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Testing a simple methylene blue method for surface area estimation in soils

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INTRODUCTION. — Specific surface area is one of the most important properties of soils that can be related to their physical or chemical behaviour. Adsorption and desorption of nutrients or pollutants by soils are examples. Surface area measurements correlate well with soil characteristics owing to their capability of integrating the properties of soils (LA FLEUR, 1973; ROSS, 1978; MARGHEIM and LOW, 1978; LOW, 1980), also providing a more direct evaluation of the physical and mineralogical properties (FRANZMEIER and MCKEAGUE, 1985). Therefore, surface area classes could result in groupings that have a narrower range of physical properties than groups based on mineral species.

The most commonly used methods to evaluate the specific surface area of soils are based on the adsorption of nitrogen (N_2), water-vapour (H_2O), or ethylene glycol monoethyl ether (EGME) (BRUNAUER *et al.*, 1938; QUIRK, 1955; CARTER *et al.*, 1965; DECHNIK and STAWINSKY, 1970). The surface area measured by the last two methods is known to represent the «total specific surface area», whereas only «external surfaces» can be determined by nitrogen adsorption, thus creating limitations with samples containing considerable amounts of expansible layer-silicates. Dye molecules have also been used for determining both the «electropositive» and «electronegative» surface area of soils and clays (BURFORD *et al.*, 1964; SEQUI and ARINGHIERI, 1977). The cationic dye methylene blue (3,7-bis dimethylaminophenazationium chloride), hereafter called MB, has also been used as a sorbate for determining the surface area of clay materials (PHAM THI HANG and BRINDLEY, 1970; LA FLEUR, 1971, 1972, 1973).

A very simple end-point procedure based on the adsorption of MB has been adapted to test bentonites in the drilling mud industry (JONES, 1964) as well as ceramic clays (NEVINS and WEIN-

TRITT, 1967; PHELPS and HARRIS, 1968).

This last method deals with the use of a MB solution added at intervals and fixed volume increments to a clay suspension until the so-called end-point, as checked up by the spot test, is reached. The end-point corresponds to the point of maximum clay flocculation and indicates that an exact coverage of clay surface is obtained. This method, devised to monitor the specific surface area of clays in the ceramic industry, could easily be used in small laboratories, including those from less developed countries, to obtain rapid evaluations of the surface area of soils.

The present work was carried out to test the suitability of this last method to evaluate the surface properties of soils of different pedogenic origins and to compare it with more classic methods.

MATERIALS AND METHODS. — The following soils ranging widely in clay mineralogy, iron oxides, amorphous alumino-silicate, and organic matter contents (Table 1) were selected:

i) The A, E and Bh horizons of a Cryorthod (SEQUI and ARINGHIERI, 1977) developed on acid schists of late Paleozoic age from Bormio (Central Alps, Italy).

ii) The A and C horizons of three Entisols (V-88, V-89, V-91) and two bare regoliths (V-90, V-01) developed on calcareous mudstones of the Cretaceous-Paleogene boundary, from Vallcebre, in the eastern Pre-Pyrenees, Spain (SOLÉ *et al.*, 1990).

iii) The A horizon of a Haplumbrept (Campeda soil) from the north-west part of Sardinia (Italy), with high contents of amorphous alumino-silicates and organic matter (SEQUI and ARINGHIERI, 1977).

iv) Montmorillonite and kaolinite samples, purchased from Ward's Natural Science Establishment Inc:, Rochester, N.Y., were also used as standards to compare the results obtained in specific surface area determinations.

Particle size analyses were performed with a Micromeritics Sedigraph apparatus. The pH was measured in a 1:2.5 soil: water suspension with a Schott 822 pH meter. Calcium carbonate and organic matter determinations were carried out by conventional methods. Mineralogy of powder and oriented aggregate specimens was analyzed with a Siemens D-500 diffractometer equipped with a graphite monochromator and a Cu-target X-ray tube operating at 40 kV and 20 mA. The diffractometer was connected to a PDP 11/37 unit through a DACO-MP interface for data processing.

«External» surface area of samples was determined by N_2-(BET) adsorption isotherms at —195°C, whereas the method of QUIRK (1955) was employed to determine their «total» specific surface area by water-

TABLE 1. — *Some characteristics of the studied soils.*

Sample	Depth	Horz	pH	$CO_3^=$	CEC	O.M.	Texture (%)			Mineralogy (%)						
	(cm)			(%)	meq/100 g	(%)	Sand	Silt	Clay	Qrz	Fld	Cal	Kao	Il.	Smc	Chl
V-88	2-10	A	8	33	12.7	2.98	23.1	50.0	22.9	24	1	53	9	6	5	2
	10-23	Cu1	8.1	33	15.1	1.9	22.9	45.4	31.6	28	2	41	13	10	5	1
	42-56	Cu2	8.4	31	19.6	0.29	31.1	38.6	30.3	28	2	39	9	11	10	1
V-89	2-12	A	7.3	44	24.7	2.96	30.9	49.0	20.0	28	1	46	8	10	7	0
	12-21	A/C	7.4	36	28.2	1.38	20.3	54.2	25.5	26	1	7	9	11	12	1
	22-30	Cu2	7.4	35	26.9	0.31	15.1	55.1	29.7	24	2	36	10	13	12	3
	42-49	Cu3	7.8	36	31	0.24	12.3	56.2	31.6	24	1	35	9	16	13	2
	>70	R	7.8	35	30.7	0.05	18.3	54.3	27.4	26	2	41	7	12	12	1
V-90		R	8	50	18.2	0.1	61.4	16.6	21.9	26	0	48	5	10	9	1
V-91	0-10	A	7.4	23	30.1	1.23	5.1	40.7	54.1	21	1	30	14	21	14	0
	10-20	C	7.8	25	29.8	0.61	10.3	38.6	51.1	21	1	28	17	21	11	1
V-01	0- 5	C/R	7.9	31	38.4	0.14	5.1	50.8	43.1	20	1	47	10	11	9	1
	5-10	R	7.9	36	39.9	0.78	5.7	58.4	35.9	20	0	45	8	19	7	1
Bormio soil	0-10	A	3.5	0	43.4	37.6	86.3	11.2	2.4	88	10	0	**	***	*	—
	10-30	E	3.8	0	19.2	1.36	69.1	21.7	3.3	89	7	0	**	***	*	—
	40-70	Bh	3.8	0	25.6	2.47	80.8	16.9	2.3	84	10	0	**	***	*	—
Campeda soil		A	5.1	0	58.9	15.3	0.2	84.5	15.2	14	13	0	28	55	18	0
Kaolinite			5.5	—	27.2	—	0	0	—	—	—	—	95	—	5	—
Montmorillonite			4.8	—	61.8	—	0	0	—	—	—	—	—	—	100	—

* scarce; ** medium; *** abundant.

vapour adsorption measurements (H_2O area).

Since the methylene blue adsorption method (MB area) has not been published in its present form, a more detailed procedure is provided: Fine earth (< 2 mm) samples were ovendried for 2 h at a temperature of 378°K to remove hygroscopic moisture. A portion of each dried sample, with a weight varying according to its clay type and content, was dispersed into a beaker containing 300 ml of water shaking for 20 min. The beaker was then placed on a variable speed laboratory mixer, stirred at moderate speed, and the pH of the suspension was measured with either a glass electrode or a pH test paper. Since the MB cation is a weak acid, the suspension was adjusted at pH 3.5 to avoid hydrolysis and facilitate the adsorption on soil particle surfaces. Portions of 1 or 0.5 ml of 0.01 N MB solution were added dropwise from a burette, mixing the suspension continuously for 2 minutes after each addition. The dyed soil particle suspension was then sampled by removing a few drops with a pipette and placing a drop on hardened filter paper. As long as no excess of dye appears in the water phase, only a compact dyed spot of soil particles is formed, the excess of water being drawn off into the surrounding paper. When the endpoint is reached, the excess of MB moves away from the soil spot and is strongly adsorbed by the cellulose of the paper thus forming a blue halo around the darker soil spot. At the same time, a light blue coating appears on the reverse side of the filter paper. To make sure that a complete exchange had occurred, the suspension at an apparent endpoint was stirred for another two minutes and the test repeated. If the second trial did not show the blue halo the titration was continued until a stable endpoint was reached. The specific surface area was determined by the amount of MB adsorbed assuming that each molecule of MB covers an area of 1.3 nm^2.

RESULTS AND DISCUSSION. — Table 1 shows marked differences in the physico-chemical and mineralogical properties of the investigated soils or clays. A different response may therefore be expected in surface area determinations according to their composition and heterogeneity.

The specific surface areas determined by low-temperature nitrogen adsorption isotherms (BET method) exhibit moderately low values in all instances (Table 2). As reported by BURFORD *et al.* (1964), soils rich in either montmorillonitic clay or organic materials can behave in a similar way when outgassed at 105°C for N_2 adsorption measurements. We observed a similar trend for the soils used. The N_2-area of the A horizon of the Bormio soil may be explained by the presence of large amounts of partially humified organic matter, in which a contraction due to the outgassing treatment is likely occur rendering many surfaces inaccessible

TABLE 2. — *Specific surface area data and relationships between characteristics of the soils.*

Sample	Depth	Spec. surf. area (m^2/g)			Er (1)
		M.B.	H_2O	N_2	
V-88	2-10	79.6	160.6	8.0	0.25
	10-23	87.9	143.8	13.9	0.18
	42-56	86.7	112.7	16.7	0.33
V-89	2-12	45.4	103.1	7.0	0.28
	12-21	58.1	119.6	12.9	0.37
	22-30	64.6	115.1	12.3	0.34
	42-49	66.3	108.7	13.0	0.35
	>70	75.8	143.4	12.2	0.39
V-90		31.2	108.4	15.6	0.38
V-91	0-10	107.8	175.0	24.3	0.29
	10-20	94.9	140.0	26.2	0.30
V-01	0- 5	75.6	312.9	22.4	0.30
	5-10	74.8	336.0	27.4	0.31
Bormio soil	0-10	66.2	324.8	11.6	—
	10-30	8.5	18.2	2.0	—
	40-70	7.8	91.7	17.5	—
Campeda soil		11.7	289.6	15.3	0.18
Kaolinite		28.3	152.7	29.9	0.00
Montmorillonite		344.5	752.7	*	1.00

(1) smectite/(smectite + kaolinite + illite).

to the nitrogen molecules; on the contrary, the same materials can swell in water and offer a larger area to water-dissolved adsorbates. The poor reactivity of non-polar molecules (viz. N_2) to exposed surfaces of partially or non humified organic residues may also contribute to lowering the values of specific surface area. The lack of relationships between N_2 (BET) area and water-vapour area for Vallcebre soils may be ascribed to the presence of an important fraction of expandable clay, thus indicating that internal surfaces dominate in these soils. The values of expandable clay to expandable plus non-expandable clay ratio (Er) reported in table 2, support this hypothesis.

Noticeable differences between water-vapour and MB area values were observed for all investigated samples. The reason for this may be the electrostatic repulsion of the cationic reactant MB by positively charged sites of soil particles which impede a complete coverage of the surfaces. On the other hand, water molecules can be adsorbed on both positively and negatively soil particle surfaces giving a more realistic value of the total specific surface area. Data obtained for the Bh horizon of the Bormio soil are therefore of particular significance because of the presence of iron and aluminum oxy-hydroxides which lead to the prevalence of positively charged surfaces (SEQUI *et al.*, 1980). The higher the positive charge at the colloid particle-solution interface, the stronger the repulsive effect to cationic reactants such as methylene blue.

Another significant example is reported in Table 2 for the Campeda soil. In this case, the water-vapour area is the result of the swelling properties of spongeous amorphous aluminosilicates formed by the Allophane-Imogolite complex as shown from the diffraction pattern (Fig. 1). At the same time, this sample reacts very little with MB because of the abundance of electropositive allophanic surfaces (SEQUI and ARINGHIERI, 1977) which strongly affect the adsorption phenomenon.

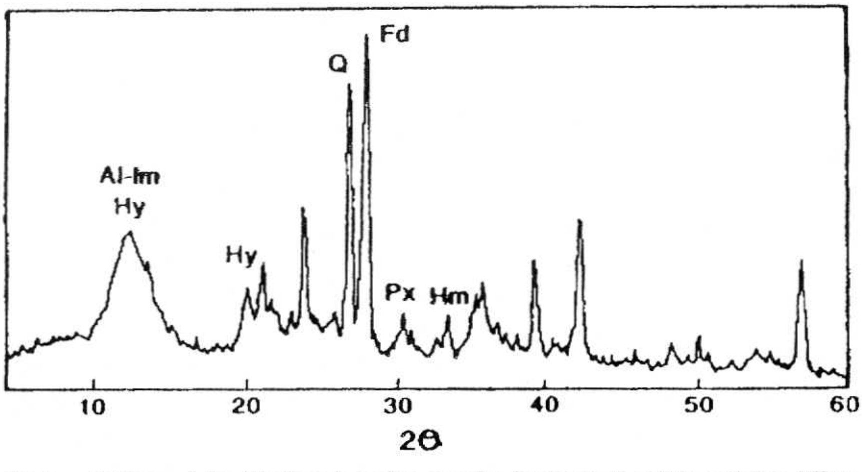

FIG. 1 — Evidence of the Allophane-Imogolite complex for Campeda soil from X-Ray diffraction pattern.

Although the electrostatic repulsion of MB cations by positively charged sites on soil particle surfaces can explain differences in the specific surface area, as determined by the MB or water-vapour adsorption method, physical restrictions such as the presence of «bottleneck-like» pores in some specific materials may prevent the penetration and, consequently, the adsorption of MB, so giving surface area values lower than those expected. The regoliths «V-89 > 70» and «V-01» show the same MB surface area whereas water-vapour adsorption gives twice the value for the «V-01» material. This water adsorption value may account for the considerably higher clay content in the «V-01» sample, which however does not explain its low MB area at the same time. Nevertheless, the microporosity of this material in the range of 0.1 to 0.007 μm (measured with a Hg-intrusion porosimeter) is much lower than the microporosity of «V-89 > 70», as reported by SOLÉ *et al.* (1990). It seems therefore likely that MB molecules cannot reach all the surfaces as water alone can do.

Another limiting factor to the use of the MB simplified method to estimate the specific surface area of soils is the dissolution of carbonates. We in fact observed that about 15% of total $CaCO_3$ present in the Vallcebre samples was dissolved during the MB adsorption process. On the other hand, negligible amounts of Fe, Al, Mg and Si were found in the supernatant after MB adsorption, thus indicating that hydrolysis and evolution with partial dissolution of some clay materials is unlikely to take place in a short time.

There are also a few instances in which N_2-BET and MB values are quite close. However, it would be erroneous to attribute a pure measure of external surface area to the adsorption of MB, as takes place with nitrogen adsorption.

The specific surface area for kaolinite, determined by the MB simplified method was slightly lower than the value reported by PHAM THI HANG and BRINDLEY (1970), who applied the Langmuir equation to MB adsorption isotherms. At the same time the water-vapour area was higher than expected, probably because of the presence of smectite impurities in the sample as indicated from its C.E.C. value and clay mineralogy (Table 1). For the same reason a higher value of MB would be expected. However, the presence of sites of pH-dependent charge at the edge faces of the clays, especially at the low pH values at which the method operates, may reduce the MB adsorption also hindering the access of MB cations to some negatively charged sites on planar sheets of the mineral.

The low MB area value found for montmorillonite may be explained in the same way even though its edge/planar area ratio is smaller than kaolinite. The MB to H_2O area ratio from both kaolinite and montmorillonite (0.19 and 0.46 respectively) reflect these conditions. Moreover, two replications on MB adsorption by montmorillonite carried out with the simplified method at pH 4.5 gave specific surface area values of 602 and 597 m^2/g respectively. This means that the presence of pH-dependent positive charges at the edges of clay mineral may reduce the MB adsorption, thus hindering a complete saturation of the available sites.

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SUMMARY. — Soils differing in clay mineralogy, iron oxides, amorphous alumino-silicates and organic matter content were investigated for their reaction in specific surface area measurements by using a simplified method based upon methylene blue (MB) adsorption. Results are compared with those obtained with more classic N_2 (BET) and water-vapour (H_2O) adsorption methods. Specific surface area values determined by the MB method were unrealistically lower than those obtained with the H_2O adsorption method.

The major limitation of tthe MB method seems to be its dependence upon the surface charge characteristics of the soils. In addition, physical restrictions such as the presence of «bottleneck-like» pores may impede MB molecules from coming into contact with adsorption sites on soil particle surface.

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