



Comparison of Methods for Measuring Cation Exchange Capacity in Clays

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Abstract

Three methods for measuring cation exchange capacity (CEC) in clay were compared. CEC measures cation exchange sites resulting from isomorphic substitution within clay minerals. Due to the effects of CEC, clay minerals possess certain properties that are useful to several fields, including the ceramics, rubber, paper, and oil industries. The three chosen methods included the ammonia electrode method, atomic absorption spectroscopy, and UV-Visible spectroscopy. Focus was placed on possible ways to improve these methods in order to lower the current acceptable percent error of $\pm 20\%$. Two standard clays with known CEC values were compared. A Wyoming clay (CEC = 80 meq/100 g) and an Arizona clay (CEC = 120 meq/100 g) were first purified before being analyzed. The first method, using an ammonia electrode, which is a direct measure, produced good accuracy and fair precision for the Wyoming and Arizona clays. A California clay with a published CEC of 140 meq/100g, which is in question, was also analyzed. Measured values for the California clay overall produced the highest percent error and standard deviation of the three clays. Varying degrees of sample size for each clay were analyzed. Finer ground clays tended to give better results, particularly for the Wyoming clay. Thus, sample preparation was likely a key factor influencing results. Compared to atomic adsorption and UV-Vis methods, which are indirect measurements, the ammonia electrode method was fairly simple, relatively inexpensive, yet somewhat tedious. Sample preparation for atomic adsorption and UV-Vis was more strenuous and possibly lead to errors in analysis, as both methods produced highly fluctuating results. Detection of analyte concentration for the UV-Vis method was particularly problematic. Overall, the ammonia electrode method, the only direct measure studied, produced the most accurate results of the three methods examined. Sample preparation likely played a key role across all methods with emphasis being placed on sample texture for the ammonia electrode method.

Conclusion

Three methods for measuring CEC in two types of clay were performed and compared. Emphasis was placed on how these methods might be refined in order to achieve greater accuracy and lower the acceptable percent error, which is currently quite high. The ammonia electrode method produced the highest accuracy among the three methods with fair precision. This method is relatively simple and inexpensive but can be somewhat tedious. Sample preparation is key for all three methods and is somewhat strenuous for the UV-Vis and AAS methods. Fluctuating numbers for these two methods could have been linked to errors in sample preparation, specifically from centrifuging, and in issues with the metal exchange complex stock solution's concentration

References

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Methods

Purification extensively purified two sets of clay through several steps. (1) *Sedimentation* separated clay from silica. (2) *Decarbonation* removed carbonates (3) *Metal removal* converted metals to a soluble citrate complex. (4) *Oxidation* removed organic matter. (5) *Saturation* with exchange complexes filled exchange sites with a certain cation. (6) *Dialysis* removed excess ion pairs.

Ammonia Electrode Method measured CEC directly by converting NH_4^+ cations on the exchange sites of NH_4^+ saturated clay to ammonia gas, which was measured by the electrode. This method was somewhat tedious but produced good accuracy and fair precision. Texture played a key factor in results.

Spectroscopy Methods measured CEC indirectly by analyzing metal ions left over in the supernatant after cation exchange with sodium saturated clay. Sample preparation was somewhat strenuous, but analysis was relatively fast.

UV-Visible Spectroscopy (UV-Vis) produced unacceptable accuracy and precision. Analyte detection was a major issue

Atomic Absorption Spectroscopy (AAS) included excellent detection limits but low accuracy. Refinements produced good precision and better accuracy though not all samples analyzed were in the acceptable percent error range. Possible reasons for inaccuracy included centrifuging to isolate the supernatant in early runs and issues with the metal stock solution used for exchange.

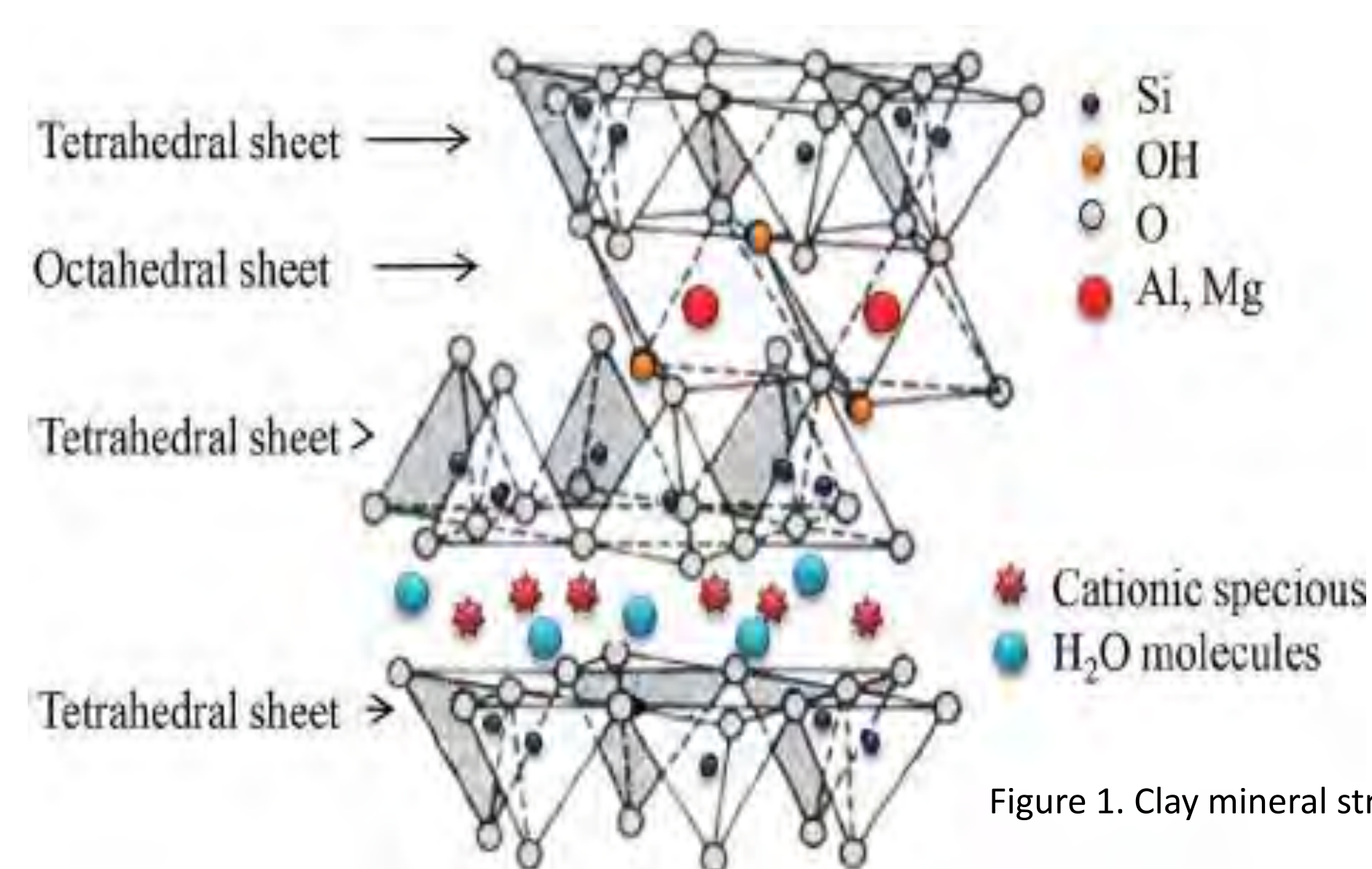


Figure 1. Clay mineral structure and CEC

www.researchgate.net/figure/Smectite-structure-of-a-2-1-clay-mineral-showing-two-tetrahedral-sheets-sandwiched_fig2_274095227

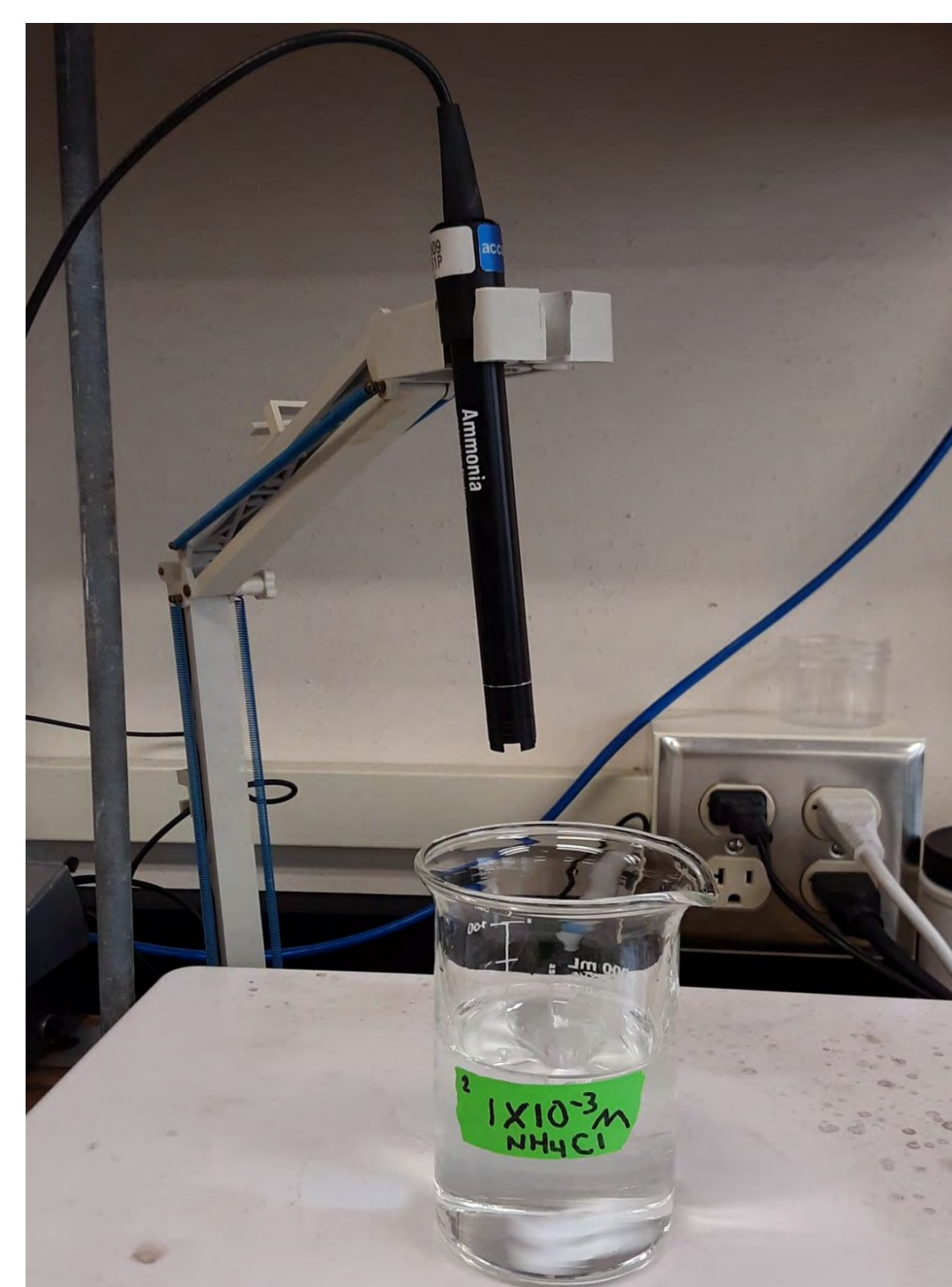


Figure 2. Setup for analysis using ammonia electrode

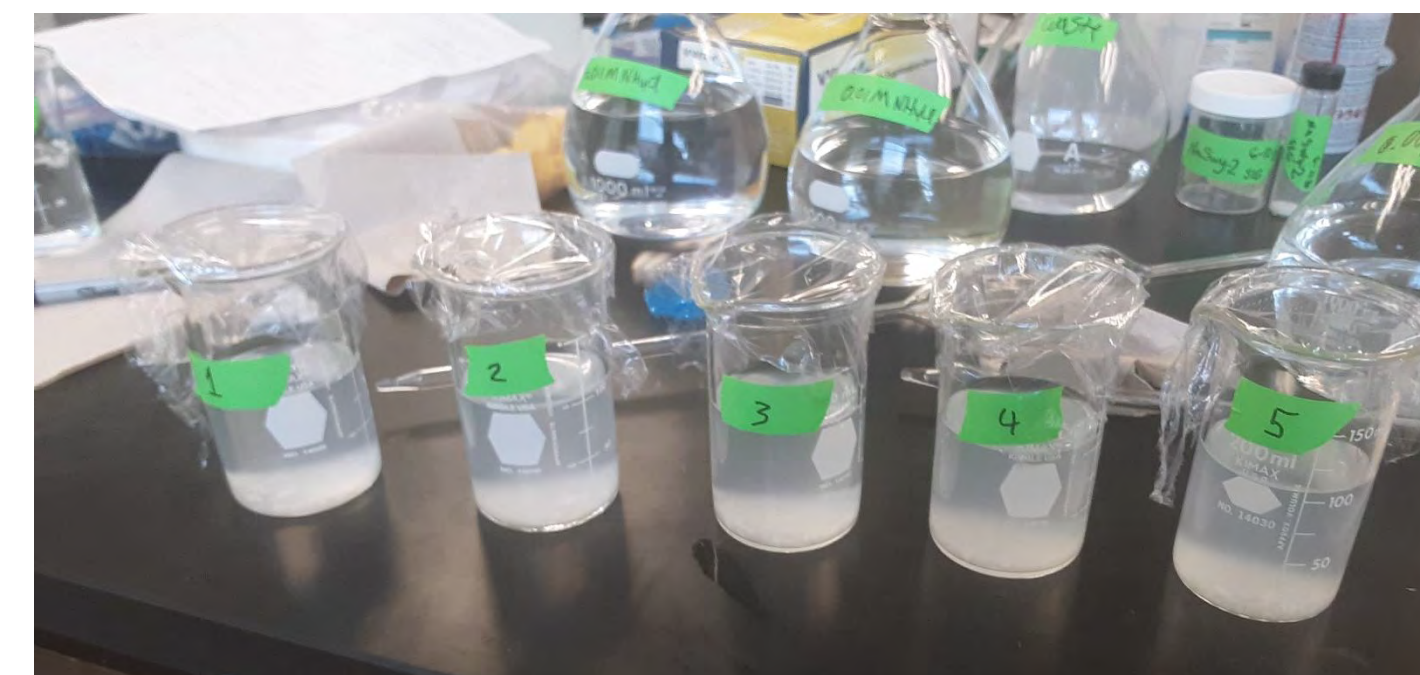


Figure 3. Clay samples ready for ammonia electrode analysis



Figure 4. Supernatants ready for spectroscopy analysis

Results

Ammonia Electrode

SWy-2 (Accepted CEC = 80 meq/100 g) & SAz-1 (Accepted CEC = 120 meq/100 g)

Clay Type	Texture	Ave. CEC (meq/100 g)	Std. Dev.	% Error
SWy-2	Fine Ground	83.5	± 0.13	4.4%
SWy-2	Coarse Ground Trial 1	81.2	± 2.69	1.50%
SWy-2	Coarse Ground Trial 2	70.1	± 1.22	12%
SWy-2	Super Coarse Ground	66.3	± 0.85	17.1%
SAz-1	Fine Ground Trial 1	105.1	± 2.31	12.4%
SAz-1	Fine Ground Trial 2	113.1	± 2.51	5.7%
SAz-1	Coarse Ground Trial 1	105.2	± 2.28	12.4%
SAz-1	Coarse Ground Trial 2	110.7	± 1.79	7.8%
SAz-1	Super Coarse Ground	109.1	± 2.29	9.11%

Atomic Absorption Spectroscopy

SWy-2 Accepted CEC = 80 meq/100 g SAz-1 Accepted CEC = 120 meq/100 g

Amount of Clay	Clay type	Stock Solution	Ave. CEC (meq/100 g)	Std. Dev.	% Error
0.5 g	SWy-2	0.02 M Cu^{2+}	148.3	± 1.21	85.4%
0.5 g	SWy-2	0.02 M Ni^{2+}	65.67	± 34.647	-17.9%
0.5 g	SWy-2	0.006 M Cu^{2+}	108.4	± 1.68	35.5%
0.25 g	SWy-2	0.02 M Cu^{2+}	208.5	± 6.44	160.6%
1 g - trial 1	SWy-2	0.02 M Cu^{2+}	106.1	± 0.42	32.6%
1 g - trial 2	SWy-2	"0.02 M" Cu^{2+}	105.9	± 0.20	32.4%
1 g - trial 2	SWy-2	0.0165 M Cu^{2+}	71.4	± 0.20	-10.8%
0.25 g	SAz-1	0.01 M Cu^{2+}	170.2	± 1.33	41.9%
1 g - trial 1	SAz-1	0.02 M Cu^{2+}	122.8	± 0.75	2.4%
1 g - trial 2	SAz-1	"0.02 M" Cu^{2+}	123.00	± 0.93	2.5%
1 g - trial 2	SAz-1	0.0165 M Cu^{2+}	88.5	± 0.93	-26.3%

UV-Visible Spectroscopy: SWy-2 (accepted CEC = 80 meq/100 g)

Metal Ion analyzed	Ave. CEC (meq/100 g)	Std. Dev.	% Error
Cu^{2+}	109	± 33.7	37%
Co^{2+}	177	± 64.9	121%
Ni^{2+}	165	± 82.2	107%

Acknowledgements

The Welch Foundation Departmental Grant (AN-0008)

SRE Welch Grant

Stephen F. Austin State University Department of Chemistry and Biochemistry

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