ADSORPTION OF ORGANIC ACIDS ON THORIA

by

Harold R. Bradford and Milton E. Wadsworth

Institute of Metals and Explosives Research
Department of Metallurgy, University of Utah
Salt Lake City, Utah

ADSORPTION OF ORGANIC ACIDS ON THORIA

by

Harold R. Bradford and Milton E. Wadsworth
Department of Metallurgy, University of Utah

ABSTRACT

The adsorption of acetic and oleic acids on the surface of thoria
was studied by means of infrared spectroscopy. An infrared analysis of
the adsorbates before and after adsorption using differential double beam
methods indicated that the adsorption of organic acids on thoria surfaces
occurs by an esterification reaction between the organic acid and the
hydroxylated thoria surface. Ammonia vapor will not adsorb on thoria,
indicating the basic character of the hydroxylated surface.

INTRODUCTION

The successful application of thoria slurries to the development
of nuclear power depends largely upon a basic understanding of the surface
properties of thoria. The results presented in this study cover the
variations observed in the infrared spectra of acetic and oleic acids
before and after adsorption on thoria. Many organic and inorganic acids
adsorb strongly on thoria surfaces and are difficult to remove. To gain
a qualitative concept of the mechanism of the acid-thoria adsorption
process, acetic acid was adsorbed from the vapor phase and oleic acid was
adsorbed by direct liquid-solid contact.

Experimental Procedure

Pellets containing thoria dispersed in a potassium bromide
matrix were used in this investigation. Special potassium bromide pre-
pared for infrared studies by the Harshaw Chemical Company was used.
Treated thoria samples, carefully weighed, were added to a 1/2" x 1"
plastic vial containing one gram of potassium bromide along with a 1/4"
diameter plastic ball to promote mixing. A press-fit plastic lid was
immediately put in place and the filled vial was rapidly agitated in a
"Wig-L-Bug" vibrating mixer for one minute. A weighed portion (400 mg)
from the mix was transferred to an evacuable die fitted with a stainless
steel ring, evacuated for five minutes, then pressed for 5 minutes at 12
tons/sq. in. pressure. The resulting window pellet was then used to
determine the infrared spectrum of the solid suspended in the KBr matrix.
Each pellet was kept in individual envelopes in a desiccator when not in
immediate use. Alteration with age did not seem appreciable with properly
made pellets.

Absorption spectra were obtained on a Perkin-Elmer 21 Double Beam
Recording Infrared Spectrophotometer using a sodium chloride prism
covering the spectral range from 2 to 15 microns wavelength. Control
settings were speed 4, response 1, resolution 1000 for differential spectra,

and 927 for non-differential runs. The double beam instrument records only the differences between sample and reference, similarities being balanced out. When the reference beam pellet contained untreated thoria and the sample beam contained a treated sample, the spectrum of bulk thoria was cancelled along with atmospheric impurities (i.e. water vapor and carbon dioxide). This differential method provides a spectrum of the surface alone.

The thoria used in the study was the D 16-650* thoria prepared by firing thorium oxalate at 650°C. The surface area determined by nitrogen adsorption was $32.4 \pm .6 \text{ m}^2/\text{g}$.

Adsorption of acetic acid from the gas phase was carried out at room temperature in a clean evacuated container by exposure for approximately 12 hours. A clean glass desiccator was used for this purpose. Reagent grade acetic acid (15 ml) in a 50 ml uncovered beaker was placed in the desiccator bottom and uncovered samples of thoria were added. Evacuation by an aspirator pump was carried to the reduced pressure condition where bubbles formed in the acetic acid, air being thus displaced by acetic acid vapor in the container. The valve was closed for the required treatment time.

After exposure, certain samples were evacuated for several hours to remove physically adsorbed acetic acid. Other samples were used immediately in making infrared absorption windows.

Oleic acid was adsorbed by adding the liquid acid directly to the thoria which was then mulled by mixing in the "Wig-L-Bug" mixer. Less oleic acid than that necessary for complete surface coverage was added in all cases. This was based upon a surface area of approximately 20 $\overset{*2}{\text{A}}$ surface area for each acid molecule adsorbed. Following mixing the thoria was washed with ethyl alcohol and dried under vacuum. A KBr pellet was then prepared and the absorption spectrum determined.

---

*Prepared by Union Carbide Nuclear Co., Chemical Technology Division, Oak Ridge, Tennessee

Experimental Results and Discussion

The infrared spectrum of 4 mg of the D-16-650 thoria as received is shown in Fig. 1, using a plain KBr reference window to cancel moisture in the KBr. The strong band at 2.9 μ (3450 cm^{-1}) is due to surface hydroxyl -OH stretching (-Th-OH) and cannot be removed without increasing the temperature above 650°C to sintering temperatures. Bands at 6.4, 7.3, 9.6 and 11.9 μ result from adsorbed carbonates,[1] and are invariably present on the surface of thoria exposed to the atmosphere. The surface -OH bending at 6.2 μ is obscured by the surface carbonates. Also included in Fig. 1 is the spectrum of acetic acid. The CH$_3$ stretching frequencies occur at 3.37 μ (2962 cm^{-1}) and 3.48 μ (2872 cm^{-1}). The additional bands in the region 3 to 4 μ are -OH stretching bonds of strongly hydrogen bonded acid dimers.[2] The bond at 5.85 μ (1710 cm^{-1}) results from the carbonyl -C = O stretching mode and is characteristic of C = O when associated with the acid carboxyl -COOH group. Ionization of the -COOH to -COO$^-$ shifts the associated C = O bond drastically. The -CH deformation modes associated with the C - CH$_3$ normally present at 6.9 μ (1450 cm^{-1}) and 7.3 μ (1370 cm^{-1}) are almost obscured by the strong band at 7.1 μ (1410 cm^{-1}) resulting from a C - O stretching mode. Additional C - O bands are in evidence in the 7.7 μ (1300 cm^{-1}) to 10 μ (1000 cm^{-1}) region. The OH deformation band of the -COOH group at 10.85 μ (920 cm^{-1}) is very weak in acetic acid.

Fig. 2 is the spectrum of acetic acid adsorbed on the surface of thoria. The dotted curve is the spectrum obtained immediately after adsorption without evacuation. The solid curve of Fig. 2 is the spectrum after evacuation for 20 hours. Only slight differences occurred, illustrating the rapid and strong attachment of acetic acid to the thoria surface. A comparison of the acetic acid spectrum of Fig. 1 with the Fig. 2, however, illustrates great differences following adsorption. The 5.85 μ (C = O) band is almost completely missing, indicating only a small amount of -COOH or acetic acid. Two new strong bands appeared at 6.45 (1550 cm^{-1}) and 6.85 (1460 cm^{-1}) corresponding to ionized carboxyl group (-COO$^-$) and represent the anti-symmetrical and the symmetrical vibrations respectively.

Also, it is noticeable that the -OH bands in the 3.2 to 4 μ region are missing, leaving only the 3.37-3.48 -CH₃ band. This is consistant with the appearance of the ionized carboxyl bands. The acetic acid C - O vibration at 7.78 μ is missing after adsorption with two new bands appearing at 7.94 μ and 9.15 μ, indicating an appreciable variation in the C - O vibrational modes.

Figure 3 is a differential spectrum of acetic acid adsorbed on thoria. The sample pellet contained 400 mg of thoria with adsorbed acetic acid and the reference contained 400 mg of thoria with no acetic acid adsorbed. Both thoria samples were treated identically except for the adsorption step. In one test the thoria with and without adsorbed acetic acid was dried under vacuum for 5 hours to remove physically adsorbed acetic acid and water resulting in the spectrum shown by the solid curve of Fig. 3. The dotted spectrum of Fig. 3 is the differential spectrum obtained immediately after adsorption without evacuation. The differential spectrum clearly illustrates reverse -OH bands at 2.97 μ and 6.2 μ indicating an excess of surface -OH in the reference sample having no acetic acid adsorbed. These results are consistant with the esterification model of acid adsorption and compare with results obtained by Eyring and Wadsworth[3] for the adsorption of hexanethiol on zinc minerals. The adsorption of the organic acid results in the splitting out of water from surface Th-OH groups by esterification or simple acid-base reaction forming a surface thorium salt. These results may be explained by the equation:

$$-O-Th \underset{OH}{\overset{OH}{<}} + HOOCR \longrightarrow OTh\overset{+}{O} \mid \overset{-}{O}OCR + H_2O \qquad (1)$$
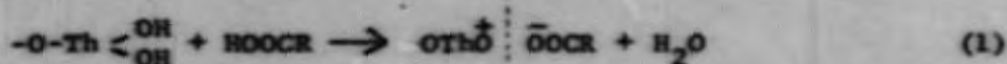
Similar results were obtained for oleic acid adsorption on thoria. The spectrum of oleic acid liquid by itself is illustrated by the dotted curve of Fig. 4. Frequency assignments are essentially the same as those for acetic acid with the exception of the presence of the -CH₂- stretching (3.53 μ) and deformation (6.83 μ) modes. Also the broad band at 10.7 μ, corresponding to an -OH out of plane deformation of the COOH group, is much

stronger in the case of oleic acid than for acetic acid. The band at 13.8 μ is caused by a $-(CH_2)_4-$ skeletal vibration.

The solid curve of Fig. 4 is a differential spectrum of oleic acid adsorbed on thoria. Again strong reverse -OH peaks are evident at 2.95 and 6.2 μ indicating the splitting out of water. The -OH submaxima in the 3 to 4 micron range are missing leaving the strong $-CH_3$ and $-CH_2$ stretching bands between 3.45 and 3.55 μ. The $C = O$ band of oleic acid at 5.85 μ is missing forming two new bands corresponding to carboxyl ion at 6.5 μ and 6.85 μ. The 6.85 μ band superimposes the $-CH_2$ deformation band at 6.83 μ but the increased depth of this band illustrates the additive effect. Also the strong -OH deformation of the $C - O$ vibration at 10.7 μ is missing after adsorption. These variations are consistant with the esterification model proposed according to equation (1).

It is interesting to note the slight reverse bands in the differential spectrum for oleic acid adsorption at 7.5, 9.6, and 11.9 μ. These correspond to the bands (Fig. 1) for carbonates adsorbed on thoria showing that oleic acid also displaces carbonates upon adsorption.

The basic character of the thoria surface was illustrated by attempts to adsorb ammonia vapor on the thoria surface. No adsorption was found to occur. An acid surface such as silicic acid with free Si-OH surface groups will adsorb ammonia[4,5] by donating a proton and forming the ammonia ion according to the reaction

$$-\overset{|}{\underset{|}{Si}}-OH + NH_3^+ \longrightarrow SiO^- \ NH_4^+ \tag{2}$$
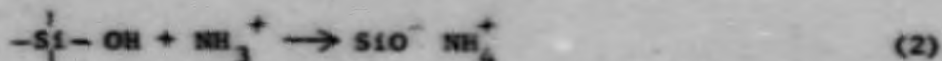
The inability of NH_3 to adsorb on thoria is indicative of its basic character.

SUMMARY

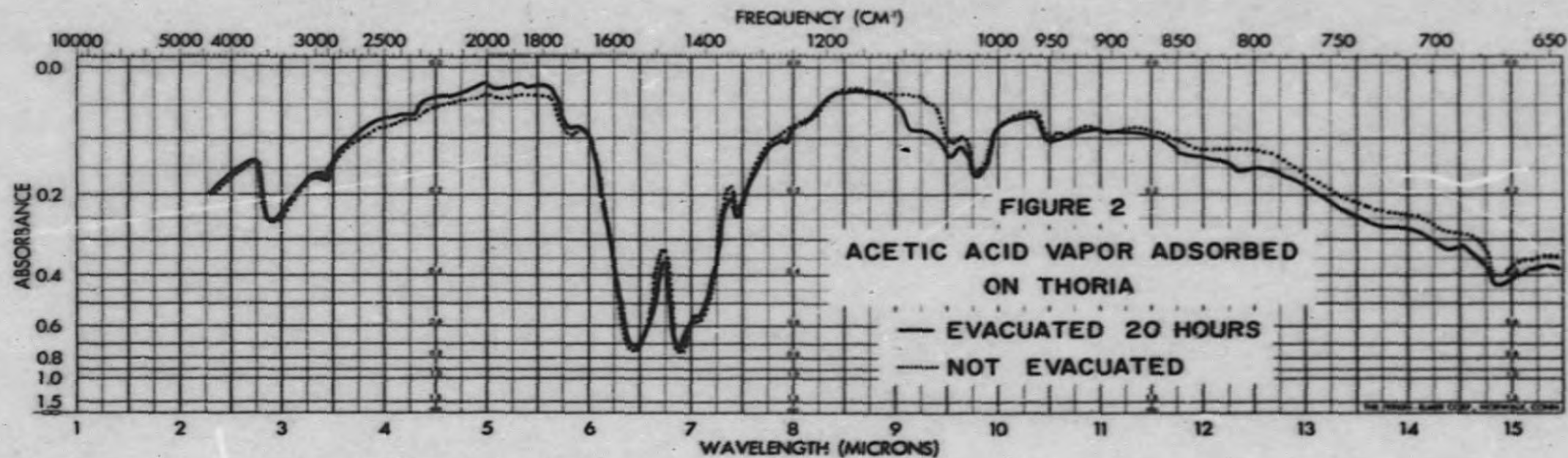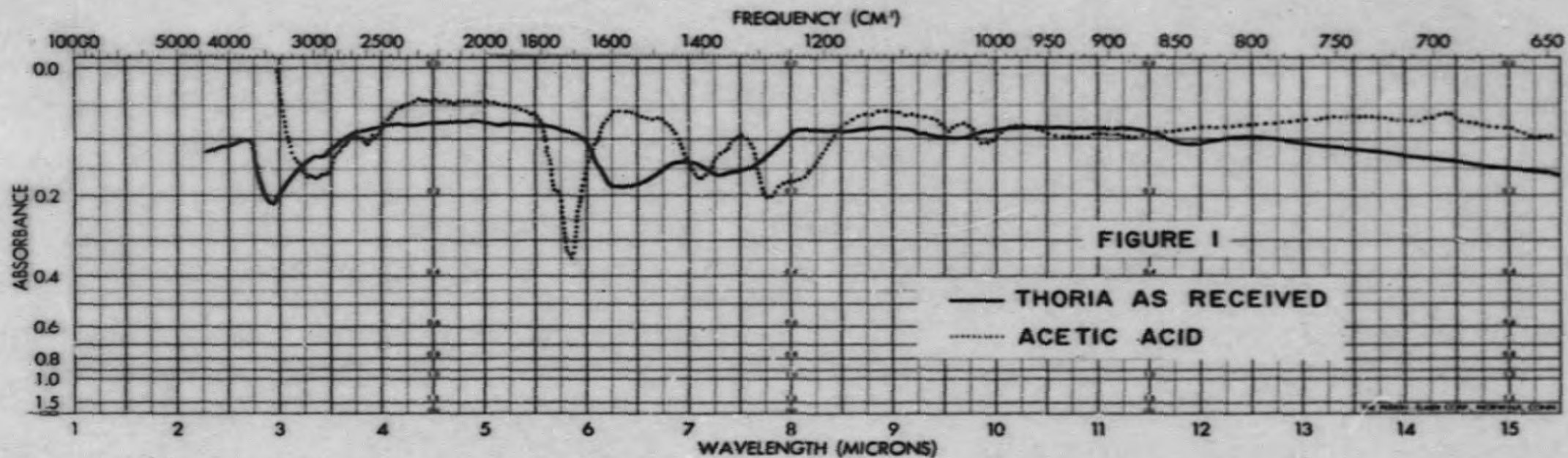1. Organic acids such as acetic and oleic acids adsorb rapidly and strongly on thoria.

2. Acetic acid cannot be removed appreciably by evacuating the sample for periods as long as 20 hours.

3. Organic acids adsorb on thoria by an esterification process forming surface ionized carboxyl groups with an associated splitting out of water according to the reaction:
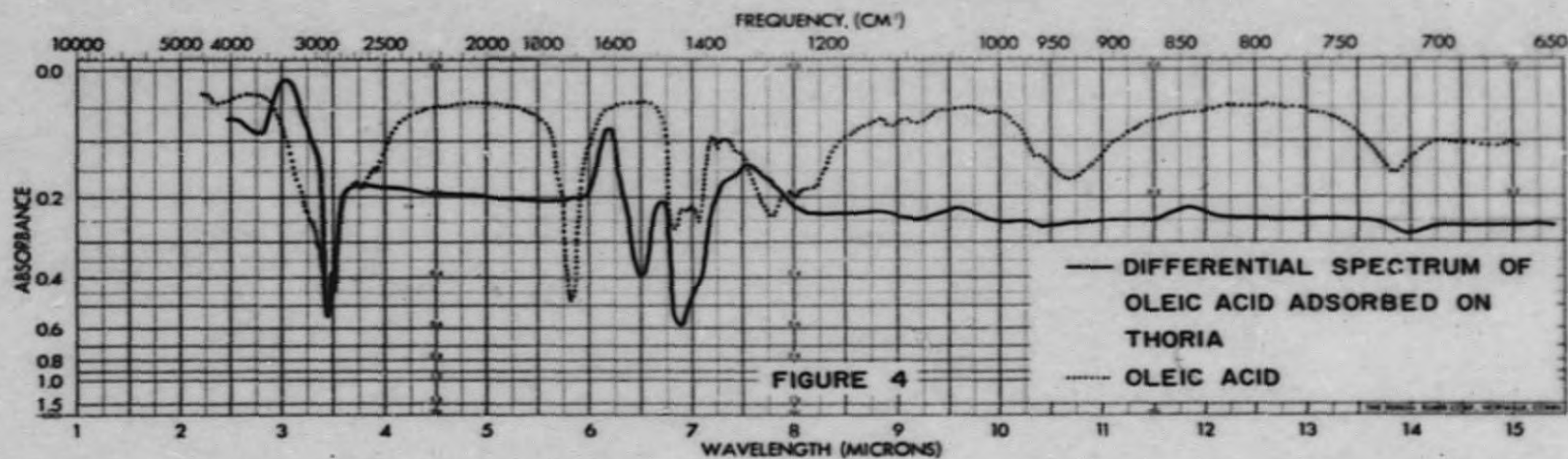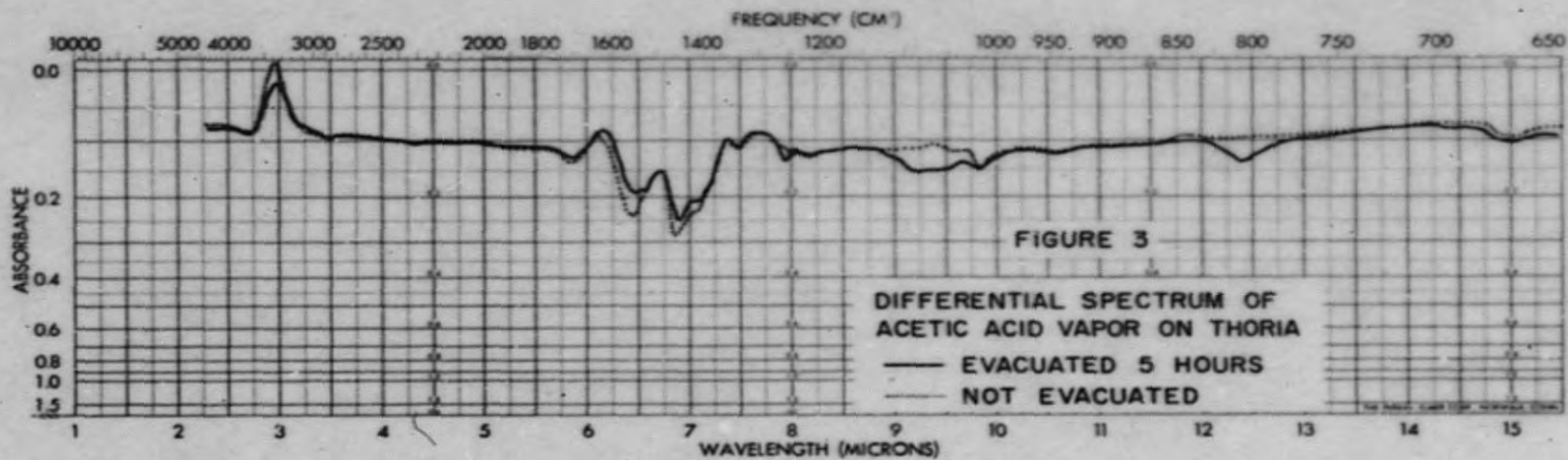
$$-O-Th\langle{}^{OH}_{OH} + HOOCR \longrightarrow -O-Th\overset{+}{O}|\bar{O}OCR + H_2O$$
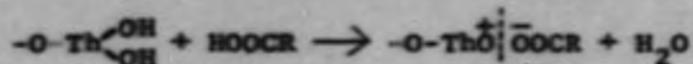
4. Ammonia vapor will not adsorb on thoria indicating the basic character of its surface.

BIBLIOGRAPHY

1. G. J. Spaepen, R. T. Wimber and M. E. Wadsworth, "Adsorption of Silicic Acid on Thoria - Determined by Infrared Spectroscopy," Technical Report No. V, June 30, 1959, University of Utah, Union Carbide Nuclear Co., Chem. Tech. Div., Res. and Dev. Subcontract 1075 Under W-7405-eng-26.

2. L. J. Bellamy, "The Infrared Spectra of Complex Molecules, John Wiley and Sons, New York, 1958.

3. E. M. Eyring and M. E. Wadsworth, AIME Trans, Mining Engineering, p. 531, 1956.

4. J. E. Mapes and R. P. Eischens, Phys. Chem., 58, 1059, (1954).

5. R. O. French, M. E. Wadsworth, M. A. Cook and I. B. Cutler, J. Phys. Chem., 58, 805 (1954).

FIGURE 1

THORIA AS RECEIVED
ACETIC ACID

FIGURE 2

ACETIC ACID VAPOR ADSORBED
ON THORIA

EVACUATED 20 HOURS
NOT EVACUATED

FIGURE 3

DIFFERENTIAL SPECTRUM OF
ACETIC ACID VAPOR ON THORIA
—— EVACUATED 5 HOURS
······ NOT EVACUATED

—— DIFFERENTIAL SPECTRUM OF
OLEIC ACID ADSORBED ON
THORIA
······ OLEIC ACID

FIGURE 4

END