THE USE OF SALTED PASTES OF SOIL COLLOIDS FOR X-RAY ANALYSIS

By

ISAAC BARSHAD

University of California, Berkeley

ABSTRACT

A new technique for the x-ray analysis of soil colloids is proposed based on the finding that the interlayer swelling of montmorillonite persists in the presence of salt solutions and that the x-ray reflection representing the d(001) spacings becomes intensified in salted gels. The technique consists in flocculating the colloid from a suspension with sodium chloride, removing the "free" Fe_2O_3, Al_2O_3, and SiO_2 by means of a solution of sodium citrate and sodium hydrosulfite, separating the cleaned colloid from the solution as a salted paste, and as such subjecting it to x-ray analysis. The method is not only more rapid than other recommended methods for x-ray analysis of soil colloids, but also — and which is of the utmost importance — yields a much more accurate picture of the mineralogical composition, particularly with respect to the content of the mica and the montmorillonite-type clays.

INTRODUCTION

An examination of the literature dealing with x-ray diffraction patterns of soil colloids reveals that very frequently the d(001) spacings of the clay minerals, particularly those of the mica and the montmorillonite type, are reported as weak or absent although these clay minerals may be present in considerable amounts in the specimens studied.

Several factors appear to contribute to the production of "poor" x-ray diffraction patterns of soil colloids. These are:

1. — *The presence, as a surface coating or as a mixture with the clay minerals, of amorphous oxides, such as Fe_2O_3, Al_2O_3, and SiO_2, and possibly amorphous silicates which are permutite-like in nature.* These affect the x-ray pattern by (a) darkening the background, (b) absorbing a considerable amount of the reflected x-ray beams and thus weakening the intensities of the lines produced, (c) producing a particularly dark halo in the vicinity of the primary beam which extends up to about 5° — the most important region for identification of the clay minerals —, and (d) favoring the formation of unoriented and fairly stable aggregates of clay particles.

2. — *The failure to employ techniques which induce the formation of oriented aggregates during the separation of the colloid from the soil suspension.* This is particularly true when colloids are dried and ground to a fine powder for use as a specimen for x-ray analysis.

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3. — *The presence of randomly interleaved clay minerals with interlayer spacings of different magnitudes.* Such interleaving causes the cancellation of the d(001) spacings of the individual clay minerals and the appearance instead of average spacings with reflections which may be weak, broad, and diffused or even absent, depending upon the kind of interleaving and the magnitude of the individual d(001) spacings of the interleaved minerals (Brown and MacEwan, 1950).

4. — *The presence of the exchangeable cations which produce poorer reflections* — Ba, Li, Na, NH_4, K, Rb, and Cs — instead of the ones which produce stronger reflections — Mg and Ca (Aldrich and others, 1944; Barshad, 1950); this is particularly pronounced when the clay is air-dry during the analysis.

5. — *The conditions inherent in the x-ray machine during analysis;* such as the intensity of the x-ray beam, collimation of beam, size of beam in relation to specimen, distance from specimen to film, distance of specimen from end of collimator, shape and size of beam stop in relation to the size of the primary beam at the surface of the film, length of exposure time, and nature of the capillary when capillaries are used for packing the specimen.

Several aids have been suggested to overcome some of the indicated difficulties (Aldrich and others, 1944; Brown and MacEwan, 1950; Brown, 1953; MacEwan, 1950; Nagelschmidt, 1941) but for many soil colloids these aids are insufficient to bring out all the d(001) spacings in the clearest manner. It is for this reason that the technique to be described in the present paper was developed. This method not only overcomes the difficulties mentioned but is also simple and rapid. However, before describing the technique and in order to facilitate its use it is advisable to indicate the findings which have led to its development. These are as follows:

1. — The d(001) reflection of montmorillonite-type clay in a gel state is strongly intensified by the presence of a soluble salt; the intensities of the d(001) reflections of such salted gels or pastes are comparable and in most instances are stronger than those of the dry powder or of the glycerol-wet form of the same clay. The effect of salt solution on the intensification of the d(001) reflection is most striking for Na^+— and Li^+— saturated montmorillonite. Whereas in a salt-free gel the d(001) reflection is barely visible or completely absent, in a salted gel or paste the d(001) reflection is very strong. The concentration of the salt solution in the paste or gel at which intensification begins is about $0.2N$; at $0.4N$ nearly the full intensification is achieved and it remains in that state up to a concentration of $2N$. The effect of higher salt concentrations was not studied.

2. — Citrate ions form a very strong complex with Al^{3+} ions, and their presence in a solution of an aluminum salt completely prevents precipita-

tion of $Al(OH)_3$. Conversely, a citrate solution at any pH dissolves freshly precipitated $Al(OH)_3$ but it does not dissolve gibbsite.

3. — Both Fe^{3+} and Fe^{2+} iron form strong enough complexes with citrate ions to prevent their precipitation as hydroxides until the solution in which they are present reaches a pH of about 6 for Fe^{3+} and about 9 for Fe^{2+}.

4. — Silicic acid and amorphous silica dissolve in a sodium citrate solution having a pH of about 10.3.

5. — Noncrystalline or amorphous permutites also dissolve in solutions of citrate salts ranging in pH from 5 to 10.

6. — An approximately normal solution of sodium citrate ranging in pH from about 5 to 9 aids in the removal of free Fe_2O_3 with sodium hydrosulfite by preventing the precipitation of FeS and by protecting the clay minerals from acid damage by its strong buffering action.

7. — Approximately normal solutions of sodium citrate ranging in pH from 5 to 10 do not seem to damage the clay minerals when they are contacted for short periods of time (2 to 5 hours) and at temperatures from 50° C to 70° C.

8. — Presence of organic matter in soil colloid does not interfere markedly with the x-ray analysis of the salted pastes.

9. — With copper radiation the d(001) reflections up to about 24 A are most clearly recorded on a flat cassette which has a circular lead stop about 2 mm in diameter and is set at a distance of 5 cm from specimen, with the specimen mounted directly on the tip of a collimator having a pinhole 0.02 inch in diameter. With such a setting and with the x-ray tube operating at 40 kv and 20 ma, an exposure of 30 to 60 minutes registers strong reflections up to 2 A in a specimen mounted in pyrex glass capillaries having a diameter as large as 1.0 mm.

PROCEDURE

Reagents: 2N citric acid, 3N sodium hydroxide, 5N sodium chloride, and crystalline sodium hydrosulfite ($Na_2S_2O_4$ — also known as sodium dithonite).

Steps involved in the procedure:

1. — To one portion of 500 ml of citric acid enough of the sodium hydroxide solution is added to raise the pH to about 8; distilled water is then added to make a volume of 1000 ml. To another portion of 500 ml of citric acid enough of the sodium hydroxide solution is added to raise the pH to about 10.3; distilled water is then added to make a volume of 1000 ml.

2. — The soil, or any other material containing the colloid to be analyzed, is brought into a stable suspension with the aid of a dispersing agent such as calgon. If x-ray analysis only is to be made, a very small amount of soil may be used for dispersion — enough to yield from 10 to 20 mg of colloid.

3. — The desired particle sizes are obtained either by means of sedimentation or centrifugation techniques.

4. — The sodium chloride solution is added to the suspension containing the desired particle sizes in an amount adequate to bring about flocculation.

5. — After the flocculated colloid settles out, with or without the aid of centrifugation, the supernatant liquid is decanted and replaced with about twice as much sodium citrate solution as the liquid left with the flocculent, at pH 8.0; it is then kept at about 60° to 70°C for an hour or two.

6. — Enough sodium hydrosulfite is then added to reduce the free Fe_2O_3 and to bring it into solution within 10 to 20 minutes. The amount of added sodium hydrosulfite should be enough to make approximately a 5 percent solution (Deb, 1950).

7. — After the colloid settles out, the supernatant liquid is decanted and the colloid is poured into a porous sintered glass-bottom crucible from which the rest of the solution is removed by suction. (This can also be accomplished by centrifuging with enough force to form a thick paste or gel in the bottom of the centrifuge tube from which the supernatant liquid can be drained off thoroughly.)

8. — As soon as the free liquid is removed and the colloid is in a wet paste or gel form, a small amount of it is placed between the forefinger and thumb as an aid in introducing it into a pyrex glass capillary, or a cellulose acetate or plastic capillary (Beu, 1951), which has a diameter of about 0.5 mm or less and as thin a wall as can be handled without breaking. At least a 3 to 5 mm portion of the capillary should be filled with the paste. The end of the capillary which contains the paste is then pushed into a slightly softened piece of beeswax or paraffin wax until the paste is about 5 to 10 mm from the end of the capillary. The other end of the capillary is then also sealed with the wax.

9. — The specimen is then placed in the x-ray machine for analysis under the conditions previously described.

In a large number of soil colloids the foregoing procedure was found to eliminate from the diffraction pattern most of the darkening in the region from the beam stop to 5°. If, however, excessive darkening still persists it can be eliminated by taking up the paste, which was separated from the solution of sodium citrate and the sodium hydrosulfite, with the solution of sodium citrate at the pH of 10.3, keeping it for an hour or two at about 50°C and then proceeding as outlined above in 7, 8, and 9.

If the colloidal separates to be analyzed are already in a powdered form, steps 2, 3, 4 and part of 5 are dispensed with and the following step is substituted: to a sample of about 10 to 20 mg of colloid 20 ml of the sodium citrate solution at pH 8.0 is added and kept at a temperature of about 60°C to 70°C for an hour or two before proceeding with steps 6, 7, 8, and 9.

DISCUSSION

The advantages which the proposed technique offers are as follows: (1) The free oxides and possibly most of the amorphous silicates are removed without affecting the clay minerals themselves. (2) Orientation of the particles is achieved without special effort during step 7 when the paste or gel is obtained and particularly during step 8 when the paste is introduced into the capillary tube (Weymouth and Williamson, 1953). (3) The interference from random interleaving on the recording of d(001) spacings of the individual minerals is eliminated to a large extent owing to the fact that the differences in the interlayer expansion of the mica and the montmorillonite clays in the salted pastes are much larger than in the air-dry state or even in the glycerol-wet state (Brown and MacEwan, 1950). In the salted pastes the d(001) spacing of the mica is about 10 A, of vermiculite about 15 A, and of the montmorillonites from 16.5 to 19.5 A. In some of the colloids studied, however, interleaving still persists, particularly between vermiculite and mica and between vermiculite and montmorillonite, as indicated by the magnitude of the d(001) spacing, by an irrational series of d(001) spacings, and by the other tools for the identification of clay minerals such as chemical and differential thermal analyses. (4) Owing to the presence of salt in the paste the effect of the exchangeable cation on the intensity of the d(001) reflection is eliminated. Consequently, the time required to saturate a clay with a desired cation and to remove the free salt is also eliminated. (5) It is considerably easier to introduce a paste than a powder into a fine capillary. (6) Time is not required to dry the colloid from a suspension or equilibrate it with water or other solvents as recommended in other methods. (7) The technique lends itself to the analysis of very small amounts of clay — from 10 to 20 mg or less. (8) The relatively small distances from specimen to film and from end of collimator to film during exposure to x-rays result in sharp, narrow, and fairly intense lines representing the d(001) spacings.

Some of the results obtained by different techniques are shown in Plates 1 and 2 and Table 1.

It is clear from these results that the proposed technique promises to yield accurate clay mineral analysis of soil colloids.

The technique has already been used to re-examine a large number of soil colloids which have been studied previously by other techniques. The results obtained give a much clearer picture of the nature of the clay minerals of these colloids and they lead to the following interesting conclusions: (1) Montmorillonite and vermiculite-type clays are much more widespread in soils than previously reported. (2) In a majority of the mineral soil colloids, montmorillonite or vermiculite is mainly responsible for their cation exchange capacity. (3) Nearly all of the clays identified previously as "hydrous mica", "illite" or "mineral x" are really
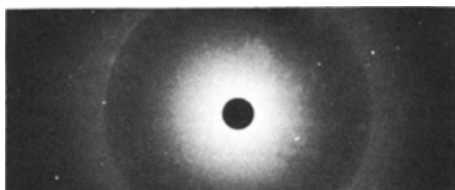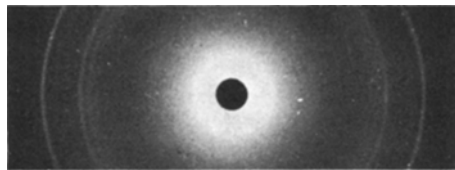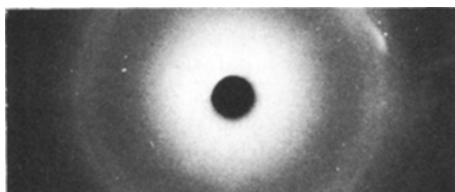
Wyoming Na-montmorillonite as a water gel
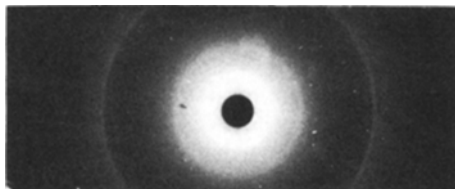
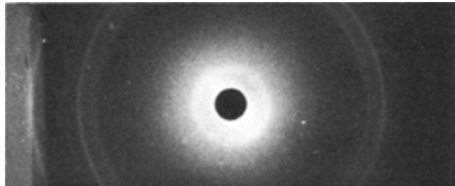Wyoming Na-montmorillonite as a gel with a $Na_3C_6H_5O_7$ and $Na_2S_2O_4$ solution at pH 7.3
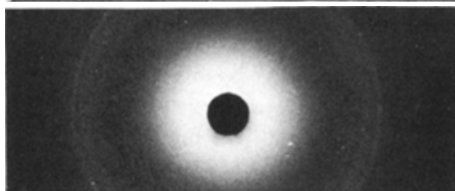
Giant Podzol —b horizon in a Mg-saturated and an air-dry state

Giant Podzol —b horizon as a gel with a $Na_3C_6H_5O_7$ solution at pH 10.0

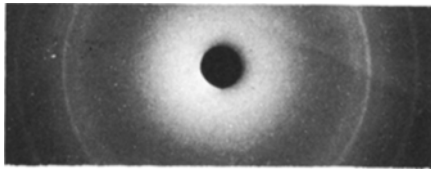Shasta no. 19 in a Ca-saturated and an air-dry state

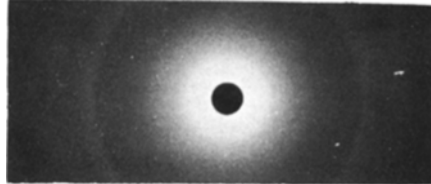Shasta no. 19 as a gel with a $Na_3C_6H_5O_7$ and $Na_2S_2O_4$ solution at pH 7.3
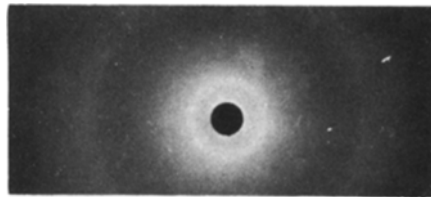
PLATE 1. — Diffraction diagrams comparing effect of condition of sample during x-radiation. (The x-ray films were printed with the main purpose of bringing out the d(001) spacings.)
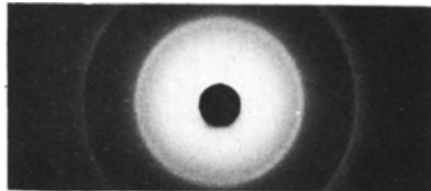
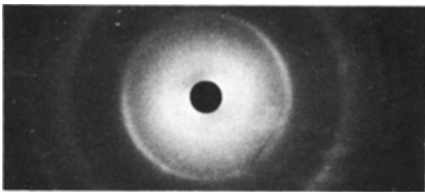Sheridan 24″ - 30″ in a Ca—, Mg-saturated and air-dry state

Sheridan 24″ - 30″ as a gel with a $Na_3C_6H_5O_7$ and $Na_2S_2O_4$ solution at pH 7
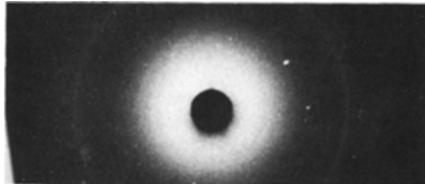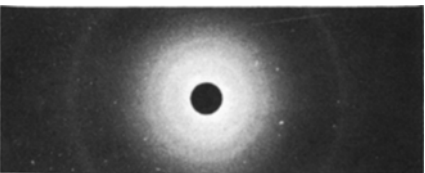
Sheridan 24″ - 30″ as a gel with a $Na_3C_6H_5O_7$ solution at pH 10.0

Redding no. 11 in a Ca-saturated air-dry state

Redding no. 11 as a gel with a $Na_3C_6H_5O_7$ solution at pH 10.0

S - 461 in a Mg-saturated air-dry state

S - 461 as a gel with a $Na_3C_6H_5O_7$ and $Na_2S_2O_4$ solution at pH 7

PLATE 2. — Diffraction diagrams comparing effect of condition of sample during x-radiation. (The x-ray films were printed with the main purpose of bringing out the d(001) spacings.)

TABLE 1. — THE d(001) BASAL SPACINGS (IN ANGSTROM UNITS) OF SEVERAL SOIL COLLOIDS AS REPORTED BY EARLIER[1] INVESTIGATIONS AND BY THE SALTED PASTE METHOD.

Sample No.	Earlier Results	Salted Paste Results	Sample No.	Earlier Results	Salted Paste Results
15607[1]		15.6 m.	16308[2]		17.1 v.w.
	10.1 w.	10.2 m.w.			10.2 m.
		7.3 w.		7.2 m.s.	7.2 m.s.
7081[1]	no basal	16.1 m.s.			
	spacings	10.1 w.	Cayucas[3]	no basal	16.9 s.
	reported	7.4 v.v.w.	0-6"	spacings	
19013[1]		19.8 w.	Sheridan[3]		16.4 m.w.
		14.6 w.	0-6"	10.3 w.	10.2 w.m.
	10.0 w.	10.2 m.			7.3 w.
		7.3 v.v.w.			
16054[2]	15.0 ?	16.7 m.	Sheridan[3]		15.4 m.
		10.6 v.v.w.	24-30"	10.1 v.v.w.	10.2 v.v.w.
	7.3 m.	7.2 m.			7.4 w.

Symbols for intensities of x-ray reflections: s. — strong; m.s. — medium strong; m. — medium; m.w. — medium to weak; w. — weak; v.w. — very weak; v.v.w. — very, very weak.

[1] Kelley and others (1941); [2] Kelley and others (1939); [3] Barshad (1946).

a mixture of montmorillonite or vermiculite, mica, and kaolinite. (4) Montmorillonite and kaolinite occur together in soils to a much greater extent than has been indicated by previous studies. This is true even in very "old" soils and in very strongly weathered soils.

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