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* To whom inquiries should be directed.

Comparison of IR Spectroscopic Analysis and X-Ray Diffraction of Aluminum Hydroxide Gel

STEVEN L. NAIL *, JOE L. WHITE †, and STANLEY L. HEM **

Abstract □ Data are presented which demonstrate that IR spectrophotometry is more sensitive than X-ray diffraction to structural changes occurring in aluminum hydroxide gel during aging. By examining changes in peak shape and position in the IR spectrum, evidence is seen for an increasing degree of order as the gel ages. The increased order may be responsible for the loss of acid reactivity observed during aging. IR analysis is also recommended for routine monitoring of aluminum hydroxide gels.

Keyphrases □ Aluminum hydroxide gel—monitoring of structural changes during aging, IR and X-ray diffraction methods compared, relationship to decreased acid reactivity □ IR spectrophotometry—monitoring, structural changes in aluminum hydroxide gel during aging, compared to X-ray diffraction method □ X-ray diffraction—monitoring, structural changes in aluminum hydroxide gel during aging, compared to IR spectrophotometric method

Aluminum hydroxide gel is an effective antacid, although many aspects of its structure and acid reactivity are not fully understood. The initial precipitate resulting from the reaction of a soluble aluminum salt with a base is probably a highly random structure. With aging, structural rearrangement occurs to

form a more thermodynamically stable system. For example, a polymerization-like process may produce a highly ordered system resistant to attack by acid (1-4). The rate of this process has been related to many factors including pH of precipitation (5), type and concentration of ions present (6-8), temperature (9), and order of addition of the reactants (10). The end-product of the aging process is usually a crystalline form of aluminum hydroxide (1-4, 6-8, 11, 12). These crystalline structures are resistant to attack even by concentrated acid.

It has been demonstrated that aluminum hydroxide gels, which are essentially nonreactive as measured by the USP acid-consuming capacity test, retain an amorphous X-ray diffraction pattern (5). Since X-ray diffraction appears to be relatively insensitive to the structural changes occurring during aging that result in a diminished acid reactivity, a more sensitive method is needed to study these structural changes. The purposes of this report are to demonstrate the usefulness of IR spectrophotometry

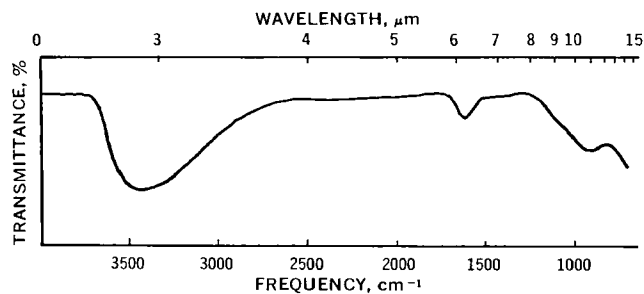


Figure 1—IR spectrum of freshly prepared aluminum hydroxide gel.

in studying the structural characteristics of aluminum hydroxide gel and to point out its application in relating structural changes to decreased acid reactivity.

EXPERIMENTAL

Materials—All chemicals used were either official or reagent grade.

Preparation of Aluminum Hydroxide Gel—Aluminum hydroxide gel was prepared by the reaction of aluminum chloride and strong ammonia solution at pH 7.0 (5).

Analytical Procedures—The acid-consuming capacity test (11) was modified by titrating to pH 3.5 rather than using bromophenol blue TS, as given in the USP. Duplicate determinations were made for each sample. The antacid property of the aluminum hydroxide gel is given as a percentage of the theoretical acid-consuming capacity.

For X-ray analysis, a sample of gel was air dried at room temperature and ground to a fine powder with an agate mortar and pestle. Powder mounts were prepared using aluminum McCreery mounts. The diffraction pattern was recorded from 6 to 30° 2θ¹ under the following conditions: CuK_α radiation, 40 kv, 20 mamp, 500 cps full scale, and 2°/min scan speed.

IR spectra² of gel samples were obtained by air drying a film of the gel on a zinc sulfide³ window. Spectra of gibbsite⁴, bayerite⁴, and boehmite⁴ standards were obtained by pressing a disk containing 1 mg of the standard material with 300 mg of potassium bromide.

RESULTS

The IR spectrum shown in Fig. 1 is typical of a freshly prepared aluminum hydroxide gel. The broad diffuse peak centered at about 3400 cm⁻¹ corresponds to the O—H stretching frequency of structural hydroxy and adsorbed water. The band at 1640 cm⁻¹ is the H—O—H bending vibration of adsorbed water. The broad peak at about 900 cm⁻¹ represents an O—H deformation vibration. A peak at 1410 cm⁻¹ is sometimes seen and is due to ammonium ion that was not totally removed by washing. Gels containing carbonate have a peak in the 1400-cm⁻¹ region as well as a peak at 1550 cm⁻¹.

The O—H stretching and O—H bending frequencies are markedly affected by their chemical environment. The broad absorption band in the 2900–3700-cm⁻¹ region of the IR spectrum of the fresh gel (Fig. 1) indicates O—H groups in many environments, thus indicating the highly disordered nature of the fresh gel (13).

The presence of adsorbed water causes some obliteration of structural detail in the O—H stretching region of the spectrum. For this reason, it is best to prepare the sample as an air-dried film on zinc sulfide or silver chloride windows. The use of a potassium bromide disk is not advisable due to the hygroscopic nature of potassium bromide. For the highly crystalline standard materials, the use of the potassium bromide pressed disk technique is satisfactory because the absorption bands are sufficiently well defined that

Table I—O—H Vibrations in Stretching and Bending Regions for Crystalline Aluminum Hydroxides

Phase	Frequency, cm ⁻¹	
	O—H Stretching Region	O—H Bending Region
Gibbsite	3612	1030
	3520	970
	3440	
	3395	
Bayerite	3650	1010
	3540	970
	3460	doublet
Boehmite	3300	1150
	3095	1070

small amounts of adsorbed water do not affect the spectrum. Air-dried films are also suitable for a vacuum heating treatment or deuteration to remove water.

The hydroxy groups in the aluminum trihydroxides, gibbsite and bayerite, are part of a highly ordered structure and have characteristic absorption bands in both the O—H stretching and O—H deformation regions. These crystalline aluminum hydroxides are easily identified by their IR spectra (Table I). Gibbsite has well-defined bands at 3612, 3520, 3440, and 3395 cm⁻¹ in the O—H stretching region. An intense peak occurs at 1030 cm⁻¹ with a smaller peak at 970 cm⁻¹, both of which are O—H deformations.

The general features of the bayerite spectrum are similar to gibbsite with peak positions shifted to 3650, 3540, and 3460 cm⁻¹. A doublet at 1010 and 970 cm⁻¹ occurs in the O—H deformation region.

Band positions for boehmite, an aluminum oxide hydroxide, are also shown in Table I. The O—H stretching frequency region is characterized by two broad peaks at 3300 and 3095 cm⁻¹. The O—H deformation frequencies are at 1150 and 1070 cm⁻¹.

Figure 2 shows X-ray diffraction patterns for the gel at various

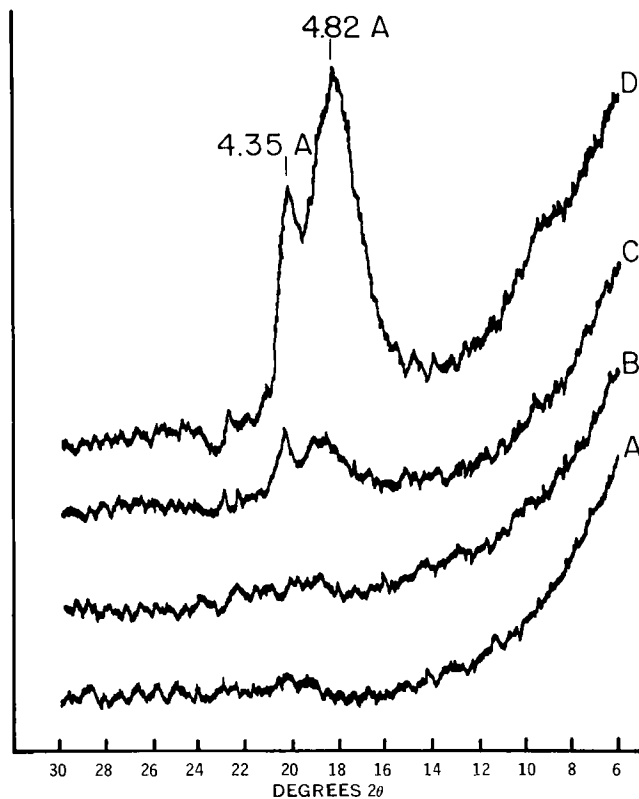


Figure 2—Change in X-ray diffraction pattern of aluminum hydroxide gel during aging at 25°. Key: A, 57 days; B, 65 days; C, 71 days; and D, 124 days.

¹ Norelco, Phillips Electronic Instruments, Mount Vernon, N.Y.

² Model 421, Perkin-Elmer Corp., Norwalk, Conn.

³ Irtan 2, Eastman Kodak Co., Rochester, N.Y.

⁴ Reynolds Metal Co., Richmond, Va.

Table II—X-ray Powder Diffraction Patterns of the Five Most Intense Peaks for Crystalline Aluminum Hydroxides^a

Gibbsite		Bayerite		Boehmite	
Interplanar Spacing, Å	Relative Intensity, %	Interplanar Spacing, Å	Relative Intensity, %	Interplanar Spacing, Å	Relative Intensity, %
4.84	100	4.72	100	6.11	100
4.34	40	4.36	70	3.16	65
4.30	20	3.19	25	2.34	53
2.37	20	2.21	67	1.86	32
2.03	12	1.71	26	1.85	27

^a Taken from K. Wefers and G. M. Bell, Alcoa Research Laboratories Technical Paper No. 19, 1972, p. 38.

aging times. The gel retains an amorphous pattern until about 70 days after preparation, at which time a rather broad peak is seen from 18.5 to 19.2° 2θ (4.77–4.62 Å) with a sharper peak at 20.4° 2θ (4.35 Å). After 124 days of aging, well-defined peaks are seen at 18.3° 2θ (4.82 Å) and at 20.4° 2θ (4.35 Å).

Table II lists the predominant X-ray diffraction peaks for gibbsite, bayerite, and boehmite. A comparison of the X-ray diffraction pattern of the 70-day sample with the spacings in Table II clearly indicates that a crystalline aluminum hydroxide phase has formed, although the X-ray diffraction pattern is too diffuse to identify the crystalline phase clearly. With further aging, the crystalline phase is clearly identified as gibbsite.

The O—H stretching frequency region of the IR spectrum is shown for various aging times in Fig. 3. The gel aged 5 days has an IR absorbance pattern characteristic of a highly disordered structure. As the gel ages, an inflection point occurs at 3520 cm⁻¹. This shoulder develops into a well-resolved peak. A shoulder is seen developing at 3612 cm⁻¹ along with a peak at 3470 cm⁻¹.

The spectral changes in the O—H deformation region are shown in Fig. 4. The fresh gel shows a broad peak centered at 900 cm⁻¹. As the gel ages, a shoulder develops at 1020 cm⁻¹ and eventually becomes a well-resolved peak.

A plot of the log of the acid-consuming capacity of the gel *versus* time at room temperature is shown in Fig. 5. The loss in acid reac-

tivity follows apparent first-order kinetics. The slope and y-intercept are $-5.93 \times 10^{-3} \text{ day}^{-1}$ and 93.5%, respectively, by linear regression analysis. The linear correlation coefficient is -0.99 .

DISCUSSION

Based on X-ray diffraction, the first evidence of crystallinity is seen after about 70 days of aging. It is not possible at that time to identify the polymorph present; however, the characteristic X-ray diffraction pattern of gibbsite developed in later samples.

By examining the same gel by IR spectrophotometry, a slight inflection is seen at 3520 cm⁻¹ after 42 days and it clearly develops into a gibbsitic peak after less than 70 days.

The O—H deformation region of the spectrum is also sensitive to the degree of order of the gel. The deformation peak undergoes a marked shift to higher frequency, and a sharpening of the band occurs as the gel ages. An absorption pattern develops characteristic of gibbsite.

The IR spectrum indicates that gibbsite or a precursor of gibbsite is the major crystalline phase that is forming as the gel ages. The sharp peak at 3650 cm⁻¹ characteristic of bayerite and the doublet at 970 and 1010 cm⁻¹ are not seen in the IR spectrum, indicating that the developing order is leading to gibbsitic material.

The value of IR analysis of aluminum hydroxide gel is also seen

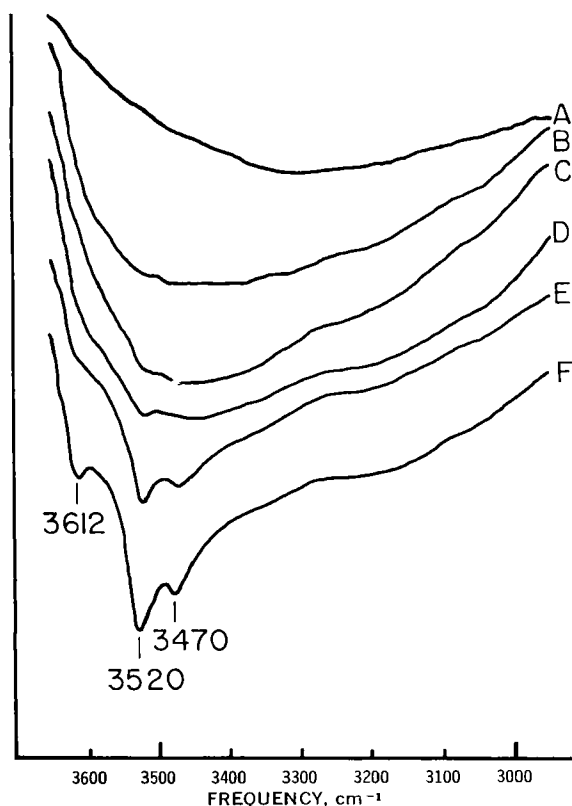


Figure 3—Change in O—H stretching frequency region of IR spectrum of aluminum hydroxide gel during aging at 25°. Key: A, 5 days; B, 42 days; C, 54 days; D, 61 days; E, 69 days; and F, 124 days.

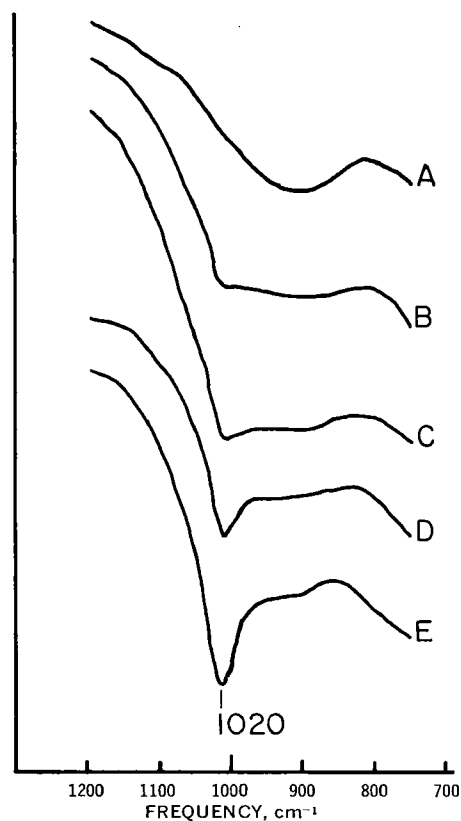


Figure 4—Change in O—H bending frequency region of IR spectrum of aluminum hydroxide gel during aging at 25°. Key: A, 5 days; B, 54 days; C, 61 days; D, 70 days; and E, 124 days.

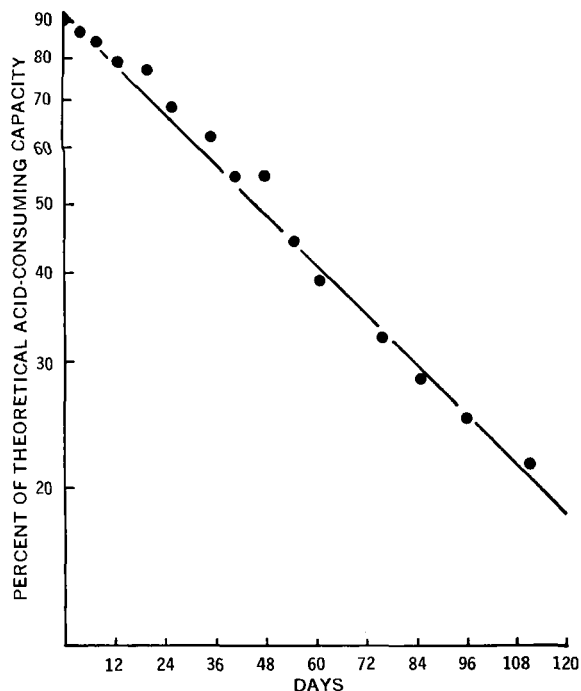


Figure 5—Change in acid-consuming capacity of aluminum hydroxide gel during aging at 25°.

when the degree of acid reactivity is compared to IR and X-ray spectral changes. When using IR spectrophotometry, evidence of crystallinity is first seen when the gel is about 50% reactive. X-ray diffraction does not indicate any structural change until the gel is less than 35% reactive. The X-ray diffraction pattern is too diffuse at this point to permit identification of the crystalline phase.

The IR spectra also yield information concerning structural changes occurring during aging. A freshly prepared gel has a diffuse band in both the O—H stretching and deformation regions, indicating a highly unordered structure with many types of environments associated with O—H. As the gel ages, definite absorption bands develop as the hydroxys become part of an ordered structure. Increasing degrees of ordering are apparent from the shape and position of the bands in comparison to the reference IR spectra. This type of analysis yields insight into the mechanism re-

sponsible for reactivity losses that occur upon aging.

IR analysis offers additional advantages over X-ray diffraction in terms of lower cost of instrumentation and more universal access to IR spectrophotometers. It is suitable for routine monitoring of aluminum hydroxide gels.

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* To whom inquiries should be directed.