

Soil colloid analysis by Flow Field-Flow Fractionation

David J. Chittleborough¹, Soheyl Tadjiki², James F. Ranville³, Finlay Shanks⁴ and Ron Beckett⁵

¹School of Earth and Environmental Sciences, University of Adelaide, Private Bag 1, Glen Osmond, SA 5064 Email David.Chittleborough@adelaide.edu.au

²CRC for Freshwater Ecology, Water Studies Centre, Department of Chemistry, Monash University, Clayton, Vic., Australia; present address

³Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 804401, USA. Email jranvill@Mines.EDU

⁴CRC for Freshwater Ecology, Water Studies Centre, Department of Chemistry, Monash University, Clayton, Vic., Australia; Email

⁵CRC for Freshwater Ecology, Water Studies Centre, Department of Chemistry, Monash University, Clayton, Vic., Australia Email Ron.Beckett@sci.monash.edu.au

Abstract

Field-Flow Fractionation (FFF) is emerging as an essential piece in the toolkit of the colloid analyst. Of all the chameleon-like forms that FFF can assume, Flow FFF appears the most versatile, not least because of its capability, in theory, of separating particles, colloids and macromolecules in a range of 15 orders of magnitude in molecular weight. Another key attribute is that separation is independent of particle density. Here we demonstrate, for the first time, that Flow FFF is capable of separating very fine illitic colloids <80nm, isolated from the lower B horizon of a soil profile. We show that marked decreases in the K/Si ratio with decrease in particle size are caused by the presence of very fine kaolinite. The theory of Flow FFF, and the linkage of a Flow FFF channel to Inductively Coupled Plasma Atomic Emission and Mass Spectrometers to produce rapid elemental concentrations as a function of particle size, is explained.

Key Words

Field-flow Fractionation, soil colloid, inductively coupled plasma-mass or atomic emission spectrometry, elemental analysis, particle size.

Introduction

Field-flow fractionation (FFF) is a relatively new technique that is capable of high-resolution separations of colloids and particles that are difficult, time-consuming and/or impractical by other techniques (Giddings 1993, 1988). One of its outstanding characteristics is the broad size range over which it is capable of separation: 5 orders of magnitude, from ~1nm to 100µm. There is a growing body of research in an array of fields testifying to the efficacy of the method but its use in soil colloid and clay mineral analysis is untested.

Over the last decade there has been considerable interest in the nature of fine particles in soils. Much of this interest has arisen from the observation that contaminants have moved through soils at a rate much faster than hydrological models have predicted (McCarthy and Zakara 1989). The process has been attributed to colloid facilitated transport, whereby a contaminant, strongly sorbed to a colloid, is 'carried' through the soil, often along preferential pathways. The colloids responsible are often <60nm, in low concentration and in the form of diverse organo-mineral complexes. These three characteristics pose a challenge for traditional separation techniques such as size exclusion chromatography, ultrafiltration and zonal centrifugation. The threefold challenge of size, concentration and nature for *separation* of fine colloids is, however amenable to *chemical* analysis by modern analytical techniques such as Inductively Coupled Plasma (ICP) spectroscopy, field emission scanning electron microscopy (FESEM), and x ray analytical techniques such as x-ray absorption near-edge structure (XANES) and x-ray absorption fine structure (XAFS) analysis. The limitations have been in the techniques to isolate the colloid-contaminant association from the fluid or solid medium without denaturing the components and fractionate the components based on critically important properties such as their surface charge, density, size and/or shape. FFF offers this prospect. An added benefit is that FFF instruments can be linked readily to analytical instruments to provide elemental analysis in real time.

For the first time Beckett (1991) introduced FFF-ICP-Mass Spectroscopy (MS) as a powerful analytical tool for characterising macromolecules and particles. Taylor *et al.* (1992) illustrated the characterisation of some inorganic colloidal particles and river-borne suspended particulate matter of size range < 1µm using sedimentation field-flow fractionation (SdFFF) and ICP-MS. In their attempt the collected

fractions from the output of SdFFF were introduced to ICP-MS for the multi-element analysis. Chittleborough *et al.* (1992) used the same methodology to analyse soil colloids of size $< 2\mu\text{m}$. However; SdFFF and ICP-MS were directly combined by Murphy *et al.* (1993) to characterise $< 1\mu\text{m}$ clay and river-borne suspended particulate matter. Ranville *et al.* (1999) used the on-line SdFFF-ICP-MS methodology to analyse soil particles in the same size range. Other analytical tools have also been tried as off-line detectors for the FFF subtechniques. Blo *et al.* (1995) used a graphite furnace atomic absorption spectrometer (GFAAS) as an off-line detector for SdFFF to analyse colloidal kaolin particles. Contado *et al.* (1997) coupled GFAAS to SdFFF to characterise river-suspended particulate matter of size $< 1\mu\text{m}$. Hasselov *et al.* (1997) utilised direct interfacing of flow field-flow fractionation (F1FFF) with electrospray mass spectrometry to characterise low molecular weight polymers.

All the work quoted above reports the success of SdFFF as a means of separation of colloids and fine particles and the efficiency and effectiveness of their elemental analysis through linkage of a SdFFF channel to an ICP Mass Spectrometer or an ICP Atomic Emission Spectrometer. Sedimentation Field-flow fractionation-inductively coupled plasma atomic emission spectroscopy (SdFFF-ICP-AES) and Sedimentation Field-flow fractionation-inductively coupled plasma mass spectrometry (SdFFF-ICP-MS) are therefore the combination of a separation and sizing technique with an analytical technique. However, the centrifuges available for SdFFF are only capable of separating down to 80nm. Many colloids of interest are considerably smaller than this. The solution may be Flow Field-Flow Fractionation (F1FFF) which is capable of separating to 1nm but has not been used previously to separate soil colloids and fine clay particles although Hasselov *et al.* (1999), von der Kammer and Forstner (1998) and Lyven *et al.* (2003) have reported the separation and analysis colloids in streams and natural waters. The purpose of our research was to test whether this was possible.

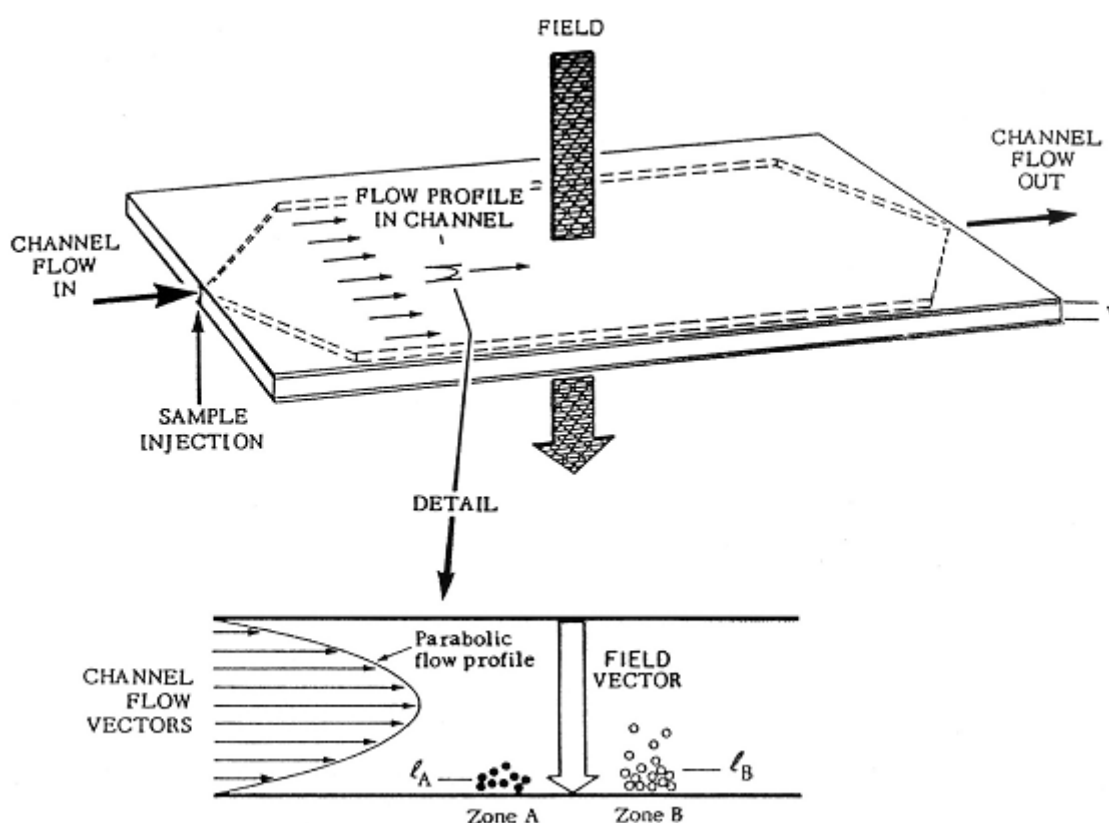


Figure 1. Field-flow fractionation channel showing laminar flow profile and field perpendicular to flow.

Our paper therefore has two prime objectives: to explain the theory of F1FFF and to demonstrate the separation of very fine soil colloids from a suspension with a diversity of sizes. A further objective was to test whether it was possible to hyphenate F1FFF and ICP-MS, and F1FFF and ICP-AES and produce elemental composition as a function of particle size as has been done with SdFFF.

The analysis of some essential elements which have a crucial role in soil mineralogy are very difficult or not possible with quadrupole or high resolution ICP-MS instruments. For example K and Ca are among those elements that cannot be easily detected because their mass number are very close to that of Ar gas which is the main component in the ICP. In this regard ICP-AES could be a good alternative for analysis of the non-detectable elements with ICP-MS, especially K and Ca (Chittleborough *et al.* 1992). In this paper, ICP-AES is tested as an on-line detector for F1FFF and SdFFF to characterise soil and clay particles for the first time.

Theory

Like chromatography, FFF is an elution-based technique. The separation mechanism in FFF is based on the physical interaction of particles with an applied field and the subsequent migration down the channel caused by the carrier fluid. The external field is applied at the right angle to the direction of carrier flow. Separation in FFF takes place in a thin ribbon-shaped channel (Figure 1). Carrier flow in this channel is laminar with the linear fluid velocity being zero at the channel walls and maximum at the centre of the channel. In the presence of the applied field, particles are forced to migrate toward the accumulation wall where they form a concentration gradient that causes diffusional migration against the direction of the field-induced flux. Particles reach equilibrium as these two motions (i.e. the field and diffusion based fluxes) balance each other. At equilibrium each particle component forms an equilibrium cloud whose average thickness ℓ depends on the magnitude of the diffusion coefficient and the strength of the interaction of the field with the particles. Lower flow velocities are found near the walls of the channel than near the centre because of frictional drag. Larger particles that possess less diffusional motion and higher interaction with the applied field, will be caught up in the slower moving streams near the channel wall and elute later than smaller particles.

FFF is therefore a general elution technique resembling chromatography in its operation but using a retention mechanism based on external fields acting in one phase. It has important advantages over chromatography in application to large macromolecules and particles. For the normal mode of FFF, the elution sequence is one in which small particles are eluted first and large particles last.

In SdFFF, the FFF technique that is in most widespread use, the centrifugal field is produced by placing the channel in a centrifuge basket. At constant field strength, the equivalent spherical diameter can be calculated from the retention parameter λ , provided the difference in density between the particles and carrier liquid, $\Delta\rho$, is known;

$$d = \left[\frac{6kT}{\pi\omega^2 r w \Delta\rho \lambda} \right]^{1/3} \quad (1)$$

where ω is the centrifuge speed (radian. s^{-1}), r is the centrifuge radius and k is the Boltzmann constant

In F1FFF, a crossflow is the driving force that induces retention and separation. The parameter controlling retention in F1FFF is the particle diffusion coefficient. The retention volume and retention time for any separated fraction is therefore a direct and calculable measure of particle diffusivity that can be related to an effective particle size termed the Stokes radius or Stokes diameter. It has been shown that the Stokes diameter is a reasonable measure of the volume of the particle for irregular particles (such as most inorganic soil colloids) having aspect ratios up to about 10.

In F1FFF the retention parameter, λ , can be defined as (Wahland *et al.* 1986),

$$\lambda = \frac{DV^0}{V_c w^2} \quad (2)$$

where V^0 is the channel void volume, V_c is the cross flow rate (field), D is the diffusion coefficient, and w is the channel thickness. The particle diameter can then be calculated from the Stokes-Einstein equation:

$$d = \frac{kT}{3\pi\eta D} \quad (3)$$

where k is the Boltzmann constant, T is the temperature, η is the carrier viscosity, and d is the particle diameter. The field in FIFFF is non specific because separation is independent of density and other physical properties of the particle, colloid or macromolecule. It is, potentially, the most versatile method in the family of FFF techniques. The field applied perpendicular to the mobile phase stream along the channel is a secondary flow that drives all sample components to the bottom of the channel surface. Separation is based on differences of diffusion.

Experimental

Flow FFF channel

Two FIFFF channels were used in this work. The channel specifications of the two systems are listed in Table 1. In both channels regenerated cellulose acetate membranes with a cut-off of 30 kD and 10 kD. Amicon YM30 and YM10 membranes were used to cover the lower frit (accumulation wall) of the channels (Figure 1). In both systems samples were injected using a Rheodyne injection loop. The channel, field, and outflow flows were maintained using HPLC pumps. The outlet of the crossflow was connected to the outflow pump working at the same flow rate as the cross flow pump. The HPLC pumps were controlled by computer using FFFractionation software. The outlet of the channel was connected to a UV-visible detector set at 254 nm. Data were recorded using an inhouse data collection program and also monitored using a chart recorder. The carrier used in FIFFF experiments was a 0.005% (w/w) FI-70 (a cationic and anionic surfactant) solution made using deionised water.

Hyphenation of FIFFF channels and ICP spectrometers

The high resolution ICP-MS instrument used in this experiment, was Finnigan Element with a Meinhard nebuliser. The ICP-AES instrument was a Perkin Elmer Optima 3300 DV model, capable of axial and radial plasma viewing. The axial viewing of plasma increases the sensitivity and analysis precision. All elements were analysed in the axial analysis mode. The general set up is shown in Figure 2 that is a schematic representation of the arrangement of the components in an on-line FFF-ICP system. In practice the FIFFF instrument was linked to an ICP-AES and then the instrument was linked to a mass spectrometer. Eluted sample components from UV detector were fed directly to the ICP unit as aerosols created by peristaltically pumping the sample through a nebuliser. In the plasma, the sample aerosols were vaporised, dissociated, atomized and ionized and then transferred to the MS or AES compartments via an Ar gas stream for the elemental analysis.

The FFF-ICP instrument had two on-line detection systems and generated two sets of data. The first set was the plot of UV response versus elution volume or time and is referred to as a fractogram (cf., chromatogram). The next was the ion intensity (cps) generated from the MS unit or emission intensity (counts) from the AES unit for each element versus the elution volume or time. The conversion of the UV and element fractograms to the particle-size and element-size distributions have been explained by Murphy *et al.* (1993) and Ranville *et al.* (1999). The same transformations were used herein for the data obtained in the FIFFF-ICP-AES and FIFFF-ICP-MS experiments.

Another way of presenting the FFF-ICP data is the molar ratio-based size-distributions where the molar ratio of two elements is plotted against the particle size. The molar ratio-based size-distributions are indicators of chemical changes which, in turn, may indicate changes in mineralogical components that must be confirmed by other techniques. Because the concentration of particles in the effluent is very low, standard techniques such as x-ray diffraction lack sensitivity and techniques such as electron microscopy, XANES and XAFS must be employed.

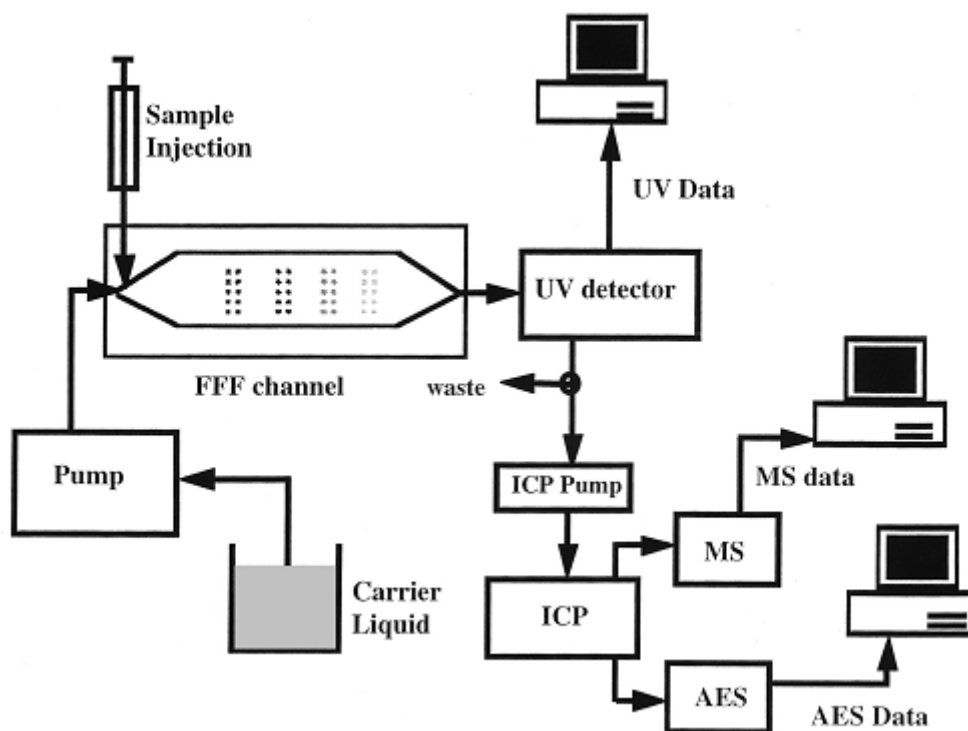


Figure 2. General setup of the Flow FFF channel for elemental analysis by ICP-AES and ICP-MS.

Sample preparation and analysis

The samples used in this work were natural clay particles in two different size ranges; <0.06 μm and 0.06-0.08 μm . The particles were isolated from the lower B horizon of Willalooka sand, a Sodosol from the Hundred of Laffer in the south east of South Australia and which is very high in illite. The horizon was chosen because of the preponderance of one mineral type. The samples were pre-fractionated by physical and chemical dispersion followed by centrifugation using the method of Chittleborough *et al.* (1992). The dried soil and clay samples were firstly sodium-saturated by adding approximately 10 mL of 1M NaCl solution for every gram of mineral component was added. The suspension was shaken overnight (~ 14 hours) following which it was centrifuged for about 30 min at 4000 rpm and the supernatant discarded. Following the addition of 150 mL of deionised water, the samples were shaken and centrifuged and the supernatant was discarded. The process was repeated until the suspension remained turbid.

The ICP-AES was capable of axial and radial plasma viewing. The axial viewing of plasma increased the sensitivity and analytical precision. All elements were analysed in the axial analysis mode. The ICP-AES and ICP-MS operating conditions are listed in Table 2. Element ion current data were collected as a series of consecutive multielement analyses, each lasting 45 and 70 seconds respectively and stored as sequentially numbered files. Each data file contained the average ion counts. Data files for each element were combined and arranged according to the time sequence.

Table 1. FFF channel specifications.

Channel	Thickness (cm)	Breadth (cm)	Length (cm)	Void volume (mL)	Membrane
F1FFF (I)	0.0122	2.0	25.9	0.635	YM-30
F1FFF (II)	0.0145	2.0	27	0.798	YM-10
SdFFF	0.02	2.1	87.1	3.65	-

Table 2. ICP-MS and ICP-AES operating conditions

ICP-MS		ICP-AES	
Resolution ($\Delta M/M$)	3000	Plasma viewing	Axial
Cool gas (mL/min)	14	RF generator (w)	1300
Aux gas (mL/min)	1.1	Plasma gas (L/min)	15
Sample gas (mL/min)	0.96	Auxilliary (L/min)	0.5
Plasma power (w)	1300	Nebuliser (L/min)	0.8
Sample uptake rate (mL/min)	0.5	Sample uptake rate (mL/min)	0.8

Results and discussion

In Figure 3 the result of the separation analysis of $<0.06 \mu\text{m}$ and $0.06\text{-}0.08 \mu\text{m}$ fractions of the Willalooka illite is presented as a plot of relative amount versus particle-size.

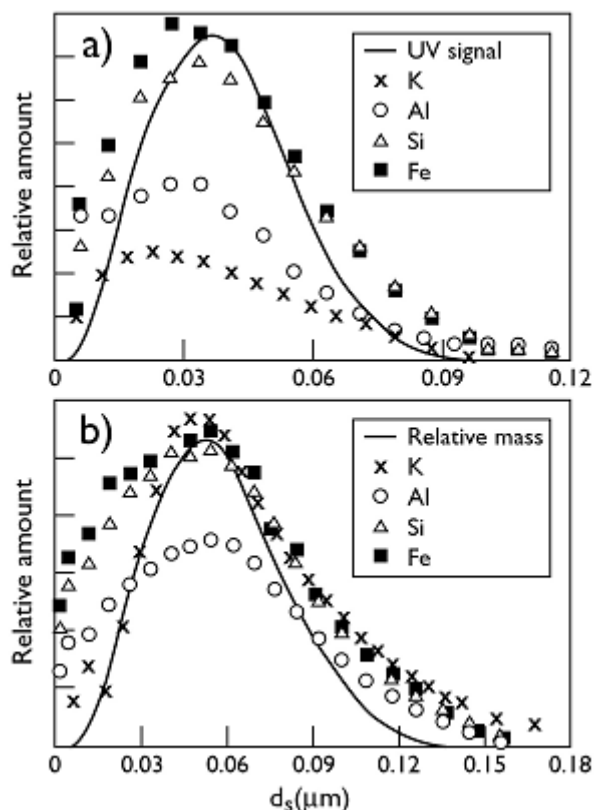


Figure 3. Element based size distribution of the $0.06\text{-}0.08 \mu\text{m}$ and $<0.06 \mu\text{m}$ fractions of the Willalooka illite following separation in a FIFFF channel and on-line analysis by ICP-MS and ICP-AES.

All the elemental profiles roughly followed the UV trace. The size-distribution obtained for the fraction $0.06\text{-}0.08 \mu\text{m}$ was $>0.08 \mu\text{m}$. The centrifugation did not produce a sharp cut-off at $0.08 \mu\text{m}$ possibly because the assumption of uniform density of the particles ($2.60 \text{ g}\cdot\text{cm}^{-3}$) was incorrect and/or there was a significant deviation from sphericity.

Figure 4 shows the molar ratio Al, Fe, and K to Si. The Al/Si ratios were approximately constant for these size fractions. Both fractions had Al/Si ratios of ~ 0.6 although there is an indication of divergence at particle sizes greater than $0.1 \mu\text{m}$. The Fe/Si ratios for both fractions had a maximum value of 0.2 at a particle diameter of $0.034 \mu\text{m}$. The ratio decreased to the value of 0.14 at a particle diameter of $0.06 \mu\text{m}$ and higher. There may be some iron oxide on the surface of the clays at the coarse end of the particle-size spectrum or the Fe may be in the crystallographic structure. Whereas the Fe, Al/Si trends are not strong, those for K/Si are highly significant. In both fractions there is a marked decrease in K/Si ratios with decrease in particle size. Either there is less K in the illite or, more likely, there is very fine-grained kaolinite present. X ray diffraction (data not shown) confirms the presence of kaolinite.

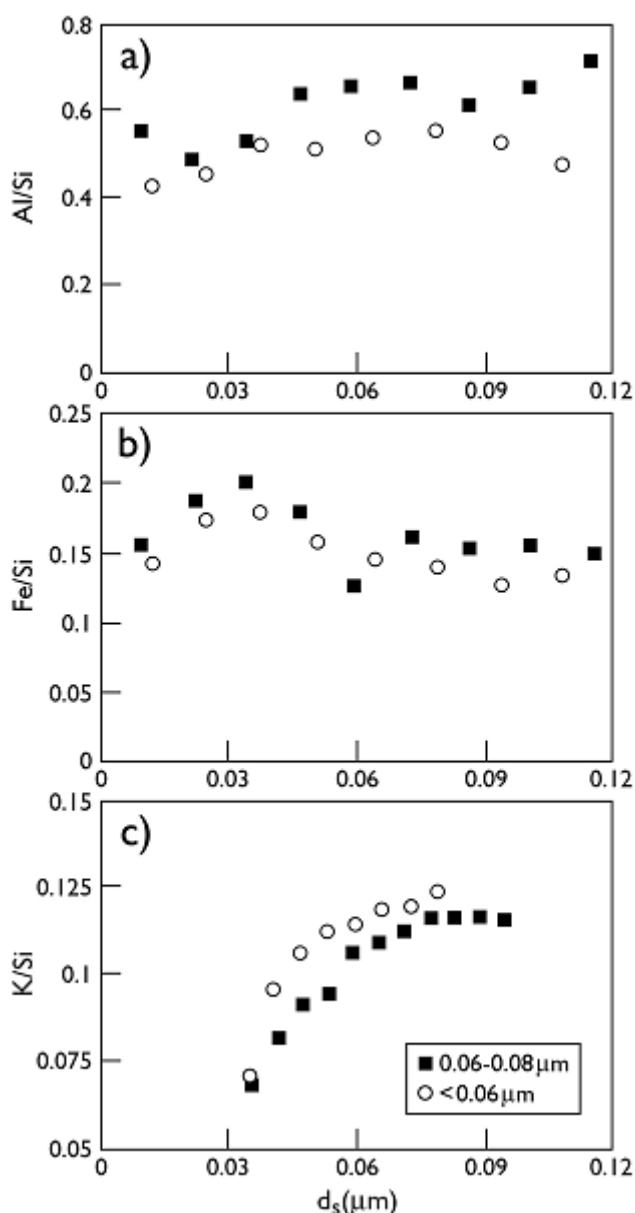


Figure 4. Molar ratios of major elements in size fractions of 0.06 μm and 0.06-0.08 μm of the Willalooka illite
a) Al/Si, b) Fe/Si, c) K/Si

Conclusion

Flow FFF is capable of rapid, high-resolution separation of very fine clay colloids. Hyphenated with ICP-MS and ICP-AES, elemental concentrations as a function of particle size can be generated in a fraction of the time of alternative techniques. FFF, and particularly FIFFF, has the prospect of joining a suite of emerging analytical techniques (such as solid state nuclear magnetic resonance spectroscopy) that will provide new insights into the properties of fine soil colloids and their behaviour. This is in no small measure because we can be confident that the properties of the sample under study have not been unduly perturbed during isolation and/or analysis.

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