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LETTER TO THE EDITOR

‘MEASUREMENT OF CLAY SURFACE AREAS BY POLYVINYLPYRROLIDONE (PVP) SORPTION: A NEW METHOD FOR QUANTIFYING ILLITE AND SMECTITE ABUNDANCE’

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Blum and Eberl (2004) presented a new technique for determining the surface area of clay minerals in sediment samples by measuring the amount of polyvinylpyrrolidone (PVP) [CAS#9003-39-8] adsorbed by a sample, and explained how the surface-area determination can be used to determine quantitatively the smectite content of the samples. In the previous method for determining surface area by PVP uptake (Blum and Eberl, 2004; also see the erratum relating to that paper published on p. 214 of the present issue), ~50 mg of Na-saturated smectite was dispersed in 5 mL of water, and 1 mL of 10 wt.% PVP-55 (mean MW 55,000) was added. The sample was centrifuged, a portion of the solution decanted, and the PVP concentration in solution determined by mass after drying. The mass of PVP adsorbed on the sample was then computed by difference. This method, while accurate, had several limitations for its practical application which have now been overcome.

One of the limitations of the procedure outlined by Blum and Eberl (2004) was that at high clay to solution ratios, samples with >90% Na-saturated high-charge smectites (but not low-charge smectites) tended to aggregate before the surfaces developed a completely adsorbed monolayer of PVP. Observations by X-ray diffraction (XRD) suggested that high-charge smectite particles became separated by only a single PVP layer at high smectite concentrations in solution, reducing the amount of PVP adsorbed (triangles in Figure 1) and, consequently, yielding an underestimate of the sample surface area. As a result, Blum and Eberl (2004) recommended running duplicate PVP-adsorption measurements of uncharacterized samples at different sample to solution ratios to confirm the absence of a sample-size artifact.

The authors have now observed that the use of Li-saturated samples (squares, Figure 1) avoids the sample-aggregation problem observed with Na-saturated, high-charge smectites. The use of Li as the interlayer cation prevents smectite aggregation over a very wide range of sample to solution ratios. During the preparation of the Li-saturated samples for the present work, care was taken not to raise the temperature above 25ºC. The observed effect is, therefore, unlikely to be the result of Li entering the octahedral sheet and decreasing the fixed charge of the clay. Rather, the larger hydration shell of the Li-saturated clay surface seems to prevent rapid aggregation, allowing enough time for complete PVP adsorption.

Blum and Eberl (2004) determined the concentration of PVP remaining in solution by measuring the mass of PVP remaining after evaporation of the solution. This method had several complications. First, PVP is strongly hygroscopic and uptake of atmospheric moisture during weighing can introduce uncertainty into the PVP mass measurement. Second, any residual material in solution will interfere with the measurement of PVP mass. For

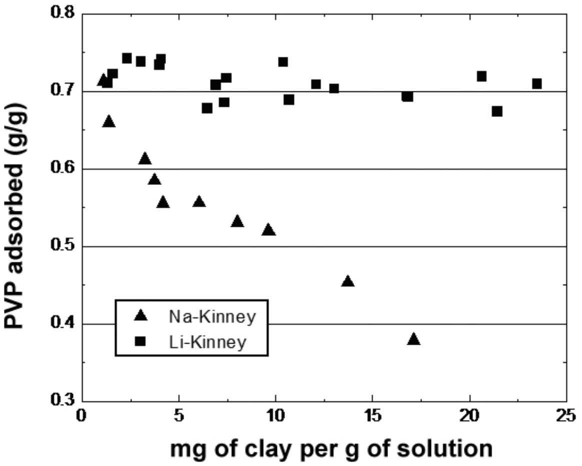

Figure 1. The mass of polyvinylpyrrolidone (PVP) adsorbed per gram of clay as a function of the mass of clay per mass of solution. PVP adsorption on a Na-saturated high-charge smectite (Kinney) is very sensitive to sample mass, whereas Li-saturated Kinney is nearly independent of sample mass.

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example, Blum and Eberl (2004) showed that PVP can solubilize organics from peat humic material. Insufficient centrifugation may also leave residual clay or colloidal particles in solution, slightly soluble minerals such as gypsum may dissolve and reprecipitate, and inadequate dialysis may leave residual LiCl from the Li saturation procedure.

The authors have found that direct determination of PVP concentration in solution by Fourier-transform infrared (FTIR) spectroscopy avoids all these difficulties. The PVP displays a pronounced mid-IR absorption feature, centered at 1295 cm^{-1}, associated with the nitrogen ring in the PVP, which is insensitive to the polymer length of the compound (Ovespyan, 1979). Conveniently, the 1295 cm^{-1} feature is within a transmission window that contains no appreciable absorption features associated with water, minerals, or natural organic matter. In addition, as the wavelength is relatively long (~8 μm), the scattering effects of submicron particles are negligible. Finally, LiCl concentrations up to 1 M had no impact on the IR spectra and standard curves. The intensity of the 1295 cm^{-1} feature was measured using the baseline-corrected integrated peak area from 1310 to 1282 cm^{-1}. Absorption values were converted to PVP concentration through a linear calibration curve constructed over the applicable concentration range.

Both transmission and attenuated total reflectance (ATR) methods were tested. For transmission, a liquid cell with ZnSe windows and a 45 μm path length was used. For the ATR-based method, an ATR attachment with a multi-bounce ZnSe prism with a liquid trough was used. In both methods, background spectra were taken through pure water under the same conditions as the samples. Transmission methods offer the greatest sensitivity, but ATR-based methods have adequate sensitivity and have the advantages of simplicity of operation and speed of measurement. Both techniques produce linear concentration-absorption relationships which conform to the Beer-Lambert Law.

The use of Li-saturated samples and the determination of PVP concentration in solution using FTIR avoids the common problems encountered in the application of the surface-area measurements of Blum and Eberl (2004). These modifications make PVP adsorption a simpler and more practical technique for determining quantitatively the smectite content of soils, sediments, and rocks.

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