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* To whom inquiries should be directed.

Differential Thermal Analysis of Aluminum Hydroxide Gel

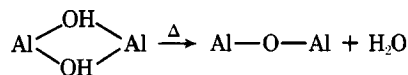
STEVEN L. NAIL *, JOE L. WHITE ‡, and STANLEY L. HEM **

Abstract □ The development of order during the aging of aluminum hydroxide gel prepared by the reaction of aluminum chloride and ammonium hydroxide to a final pH of 7.0 can be monitored by differential thermal analysis. The loss of acid reactivity upon aging is accompanied by an increase in the temperature and intensity of the dehydroxylation endotherm and an accompanying decrease in the intensity of the water of hydration endotherm. With continued aging, the thermogram develops the characteristics of a crystalline aluminum hydroxide.

Keyphrases □ Aluminum hydroxide gels—differential thermal analysis, development of order during aging □ Gels, aluminum hydroxide—differential thermal analysis, development of order during aging □ Aging—aluminum hydroxide gels, monitored by differential thermal analysis □ Differential thermal analysis—aging of aluminum hydroxide gels monitored

In previous investigations (1, 2), IR spectroscopy and X-ray diffraction were used to monitor the structural changes in aluminum hydroxide gel which occurred upon aging and were associated with a decreased rate of acid reactivity. The initial highly random structure changed during aging as the hydroxyls became part of an ordered structure. The degree of order increased until a crystalline form of aluminum hydroxide developed. This report demonstrates the utility of differential thermal analysis in monitoring the aging of aluminum hydroxide gel and relates the thermal behavior to a recently proposed structure of aluminum hydroxide gel (3, 4).

The physical changes detectable by differential thermal analysis when aluminum hydroxide gel is heated are the loss of water of hydration in the range of



Scheme I

100–120° and the loss of structural hydroxyl as water (Scheme I). The temperature at which the dehydroxylation of the double hydroxide bridges occurs is a characteristic that allows the identification of crystalline aluminum hydroxide (5–10), although the aluminum hydroxide polymorphs cannot be distinguished from one another. Gibbsite and bayerite both have dehydroxylation endotherms at about 300°. Pseudoboehmite and boehmite undergo dehydroxylation at about 450° (9).

EXPERIMENTAL

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

Aluminum Hydroxide Gel Preparation—A 4-liter batch of gel was prepared by the addition of 13% (v/v) strong ammonia solution to a solution of 287.2 g of aluminum chloride hexahydrate in 3340 ml of distilled water. Strong ammonia solution was added, with continuous stirring, at a rate of approximately 120 ml/min to a final pH of 7.0. After precipitation, the gel was divided into equal portions prior to washing. The first portion (I) was washed with 1 liter of distilled water by draining through a canvas bag, the second (II), was washed with 3 liters of distilled water, and the third (III) was washed with 5 liters of distilled water. The three gels were diluted to 1 liter with distilled water and were then stored in tightly closed glass containers and aged at 25°.

Differential Thermal Analysis Thermograms—The differential thermal analysis thermogram¹ was recorded from room temperature

¹ Model III, Deltatherm Instrument Co., Denver, Colo.

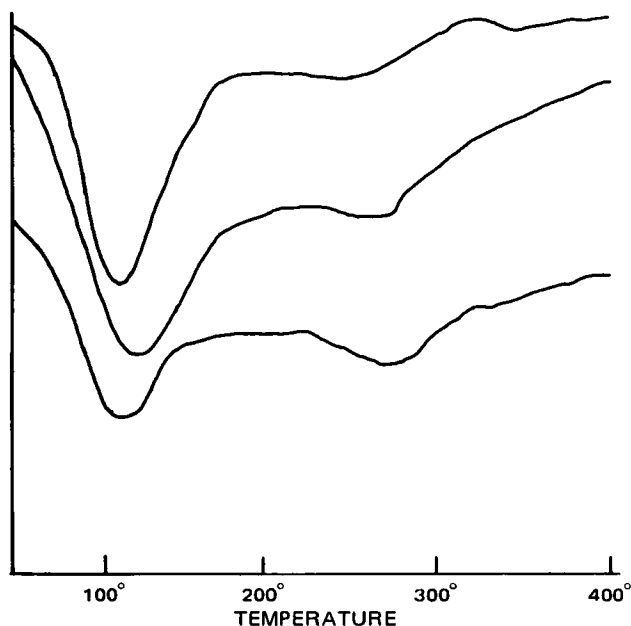


Figure 1—Change in differential thermal analysis thermogram of Gel I during aging at 25°. Key: top, 15 days; middle, 66 days; and bottom, 161 days.

to 500° for each gel at various times during aging. Samples were prepared by placing 5 ml of gel in a plastic centrifuge tube² and diluting to 12 ml with 2 N NaCl. Samples were then centrifuged³ at 4000 rpm for 15 min. The supernate was discarded and replaced with 50% ethanol, and the samples were again centrifuged at 4000 rpm for 15 min.

The purpose of this washing process was to remove any residual ammonium chloride from the gel samples. It was found that 2 N NaCl and 50% ethanol permitted the gel to be separated by centrifugation because these vehicles prevented dispersion of the gel which occurred if the gel was washed with distilled water. Ammonium chloride sublimates at 340°, resulting in an endotherm that interferes with the detection of the dehydroxylation endotherm of the sample.

After washing, the sample was air dried at room temperature and ground to a fine powder with an agate mortar and pestle. The sample cup was filled with 40 ± 3 mg of sample and packed uniformly. The thermogram was recorded under the following conditions: heating rate, 10°/min; ΔT sensitivity, 2°/2.54 cm; and upper temperature limit, 500°. The reference was calcined alumina. The thermogram of gibbsite⁴ was recorded similarly.

The temperature of the dehydration endotherm was somewhat variable due to the variable heating rate of the instrument below 100°. Daily replications indicated that the temperature of the dehydroxylation endotherm in the 200–300° range varied by less than ±1°.

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. All determinations were made in duplicate. The antacid property of each gel is given as the percentage of the theoretical acid-consuming capacity, which is based on the stoichiometric reaction of hydrochloric acid with the equivalent aluminum oxide in the sample as determined by the official chelatometric assay (11).

RESULTS AND DISCUSSION

Differential thermal analysis thermograms for the three gels studied are shown in Figs. 1–3. The earliest thermogram of each gel is characterized by an endotherm at about 100°, corresponding to loss of bound water, and by a broad, poorly defined endotherm centered at about 250°, appearing as a shoulder on the dehydration endotherm. The later endotherm is the loss of structural hydroxyl as water, resulting in an oxo linkage, Al—O—Al.

As a gel ages, the dehydroxylation endotherm becomes more de-

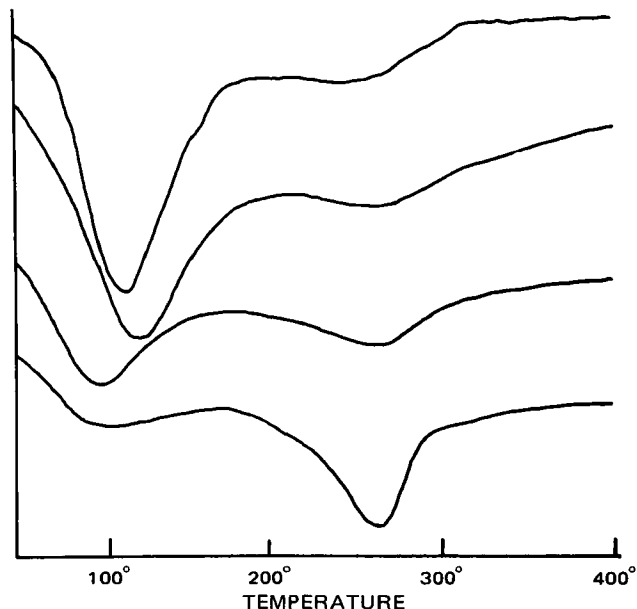


Figure 2—Change in differential thermal analysis thermogram of Gel II during aging at 25°. Key: top, 15 days; upper middle, 64 days; lower middle, 113 days; and bottom, 161 days.

finer, appears at a higher temperature, and is more intense. The fact that the endotherm is observed at a higher temperature indicates that, as the gel ages, more thermal energy is required for dehydroxylation. This is evidence that the structure is becoming more ordered with age. The differential thermal analysis thermogram of gibbsite is shown along with the thermograms of Gel III in Fig. 3. As the gels age, the features of the thermogram approach those of the highly crystalline material.

The relative rate of development of order as measured by the intensity of the dehydroxylation endotherm was greatest in Gel III (Fig. 3), which was washed with 5 liters of distilled water, and least in Gel I (Fig. 1), which was washed with 1 liter of distilled water. This rank order is the same as the loss of acid reactivity as measured by the percent of theoretical acid-consuming capacity (Table I). The crystalline aluminum hydroxide polymorphs are virtually unreactive in 0.1 N HCl, so the development of an ordered system leading to a

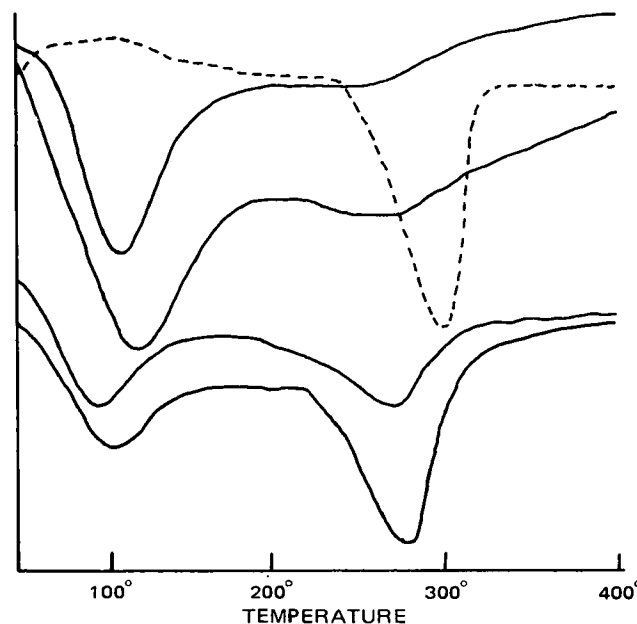


Figure 3—Change in differential thermal analysis thermogram of Gel III during aging at 25°. Key: - - -, gibbsite; top, 13 days; upper middle, 66 days; lower middle, 113 days; and bottom, 161 days.

² Polypropylene tubes, 16.0 × 102.2 mm, Ivan Sorvall, Inc., Newton, Conn.

³ Model GLC-1, Ivan Sorvall, Inc., Newton, Conn.

⁴ Reynolds Metal Co., Richmond, Va.

Table I—Change in Acid-Consuming Capacity during Aging at 25°

Days	Percent of Theoretical Acid-Consuming Capacity		
	Gel I	Gel II	Gel III
13	—	—	78
15	78	81	—
64	—	61	—
66	63	—	57
113	—	53	41
161	55	34	28

crystalline aluminum hydroxide polymorph results in a decreased acid-consuming capacity. The behavior supports the earlier hypothesis (12–14) that anions present at the time of precipitation stabilize the gel structure. The removal of these stabilizing anions by washing results in an increased rate of development of order in the gel structure, with an associated decrease in the acid reactivity.

The sequence of thermograms showing the aging process of each gel (Figs. 1–3) indicates that, as aging proceeds, the intensity of the dehydration endotherm decreases and the intensity of the dehydroxylation endotherm increases. As the gel becomes ordered, less water is bound to the gel and the structural hydroxyl content increases. The bound water is probably replaced by structural hydroxyl in the form of double hydroxide bridges.

The proposed (15) polymer model for aluminum hydroxide suggests that particle growth occurs by a deprotonation–dehydration mechanism, which results in the conversion of bound water molecules into double hydroxide bridges. This process continues until a crystalline form of aluminum hydroxide is produced. With gibbsite, a highly crystalline form of aluminum hydroxide, the thermogram (Fig. 3) indicates that virtually no bound water is present.

In summary, it appears that differential thermal analysis is a useful technique for studying aluminum hydroxide gel. It is sensitive to the structural changes that occur during aging which are responsible for the decreased acid reactivity of the aluminum hydroxide gel. Analysis of the thermograms indicates that bound water in the gels was replaced during aging by structural hydroxyl groups in the form of double hydroxide bridges. This change results in a more ordered structure which is more resistant to reaction with acid. As aging

progresses, the gel assumes the characteristic thermogram of a crystalline aluminum hydroxide.

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* To whom inquiries should be directed.

Extraction and GLC Analysis of Pyrithyldione in Highly Putrified Human Postmortem Samples

FRANK K. MARTENS*, MARK A. MARTENS, JOHAN DEMETER, and AUBIN HEYNDRIKX

Abstract □ Pyrithyldione was isolated from highly putrified human brain and small intestine samples by ether extraction followed by alumina column cleanup. The total yield was $90 \pm 5\%$. No derivatization was necessary prior to GLC analysis.

Keyphrases □ Pyrithyldione—GLC analysis, putrified brain and intestine □ GLC—analysis, pyrithyldione in putrified brain and intestine □ Sedatives—pyrithyldione, GLC analysis in putrified brain and intestine

In forensic toxicology, many methods have been reported for extracting pyrithyldione and glutethimide from postmortem samples. Most of these methods consist of a single extraction step with chloroform, petroleum ether, or methylene chloride followed by TLC, UV spectrophotometry, or spectrofluorometry (1–4).

Impurities may be removed by gel permeation chromatography (5) or direct analysis by GLC, using various

liquid phases (6, 7). If impurities interfere too much after direct extraction, ethylation with tetraethylammonium hydroxide may solve this problem (8). Three-month-old postmortem samples are difficult to analyze, and special cleanup requirements may be necessary for final unambiguous identification. To prevent interference with barbiturates and other hypnotics or sedatives, OV-275 was selected for the GLC analysis.