

NOTE

CHEMICAL DETERMINATION OF CLAY CONTENT OF MINERALOGICAL SAMPLES WITH NICKEL (II) AMMINE COMPLEXES

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INTRODUCTION

The determination of the clay content and cation exchange capacities of soils, sediments, and hard rock samples has received much attention (Busenberg and Clemency, 1973; and references therein). These methods have as their basis the saturation of the clay component of the sample with a single ion, such as Na^+ , Ca^{2+} , K^+ , or NH_4^+ . The ionic uptake is measured either by differences in initial and final solution composition, or by displacement from the solids with subsequent measurement of the saturating ion in the displacing solution.

The shortcomings of these methods include:

1. Nonuniqueness of the saturating ion with respect to ions already present in the sample, which confounds the attempt at ion balancing. The alkalis and alkaline earths (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) suffer most in this regard.
2. Interferences from solubilized components in the sample. To overcome the previous (nonunique) shortcoming a completely "foreign" ion may be used as the "probe" ion. Busenberg and Clemency (1973), for example, utilize the NH_4^+ ion. In order to saturate the clay, however, competing ions, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} must be reduced to low levels in order to maximize the NH_4^+ , competing ion ratio. This is achieved by repetitive contact, followed by exhaustive rinsing of the saturating solution. In their method, for example, the sample is subjected to two saturating contacts, alcohol washes and drying before a measurement can be made.

Other workers (El-Sayed et al., 1971; DeMumbrum and Jackson, 1956) have attempted unsuccessfully to overcome these limitations by the use of transition metal–ammine complexes such as $\text{Zn}(\text{NH}_3)_4^{2+}$ and $\text{Cu}(\text{NH}_3)_4^{2+}$. The metals were unique to the samples and the high selectivity of the clay reduced, but did not eliminate solubilized interferences. In addition, changes in pH caused hydrolysis of the probe ions giving spurious results, and it was concluded (El-Sayed et al., 1971) that transition metal ion amines could not be used as probes of clay content.

In the present method both shortcomings are eliminated by use of a simplified test method which requires only one solution–solid contact and initial and final determinations of solution phase metal ion. The novelty of the present technique lies in the use of a buffered transition metal–ammonia–ammonium ion system.

EXPERIMENTAL

In the present case, 20 g of a nickel-free Wyoming sandstone sediment were contacted with 80 ml of 0.017 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ –0.25 M $(\text{NH}_4)_2\text{SO}_4$ –0.5 M NH_3 (pH 9.4) solution for periods of 2 and 24 hr. Under these conditions, the NH_3 is ligated to the Ni^{2+} forming the

Table 1. Clay determination via Ni–ammine uptake.

Trial	Ni Initial (g/l)	Ni Final (g/l)	Ni Uptake (mg/20 g rock)	Equilibration Time (hr)
1	0.965	0.635	26.4	2
2	0.965	0.630	26.8	24

These results are combined with the following information to yield clay (montmorillonite) contents of the samples.

Table 2. Ni uptake on montmorillonite.

Trial	Solution (ml)	Clay (g)	Ni Initial (g/l)	Ni Final (g/l)	Ni Uptake (mg/g)
1	80	1.0	1.000	0.820	14.4
2	80	2.0	1.000	0.680	12.8
3	80	3.0	1.000	0.550	12.0

(Solution: 0.017 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ –0.25 M $(\text{NH}_4)_2\text{SO}_4$ –0.5 M NH_3 ; contact time 4 hr, room temperature. Metal analysis by Atomic Absorption Spectroscopy.)

$\text{Ni}(\text{NH}_3)_4^{2+}$ and $\text{Ni}(\text{NH}_3)_5^{2+}$ complexes. For simplicity these are referred to below as the $\text{Ni}(\text{NH}_3)_x^{2+}$ species. The results are given in Table 1.

Table 2 shows the Ni uptake on a commercial bentonite (Fisher Scientific). The use of sulfate salts helps minimize the competitive reaction from displaced Ca^{2+} ions via gypsum precipitation. The NH_4^+ ion serves two purposes. First, by maintaining an essentially constant $\text{NH}_3/\text{NH}_4^+$ ratio the pH of the system is buffered at pH 9.40. Second, and most important, the NH_4^+ ion, by virtue of its concentration and affinity for the clay phase, swamps the competitive effect of other solubilized ions. That is, the ion selectivity is in the order $\text{Ni}(\text{NH}_3)_x^{2+} \gg \text{NH}_4^+ \gg \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$ so that the $\text{Ni}(\text{NH}_3)_x^{2+}$ uptake is measured in a constant NH_4^+ environment. The $\text{Ni}(\text{NH}_3)_x^{2+}$ uptake, then, should be a function of the equilibrium $\text{Ni}(\text{NH}_3)_x^{2+}$ concentration, as is seen in Table 2. The data were fit to a linear equation by a least squares method. The resulting equation

$$\text{Ni uptake (mg Ni/g clay)} = 8.92 \times \text{Ni concentration (g/l)} + 6.97$$

describes the data in the range 0.55 to 0.82 g/liter Ni with an r^2 (confidence) value of 0.97.

In the present case (experiments of Table 1) a value of 12.62 mg Ni/g of clay was used to calculate an average clay value of 10.5% for the two samples. For comparison the Busenberg method was applied to samples of the same origin yielding a clay value of 9.90%.

Because of the ease of Ni analysis by Atomic Absorption and the stability of the +2 oxidation state, Ni(II) ammine complexes in $(\text{NH}_4)_2\text{SO}_4$ buffered solutions can be used as probes of expanding lattice type clay content of mineral samples.

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