

AN IMPROVED PRETREATMENT FOR MINERALOGICAL ANALYSIS OF SAMPLES CONTAINING ORGANIC MATTER¹

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ABSTRACT

Organic matter removal is accomplished rapidly and efficiently without removing carbonates by treating samples with a sodium hypochlorite solution. Quantities of organic matter left in samples by this treatment are commonly less than remain after hydrogen peroxide treatment of acidified samples.

Stable suspensions result from the use of a sodium carbonate-sodium bicarbonate solution to wash and sodium saturate the samples without dissolving or complexing sesquioxides.

INTRODUCTION

Purposes and Nature of Pretreatments

Samples for clay mineralogical analyses are commonly pretreated to remove organic materials, disaggregate mineral particles, and increase the zeta potential. Increasing the zeta potential makes possible the formation of stable suspensions in water and subsequent particle size separations.

Some commonly used pretreatments involve removal of calcium and magnesium carbonates, sesquioxide coatings, and silica coatings. Others are much less drastic; some consist simply of dispersing the sample by shaking in distilled water. In many cases the choice of a method appears to depend on the investigator rather than on the sample.

Undoubtedly it is desirable to vary the pretreatment to suit varying sample characteristics. Pretreatments must also be varied to permit the investigator to obtain the desired analytical information about the sample.

In order that the investigator may be sure of the total effect of any pretreatment, its effects on all components of the sample must be understood. In general, the effects can be understood only if all reactions are complete, and this is rarely achieved.

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Proposed Method

The proposed method consists of treatments with a sodium hypochlorite solution for oxidation of organic matter followed by washes with a sodium carbonate–bicarbonate solution for final reduction of salt content and sodium saturation. It is the result of an attempt to devise a method which was suitable for many samples, and which would give complete removal of organic matter and complete sodium saturation without removing or complexing carbonates, sesquioxide coatings, or silica. It is intended to be a basic method to which procedures for the removal of other components can easily be added if desired. Although various washing procedures could be used, the one proposed has been found easy and effective. It is based largely on methods described by Jackson (1956), but it eliminates boiling and uses a pH of 9.5. The purposes are to decrease the salt content and remove chloride ions. It has been used to produce stable suspensions of a great variety of samples.

Hypohalous Acid Systems

The use of sodium hypobromite for oxidation of soil organic matter was described by Atterberg in 1912 (Troell, 1931), and more recently by Troell (1931) and Bourget and Tanner (1953). The use of sodium hypochlorite as

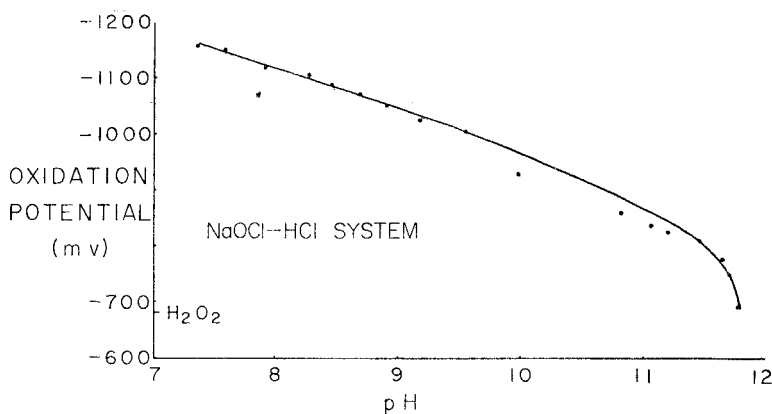


FIGURE 1.—Variation of the oxidation potential of NaOCl solution with pH.

chlorox to remove organic matter from shale samples has been described recently (Cassidy and Mankin, 1960).

The advantages of the salts of hypohalous acids for this purpose include ease of use and apparent freedom from such undesirable effects of hydrogen peroxide as exfoliation of mica (Drosdoff and Miles, 1938) and formation of calcium oxalate (Martin, 1954). An advantage of hypochlorous acid is the fact that its oxidation potential is the highest of the hypohalous acids.

The sodium hypochlorite solution used in this study was obtained from the Fisher Scientific Company and is described by them as calcium and phosphorus-free solution containing 5–6 percent available chlorine. The variation of oxidation potential with pH was determined by using a pH meter with a platinum and calomel electrode pair. The results with the standard oxidation potential for hydrogen peroxide added for comparison are shown in Fig. 1. The titration curve for the solution used and hydrochloric acid is shown in Fig. 2.

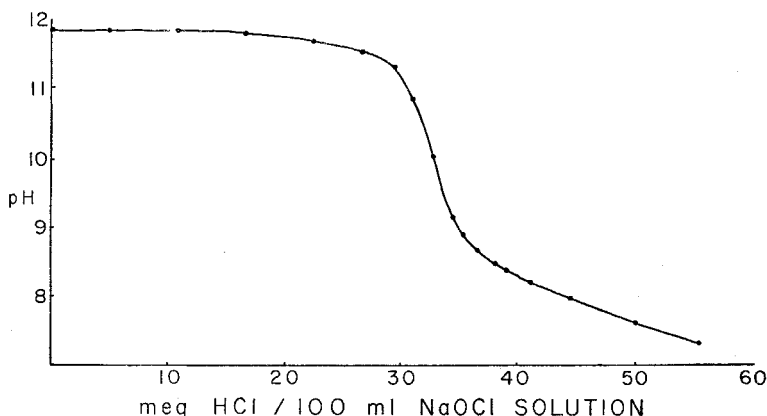


FIGURE 2.—Titration curve for NaOCl solution.

PROCEDURE

Oxidation of Organic Matter

A 20 ml aliquot of sodium hypochlorite solution freshly adjusted to pH 9.5 is added to a 10 g sample in a Truog centrifuge tube. The tube is placed in a boiling water bath for 15 min, then centrifuged for 5–10 min at 800 rpm (RCF = 178). The solution is decanted and the treatment is repeated for a total of three treatments.

Washing and Dispersing

A 50 ml aliquot of 2 percent sodium carbonate–sodium bicarbonate solution with a pH of 9.5 is added to the sample in the centrifuge tube. This is stirred using the rubber plunger technique described by Jackson (1956, p. 34), heated in a boiling water bath to promote flocculation, and centrifuged for 10 min at 800 rpm (RCF = 178). The solution is decanted, and the treatment is repeated for a total of three treatments. At the end of the third treatment centrifugation is for 10 min at 2500 rpm (RCF = 1747). After the final decantation the sample is shaken for 12 hr with distilled water.

EXPERIMENTAL RESULTS

Removal of Organic Matter

Means of evaluation.—Effectiveness of this treatment was evaluated by comparing the organic matter contents of samples that received it with those of identical samples which received two other kinds of treatments. Organic matter contents were determined by a wet-combustion procedure (Allison, 1960) which is believed to give complete oxidation of organic carbon. All determinations were made in duplicate. The treatments used for comparison were hydrogen peroxide preceded by destruction of carbonates with a pH 5 buffer (Jackson, 1956, p. 33), and hydrogen peroxide alone. The hydrogen peroxide treatments consisted of three consecutive treatments with 30 percent

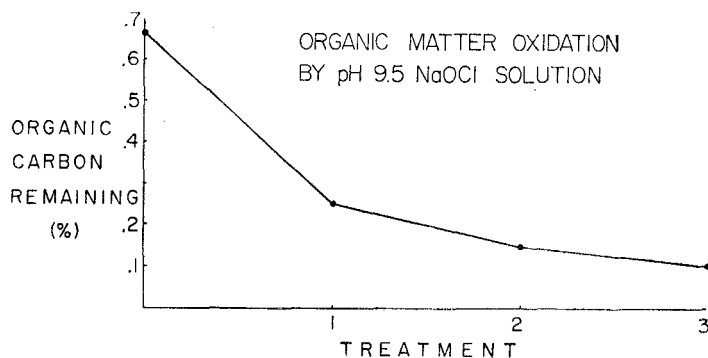


FIGURE 3.—Effects of consecutive NaOCl treatments on organic matter content of a calcareous loam sample.

reagent, each followed by digestion and evaporation to near dryness on the steam bath. Chamberlain filters were used to wash all samples free of soluble salts.

Effects of consecutive treatments.—The effects of three consecutive sodium hypochlorite treatments on a single sample are shown by Fig. 3. It appears that, at least for this sample, which is a calcareous loam, little additional oxidation of organic matter could be expected from additional treatments.

Data.—Quantities of organic matter remaining after treatments are shown by Table 1. The sodium hypochlorite treatment appears to be about equally as effective for most of the samples as the hydrogen peroxide treatment preceded by carbonate destruction. For the soil samples from the Mid-west, it appears more effective. The sodium hypochlorite treatment is much more effective than hydrogen peroxide used alone except for the most acid samples for which the difference between the treatments is small. Hydrogen peroxide used alone is, as expected, quite ineffective for calcareous samples. The efficiency of the sodium hypochlorite treatment does not appear to be a function of the $< 2 \mu$ clay content of the sample.

TABLE 1.—ORGANIC CARBON CONTENTS IN SAMPLES AFTER TREATMENTS

Soil series	Soil horizon	< 2 μ clay (%)	pH	CaCO ₃ (%)	Organic carbon after			
					No treatment (%)	H ₂ O ₂ (%)	NaOCl (%)	pH 5 H ₂ O ₂ (%)
<i>Mesilla Valley Samples</i> (Rio Grande Alluvium, Southern New Mexico)								
Glendale	A _p	24	7.9	1.8	0.67	0.35	0.10	0.10
Glendale	A ₁₂	14	8.1	9.1	0.34	0.34	0.23	0.05
Glendale	C	3	8.5	2.6	0.16	0.13	0.09	0.02
Glendale	A ₁	32	7.9	8.0	1.81	0.99	0.20	0.20
Glendale	C	65	7.7	7.8	0.65	0.63	0.07	0.10
Glendale	D	10	7.9	8.0	0.46	0.38	0.16	0.08
<i>High Plains Samples</i> (Eastern New Mexico)								
Pullman	A _p	20	7.0	< 0.05	0.68	0.17	0.03	0.06
Pullman	B ₂₂	36	7.9	< 0.05	0.64	0.47	0.04	0.06
Pullman	A ₁	18	6.9	0.2	1.19	0.33	0.07	0.14
Pullman	B ₂₁	35	7.1	0.4	0.56	0.35	0.06	0.06
<i>Zuni Mountain Samples</i> (Northwestern New Mexico)								
Ft. Wingate	A ₂	13	5.9	< 0.05	0.85	0.13	0.04	0.09
Zuni	B ₂	34	6.9	< 0.05	0.27	0.06	0.03	0.03
<i>Midwest Samples</i> (Indiana and Michigan)								
Coldwater	A _p	—	6.8	< 0.05	1.49	0.28	0.07	0.22
Crosby	A ₂	—	5.2	< 0.05	0.92	0.21	0.09	0.15
Crosby	B ₂	—	5.2	< 0.05	0.39	0.06	0.06	0.13
Brookston	BG ₃	—	7.5	< 0.05	0.10	0.08	0.05	0.08

X-Ray Diffraction Patterns

X-ray diffraction patterns were made in order to evaluate the effects of various treatments on the clays. The patterns presented here are for fractions from three of the samples used to study organic matter oxidation. All are calcium saturated; none are solvated. Copper $K\alpha$ radiation was used. Comparisons were made of the method described in this paper and the dispersion method described by Jackson (1956) which consists of consecutive treatments with a pH 5 buffer, hydrogen peroxide, and boiling 2 percent sodium carbonate.

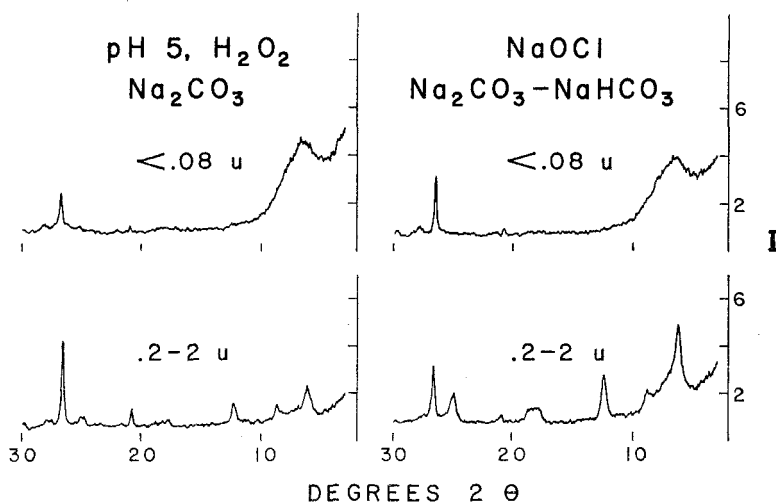


FIGURE 4.—X-ray diffraction patterns for clay fractions from Coldwater A_p , showing effects of two pretreatments.

Inspection of Figs. 4, 5, and 6 reveals distinct differences in patterns resulting from differences in pretreatment of samples. In most instances peak height/background ratios for 14 \AA components are higher for the proposed method than for the method used for comparison. For the other clay fractions, this ratio differs very little for the pretreatments considered.

Variations in height of the 3.35 \AA quartz peak do not appear to follow a consistent pattern. Although it does not appear likely, the observed variations may have resulted from the use of ceramic tile specimen mounts which contain quartz.

In Fig. 6 a carbonate peak is shown at $29.3^\circ 2\theta$ for the proposed method. This has been eliminated from the analogous pattern which involves carbonate destruction. Although an abundant supply of calcium ions is available during treatment of calcareous samples, no diffraction patterns gave evidence

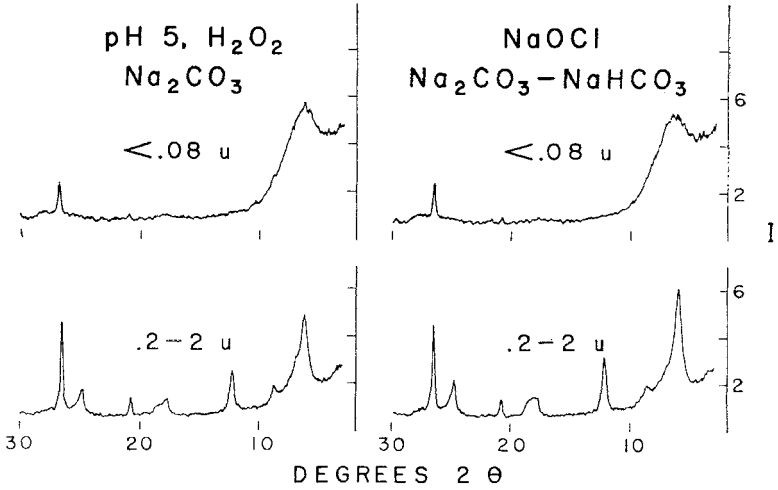


FIGURE 5.—X-ray diffraction patterns for clay fractions from Crosby A₂ showing effects of two pretreatments.

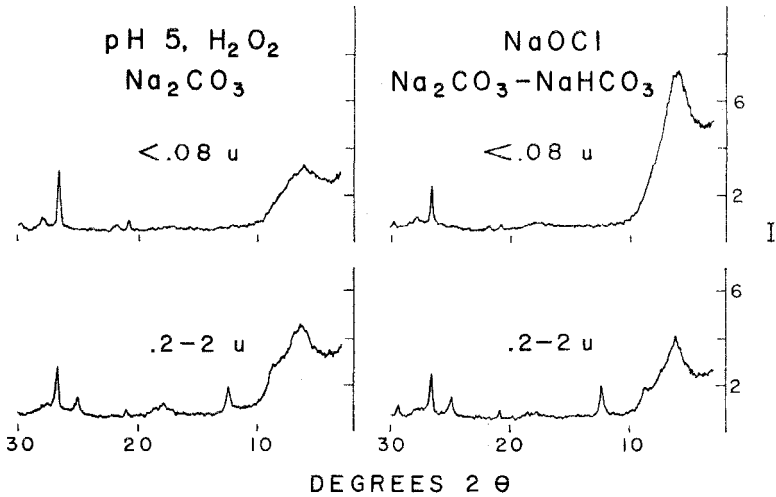


FIGURE 6.—X-ray diffraction patterns for clay fractions from Glendale A_p showing effects of two pretreatments.

of calcium oxalate formation. No indication of reduction of particle size of mica or illite by the method utilizing hydrogen peroxide was observed.

Differences appearing in these patterns can be attributed in part to differences in organic matter content for the Coldwater and Crosby samples. However, Table 1 shows that identical quantities were left in the Glendale sample. No data are available for total quantities of clay dispersed from the Coldwater or Crosby samples. For Glendale, 21 percent $<2\mu$ clay was dispersed by the proposed method. The value for the method used for comparison was 24 percent. Greater differences have been observed for other samples. The observed differences in diffraction patterns could thus be accounted for by an "X-amorphous" material which is dispersed by one treatment, but not by the other. However, existing information does not justify such a conclusion.

DISCUSSION

The pH level of 9.5 was selected because it is believed to be high enough to cause complete sodium saturation but not high enough to cause appreciable solution of aluminum. The fact that this is the inflexion point of the sodium hypochlorite titration curve may be considered a disadvantage of the procedure. However, since three consecutive treatments with a concentrated solution are involved, it has not been found a disadvantage in practice.

The sodium hypochlorite treatments have been limited to 15 min because the hypochlorite decomposes rapidly at high temperatures. Additional treatments would be expected to be more effective than three prolonged treatments for samples containing highly resistant organic matter.

An important advantage of this method is the nearly complete freedom from frothing and boiling over which commonly accompanies the use of hydrogen peroxide. A striking phenomenon which has been observed in treating many of the samples is the development of a distinct pink color in the supernatant liquid during the second or third treatment. It has not been identified.

CONCLUSIONS

The proposed method is both efficient and rapid for the destruction of organic matter in samples, and accomplishes this without destruction of carbonates or removal of sesquioxide or silica coatings. It can be used easily with other treatments to accomplish these purposes if desired. It produces stable suspensions of a great variety of samples.

X-ray diffraction patterns resulting from this treatment have been shown to have generally higher peak/background ratios for 14 Å minerals than those from other treatments.

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