Relationships Between Surface Areas of Red Tropical Soils Measured by Different Methods†

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Abstract

A variety of tests are currently used to determine surface area in different branches of engineering and industry. This paper analyzes the relationships between these tests based on the results obtained by each test for a group of nine red tropical soils collected in the north east of Brazil. The ethylene glycol monoethyl ether (EGME) method that showed a good correlation with direct measurement of particle size by electron microscopy, is taken as a base for the graphical representation of results. Conversion factors between the tests and the EGME test and the standard deviation of the conversion factors are calculated.

The results show that test procedures can be divided into three groups in terms of increasing spread in the test results - polar molecules and direct measurement tests with a spread of less than 15%, methylene blue and BET tests with a spread of about 30% and Blaine, Fisher and granulometric tests with a spread of about 50% when plotted against EGME data. It is noted that the test methods that gave a larger spread are used in industry and process control, because they may be performed quickly at a modest cost. The more accurate methods are slower and in some cases more expensive.

1. Introduction

Surface area is used in the engineering practice to correlate the size of particles of granular materials with other engineering properties. These correlations can be used as a measure of associated properties and as a control parameter in a wide variety of engineering processes.

At present, a variety of methods using different physical and chemical principles are used to measure surface area in different industries. Each of these methods has evolved in response to the need to control a specific process or evaluate a specific product. Unfortunately, the surface area values obtained using these different methods vary widely. In some cases (Ferreira and Brito, 1984) there even seems to be little or no correlation between the values given by different methods.

The various granulometric methods of calculating surface area (arithmetic mean diameter, geometric mean diameter and Mellor's mean diameter) which use grain sizes determined by sedimentation are no longer in use for the control of engineering processes. However, the grain size curves are still used to classify soils. The precision and repeatability of surface areas calculated by these methods is not adequate for most engineering applications.

The Blaine (Blaine, 1943) and the Fisher (Carman, 1939) air permeability methods, both compare the time required for a given volume of air to pass through a cylindrical sample of the compacted material with the time taken for the same volume of air to pass through a sample of known surface area.

The Blaine method is used to measure the fineness of Portland and other cements. Fisher’s method is used to determine the fineness of metal powders and oxides. Both methods are quick giving results in about five minutes per test. This allows continuous monitoring of industrial processes. However the precision of these methods is low. The Fisher method which uses more sophisticated and expensive equipment than the Blaine method is somewhat more precise.
The Hang and Brindley (1970) method based on the adsorption of methylene blue dye has for some time been used to control the fineness of raw materials in the ceramics industry and has recently been utilized to characterize soils in soil mechanics applications (Casanova, 1986). This method is quick, taking about one half hour per test, but its precision and repeatability are low.

The adsorption of polar molecules of ethylene glycol, glycerol and ethylene glycol monoethyl ether (EGME) (Bower and Gschwend, 1952) is the traditional method for measuring surface area in soils and agricultural studies. This method is characterized by a relatively high degree of precision and repeatability, but is slow and time consuming making it unsuitable for such applications as process control where a rapid feedback is required.

The classic BET method for measuring surface area (Brunauer, Emmett and Teller, 1938) is based on the adsorption of gaseous hydrogen and nitrogen. It is widely used in the chemical industry and materials technology. Its precision and repeatability are good. Each test requires about two hours, a reasonable time for most purposes, but perhaps somewhat slow for a process control. Another disadvantage of this method for industrial applications is that the equipment required for the tests is relatively expensive.

Direct measurements of particle sizes using transmission or scanning microscopy gives very accurate determinations of particle cross section areas. The former does not allow a direct measurement of particle thickness. The latter, at least in theory, allows particle thickness to be determined by changing the sample orientation. However, for materials with unregulated crystallography, it is difficult to separate the particles in the photographic images. This method, although potentially very accurate, is used mainly in research. It is one of the slowest methods for measuring surface area and requires very expensive electron microscopes.

This paper analyzes the degree to which the results of the surface area measurements obtained by different methods can be related with each other. The model materials used in this study were samples of fines fractions of a group of red tropical soils collected in three states in the north east of Brazil. Data obtained by the EGME method which demonstrated good correlations with other measurements using polar molecules, as well as with direct measurements have been used as a base for graphical presentations of data obtained by other methods.

2. Materials and Experimental Procedures

Soil Samples – The red tropical soils from the north east of Brazil used in this investigation were taken from samples stored in the soils laboratory, Solos II, of the Civil Engineering Department, Centre of Science and Technology of the Federal University of Paraíba. The samples were collected from locations in the States of Maranhão, Paraíba and Piauí and identified by the abbreviations BUPI, CAPI, PDMA, VGMA, SLMA, JPPB, TEPB, ARPB and CTPB. A detailed description of the samples and their location of origin is available in Ferreira and Brito (1981).

Sample Preparation – In order to increase the clay fraction the wet soil samples were screened through the ABNT n°200 (0.074 mm) screen. Then they were air dried under the incandescent bulbs that accelerated the drying process by raising the material temperature to about 50°C. The dry samples were comminuted by a porcelain pestle, screened through the ABNT n°200 (0.074 mm) screen and dried in an oven to a constant mass. These specially prepared samples were used in the various procedures for measuring the surface area as it is described below.

Granulometric Method – Surface areas were derived from granulometric analysis by sedimentation performed by Lima (1983) using the method of BS1377 (1975) commonly called the densimeter method. The calculations of surface area were conducted in accordance with Singer and Singer (1975) and gave numerical values in m$^2$/g accurate up to 0.01 m$^2$/g.

Blaine’s Method – Surface areas were determined using the Blaine permeameter in accordance with MB – 348 of ABNT (1966). The standard used was the cement sample obtained from the Brazilian Portland Cement Association which had a surface area of 0.342 m$^2$/g and a specific mass of 3.21 g/cm$^3$. Values of surface area in m$^2$/g were calculated to an accuracy of 0.01 m$^2$/g.

Fisher’s Method – Fisher model 95 permeameter and a reference sample having a surface area of 0.3030 m$^2$/g and a specific mass of 3.15 g/cm$^3$ obtained from the National Bureau of Standards “NBS” were used in the surface area determination. The methods used are those described by Neves (1989) and the numerical values of surface area in m$^2$/g were calculated to an accuracy of 0.01 m$^2$/g.

Methylene Blue Method – The methodology described by Chen et al (1974) was applied in the surface area determination using methylene blue. A conversion factor of 7.8043 based on molecules of methylene blue having a face area of 130Å$^2$ as suggested by
Hang and Brindley (1970) was used in the equations for the calculation of surface area, where surface area is a product of cation exchange capacity by the conversion factor. Surface areas were calculated in m²/g to an accuracy of 0.01 m²/g.

Adsorption of Polar Molecules Method—The determination of surface area using polarized molecules was performed in accordance with the methodology of Diamond and Kintner (1968) for glycerol, that of Carter et al (1965) for ethylene glycol monoethyl ether (EGME) and that of Bower and Gschwend (1952) for ethylene glycol. A detailed description of these methods and their application is also available in Guedes and Ferreira (1992). As with the other methods the surface areas for these cases were calculated in m²/g to an accuracy of 0.01 m²/g.

The BET method—The surface areas of the fines fraction of the red tropical soil samples were determined using the methodology described by Brito and Ferreira (1984). This method, which for the first time was described by Brunauer, Emmett and Teller in 1938, gives numerical values of surface area in m²/g to the nearest 0.01 m²/g.

Direct measurement—Surface areas were determined from measurements based on a planimeter of cross sectional areas in images taken in a transmission electron microscope (TEM). A description of the details of the measurement and calculation procedures is available in Conciani and Ferreira (1988). The TEM procedure used did not allow the accurate measurements of the particle thickness and evaluation of the surface area was made assuming a series of thicknesses within the range reported in the literature for this class of materials. The thicknesses chosen were D/3, D/5, D/10 and D/15 where D is the mean diameter of the cross sectional area examined. The surface areas were calculated in m²/g accurate to within 0.01 m²/g.

3. Results and Discussion

The results of the surface area determinations for the fines fraction of the various red tropical soils samples are given in Table I. The statistical correlations based on the assumption of a linear relationship between the various surface area measurements are given in Table II for those cases where the coefficient of correlation was greater than 0.70. The best correlations are between the three methods using polar molecules of EGME, ethylene glycol and glycerol, all of which gave a coefficient above 0.96 at a significance level of 0.002%. Also, as it may be seen from Table I, the numerical values given by the three methods are similar. Figure 1 gives values of surface area of ethylene glycol and glycerol plotted against those for EGME. With the exception of one test result all the data obtained is lined up at the equal values of the dependent and independent variables. In the exceptional case, the ethylene glycol and glycerol data are positioned close to each other. This is consistent with the slightly higher coefficient of correlation between these two test methods compared with the EGME results. The factor correlating the results of determinations by these three methods is approximately equal to one (1.05 for ethylene glycol and 1.02 for glycerol); the standard deviation of the factor is 12% of the mean value for ethylene glycol and 8% of the mean value for glycerol.

Because the EGME method is not as time consuming as very slow (but accurate) polar methods, it was used as a base to plot the data obtained by the other methods. Figure 2 displays data obtained by
Table I  Surfaces Area of the Fines Fraction of Red Tropical Soils from the Northeast of Brazil.

| Samples | Granulometric Methods | Blaine Diameter Standard 0.045 μm²/g | Fisher NBS Standard 0.082 μm²/g | Methylene Blue Molecular Diameter 130AB | EGME Molecule of 52A² | Ethylene Glycol | BET | Direct Measurement |
|---------|-----------------------|--------------------------------------|---------------------------------|------------------------------------------|-----------------------|----------------|-----|-------------------|
|         | Meß Or Arithmetic Mean Diameter | Geometric Mean Diameter | | | | | | C = D/3 | C = D/5 | C = D/10 | C = D/15 |
| BUPI    | 0.08 | 0.09 | 0.10 | 0.70 | 0.50 | 20.29 | 33.54 | 33.87 | 33.34 | 14.92 | 16.03 | 20.66 | 32.70 | 77.28 |
| CAPT    | 0.08 | 0.09 | 0.10 | 1.05 | 0.85 | 21.85 | 46.15 | 48.39 | 46.77 | 22.22 | 32.47 | 45.30 | 77.10 | 110.21 |
| PDMA    | 0.09 | 0.11 | 0.12 | 1.29 | 1.23 | 39.02 | 33.22 | 34.14 | 35.30 | 25.18 | 9.17 | 32.39 | 55.02 | 78.01 |
| VGMA    | 0.08 | 0.10 | 0.11 | 0.68 | 0.50 | 40.58 | 49.20 | 49.68 | 49.24 | 25.23 | 29.00 | 43.09 | 69.48 | 98.61 |
| SLMA    | 0.07 | 0.08 | 0.10 | 0.78 | 0.77 | 15.61 | 23.08 | 32.26 | 28.24 | 21.48 | 12.39 | 17.32 | 29.71 | 42.11 |
| JPPB    | 0.08 | 0.09 | 0.10 | 1.90 | 1.32 | 26.53 | 50.00 | 50.97 | 51.18 | 34.95 | 28.27 | 39.62 | 67.72 | 96.16 |
| TEPE    | 0.10 | 0.12 | 0.13 | 1.14 | 0.92 | 48.39 | 53.15 | 50.32 | 52.95 | 39.12 | 29.96 | 41.49 | 71.92 | 101.96 |
| ARPB    | 0.06 | 0.06 | 0.07 | 1.05 | 0.81 | 24.97 | 44.76 | 46.13 | 44.83 | 42.64 | 34.05 | 47.55 | 82.79 | 114.67 |
| CTPB    | 0.09 | 0.11 | 0.12 | 1.48 | 0.82 | 29.66 | 53.85 | 51.94 | 49.42 | 28.73 | 31.11 | 43.66 | 74.61 | 105.88 |

Table II  Linear Correlation Between the Various Surface Areas of Fines Fraction of Red Tropical Soils from the North East of Brazil.

| VARIABLE Y | VARIABLE X | LINEAR EQUATION y = ax + b | COEFFICIENT OF CORRELATION (R) | SIGNIFICANCE LEVEL (%) |
|------------|------------|----------------------------|-------------------------------|------------------------|
| EGME ETHYLENE GLYCOL EGME | GLYCEROL ETHYLENE GLYCOL | y = -8.29 + 1.18x | 0.98 | 0.001 |
| D/3 | ETHYLENE GLYCOL EGME | y = -21.74 + 1.05x | 0.82 | 0.049 |
| D/15| ETHYLENE GLYCOL EGME | y = -11.27 + 1.87x | 0.88 | 0.187 |
| D/5 | ETHYLENE GLYCOL Glycerol | y = -14.75 + 1.16x | 0.88 | 0.214 |
| D/5 | EGME Glycerol | y = -10.24 + 1.08x | 0.87 | 0.239 |
| D/3 | Glycerol Glycerol | y = -1.78 + 0.96x | 0.86 | 0.266 |
| D/3 | EGME Glycerol | y = -15.39 + 0.92x | 0.86 | 0.288 |
| D/3 | ETHYLENE GLYCOL Glycerol | y = -8.34 + 0.77x | 0.86 | 0.267 |
| D/10 | ETHYLENE GLYCOL Glycerol | y = -16.01 + 1.79x | 0.86 | 0.256 |
| D/15 | Glycerol Glycerol | y = -2.43 + 2.16x | 0.85 | 0.398 |
| D/15 | ETHYLENE GLYCOL Glycerol | y = -7.32 + 1.62x | 0.84 | 0.488 |
| D/10 | ETHYLENE GLYCOL EGME | y = -8.99 + 2.28x | 0.83 | 0.557 |
| D/10 | ETHYLENE GLYCOL Glycerol | y = -6.45 + 1.32x | 0.82 | 0.684 |
| FISHER METHYLENE BLUE BET | BLAINE ARITHMETIC MEAN DIAMETER D/10 | y = 0.20 + 0.59x | 0.85 | 0.383 |
| | | y = -11.39 + 43.46x | 0.73 | 1.310 |
| | | y = 4.34 + 0.37x | 0.72 | 2.970 |

direct measurement assuming the thickness of the soils particles is equal to one fifth of their diameter (D/5). Table I shows the D/5 results give the closest numerical values to those obtained by the polar molecules methods. The spread of the results relatively, to the linear curve is small. The factor relating D/5 direct measurement and the EGME results is 0.85 and the standard deviation of this factor is 15% of the mean value. Interpolation of the data obtained for the various ratio values of the thickness-to-diameter indicates that the ratio of D/6.3 will result in a correlation factor of one between direct measurement and the EGME data. If the average thickness of particle can be determined precisely when using scanning microscopy, the direct measurement can offer a promising standard which can be used as a reference for calibration of surface area measurement by other techniques. Although it does not account for surface topography the spread due to this factor should be small compared to that observed with other techniques. The main advantage of the method is the fact that it doesn't depend on the many assumptions required by other techniques.

Figure 3 presents a plot of data obtained by the methylene blue and BET methods versus the EGME data. The spread of the data is approximately ± 30% in relation to central line. The same central line and the spread region can be used to characterize results obtained by both methods, but the individual data points for these two methods show no tendency.

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to converge indicating that their correlation with each other is no better than that of each of them with the EGME results. The factors relating the methylene blue and BET methods to EGME are 0.70 and 0.67 respectively with standard deviations of 33% and 28% of the mean values accordingly.

Figures 4 and 5 give values of surface area obtained by the Blaine and Fisher methods plotted against the EGME data. The spread is about 40% and 50% correspondingly. The factors relating Blaine and Fisher measurements to those of the EGME method are 0.03 and 0.02 respectively. The standard deviations are 33% and 50% for the mean values. It should be noted that the numerical values obtained by these methods are much smaller than those given by the other methods. Figure 6 represents a plot of the Blaine surface area measurements versus those obtained by the Fisher method. The correlation factor is 1.31 (Blaine value = 1.31 x Fisher value) and the standard deviation of the factor is 18% for the mean value. The spread of about ±25% is somewhat smaller in magnitude than that of data for each of these methods plotted against the EGME method.

The surface area values obtained by the Mellor calculation based on the granulometric data is plotted versus EGME data in Figure 7. The factor relating the Mellor values to the EGME values is 0.002. The standard deviation of the factor is 30% for the mean value. The data on the graph exhibits a spread of about ±40% in relation to the mean curve. A similar but slightly greater spread was obtained when the geometric mean diameter was calculated from the granulometric data and plotted versus the EGME
Fig. 7 Surface Areas Determined by Granulometric Methods Techniques Versus Those Determined by EGME Technique.

values. Visual analysis of the data, however, can bring one to the conclusion that there is little or no correlation between the Mellor and the EGME data.

Data obtained by the polar molecules methods not only have demonstrated nearly identical results for the samples tested (with coefficient of correlations among them greater than 96%) but also correlate very well with the physically meaningful direct measurement data (with the correlation coefficient of approximately 87% for D/5) which can be further improved by using the thickness-to-diameter ratio equal to D/6.3. Data for the EGME method was taken as a basis for the graphical comparisons. These comparisons show that the methods of determining surface area can be divided into three groups in terms of increasing dispersion of the data in the graphs and presumably decreasing precision of the method. The first group includes the polar molecules and direct measurement techniques, the second—the adsorption of methylene blue and BET methods and the third—the Blaine and Fisher methods and the granulometric methods.

The degree of spread of data observed in the BET versus the EGME plot and a relatively poor correlation between the BET and the data obtained by polar molecules methods were unexpected since both the BET and the polar molecules methods are based on the isotherms of adsorption.

The methods currently used in the control of industrial processes, namely the Blaine, Fisher and the methylene blue (which are utilized in the production of cement, metal and ceramic powders) are among those that showed the greatest spread of data in the graphical plots. However, replacing them with a more accurate method such as one of the polar molecules methods would significantly increase the cost and time consumed for testing. The present results do not seem to confirm the supposition that the BET method, which is intermediate in terms of testing time is much more accurate than the Blaine and Fisher methods.

The very slow and expensive direct measurement techniques are promising for the scientific applications.

4. Conclusions

(1) The three polar molecule methods of measuring surface area using EGME, ethylene glycol and glycerol gave almost identical surface area values for all of the samples.

(2) The direct measurement by electron microscopy technique gives results that, for an appropriate thickness assumption, are almost the same as the results given by the polar molecules methods.

(3) The spread of the results for the methylene blue and BET methods, when plotted against EGME data, is significantly greater than for the polar molecules or direct measurement techniques. The Blaine, Fisher and granulometric methods show still a greater spread.

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