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ELECTROSTATIC METHOD OF DETERMINING THE EXTERIOR SPECIFIC SURFACE OF SOILS

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Consideration is given to the underlying principle of the method of determination of the exterior specific surface of soils using an electrostatic field. The results obtained by the electrostatic method are shown to correlate with data obtained in determining the total specific area by the method of steam sorption.

The majority of the physical and chemical processes in disperse media and soils depend on the magnitude and properties of the surface of their solid phase, a quantitative characteristic of which is the specific surface. Being the fundamental parameter of soils and disperse media, to many properties of which it is functionally related, the specific surface is widely employed to solve various problems in the theory and practice of soil science, agriculture, colloid chemistry, etc. [1-3].

Data on the specific surface are obtained experimentally. For this purpose, adsorption-statistical methods of calculation by the BET (Brunauer, Emmett, and Teller) equation and the method of a "single point" find widest application. The latter is based on the assumption that formation of a monolayer on the surface of the solid phase of soil is completed at 20% relative air humidity. These methods allow determination of the total specific surface [2]. It is pertinent to note that methods based on steam sorption are rather laborious and time-consuming when used. The experiment lasts 1.5 to 2 months and requires rigorously thermostated conditions. This does not allow prompt obtaining of information on the specific surface of soils when it is subjected to various factors limited to a certain time interval or in carrying out mass analyses. As noted above, the indicated methods allow determination of just the total specific surface, which includes the exterior and interior specific surfaces. The exterior surface means the area of convex and plane elements of the surface and pores whose width is larger than their depth.

D. Farrar [4] adopts another position in determination of exterior and interior surfaces. Taking data of an x-ray analysis as a basis, he points out that at a relative steam pressure ranging from 0.4 to 0.8 in minerals with a mobile lattice the process of moisture sorption occurs only over the exterior surface. The area of the monolayer covering it is calculated from sorption isotherms. The interior specific surface is found as the difference between the total and exterior specific surfaces. To determine the total specific surface and its components, it is necessary to construct a sorption isotherm, which increases the measurement process to 3 to 4 months.

At the Agrophysical Institute, an electrostatic method has been developed that allows determination of the exterior specific surface of soils by electrical conversion of the magnitude of its area into an electrical signal [5, 6]. The method is based on the effect of the charge of soil particles in contact with electrodes to which a potential difference is applied. The electrodes must have a specially contoured surface or a structure for creation of conditions for a stable position of the particles in the electric field. Soil particles are placed on the lower electrode, if it is planar, or on the interior surface of the external electrode, if it is manufactured in the form of a cylinder (Fig. 1). In the case of a potential difference U between the electrodes, an electric charge q is formed on a particle and an electric force F acts that tends to separate the particle from the lower electrode. With increase in the intensity, the following condition is fulfilled:

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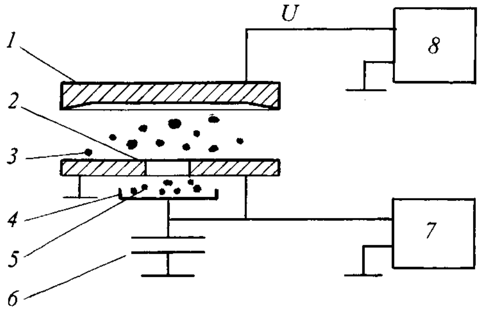

Fig. 1. Schematic of the device used to determine the exterior specific surface by the electrostatic method: 1, 2) electrodes; 3) particles moving in the interelectrode space; 4) cup for collecting particles; 5) collected particles; 6) capacitor; 7) electrometer; 8) high-voltage source.

$$F = m_i g + F_{\text{adh}} . \tag{1}$$

The particle leaves the lower electrode, moves toward the upper electrode, gives its charge to the latter, recharges to an opposite charge, and moves back to the lower electrode. Thus, charge transfer and a convective current are created in the circuit. Having determined an electrical parameter of this system, e.g., the electrical conductivity, the charge, and so on, we can obtain information on the degree of dispersion of the material. The basis of all physical properties of these systems is the electrical conductivity of the disperse material. First of all, it determines the value of the particle charge.

For soil, the electrical conductivity is a complicated and highly variable characteristic. Its value depends on a large number of factors: the moisture content, chemical and morphological composition, temperature, structure, etc. As a consequence of this, the electrical conductivity varies within rather wide limits, i.e., namely, 6–8 orders of magnitude, which is incomparably larger than the variation in any other characteristic of soil. The elements constituting the soil composition possess various electroconductive properties: from metals to dielectrics. However, ideal conductors are represented in very small amounts, although ferrous and manganic compounds, metal oxides, and graphites always enter into the mineralogical composition of soil. Minerals with such a content of elements possess a rather high electrical conductivity, namely, 10^{-1}–10^{2} S/m [7]. In turn, the primary minerals, namely, quartz, feldspar, and micas, entering into the soil composition are characterized by high dielectric properties. Their electrical conductivity is within the limits 10^{-12}–10^{-17} S/m. It should be noted that the particles of such minerals are not present in soil in a pure form since they are covered with a layer of substances whose conductivity is many orders of magnitude higher: metal oxides, metals, carbon, and various salts.

The reported values of the conductivity have been obtained in a measurement cell for low intensities of the electric field – no more than hundreds of volts per meter. In the course of the investigations it has been established experimentally that the electrical conductivity of soil in the air-dry state increases with the intensity of the electric field in the working gap of the measurement cell by 2–3 orders of magnitude. Thus, the electrical conductivity of soil in the air-dry state can reach 10^{-3}–10^{-4} S/m. This value will be determined foremost the first place by the surface electrical conductivity [5, 8, 9]. Therefore, as a model, we can represent a soil particle in the form of a dielectric sphere covered with a layer of thickness from several tens of angstroms to several micrometers whose conductivity is several orders of magnitude higher than that of the particle material and the surrounding air.

Since in our case the particle is in air, whose electrical conductivity is no higher than 10^{-14} S/m, then in a constant electric field during induction (contact) charging it acquires a charge that corresponds to the case where it seemingly consists of a conducting material. However, this is true only for a certain duration of contact of the particle with the electrode. Under the given conditions, in the regime of collision of the particle and the electrode the change in its charge is described in a firstapproximation by an ordinary exponential equation with a charging time constant τ:

$$\tau = 3\varepsilon_0 \,(\varepsilon_1 d + 1 - d)/[\gamma_1 d + \gamma_2 \,(1 - d)] \,. \tag{2}$$

For the case under consideration, $\tau = 10^{-7}$–10^{-9} sec, whereas in conformity with the theory of impact the contact time is no less than 10^{-5} sec. Even from these considerations, this time is sufficient for the particle to obtain the limiting charge [5].

In the literature, various models for determination of the charging time constant are considered; however, they produce only a qualitative result. This is explained by the dependence of the electrical conductivity, as has been indicated above, on numerous factors, in particular, on the variation in the humidity of the surrounding air. The electrical conductivity of the surface layer of the particles, as of any other hydrophilic film representing a mixture of metals, oxides, and carbonic compounds, varies by approximately four orders of magnitude depending on the fluctuations of the relative humidity within the range of 20–80%. Therefore at a rather low electrical conductivity the relation between the charge formed on the particle and the relative humidity of the air would inevitably be revealed. However experimental studies have not found such an interrelation in the case of particle charging by induction in a high-intensity field. Moreover, measurements of the charge have been made for narrow soil fractions and other disperse materials that are also described rather closely by the charge model of a conducting sphere (with allowance for the existing polydispersity of the fraction). Thus, we can draw the conclusion that the time of contact of the particles with the electrode is sufficient for "inleakage" of the maximum possible charge onto a particle and that the model of a conducting particle is applicable for soil particles [5, 6].

Moving particles form a quite stable ensemble and are in the region (or tend to find their way there) with a lower intensity of the electric field. Consequently, their energies, both potential and kinetic, are minimum. An intensity gradient of the electric field at the edges of the electrodes is created by their profiling or by using an additional electrode, isolated from the upper electrode, and applying a higher potential to it. For the chosen model of a soil particle in the form of a sphere that is in contact with a planar electrode in an electric field the charge q_i that appears on it is equal to

$$q_i = 0.66\pi^3 \varepsilon_0 r_i^2 U/h \,. \tag{3}$$

According to (3), the charge is proportional to the surface area of the particle. The simplest method of conversion of the dispersion characteristics of soil into an electrical signal is determination of the total charge of the particles acquired by them as a result of contact with the electrode, which is proportional to their surface area.

To determine the total charge, a hole is made in the lower electrode through which particles leave the interelectrode space after a number of flights from electrode to electrode. The motion proceeds from the upper electrode. Each emitted particle has a charge q_i. The particles are collected in a cup connected to a capacitor of capacitance C. Upon completion of the process of particle escape their total charge is

$$Q = \Sigma\, q_i = \pi^2 \varepsilon_0 U \,\Sigma\, s_i/(6h) = \pi^2 \varepsilon_0 U S_N/(6h) \,. \tag{4}$$

The charge is accumulated on the capacitor and is measured by an electrometer:

$$Q = CU_1 \,. \tag{5}$$

Having determined the mass M of the particles collected in the cup, we obtain an expression for the exterior specific surface:

$$S_{\mathrm{e}} = S_N/M = 6hCU_1/(\pi^2 \varepsilon_0 UM) \,. \tag{6}$$

For the adopted model, this method is absolute.

TABLE 1. Determination of the Mean Size of Narrow Sand Fractions Obtained by the Sieving Method

Sample	Fraction size, μm	Electrodynamic method 2 r, μm
Loose sand	250–300	393
	100–250	280
	60–100	120
Quartz sand	100–250	330

TABLE 2. Total and Exterior Specific Surfaces of Soddy-Podzolic Soils (Leningrad Region) of Different Granulometric Composition

Method of determination	Soil									Quartz
From steam-sorption isotherms $S \cdot 10^3$, m^2/kg	17	22	23	28	28	35	36	42	43	1.1
Electrostatic method S_e, m^2/kg	9.2	12.5	13.5	15	14.5	18.4	27.6	27.6	34	2.3

In [10], it was noted that there is no available all-purpose method for determination of the dispersity of soils. Each method has certain merits and drawbacks. The electrostatic method allows conversion of the surface area into an electrical signal and it is practically the only rapid method for determination of dispersity.

Using the well-known relation

$$r = 3/(\rho S_e)\,, \tag{7}$$

we can obtain the mean size of the soil particles in a specimen:

$$r = \pi^2 \varepsilon_0 UM/(2\rho hCU_1)\,. \tag{8}$$

Dependence (8) was used to test the method on sieved fractions. The results are presented in Table 1. The values found exceed the mean size of the fraction. This is attributable to the fact that the particles are not spherical. As a result, if such a particle is represented in the form of an equivalent sphere with the same volume, its equivalent size will be larger. For various geometric forms, we obtained coefficients that relate the equivalent size to the parameter of this geometric form. For instance, for a cube, it is equal to 1.5 a (a is the length of the cube edge); for a parallelepiped, $0.5(a+b+c)$ (a, b, and c are the lengths of the parallelepiped edges); for a cylinder, it is $0.5(l+R)$ (l and R are the cylinder height and the radius of its base, respectively); for a thin rod, 0.5 l; for a disk, 1.6 R; and so on [8].

The goal of the present work was to determine experimentally the exterior specific surface of soils by the method described above and to establish the relation between the latter and the total specific surface determined by the method of steam sorption.

In the investigation, we used samples of soddy-podzolic soil (arable horizons) of different granulometric composition (Leningrad Region), samples of sandy sierozem (Kazakhstan), and quartz sand with particles of size 0.25–0.5 mm. Experiments were carried out with air-dry samples screened through a sieve with a mesh size of 0.5, 0.25, and 0.1 mm.

The intensity of the electric field was 10 kV/cm, the interelectrode space was 1 cm. The total specific surface was determined from the sorption of steam by the soil in a closed space with a 20% relative air humidity [3].

A comparative evaluation of the results obtained (Table 2) showed that a rather high correlation exists between the values of the total and exterior surfaces determined by the different methods. The coefficient of correlation increases with decrease in the fraction dimension and reaches 0.9 for a fraction less than 0.1 mm.

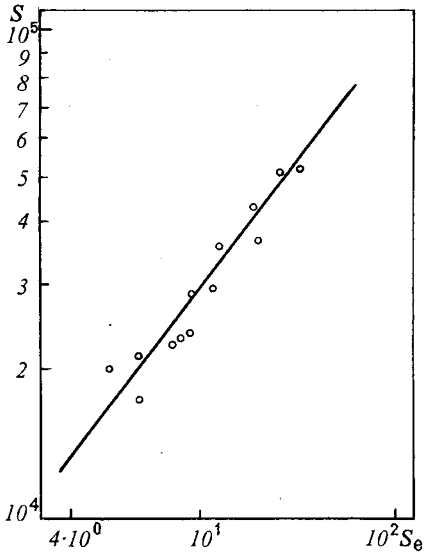

Fig. 2. Total specific surface S vs. exterior specific surface S_e.

The logarithm dependence between the total and exterior specific surfaces is linear (Fig. 2) and is described by the relation

$$S = kS_e^n . \tag{9}$$

With account for (6) and (7) we obtain the expression

$$S = k\,[6hCU_1/(\pi^2\varepsilon_0 UM)]^n , \tag{10}$$

which is used to determine the total specific surface of soils and disperse media within the range (10–45)·10^3 m^2/kg.

In [11], it is shown that the total surface area of many disperse media, including soils, determined from steam-sorption isotherms is fractal relative to the size of the particles constituting the disperse medium. Here, the fractal dimension D is in the range D = 2–3. The surface area and the radius of the particles are related as

$$S \approx r^{D-3} \tag{11}$$

or with account for (7)

$$\log S \approx (3 - D)\log(\rho S_e/3) . \tag{12}$$

An analysis of the experimental data obtained showed that the values of the fractal dimension for the investigated disperse media and those given in [11] are rather close. Now, we will determine how the results obtained are related in our case. After taking the logarithm of (9) we obtain

$$\log S = 3.68 - 0.65\log S_e . \tag{13}$$

Having equated the coefficients of the logarithms on the right-hand sides of Eqs. (12) and (13), we obtain a fractal dimension of 2.35 for the soils investigated. This coincides, with allowance for the experimental error, with the values of D found for similar media (soils), which are equal to 2.29 ± 0.6 [11].

The presented results of a comparison of the fractal dimensions confirm that the obtained correlations between S and S_e are physically reasonable and can be used for rapid determination of not only the exterior but also the total specific surface of soils.

Further investigations will be aimed at extending the domain of applicability of the developed method, including moderate and heavy loamy soils with respect to granulometric composition.

Thus, the experimental determination of the exterior specific surface of soils performed by the electrostatic method has provided the possibility of revealing the functional relation between the latter and the total specific surface determined by the method of steam sorption. This, in turn, has enabled us to develop a calculational-experimental method for determining on the basis of the electrostatic method the total specific surface of soils that are light with respect to granulometric composition.

NOTATION

m_i, particle mass, equal to $4/3\pi r^3\rho$; g, acceleration of gravity; F_{adh}, force of adhesion of the particle to the electrode; ρ, material density; ε_0, dielectric constant; ε_1, dielectric permeability of the particle material; γ_1 and γ_2, electrical conductivity of the particle and the surrounding medium; d, depolarization coefficient, for a sphere $d = 0.33$; q_i, particle charge; r_i, particle radius; h, interelectrode spacing; s_i, exterior-surface area of one particle; S_N, exterior-surface area of N particles; S_{e}, exterior specific surface; U_1, electrometer reading; C, capacitor capacitance; k and n, numerical coefficients, equal to $4.8 \cdot 10^3$ and 0.65, respectively; D, fractal dimension. Subscripts: e, exterior specific surface; i, particle number: 1, 2, 3, etc.; adh, adhesion.

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