescence, neutron activation analysis, and arc spectroscopy have been used for the chemical analysis of clay minerals. The first two methods require dissolution of the samples before analysis and are generally single-element techniques with significant chemical interferences present in the solution matrices. The other techniques are applicable to solid phases, but require calibration standards of similar chemical composition. Some require fairly extensive calculations to correct for spectral and matrix interferences. A new analytical method for elemental analysis of clays is inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This method is suitable for most elements in the periodic table and has low detection limits, high precision, and linear calibration over several orders of magnitude. ICP-AES enables simultaneous analysis of major, minor, and trace elements in a matter of seconds.

The plasma excitation source is a relatively new advance in emission spectrometry (Boumans, 1978). In an inductively coupled argon plasma a stream of argon atoms is ionized by a Tesla coil. Then electrons which are passing through the radio-frequency (1.65 kW) induced magnetic field rotate in an annular path. Collision between these electrons and the argon gas causes further ionization and Ohmic heating. This argon plasma has a temperature of 6000–10,000°K in its central region. The analyte solution is then aspirated into a nebulizer where the flow of argon gas converts a proportion of the solution into an aerosol which is sprayed into the center of the argon plasma. The analyte solution is thus introduced into a stable plasma in which the temperature is sufficient to dissociate chemical bonds and excite atoms. In such an environment, the elements in the analyte solution emit their characteristic radiation which is focused into a conventional air-path spectrometer where the spectral lines are diffracted from the main grating and detected by fixed photomultipliers mounted along the Rowland circle of the spectrometer.

The technique has found some usage in the earth sciences for geochemical analyses (Burman, 1977; Floyd *et al.*, 1980; Odegrad, 1979; Walsh and Howie, 1980), for the determination of the bulk composition of soils and sediments (Larson *et al.*, 1979; McQuacker *et al.*, 1979; Spiers *et al.*, 1983), and for extractable nutrient determinations for a wide range of soils (Dalquist and Knoll, 1978; Jones, 1977; Soltanpour *et al.*, 1979). All of these applications, however, required that samples be converted to solution form prior to analysis.

Boumans (1978) indicated that ICP-AES, although primarily suited for the analysis of liquid samples, may be adapted for the direct analysis of solids. Solid or suspension analysis would eliminate the costly and time-consuming chemical dissolution for geological materials. The objective of the current study was therefore to determine whether ICP-AES is, indeed, suitable for direct analyses of clay suspensions without sample dissolution.

### MATERIALS AND METHODS

Clay separates (<2  $\mu\text{m}$ ) were obtained from 22 soils formed on glacial till and lacustrine parent materials in northeastern

Alberta (Spiers, 1982). Subsamples (100 g) of soil were dispersed in distilled water for 3 min by ultrasonification at 400 W using a probe-type vibrator (Edwards and Bremner, 1967). The <2- $\mu\text{m}$  fraction was then separated from the suspensions by a combination of gravity sedimentation and centrifugation techniques (McKeague, 1978). The separated clays were flocculated using 1 M  $\text{CaCl}_2$  solution, washed of excess electrolyte with distilled water, and freeze-dried for storage prior to subsequent analysis. The clay separates contained a mixture of smectites, micas, and kaolinite in approximately equal amounts, with lesser amounts of chlorite, and X-ray-amorphous aluminosilicates and iron oxides (Spiers, 1982).

Digests of the clay separates were prepared using a modification of the HF-HCl dissolution method (Pawluk, 1967). One-gram portions of each sample were ignited at 550°C in porcelain crucibles for 8 hr. The samples were transferred to Teflon beakers and treated with 20 ml of concentrated HCl and 20 ml of concentrated HF. The mixture was evaporated to dryness on a sand bath at 85°C and the digestion procedure repeated using 10 ml of each of the two acids. Finally, an additional 10 ml of HCl only was added to the residue and again evaporated to dryness to ensure complete volatilization of the HF. The residue was then dissolved in 25 ml of 4 N HCl over the sand bath, cooled, transferred to a 50-ml volumetric flask and made to volume with distilled water.

Suspensions of the clays were prepared by dispersing known quantities of the freeze-dried samples in both distilled water and 2 N HCl using a 15-sec treatment with the ultrasonic probe. These suspensions were prepared over a concentration range of 2% to 0.05% to evaluate the effect of colloidal concentration on the analyte nebulization rate. This was done because the most critical factor as far as analytical precision is concerned with any technique requiring aspiration is to have the aspiration rate of both standards and analyte solutions identical. The samples were agitated gently before and during aspiration in order to maintain a uniform suspension.

Elemental abundances were determined with an ARL QA-137 direct-reading spectrometer with an inductively coupled argon plasma-excitation source. Instrumental operating conditions outlined in Table 1 are those recommended by the manufacturer for obtaining optimal results for all analyzed elements. Samples aspiration was natural with a –5 cm head on the uptake capillary. Elemental concentration ranges of sets of combined liquid standards (Table 2) were chosen to bracket the elemental concentration ranges expected for the clay digests and suspensions. The elemental groupings for standards were chosen to minimize possible interelement effects during instrument standardization. The data-processing package supplied by ARL for use with the PDP 1104 mini-computer which is interfaced with the ICP-AES instrument was used at all stages of this study.

### RESULTS AND DISCUSSION

Preliminary experiments indicated that suspensions at the higher concentrations gave a 25% or greater reduction in aspiration rate as compared to the dissolved samples. No apparent difference was observed between suspensions in HCl (2 N) made to match the standard matrix and those in distilled water. On the basis of these findings suspensions containing

Table 1. Operating procedures for routine analysis using the Applied Research Laboratories QA-137 ICP-AES instrument.

Incident power	1650 W
Reflected power	10 W
Entrance slit width	12 $\mu$ m
Argon flow rates:	
Coolant	10.5 liter/min
Sample carrier gas	1 liter/min
Plasma	1.5 liter/min
Sample aspiration rate	2.4 ml/min
Observation height	0.63 coil height
Nebulizer	Meinhart concentric
Operating temperature	24°C.

0.1–0.2 g of clay in 100 ml of distilled water were used in subsequent analyses to produce minimal aspiration-rate effects while maintaining levels of several minor and trace elements above instrumental detection limits. Clay suspensions at this concentration gave a 7–9% decrease in aspiration rate.

The results of analyses of the clay suspensions were compared with those obtained following routine chemical dissolution procedures (Figure 1). The high coefficients of determination ( $r^2$ ) for all elements demonstrate clearly the potential of suspension aspiration for rapid and comparable analysis of the bulk chemistry of clay separates. This close agreement in analytical results indicates that ICP-AES is able to dissociate the structural bonds of the clay species in the analyte suspensions to produce an atomic vapor in which the constituent atoms are excited to emit their characteristic spectra. The  $b$  values (slopes) were not significantly different among the 13 elements determined. All  $b$  values were between 1.07 and 1.09 indicating higher recorded concentrations in the solutions than the suspensions. The deviation of the slopes

Table 2. Spectral lines, detection limits, and standard groups used for instrumental calibration.

Element	Spectral line (nm)	Detection limit <sup>1</sup> (ppm)	Group number	Standard concentration range (ppm)
Cu	3247.5	1.0	1	0–10
Co	2388.9	1.0	1	0–10
B	2497.7	0.5	1	0–10
Cr	2677.2	0.5	1	0–10
As	1937.7	5.0	1	0–10
Pb	2203.5	4.0	1	0–10
Cd	2265.0	0.5	1	0–10
Zn	2025.5	0.1	2	0–100
Mn	2576.1	0.1	2	0–100
Mo	2020.3	0.1	2	0–100
V	3102.3	0.5	2	0–100
Sr	2136.2	0.1	2	0–100
P	4077.7	4.5	2	0–100
Ca	3158.9	2.5	3	0–1000
Na	5895.9	5.0	3	0–1000
Mg	2790.8	3.0	4	0–1000
K	7664.9	8.0	4	0–1000
Fe	2599.4	1.5	5	0–2000
Al	3082.2	5.0	6	0–2000

<sup>1</sup> Extrapolated to indicate minimum concentrations in clay materials using dissolution technique described in this paper.

Table 3. Analysis of A.P.I. Garfield nontronite (H 33a) illustrating agreement between analyses by electron microprobe and by suspension aspiration with inductively coupled plasma-atomic emission spectroscopy.

Element	Electron microprobe	ICP-AES <sup>1</sup> (%)
Si	24.571	24.674 $\pm$ 0.005
Al	3.865	3.742 $\pm$ 0.006
K	0.00	100 ppm
Mg	0.398	0.381 $\pm$ 0.003
Ca	1.358	1.365 $\pm$ 0.004
Fe	26.153	26.217 $\pm$ 0.002

<sup>1</sup> Based on 10 analyses.

from unity probably arose from differences in viscosity of the suspensions and solutions. The increased viscosity of the clay suspensions was shown to induce an aspiration rate 7–9% slower than that of both digest and standard solutions. Such a rate would cause a decrease in the number of atoms reaching the plasma region of the instrument. This decrease in aspiration rate appears to be directly responsible for the analytical variation observed and must be corrected by use of a factor of 1.08.

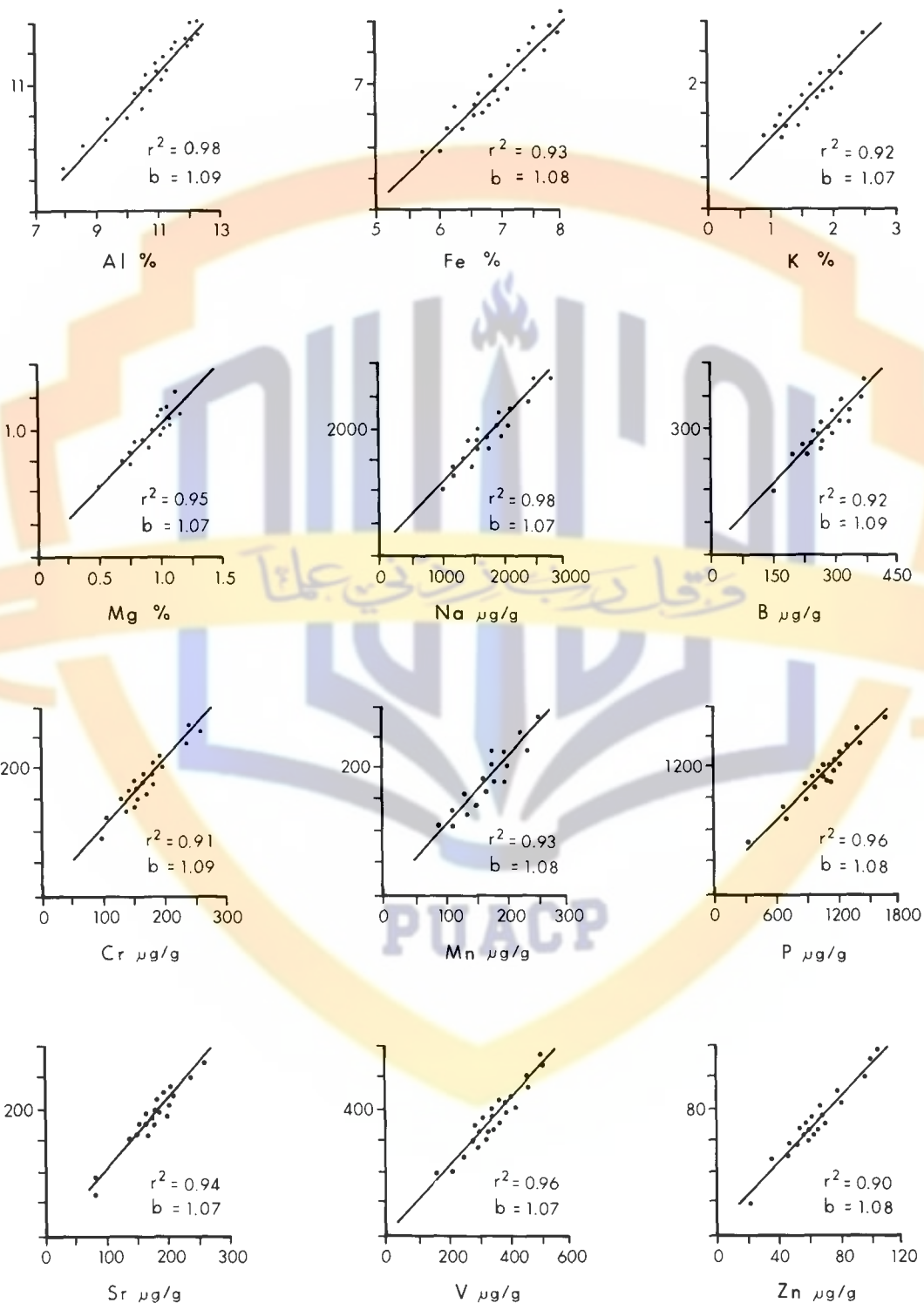
The analyses described above indicate that it is possible to obtain data using suspension aspiration which are comparable to those obtained by analysis of dissolved clay separates, but they do not indicate the degree of accuracy of the data. For this purpose five API reference clay minerals, previously analyzed for all major elements using an electron microprobe technique (Smith and Cavell, 1980), were used to create clay suspension standards which would not show the viscosity differences noted for chemical standards. Suspensions of other API clays for which microprobe analyses were available were then analyzed to determine the utility of the clay standard curves for analysis of unknown clay separates. An example of both the accuracy and reproducibility of these analyses is shown in Table 3. This method of analysis has the added advantage of providing accurate data for Si, an element which cannot be determined by the dissolution method used in this study as it is volatilized as silicon tetrafluoride.

This study shows that ICP-AES is capable of decomposing crystalline clay materials to provide accurate elemental analyses of clay suspensions. Furthermore, matrix effects resulting from viscosity differences between chemical standards and sample clay suspensions can be eliminated by using reference clay minerals as suspension standards. For routine analyses of composition of clay separates, the main advantages of this technique are its simplicity, speed, and accuracy. An operator can analyze 20–25 samples per hour for a wide range of elements with no tedious sample digestion being required.

The technique described here indicates that it is possible to sample a clay suspension of unknown composition, gravimetrically determine its concentration, and proceed with analysis using ICP-AES following dilution of a subsample to the required concentration. Saturation of subsamples of the original suspensions with different index cations and anions would enable the calculation of both anion- and cation-exchange capacities of the separates, with the added advantage of producing replicate analyses for all other compositional elements. The remaining portion of these suspensions could then be filtered onto ceramic disks or smeared onto glass slides for X-ray powder diffraction analysis for determination of the mineralogical composition. In essence, a rather complete chemical and mineralogical characterization could be obtained on a single suspension sample.



SOLUTION ANALYSIS



SUSPENSION ASPIRATION

Figure 1. Comparative plots showing total elemental abundances obtained by direct aspiration of suspensions and by solution analysis of dissolved clay separates.

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