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THE ETHYLENE GLYCOL MONOETHYL ETHER (EGME) TECHNIQUE FOR DETERMINING SOIL-SURFACE AREA

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Total surface area is an important fundamental soil property. This property is measured to estimate the proportion of lattice expandable layer silicates in soils and to assess soil physical and chemical properties. Dyal and Hendricks (4) introduced a method for measuring surface area of layer silicates. This method was modified and adapted to soils by Bower and Gschwend (1). Subsequently, Martin (5) proposed a modification of the Dyal and Hendricks method (4) for layer silicates. His modification included a source of free ethylene glycol in the evacuated desiccator to control the vapor pressure of ethylene glycol at the mineral sorption surfaces. Bower and Goertzen (2) modified the method proposed by Martin (5) and adapted it for measuring soil surface area. This latter method is considered to be an equilibrium method (2) and is widely used today. A similar but more complex method was introduced by Sor and Kemper (7). All these methods utilize ethylene glycol, a highly polar molecule, as the absorbed phase. They all have the common disadvantage of being very time-consuming.

Recently, Carter *et al.* (3) introduced a method for determining the surface area of layer silicates in which the adsorbed phase was ethylene glycol monoethyl ether (hereafter referred to as EGME). The method is similar to but much more rapid than ethylene glycol methods. This paper reports results of adapting the EGME method to soils, the agreement between the glycol and EGME methods for soils, and a proposed routine method for determining soil surface area with EGME.

METHODS AND MATERIALS

The soils studied included four horizons from each of eight irrigated soils of the Lower Rio Grande Valley of Texas. Soil samples from four horizons, which represented the range of properties in the profile of each soil type, were selected for study. These included the two surface horizons, the textural B or a horizon near a depth of 36 inches, and a horizon from below 48 inches, where little weathering had occurred. In addition, four surface soils used in previous surface-area studies at the U. S. Salinity Laboratory were included. The soils, horizons, and depths are listed in table 1.

Air-dry soil samples were ground to pass a 60-mesh sieve, treated with H_2O_2 to destroy organic matter, and washed with successive quantities of N $CaCl_2$ for Ca-saturating. Excess salt was removed by three successive water washings. Then the samples were dried and again ground to pass a 60-mesh sieve.

Six replicate 1.1-g. samples of each soil were placed in shallow aluminum weighing cans and dried to constant weight in evacuated desiccators over P_2O_5. One group of duplicate samples was treated with approximately 3-ml. portions of reagent-grade ethylene glycol for determining the glycol retention and surface area by the Bower and Goertzen method (2). A glycol-$CaCl_2$ solvate was prepared and placed in a culture dish beneath a supporting screen. The sample cans were placed on the screen, and the lid was placed on the culture dish, using a small block to leave an approximately 2-mm.-wide space between the lid and dish for gases to escape. The entire culture dish was placed in a vacuum desiccator containing $CaCl_2$. The purpose of the culture dish and solvate was to maintain a constant glycol vapor pressure at the sorption surfaces of the soil. The glycol-soil slurry was allowed to equilibrate overnight before the desiccator was evacuated for 45 minutes with a high-vacuum pump. The vacuum attained after 45 minutes was approximately 0.250 mm. Hg, and the stopcocks were closed to retain the vacuum. The first weighing was made approximately 72 hours after the first evacuation. After each weighing, the desiccators were re-evacuated for 45 minutes. Weighing was continued at 24-hour intervals until a constant weight was attained.

Approximately 3-ml. portions of reagent grade

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[1] Weslaco, Texas.

TABLE 1

Soils used for comparing methods of determining soil-surface area

Soil No.	Horizon Depth	(in.)
	Laredo silty clay loam	
567	A1p	0–9
568	AC	9–20
570	C2	31–41
573	C5	61–75
	Cameron silty clay	
596	A1p	0–11
597	A12	11–22
599	C2	33–39
602	C5	60–74
	Harlingen clay	
616	A1p	0–11
617	AC	11–23
619	C2	35–47
622	Cca2	71–78
	Willacy fine sandy loam	
623	A1p	0–9
624	A12	9–17
626	B22	24–37
628	Cca	49–64
	Brennan fine sandy loam	
651	A1p	0–7
652	A12	7–14
654	B22	26–36
657	Cca2	62–72
	Hidalgo fine sandy loam	
687	A1p	0–10
688	A12	10–23
690	AC2	34–46
692	Cca2	56–67
	Hidalgo clay loam	
708	A1p	0–10
709	A12	10–19
711	AC2	27–38
713	Cca2	49–60
	Hidalgo sandy clay loam	
735	A1p	0–9
736	A12	9–17
738	AC2	30–39
740	Cca2	51–65
	*Riverside samples**	
3280	surface	Pachappa†
60	surface	Aiken
2738	surface	Sebree
3284	surface	Chino

* Soil type and depth unknown.

† Series name.

EGME were added to each of another set of duplicate samples. The retention of EGME was determined by the method proposed for layer silicates by Carter *et al.* (3). This method included an EGME-$CaCl_2$ solvate placed in culture dishes, as described previously, to maintain a constant EGME vapor pressure at the sorption surfaces. In contrast to the glycol method, the EGME-soil slurries were allowed to equilibrate for only 30 minutes before the desiccator was evacuated. The first weighing was made from 4 to 6 hours after the first 45-minute evacuation. The desiccators were evacuated for 45 minutes after each weighing, and weighings were continued at intervals of 2 to 4 hours until a constant weight was attained. Data obtained by this method are identified as EGME$_s$ in figures and tables.

A third group of duplicate samples was treated with approximately 3-ml. portions of reagent-grade EGME and evacuated and weighed by the same procedure as that described for the other samples receiving EGME, except that samples in weighing cans were placed directly into desiccators containing $CaCl_2$. No attempt was made to maintain a constant EGME vapor pressure. Data obtained by this method are identified by EGME in tables and figures.

For routine determinations, retention of EGME by samples was determined by weighing samples at the beginning and end of each workday. Varying numbers of samples were placed in desiccators to determine the effect of number of samples on time required to attain constant weight.

The total surface area for each sample was calculated by dividing the grams of adsorbate retained per gram of soil by 0.00031 g./m^2. for glycol and by 0.000286 g./m^2. for EGME (3).

RESULTS AND DISCUSSION

The glycol and EGME methods using $CaCl_2$-adsorbate solvates to control vapor pressure gave essentially the same surface area for all the soils studied (fig. 1). The greatest variation occurred in two soils with large surface areas. Since these same two soils gave variable results between replicated samples within the glycol method, the glycol values may be in error.

Surface-area values obtained with EGME without the use of $CaCl_2$-EGME solvate for controlling vapor pressure were the same as those obtained using glycol with controlled glycol vapor pressure (fig. 2). These results indicate that the control of vapor pressure is not important when EGME is used as the adsorbed phase. Actually, the values reported previously for glycol, with and without $CaCl_2$-glycol solvates to control vapor pressure, did not differ greatly (2). Since only a few hours are required for attaining monolayers of EGME, control of vapor pressure appears unnecessary.

Surface area values determined by EGME methods with and without $CaCl_2$-EGME solvates for vapor pressure control also were compared. The relation is illustrated in figure 3 ($EGME_s$ refers to the use of the $CaCl_2$-EGME solvate). Some variation occurred, but it was no greater than the random variation that occurred between duplicate runs within any of the three methods (table 2). The variation between duplicate runs using glycol was greater than that found between methods (table 2). The probable explanation for this variation is that samples are handled and exposed to the atmosphere more during a several-day run with glycol than they are with a single-day run with EGME. Also, averaging duplicate runs within each method before methods were compared decreased the random variation.

The regression coefficients, intercept values, and correlation coefficients for comparisons between methods for milligrams adsorbate retained per gram of soil are also presented in table 2. The intercepts for all regressions are near the origin, and the slopes approximate unity. As reported previously, a slightly greater mass of glycol than EGME is required to form a monolayer per unit surface (3). This difference, however, is only about 7 per cent and is one that is not evident because of random variation among samples.

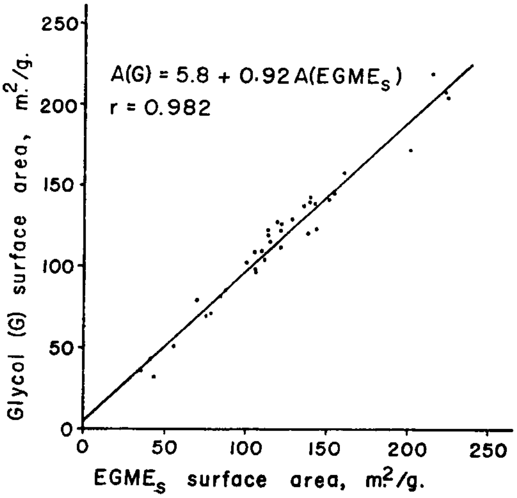

FIG. 1. Relation between soil surface area determined by the glycol and the $EGME_S$ methods with controlled vapor pressure.

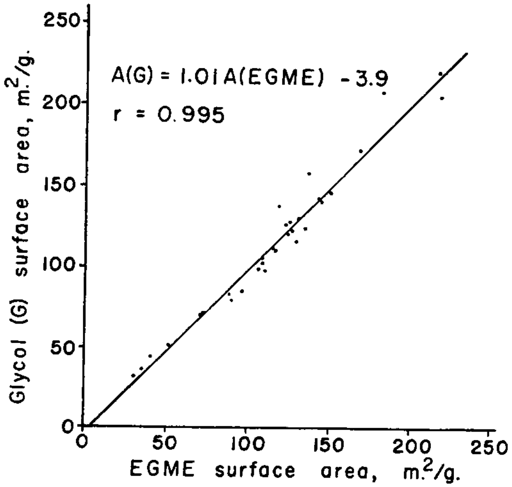

FIG. 2. Relation between soil-surface area determined by the glycol method with controlled vapor pressure and the EGME method with no vapor-pressure control.

Since methods using EGME and glycol give the same results for soil-surface area, the most convenient method should be used. In our laboratory, the glycol method required from 4 to 8 days to obtain equilibrium monolayers on the P_2O_5-dried soils studied. In contrast, the maximum time required for EGME was 2 days, and many samples could, if desired, be completed within one day. Using EGME saves considerable time and is more convenient than the glycol method. When using EGME, the P_2O_5 drying becomes the most time-consuming part of the procedure. It may be possible to oven-dry samples to save time, but the effect of oven-drying on surface area would have to be evaluated.

Studies with different numbers of samples per desiccator indicated that samples should not be crowded. Precision was increased and time saved by placing a maximum of 6 samples per desiccator (250-mm. I.D.). When greater numbers of samples were used, precision decreased, because samples in the unevacuated desiccator adsorbed moisture while other samples were being weighed. The greater the exposure time to the atmosphere the greater was the amount of moisture adsorbed.

Recently, McNeal (6) reported that the saturating cation was important in surface-area determinations by the glycol method because of multiple association of glycol molecules with certain saturating cations. It is probable that EGME molecules similarly associate with saturating cations, because the two materials gave the same results for Ca-saturated samples.

The EGME method, with or without $CaCl_2$-EGME solvates to control vapor pressure, is considerably more rapid than the glycol method, and it gives results that are equally useful. Neither material is the probable ultimate for measuring the actual surface area of soils and minerals. There is a need for a more direct measure of the actual soil and mineral surface area, but no such method has been developed. Until such a method is introduced and proven, the EGME procedure appears to be the most convenient method to obtain results that are useful and that can be related to other mineral and soil properties.

A convenient procedure for soil-surface area, using the EGME method with or without a $CaCl_2$-EGME solvate, has been developed at this laboratory. The procedure could be altered somewhat without loss of precision.

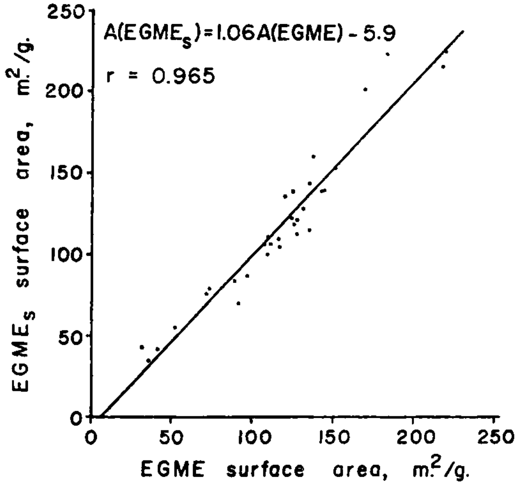

FIG. 3. Relation between soil-surface area determined by EGME methods with and without vapor pressure control. $EGME_s$ indicates the use of a $CaCl_2$-EGME solvate for vapor pressure control.

TABLE 2

Regression constants and correlation coefficients relating sorbate retention between different methods and between duplicate determinations of surface area within a given method

Y	*X*	*a*	*b*	*r*
Relation between methods				
mg./g.	*mg./g.*	*mg./g.*		
Glycol	$EGME_s$*	2.1	0.99	0.975
Glycol	EGME	−0.9	1.08	0.976
$EGME_s$	EGME	−2.0	1.06	0.968
Variation within a method				
m^2./g.	*m^2./g.*	*m^2./g.*		
Glycol, Rep. 1	Glycol, Rep. 2	−2.3	1.05	0.948
$EGME_s$, Rep. 1	$EGME_s$, Rep. 2	1.3	0.97	0.968

* The subscript *s* refers to the use of a $CaCl_2$-EGME solvate to maintain a constant vapor pressure at the sorption surfaces.

Recommended procedure

Approximately 1-g. samples are dried to constant weight over P_2O_5 in an evacuated desiccator. At the beginning of a working day, samples are treated with approximately 3 ml. of EGME to form a soil-EGME slurry that is placed in a desiccator over $CaCl_2$ and allowed to equilibrate 30 minutes. The desiccator is then evacuated for approximately 45 minutes. About one hour before the end of the working day, the samples are weighed and the desiccator reevacuated for 45 minutes. At the beginning of the next working day, the samples are again weighed. Generally this latter weight will agree very closely with the previous weight, indicating that a constant weight has been attained. If all samples have attained a constant weight, a new group can be started. Samples that have not attained a constant weight are returned to the desiccator, which is again evacuated. Another weighing can be made about midday or at the end of the workday. Samples seldom require more than three weighings. If results are required within the same day, the first weighing can be made near midday and the second weighing near the end of the day.

SUMMARY

Ethylene glycol and EGME (ethylene glycol monoethyl ether) give the same measure of soil surface area. The EGME method is convenient and much more rapid than the ethylene glycol method. EGME can be used as the adsorbed phase in the presence or absence of a $CaCl_2$-EGME solvate to control vapor pressure with equal measurements of surface area. A procedure is presented for using the EGME method routinely in the laboratory.

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