DIVISION S-2—SOIL CHEMISTRY

A Clay Suspension Stability End Point Titration Method for Measuring Cation Exchange Capacity of Soils[1]

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ABSTRACT

The silver–thiourea (AgTU) method for cation exchange capacity (CEC) measurement of soils involves the assessment of Ag in the AgTU soil extracts. Silver can be easily measured by an atomic absorption spectrophotometer or with a radio isotope and scintillation counter. Laboratories for soil analysis in developing countries often do not have access to such instruments. A simple method for measuring Ag in the AgTU soil extracts was, therefore, developed. The method involves a stability end point titration of a stable montmorillonite clay suspension calibrated with AgTU solutions ranging from 5×10^{-4} to 10^{-2} mol L^{-1}. The AgTU-CEC measured by this clay titration method was compared with the "effective" CEC by NH_4OAc and KCl extractions and with the AgTU-CEC measured by an atomic absorption spectrophotometer. The correlation coefficients were 0.95 and 0.97, respectively.

Additional Index Words: **African soils, turbidimetric titration, base saturation, field measurement, flocculation of clays, lime requirement.**

Pleysier, J., J. Janssens, and A. Cremers. 1986. A clay suspension stability end point titration method for measuring cation exchange capacity of soils. Soil Sci. Soc. Am. J. 50:887–891.

WE HAVE REPORTED before that the silver–thiourea (AgTU) complex can be used as an index cation for measuring the cation exchange capacity (CEC) and exchangeable cations of various types of soils, including soils with variable charges (Chhabra et al. 1976; Pleysier and Juo, 1980). The AgTU CEC is determined by equilibrating the soil with a 0.01 *M*

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solution of AgTU, measuring the amount of Ag (as AgTU) in the equilibrium extract, and calculating the amount of AgTU adsorbed by difference. The amount of Ag in the equilibrium extract is usually measured by an atomic absorption spectrophotometer or with a radio isotope and scintillation counter. Most laboratories in developing countries do not, however, possess such sophisticated instruments. A simple method for measuring AgTU in the equilibrium soil extracts is therefore needed.

Adsorption of the AgTU complex on a montmorillonite clay has a very marked effect on the stability of the clay suspension (Cremers and Pleysier, 1973). Large, rapidly sedimenting clay flocs are formed when AgTU is added to a stirred montmorillonite suspension. This flocculation with AgTU continues until all the clay is flocculated, leaving a clear supernatant when stirring is stopped. The critical amount of AgTU necessary for complete flocculation coincides almost exactly with the CEC of the clay. One could, therefore, use a stable montmorillonite suspension of known CEC and concentration to titrate AgTU in a solution, i.e., the equlibrium soil extract. The titration can be performed in two ways. The first is to titrate a given amount of a stable montmorillonite suspension of known AgTU-CEC with the unknown AgTU soil extract. The end point is reached when all the clay is flocculated and the supernatant has become clear. The volume of added AgTU extract required for complete flocculation of the known equivalents of clay allows one to calculate the AgTU in the equilibrium soil extract. With the second method of titration, a given volume of the unknown AgTU extract is titrated with the clay suspension of known AgTU-CEC. At the end point the supernatant changes from clear to turbid because all the AgTU has been adsorbed and any excess suspension added remains dispersed, causing a turbid supernatant. The second method was used in this study.

This method of titrating Ag (as AgTU complex) in soil extracts or in other solutions can be considered as a clay suspension stability end point titration (CSSET). The remarkable effect of AgTU on the stability of a montmorillonite suspension is probably due to the high adsorption affinity of the AgTU complex for the clay and the very efficient neutralization of the negative charges on the clay particles. Rapid flocculation by AgTU is also observed for suspensions of other clay minerals such as kaolinite and illite. Montmorillonite clay suspensions give large flocs, while kaolinite and illite flocculate as small flocs with the AgTU complex. The different flocculation patterns with AgTU are also observed on suspensions of soils rich in these clay minerals. The patterns could serve as a rapid qualitative test for these minerals in soils.

Other heavy metals (i.e., Cu, Zn, Cd, etc.) also form stable positively charged complexes with uncharged organic ligands (i.e., thiourea, ethylenediamine, etc.). Adsorption of these complexes causes rapid flocculation of stable montmorillonite suspensions. The CSSET method could therefore be developed for measuring these metals in solution.

In this study, AgTU-CEC measured by CSSET is compared with the effective CEC (ECEC) and the AgTU-CEC measured by atomic absorption spectrophotometer for a selection of mainly African soils.

MATERIALS AND METHODS

Soil Samples

Samples were taken from a wide variety of surface and subsoils, which included alfisols, ultisols, oxisols, entisols, inceptisols, and vertisols. Most samples were from Nigeria, but some came from Togo (soil 105), Tanzania (soil 111), Ghana (soil 116), the Ivory Coast (soil 117), Liberia (soil 119), Kenya (soil 138), Brazil (soil 151), Cameroon (soil 155), Sao Tome (soil ST8), and Sierra Leone (SL5 and SL7). Some properties of the soils are given in Table 1. The samples were air-dried, ground, and passed through a 2-mm sieve. Subsamples were pulverized to pass a 0.5-mm sieve for organic C analysis. Clay content was measured with a hydrometer after oxidation of organic matter and dispersion with calgon. The pH was measured in a 1:1 soil/water suspension. Organic C was measured according to the Walkley-Black method (Page et al., 1982).

The CSSET Method

The AgTU solution was prepared as described previously (Pleysier and Juo, 1980). The soil (0.5–10.0 g) was equilibrated for 2 h with 30 mL of 0.01 mol AgTU L^{-1} solution. Five milliliters of the filtered AgTU soil extract was added to a test tube, together with 5 mL of a 0.03 mol L^{-1} solution of disodium-EDTA. The latter was added to complex the multivalent cations (i.e., Al, Ca, Mg) in the soil extract. These cations would otherwise have caused some flocculation of the clay suspension and affected the end point. This mixture was then titrated with a stable montmorillonite suspension. The suspension was added with a graduated syringe of 6 ± 0.2) 10^{-3} L. The test tube was shaken by hand for a few seconds after every increment of suspension was added. The montmorillonite suspension (titrant) was prepared by dispersing 10 g of a montmorillonite clay powder in 1 L of distilled water. In this study, a bentonite powder (no. 26022, technical grade) from British Drug Houses, Ltd., was used. This suspension was standardized by titrating a series of AgTU solutions ranging from 5×10^{-4} to 10^{-2} mol L^{-1}

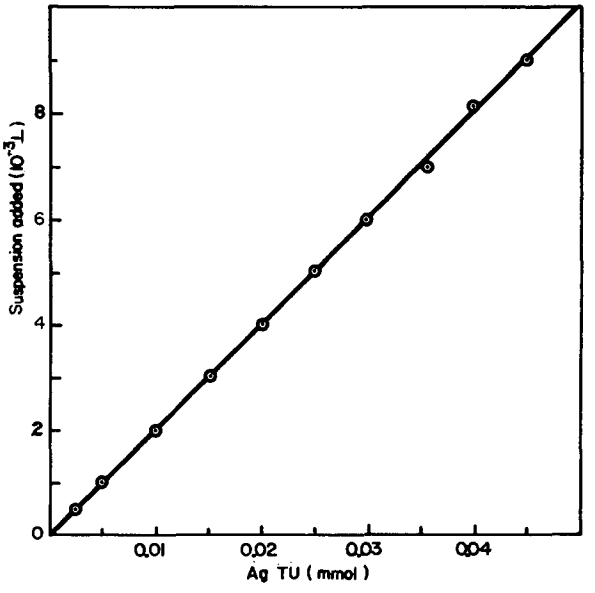

Fig. 1. Calibration of a montmorillonite clay suspension (10 g L^{-1}) with AgTU solutions ranging from 5 10^{-4} mol L^{-1} to 10^{-2} mol L^{-1}.

with the clay suspension (Fig. 1). The bentonite was found to adsorb 1 mmol of AgTU per 200-mL suspension, which corresponds with a CEC of the bentonite clay of 0.50 mol(+)kg^{-1}. The low CEC of the bentonite clay is due to the presence of silt and sand in this technical grade clay mineral.

The end point of the titration is detected visually by continuously observing the supernatant above the flocculated montmorillonite clay. The end point is reached when the clear supernatant becomes turbid. This occurs when sufficient suspension was added to adsorb all the AgTU in the soil extract, leaving a supernatant virtually free of AgTU. Any amount of clay suspension added in excess will remain dispersed and will cause the supernatant to become turbid. When the concentration of AgTU in the equilibrium soil extract is rather high (i.e., for soils with low CEC), quite a lot of clay suspension has to be added to reach the end point. In this case the volume of supernatant above the flocculated clay will be small and because of this, detection of the end point may be difficult. These soil extracts should therefore be diluted with distilled water before titration.

Cation Exchange Capacity and Base Saturation

Percent base saturation was calculated from total exchangeable acidity and AgTU-CEC or ECEC. The ECEC was determined by three extractions with 1.0 mol L^{-1} NH_4OAc at pH 7 for exchangeable bases and with unbuffered 1.0 mol L^{-1} KCl for exchangeable acidity (Coleman and Thomas, 1967). Exchangeable Ca and Mg in NH_4OAc extracts and Ag in AgTU extracts were determined by an atomic absorption spectrophotometer. Exchangeable acidity in the KCl extracts was titrated with 0.05 mol L^{-1} NaOH, using an automatic end point titrator, to pH 7. Exchangeable acidity in the AgTU extracts was determined by titration with 0.01 mol L^{-1} NaOH to phenolphtalein end point.

RESULTS AND DISCUSSION

Table 1 and Fig. 2 compare the results of CEC measurement with AgTU and those with the ECEC. There is good agreement between CEC by clay titration (CSSET) and ECEC for soils that differ widely in pH, organic C and clay content. The intercept of the correlation line shows that the ECEC values are slightly higher than the AgTU-CEC (CSSET). This is perhaps because some soil components (i.e., organic matter, carbonates, and sulfates) are more soluble in 1.0 mol L^{-1} NH_4OAc than in 0.01 mol L^{-1} AgTU solution (van Rosmalen, 1980). This results in an overestimation of the exchangeable bases and consequently of the ECEC. Two soils show very large differences in CEC by both methods (N50–1 and 155–1). The first is a hydromorphic soil and contains some soluble salts for which no correction was made in the NH_4OAc extract. Soil 155–1 is a volcanic soil with very high organic matter content. The reason for its considerably higher AgTU-CEC is not known.

When the clay titration is done without EDTA, the AgTU-CEC values are about 25% lower overall. In the absence of EDTA, the multivalent cations in the AgTU soil extract lead to some flocculation of the titrant,

Table 1. Cation exchange capacity, total acidity (Al + H), and some properties of the soils.

Soil no.	Clay	O.C.	pH_w (1:1)	ECEC	AgTU-CEC (CSSET)	AgTU-CEC (AAS)	TA (KCl)	TA (AgTU)
	%	g kg^{-1}		mmol(+)kg^{-1}			mmol(+)kg^{-1}	
185-7	44	3.2	8.5	434.2	430 360†	735.1	0	16.2
188-7	15	1.3	5.0	34.0	36	46.5	8.7	3.2
185-1	44	10.4	7.3	369.6	336†	735.0	2.1	21.0
305-1	58	45.4	4.9	339.8	332	380.0	7.5	13.6
305-3	76	7.8	6.0	379.9	348	395.0	3.8	8.2
111-1	17	16.3	6.6	147.0	143	183.8	3.3	9.1
116-1	38	16.5	7.0	271.1	274 216†	360.0	6.9	11.4
105-1	7	3.7	7.0	41.7	29	46.5	3.0	2.0
105-3	19	2.4	6.2	26.2	21	31.1	4.9	1.2
117-1	13	19.7	4.6	53.3	41	55.8	15.2	9.3
119-4	30	4.9	4.2	19.0	12	25.7	14.4	13.2
ST8-1	–	34.8	–	70.8	64	61.6	18.2	7.1
N50-1	–	20.5	4.9	350.1	200	140.5	29.7	20.2
N45-4	–	4.7	4.6	54.0	49	43.7	49.7	42.0
N51-1	17	16.1	4.4	34.5	21	21.0	22.3	10.2
80-5	45	2.9	5.3	57.3	38	47.2	2.4	1.5
286-1	56	21.5	5.4	61.1	59	85.0	5.6	3.2
84-1	5	7.6	5.9	88.5	63	76.2	1.6	2.2
84-4	40	2.0	6.2	285.1	281	300.0	2.2	5.7
82-1	17	29.4	6.5	160.9	92	129.4	1.9	3.7
314-1	6	5.7	6.4	31.1	27	33.7	1.4	1.6
297-3	37	2.9	4.7	74.5	75	93.7	47.3	49.1
138-3	76	12.1	4.6	41.2	43	60.0	24.2	2.0
151-1	86	13.8	3.9	66.7	56	65.1	47.6	34.5
155-1	9	65.0	6.1	214.6	300	268.6	7.4	8.7
155-3	–	79.0	5.3	159.1	119	88.9	8.8	6.9
71-1	23	48.0	5.7	176.8	124	112.0	2.8	14.4
71-5	31	2.9	4.4	30.6	28	25.0	22.1	21.6
79-1	9	18.3	6.1	120.6	63	60.0	5.3	2.6
79-4	30	2.8	4.7	34.1	34	32.9	19.1	17.6
95-2	35	11.9	4.5	31.8	23	18.0	27.9	19.5
118-4	29	5.8	4.5	29.7	22	19.3	27.7	20.7
SL5-2	47	13.0	4.2	76.5	68	53.3	53.4	60.5
SL7-3	15	1.0	4.6	37.4	25	23.9	34.3	19.7
116-2	38	9.7	7.4	292.5	276†	397.5	0.1	13.5

† Titration done in absence of EDTA.

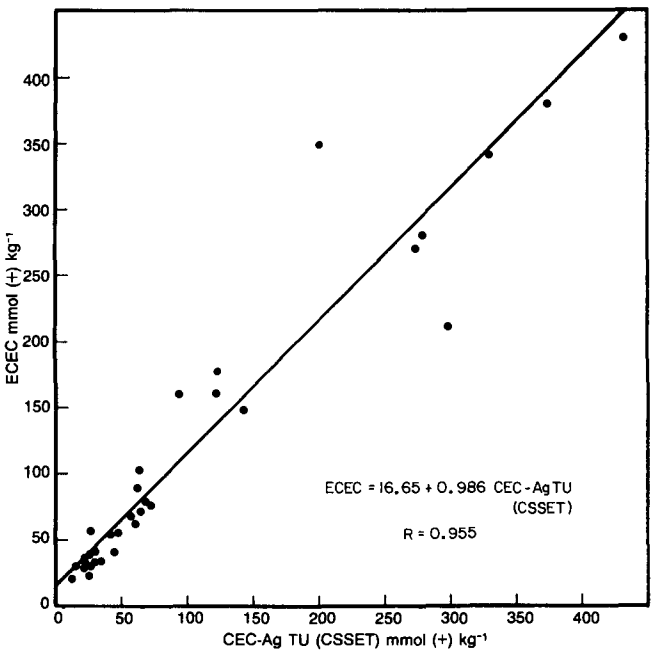

Fig. 2. Comparison of effective CEC with AgTU-CEC by clay titration (CSSET).

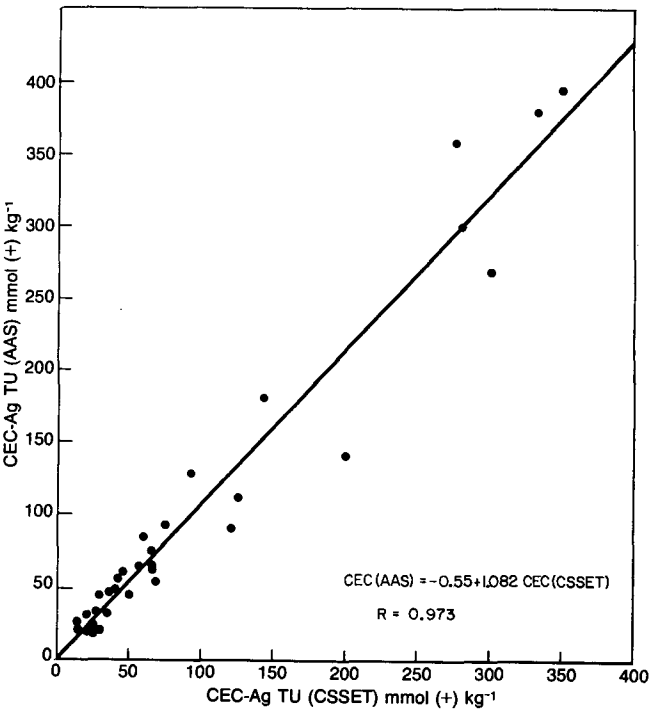

Fig. 3. Comparison of AgTU-CEC by atomic absorption spectrophotometer (AAS) with AgTU-CEC by clay titration (CSSET).

causing the AgTU-CEC by clay titration to be underestimated. This effect is larger for acid soils and calcareous soils.

Figure 3 and Table 1 show the AgTU-CEC by atomic absorption spectrophotometer (AAS) and by clay titration (CSSET). The agreement between these methods is good, indicting that a simple clay titration of the AgTU in the soil extract can be used instead of an atomic absorption spectrophotometer to measure the CEC of various types of soils. Table 1 shows that soils 185–1, 185–7, 116–1, and 116–2 have a much higher AgTU-CEC measured by AAS than by CSSET or ECEC. In soils such as these that have a high pH, as reported earlier (Chhabra et al. 1976), the AgTU complex in solution becomes unstable, and Ag is probably precipitated as Ag_2S. Precipitation is rather slow at pH 7 to 8 and occurs mainly after the separation of the extract from the soil. However, AgTU-CEC by CSSET of the same AgTU extract is not much affected by this high pH and Ag_2S precipitation. Clay titration of the AgTU extracts from these high pH soils with and without EDTA (Table 1) shows that EDTA does not much affect the solubility of Ag_2S. Therefore the Ag_2S is probably dissolved during titration of the AgTU extract with the montmorillonite suspension. This seems possible since the AgTU complex is about a thousand times more stable when adsorbed on the montmorillonite clay than in solution (Pleysier and Cremers, 1975). A buffered AgTU extractant can be used for measuring the CEC of soils with high pH (Chhabra et al. 1976; van Rosmalen, 1980).

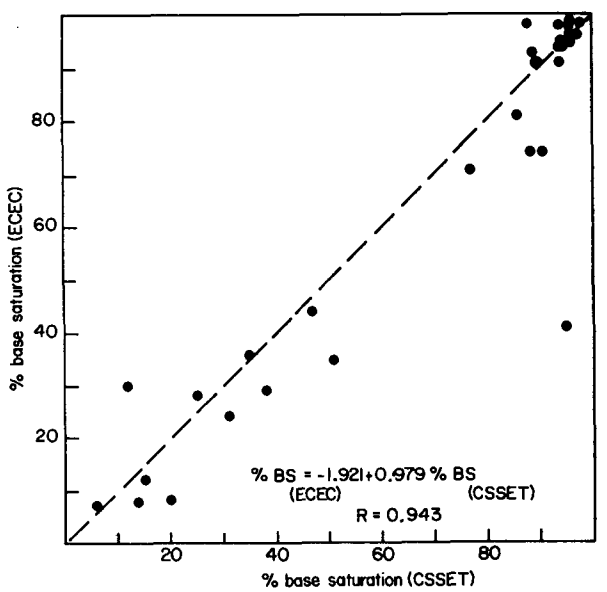

Fig. 4. Comparison of percent base saturation calculated from total acidity and ECEC or AgTU-CEC by clay titration (CSSET).

Table 1 shows the values for total exchangeable acidity by KCl and by AgTU. The agreement between both methods is generally good. The large differences in exchangeable acidity by AgTU and by KCl observed for a few soils (i.e., 116–2, 71–1, 138–3, 185–7) requires further investigation.

Figure 4 shows the percent base saturation calculated from ECEC, AgTU-CEC (CSSET), and exchangeable acidity in KCl or in AgTU extracts. The agreement is also rather good. Data shown in Fig. 4 were obtained from analysis of a given weight of soil (0.5–10 g). However, one can also calculate the percent base saturation from AgTU-CEC (CSSET) and total acidity (phenolphtalein) measured on a given "volume" of soil (because percent base saturation is a dimensionless value). The AgTU-CEC (CSSET) and total acidity (phenolphtalein) are measured on the same extract. Therefore, percent base saturation cal-

culated from these measurements will not be affected by moisture and gravel content of the sample nor by the exact amount (weight or volume) of sample analyzed. This makes the AgTU method suitable for measuring base saturation in the field since drying, crushing, sieving, and weighing of samples will not be necessary. A certain volume of fresh soil can be extracted with the AgTU solution by shaking the mixture for 1 min at regular intervals (i.e., 5 min) during about one-half hour. This is sufficient to saturate the exchange complex of the soil with AgTU and to displace the exchangeable acidity (Janssens, 1984). A rapid test of percent base saturation in the field could be helpful in soil classification or for testing lime requirement.

CONCLUSIONS

In this study it was shown that the CEC and base saturation of various types of soils could be determined by a simple end point titration of the AgTU extract with a calibrated, stable montmorillonite suspension. Since the method requires only simple laboratory ware such as test tubes, funnels, syringe, and common chemicals, it should be suitable for testing of CEC and base saturation of soils in small laboratories or in the field.

ACKNOWLEDGMENT

The authors are grateful to Drs. A.S.R. Juo and T. Kosaki for providing a selection of soil samples and to Miss C. Musvoto for assistance with the laboratory work.

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