AN ULTRAVIOLET SPECTROSCOPIC METHOD FOR MONITORING SURFACE ACIDITY OF CLAY MINERALS UNDER VARYING WATER CONTENT

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Abstract—The ability of a clay mineral surface to function as an acid is not represented by bulk pH measurements. A method using u.v. analysis and organic indicators has been developed to monitor surface acidity. The u.v. organic indicator method enables sensitive *in situ* quantification of surface-induced protonation in wet or dry clay systems. The clay preparation procedure used yields reproducible acidic behavior.

INTRODUCTION

THE SUBJECT of acid properties of clay mineral surfaces has been an area of intensive research for the past two decades, especially in the fields of surface catalysis, clay mineralogy and soil science. Surface acidity is inherently related to spontaneous chemical change within and on the edges of the clay lattice (Paver and Marshall, 1934; Kerr *et al.*, 1955), and plays a governing role in the chemical and physical behavior of many surface-adsorbed molecules (McAuliffe and Coleman, 1955; Dodd and Satyabrata, 1960; Fripiat *et al.*, 1964; Swoboda and Kunze, 1964; Russell, 1965; Serratosa, 1966; Farmer and Mortland, 1966; Talhoun and Mortland, 1966; Mortland, 1968; Harter and Ahlrichs, 1969; Yariv *et al.*, 1969).

The two fundamental approaches to the study of surface acidity are:

1. To introduce a basic molecule (indicator) into the clay system and monitor the ability of the surface to induce an observable change in the indicator that reflects the acidic properties of the surface. The structural nature of the acid source is subsequently inferred from the response to the indicator. This approach has been employed extensively in the qualitative characterization of acid properties (Walling, 1950; Harter and Ahlrichs, 1967; Swoboda and Kunze, 1968; Raman and Mortland, 1969).

2. To look directly at the clay system and try to characterize structurally the acid source. Acidic behavior is inferred from the physical nature of the source. For example, Brönsted acidity is inferred from protonic behavior as reflected by infrared spectroscopy (Uytterhoeven *et al.*, 1965), n.m.r. spectroscopy

(Trouillaux *et al.*, 1968), or conductometric measurements (Fripiat *et al.*, 1965).

Acidity in wetted clay systems is predominantly Brönsted, or protonic in nature. Lewis acid sites are converted by water to Brönsted sites unless a Lewis base stronger than OH^- is present. Protons may be available from the dissociation of chemisorbed water or the hydrolysis of edge sites, or may be present as exchangeable cations. The behavior of water and acidic protons in the inner adsorption sphere (interfacial region) differs markedly from bulk solution behavior, and depends upon the surface and near surface constituents (i.e. clay lattice framework, saturating cations and other surface-adsorbed species).

Because of the complexity and heterogeneity of the surface environment giving rise to this acidity, the use of indicators is the only viable approach to quantifying surface acid properties in wetted clay systems. Any molecular species that reacts reversibly with the acidic surface to form a conjugate species distinguishable from its precursor is a potential indicator; any experimental technique capable of distinguishing between the conjugate species constitutes a potential acidity monitor. However, indicators differing in their adsorptive properties can yield differing 'effective' acidities for that surface. That is, indicator pK_a is not the sole determining factor for surface protonation. Likewise, different techniques involved in preparing a surface for measurement or in monitoring a given indicator on a given surface can show differing acidities; i.e. the preparation or measurement perturbs the variable measured.

The described u.v. indicator method provides a reproducible, *in situ* method of monitoring protonation over a continuous range of water content from

471

suspensions to dry films. The major advantages over other indicator methods are (a) ability to measure protonation *in situ* under wet or dry conditions, and (b) sensitivity; i.e. low levels of indicator loading [< 0·1 per cent cation exchange capacity (CEC) for some indicator/clay systems] can be quantitatively and reproducibly monitored.

EXPERIMENTAL

Clay preparation

Clay minerals from Wards Scientific Establishment* were fractionated by sedimentation; particles <2 μm in equivalent spherical dia. were isolated and washed twice with distilled water to remove water-soluble materials. Although a large number of clays was studied, data are presented only for hectorite No. 34 and montmorillonite No. 25. To remove insoluble carbonates, the clay suspensions (0·1–1 per cent by weight) were percolated through an H-saturated cationic exchange column, degassed by stirring under vacuum, and passed through an OH-saturated anionic exchange column. The suspension was then passed through a Na-column, degassed again, and stored in the Na form for brief periods prior to use. The clay was not permitted to remain in the acid form for more than 10 min to minimize chemical aging, which is accelerated in the H–clay form. Fresh samples were prepared just prior to indicator treatment, either by percolating the Na-suspension through cationic exchange column

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* Reference to trade names is for information only and does not constitute endorsement by the U.S. Environmental Protection Agency.

saturated with the desired cation, or by batch washing in a 1N solution of a salt of the desired cation followed by anion and excess cation removal. Rexyn AG-50 cation resin and Rexyn 201 anion resin were used throughout.

Indicators

Stock solutions of indicators (Table 1) were prepared using reagent grade organics and degassed water. Spectroscopic absorbtivities of the neutral and protonated forms of the indicators were determined both in water and in hectorite suspensions containing approximately 5 mg/l hectorite and 0·1 to 5 mg/l indicator. Dilute NaOH and HCl were used as needed to achieve the desired indicator forms.

Indicator-clay mixing

Indicator-clay suspensions were prepared by mixing (on a drop-wise basis) aliquots of bulk clay and indicator solutions. Indicator-clay films were prepared by pipetting 1 ml aliquots of the indicator-clay suspensions onto quartz discs (22 mm dia.) and drying in desiccators over silica gel or magnesium perchlorate. Spectroscopic blanks were prepared for all samples by substituting water for indicator in the sample preparation procedures. Care was taken to maintain degassed conditions throughout preparation and analysis to avoid CO_2 effects on acidic behavior.

Spectroscopic analysis

All spectra were obtained on a Perkin–Elmer 356 Spectrophotometer using an R-189 photomultiplier tube. Suspensions were run in sealed quartz cells (1 cm path length) placed approx 5 mm from the phototube.

Table 1. Indicators and humidity control salts

Indicator*	pK_a^1†	Salt	%r.h. at 25°C‡
3-Aminopyridine	6·03	NaOH	7·0
5-Aminoquinoline	5·42	LiCl	11·3
2-Amino–5-chloropyridine	4·83	$MgCl_2$	32·7
2,6-Dimethylaniline	3·94	NaCl	75·1
3-Chloroaniline	3·50	KCl	84·2
m-Nitroaniline	2·50	K_2SO_4	97·0
Pyridazine	2·30		
Pyrimidine	1·30		
Phenazine	1·20		
p-Nitroaniline	1·00		
Quinoxaline	0·70		
Pyrazine	0·60		
o-Nitroaniline	−0·20		
4-Chloro–2-nitroaniline	−1·0		
4-Nitrodiphenylamine	−2·4		

* Indicator concentration approximately 10 ppm.
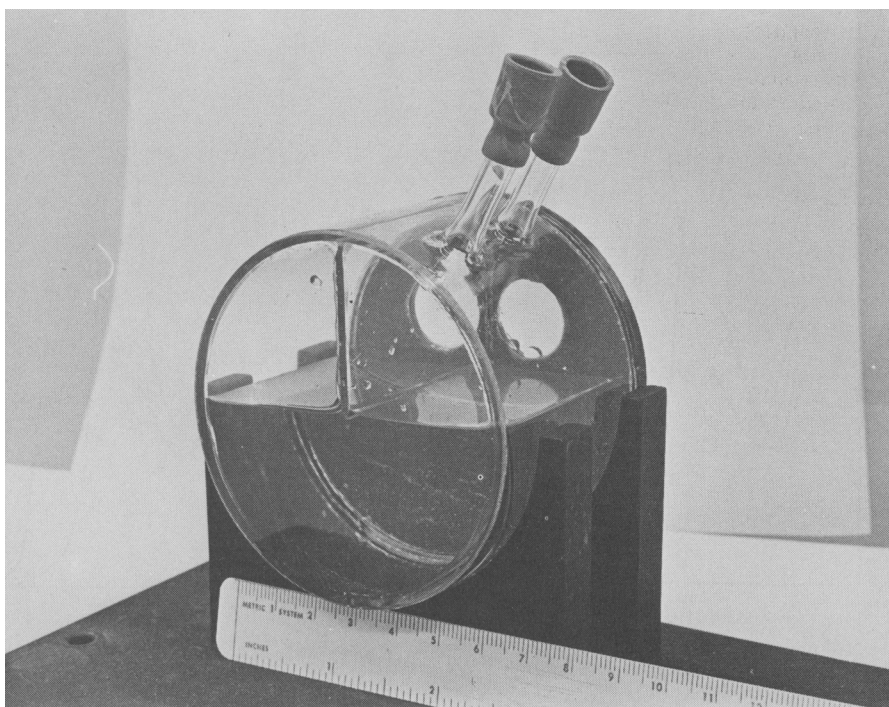† Perrin (1965).
‡ Young (1967).

Fig. 1. Humidity control cell for clay films. The quartz discs containing the sample films were recessed into the front face of the cell; the rear face is optical quartz.

Indicator-clay and blank films were mounted in a cylindrical cell (Fig. 1) with the clay samples facing the cell interior. The cell was partially filled (below the sample level) with the saturated salt solution required to achieve the desired humidity control (Table 1). Gas ports on the cell allowed further atmospheric control on the film surface. The entire cell was placed in the instrument with the films contiguous to the phototube (samples were approx 3 mm from phototube). Films taken from the drying desiccators were allowed to equilibrate in the cell for approximately 30 min. Equilibration was judged to be complete when a stable spectroscopic response was obtained. The proximity of the samples to the phototube substantially reduces light-scattering problems, which have hampered u.v. studies of turbid media in the past; the high sensitivity characteristic of u.v. absorption can now be realized in clay media. To date, all spectra have been run at room temperature, but temperature variation and control have been designed into the experimental setup.

RESULTS AND DISCUSSION

The indicators listed in Table 1 span the acidity range of the clay systems studied, and their protona-

tion reactions can be monitored spectroscopically. Figures 2–6 illustrate the ability of the described technique to quantify the degree of protonation of organic molecules by acidic clay surfaces. Although the protonic behavior of the surface is very sensitive to surface contamination, organic or inorganic, the clay system preparation outlined produces a surface that shows very reproducible behavior.

Each species (neutral and protonated) of the two indicators, 5-aminoquinoline and phenazine, shown in Figs. 2–6 can be independently determined quantitatively without resorting to difference calculations that assume mass balance. The concentration ratio of any two of the indicator forms (neutral, monoprotonated, diprotonated) in equilibrium can be related to the ratio of two spectral peaks on the same spectrum, assigned to the respective indicator forms. Figure 2 shows the monoprotonated–neutral species equilibrium in a 5-aminoquinoline–Ca–hectorite suspension; Fig. 3 is the diprotonated–monoprotonated species equilibrium with the same indicator in Na–montmorillonite and H–hectorite suspensions. Surface acidity in the film state is illustrated in Figs. 5 and 6 using phenazine as the indicator.

The effect of traces of carbonate salts on the suspension acidity of Na–hectorite is shown in Fig. 4 by the
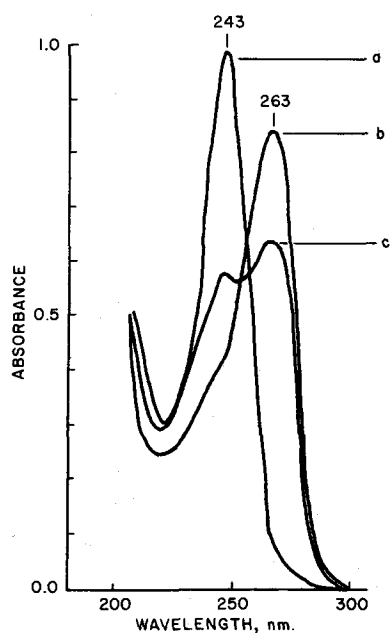
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Fig. 2. Monoprotonation of 5-aminoquinoline by clay suspensions: (a) Neutral 5-aminoquinoline (5·5 mg/l) in 1 per cent Na–hectorite suspension; (b) Monoprotonated 5-aminoquinoline (5·5 mg/l) in 1 per cent Na–hectorite suspension; (c) 5-aminoquinoline (5·5 mg/l) equilibrated 5 min with a fresh Ca–hectorite suspension (3·4 mg/l).
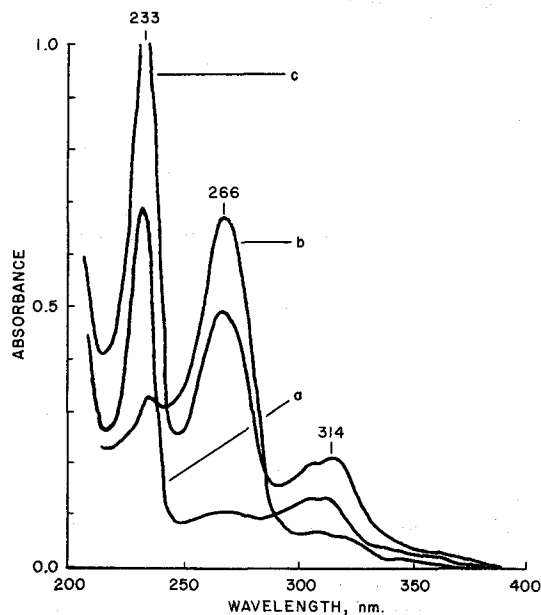

Fig. 3. Diprotonation of 5-aminoquinoline by clay suspensions: (a) Diprotonated 5-aminoquinoline (2·5 mg/l) in 1 per cent H–hectorite suspension; (b) 5-aminoquinoline (3·7 mg/l) equilibrated 5 min with fresh Na–montmorillonite suspension (1·2 mg/ml); (c) 5-aminoquinoline (3·7 mg/l) equilibrated 5 min with fresh H–hectorite suspension (6·4 mg/ml).
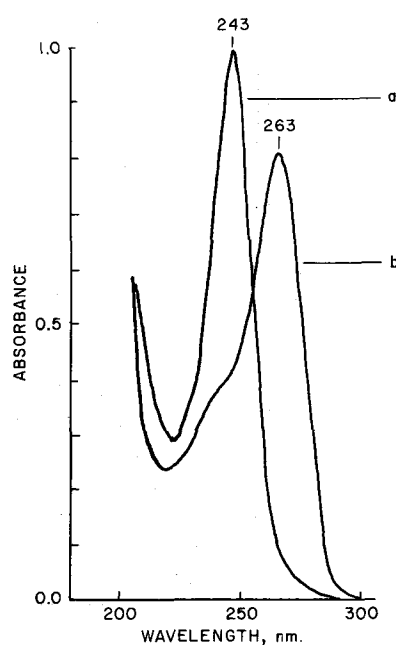

Fig. 4. Carbonate effect on suspension acidity: 5-aminoquinoline (5·5 mg/l) equilibrated 5 min with a fresh Na–hectorite suspension (3·2 mg/ml). (a) Prior to carbonate removal; (b) Subsequent to carbonate removal.

pre- and post-carbonate removal spectra. Not all clays, and not all batches of the same clay, show carbonate contamination. In order to achieve reproducibility in the method, all clays were subjected to the sequential column preparation consisting of the acid column, degassing, and OH^- column, to remove traces of carbonate, bicarbonate and carbon dioxide.

Surface acidity

Some acidity function must be found to relate the degree of protonation data to the clay–water system characteristics. For acidities outside the scope of the pH meter, it is common practice to adopt a Hammett-type acidity function (h_0). For the general surface equilibrium

$$I \xrightleftharpoons[K_{eq}]{H^+ \text{ surface}} I_c$$
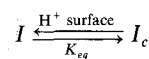
$$h_0 = -\log K_{eq} + \log \frac{(I)}{(I_c)}.$$

I and I_c denote conjugate indicator species differing by a proton and K_{eq} is the acidity constant describing the equilibrium between the indicator species under ideal aqueous solution behavior. In this case, h_0 reflects not only surface proton availability which is characteristic of the clay–water system, but also the deviations from ideal solution behavior of the indicator species.
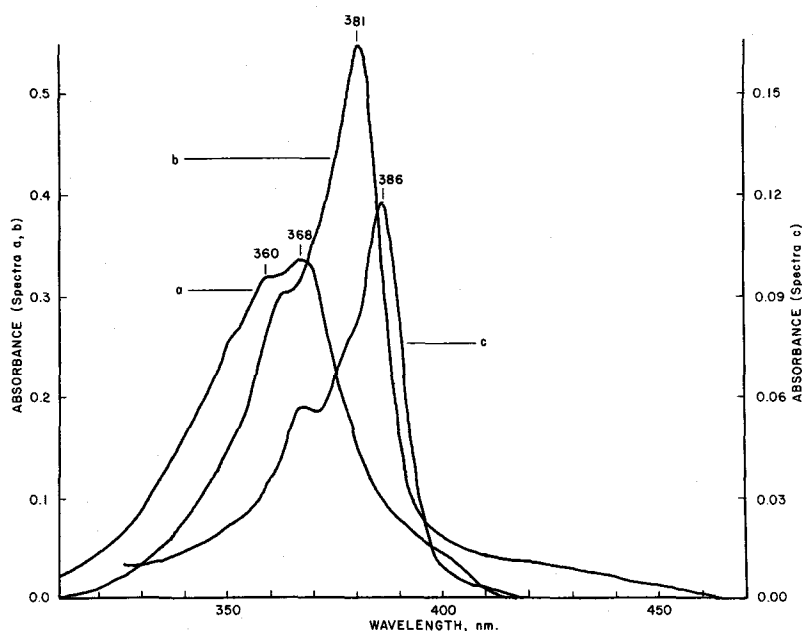
Fig. 5. Phenazine as an indicator: (a) Neutral phenazine (5·0 mg/l) in solution; (b) Protonated phenazine (5·0 mg/l) in solution; (c) Phenazine (1·2 μg/cm^2) on a Na–montmorillonite film (0·8 mg/cm^2) equilibrated at 32·7 per cent r.h. at 25°C.

The most significant indicator property, as reflected in h_0, is the charge type of the conjugate pair (I, I_c); i.e. (neutral, monocation), (monocation, dication), or (anion, neutral). These charge pairs show significantly

Fig. 6. Phenazine protonation by clay films: (a) Phenazine (1·3 μg/cm^2) equilibrated on a Ca–hectorite film (2·1 mg/cm^2) at 97 per cent r.h. and 25°C; (b) Phenazine (1·3 μg/cm^2) equilibrated on a Ca–hectorite film (2·1 mg/cm^2) at 32·7 per cent r.h. and 25°C; (c) Phenazine (1·3 μg/cm^2) equilibrated on a H–hectorite film (2·3 mg/cm^2) at 32·7 per cent r.h. and 25°C.

different adsorptive behavior that should be reflected in different h_0 values. Charge distribution in the indicator species also affects h_0, but to a lesser extent. The selection of indicators in Table 1 was designed to ascertain the indicator properties and clay–water properties most significantly affecting h_0. The clay–water variables, such as clay preparation, clay type, saturating cation, and water content have a significant effect on surface acidity. Publications describing these effects are being prepared.

Indicator techniques

Ideally, an indicator not only provides information about the reaction of a surface to an incoming basic molecule, but also yields insight into the structural character of the surface. The ability of u.v. spectroscopy to monitor trace amounts of indicator in clay systems (<0·1 per cent of CEC for hectorite) makes possible the study of a surface with minimal organic contamination. By contrast, i.r. methods require from 10 to 100 times more indicator; the increased concentration produces surfaces having significant organic character. Studies to date indicate that the degree of protonation in a given indicator-clay system varies significantly with indicator loading when indicator levels in excess of 10 per cent of the clay CEC are used.

Surface acidity of clay minerals may play a dominant role in the movement and persistence of
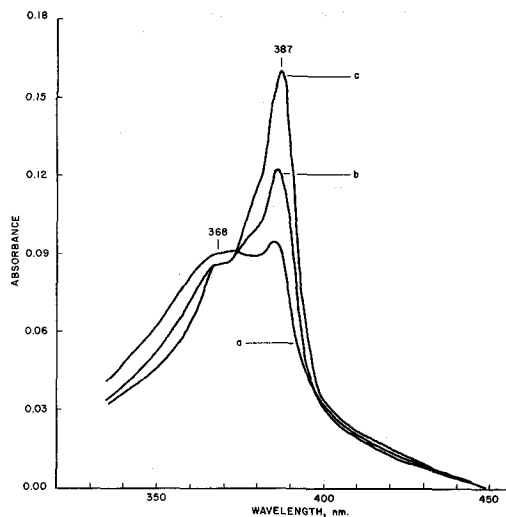
many pesticides in soils (Bailey and White, 1964, 1970; Bailey *et al.*, 1968; Russell *et al.*, 1968a, b). The sensitivity of the u.v. technique enables studies of protonation of indicators or pesticides in the concentration range characteristic of field application. The low solubility in water of many pesticides presents a problem for i.r. analysis. In order to prepare clay minerals containing the high pesticide levels necessary for i.r. monitoring, organic solvents are commonly used as the solvating medium. The effect of organic solvents on the measured surface properties has not been determined. The u.v. sensitivity makes it possible to work within the water solubility limits of many of these compounds.

U.V. spectroscopy enables *in situ* monitoring at any water content. In suspensions the indicator is in equilibrium with the surface, although it may not be 'adsorbed' in the sense that it will remain with the solid upon separation of the liquid and solid phases; yet, the indicator is responsive to surface proton activity. Since ordinary infrared techniques cannot monitor aqueous suspensions, the clay–organic system must be dried to produce a sample suitable for i.r. analysis; the drying technique used may drastically alter the indicator-surface equilibrium. Acidities measured *in situ* and those measured after isolation of the solid most definitely will differ.

The proposed u.v. organic indicator technique provides sensitive and reproducible *in situ* monitoring of degree of protonation in wet or dry systems, and has many ramifications in the study of clays and clay–organics.

REFERENCES

Bailey, G. W. and White, J. L. (1964) Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity: *J. Agr. Food Chem.* **12**, 324–332.

Bailey, G. W. and White J. L. (1970) Factors influencing the adsorption, desorption and movement of pesticides in soil: *Residue Rev.* **32**, 29–92.

Bailey, G. W., White, J. L. and Rothberg, T. (1968) Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate: *Soil Sci. Soc. Am. Proc.* **32**, 222–234.

Dodd, C. G. and Satyabrata, R. (1960) Semiquinone cation adsorption on montmorillonite as a function of surface acidity: *Clays and Clay Minerals* **8**, 237–251.

Farmer, V. C. and Mortland, M. M. (1966) An infra-red study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite: *J. Chem. Soc. (Lond.) A.* 344–351.

Fripiat, J. J., Helsen, J. and Vielvoye, L. (1964) Formation de radicaux libres sur la surface des montmorillonites: *Bull. Groupe Fr. Argiles* **15**, 3–10.

Fripiat, J. J., Jelli A., Poncelet, G. and Andri, J. (1965) Thermodynamic properties of adsorbed water molecules and electrical conduction in montmorillonite and silicates. *J. Phys. Chem.* **69**, 2185–2197.

Harter, R. D. and Ahlrichs, J. L. (1967) Determination of clay surface acidity by infra-red spectroscopy: *Soil Sci. Soc. Am. Proc.* **31**, 30–33.

Harter, R. D. and Ahlrichs, J. L. (1969) Effect of acidity on reactions of organic acids and amines with montmorillonite clay surface: *Soil Sci. Soc. Am. Proc.* **33**, 859–863.

Kerr, G. T., Zimmermann, R. H., Fox, H. A. and Wells, F. H. (1955) Degradation of hectorite by hydrogen ion: *Clays and Clay Minerals* **4**, 322–329.

Low, P. F. (1955) The role of aluminum in the titration of bentonite: *Soil Sci. Soc. Am. Proc.* **19**, 135–139.

McAuliffe, C. and Coleman, N. T. (1955) H-ion catalysis by acid clays and exchange resins: *Soil Sci. Soc. Am. Proc.* **19**, 156–160.

Mortland, M. M. (1968) Protonation of compounds at clay mineral surfaces: *Trans. 9th Internat. Congr. Soil Sci.* **1**, 691–699.

Paver, H. and Marshall, C. E. (1934) The role of aluminum in the reactions of the clays: *J. Soc. Chem. Ind.* **53**, 750–760.

Perrin, D. D. (1965) *Dissociation Constants of Organic Bases in Aqueous Solution*: Butterworths, London.

Raman, R. V. and Mortland, M. M. (1969) Proton transfer reactions at clay mineral surfaces: *Soil Sci. Soc. Am. Proc.* **33**, 313–317.

Russell, J. D. (1965) Infra-red study of reactions of ammonia with montmorillonite and saponite: *Trans. Faraday Soc.* **61**, 2284–2294.

Russell, J. D., Cruz, M. I. and White, J. L. (1968a) The adsorption of 3-aminotriazole by montmorillonite: *J. Agr. Food Chem.* **16**, 21–24.

Russell, J. D., Cruz, M., White, J. L., Bailey, G. W., Payne, W. R., Jr., Pope, J. D., Jr. and Teasley, J. I. (1968b) Mode of chemical degradation of *s*-triazines by montmorillonite: *Science* **160**, 1340–1342.

Serratosa, J. M. (1966) Infra-red analysis of the orientation of pyridine molecules in clay complexes: *Clays and Clay Minerals* **14**, 385–391.

Swoboda, A. R. and Kunze, G. W. (1964) Infra-red study of pyridine adsorbed on montmorillonite surfaces: *Clays and Clay Minerals* **13**, 277–288.

Swoboda, A. R. and Kunze, G. W. (1968) Reactivity of montmorillonite surfaces with weak organic bases: *Soil Sci. Soc. Am. Proc.* **32**, 806–811.

Talhoun, S. A. and Mortland, M. M. (1966) Complexes of montmorillonite with primary, secondary and tertiary amides—I. Protonation of amides on the surface of montmorillonite: *Soil Sci.* **102**, 248–254.

Trouillaux, R., Salvadore, P., Vandermeersche, C. and Fripiat, J. J. (1968) Study of water layers adsorbed on Na- and Ca-montmorillonite by the pulsed nuclear magnetic resonance technique: *Israel J. Chem.* **6**, 337–348.

Uytterhoeven, J. B., Christner, L. G. and Hall, W. K. (1965) Studies of the hydrogen held by solids—VIII. The decationated zeolites: *J. Phys. Chem.* **69**, 2117–2126.

Walling, C. (1950) The acid strength of surfaces: *J. Am. Chem. Soc.* **72**, 1164–1168.

Yariv, S., Heller, L. and Kaufherr, N. (1969) Effect of acidity of montmorillonite interlayers on the sorption of aniline derivatives: *Clays and Clay Minerals* **17**, 301–308.

Young, J. F. (1967) Humidity control in the laboratory using salt solutions—A review: *J. Appl. Chem.* **17**, 241–245.

Résumé—L'aptitude de la surface d'une argile à fonctionner comme un acide n'est pas représentée par des mesures de pH effectuées sur la masse du produit. Une méthode utilisant l'analyse u.v. et des indicateurs organiques a été développée pour évaluer l'acidité de surface. La méthode u.v.-indicateur organique permet une quantification sensible *in situ* de la protonation induite par la surface dans les systèmes argile humide ou sèche. Le procédé utilisé pour la préparation de l'argile permet d'obtenir un comportement acide reproductible.

Kurzreferat—Die Fähigkeit einer Tonmineraloberfläche als Säure zu wirken, wird durch eine pH-Messung an der Gesamtprobe nicht widergegeben. Es wurde eine Methode entwickelt, um unter Verwendung der u.v.-Analyse und organischer Indikatoren die Oberflächenacidität zu bestimmen. Die u.v.-Indikatormethode ermöglicht empfindliche *in situ* Bestimmung oberflächeninduzierter Protonierung in nassen oder trockenen Tonsystemen. Das zur Präparation der Tone benutzte Verfahren liefert reproduzierbare Aciditätseigenschaften.

Резюме — Способность поверхности глинистого минерала функционировать в качестве кислоты не выражается измерением pH в общей массе. Для проверки кислотности поверхности разработали метод анализа ультрафиолетовым спектром и органическими индикаторами. Метод ультрафиолетового органического индикатора дает возможность квантифицировать на месте протонацию, вызванную на поверхности влажной или сухой глины. Процедура приготовления глины дала возможность воспроизведения кислотного поведения поверхности.