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ABSTRACT

The major source of man-made SO_2 in the atmosphere is the burning of coal for electric power generation. Coal-fired utility plants are also large sources of NO_x pollution. Regenerable flue gas desulfurization/NO_x abatement catalysts provide one mechanism of simultaneously removing SO_2 and NO_x species from flue gases released into the atmosphere.

The purpose of this project is to examine routes of optimizing the adsorption efficiency, the adsorption capacity, and the ease of regeneration of regenerable flue gas cleanup catalysts. We are investigating two different mechanisms for accomplishing this goal. The first involves the use of different alkali and alkaline earth metals as promoters for the alumina sorbents to increase the surface basicity of the sorbent and thus adjust the number and distribution of adsorption sites. The second involves investigation of non-aqueous impregnation, as opposed to aqueous impregnation, as a method to obtain an evenly dispersed monolayer of the promoter on the surface. The thermal gravimetric analysis (TGA) coupled with atomic absorption analysis for metals provide the quantitative data: how much SO_2 or NO/NO_2 is adsorbed versus the amount of alkali or alkaline earth on the surface and at what temperature or temperatures the surface complexes decompose. The infrared data tell us which types of adsorbed SO_2 are present on the surface during adsorption, in what order they form, and, in an approximate way, the relative amounts which are generated. During regeneration, the FT-IR results can be directly correlated with the TGA data to determine which surface structures decompose to give rise to the greatest amount of desorbed SO_2 and the greatest extent of regeneration of the catalyst, and in what order and to what extent the surface complexes decompose as a function of alkali/alkaline earth additive and dispersion.

We have purchased the infrared diffuse reflectance cell and interfaced it to a vacuum manifold for the supply of gases and a pumping station for evacuation of the cell. We have configured the cell for accurate temperature control over the range from room temperature to 600°C. The TGA has been modified to monitor low temperature SO_2 adsorption. We have characterized a commercial alumina for surface alkali content by x-ray photoelectron spectroscopy (XPS). We have carried out initial dehydration experiments (obtaining both gravimetric and infrared spectroscopic data) on two model aluminas which we have chosen on the basis of their purity and alkali content.

INTRODUCTION

The major source of man-made SO_2 in the atmosphere is the burning of coal for electric power generation.[1] Coal-fired utility plants are also large sources of NO_x pollution from oxidation of nitrogen in the fuel as well as atmospheric N_2. In order to comply with present and future "acid-rain" legislation restricting SO_2 and NO_x emissions from industrial plants, there is a great deal of interest in improving flue gas desulfurization technology. The most desirable technology would be one that can be applied with relatively little initial capital investment to older plants, and one which requires low annual operating expenses. Injection techniques using lime and limestone have been commercialized but these methods have high cost and disposal limitations.[2] Regenerable flue gas desulfurization/NO_x abatement catalysts provide one mechanism of simultaneously removing SO_2 and NO_x species from flue gases released into the atmosphere.[2]

The purpose of this project is to examine routes of optimizing the adsorption efficiency, the adsorption capacity, and the ease of regeneration of regenerable flue gas cleanup catalysts. Previous investigations directed toward optimization of flue gas desulfurization catalysts have assumed that the limiting regeneration consideration involved decomposition of adsorbed sulfate. We are investigating the possibility that this assumption is not necessarily accurate. If we can, by a judicious choice of additive, create a surface where the predominant form of adsorbed SO_2 is sulfite or some other chemisorbed form of SO_2, both of which should decompose at lower temperature than surface sulfate (and correspond to active desulfurization sites at flue gas temperatures),[3-6] we will be able to design a catalyst with comparable sorbent capacity but much more favorable regeneration characteristics. If, on the other hand, it becomes clear that formation of surface sulfate is preferred, we will be able to design a formulation to maximize sorbent capacity while minimizing the effect on regeneration kinetics.

We are investigating two different mechanisms for accomplishing this goal. The first involves the use of different alkali and alkaline earth metals as promoters for the alumina sorbents to increase the surface basicity of the sorbent and thus adjust the number and distribution of adsorption sites. The second involves investigation of non-aqueous impregnation, as opposed to aqueous impregnation, as a method to obtain an evenly dispersed monolayer of the promoter on the surface.

Alkalized Aluminas

One of the first regenerable flue gas desulfurization catalysts was developed at the Bureau of Mines in Pittsburgh for the Department of Energy by Bienstock et al.[7-10] This catalyst consisted of an alkali deficient sodium aluminate (8% less Na than stoichiometric). This catalyst suffers from relatively high attrition losses due to loss of structural integrity during successive adsorption/regeneration cycles. As a way to avoid this problem, the alkali can be

deposited over the surface of an alumina support. When calcined, this material is thought to form a surface aluminate. This is the basis of the NOXSO catalyst[11] (3.1% Na_2CO_3 on γ-alumina) and other alkalized aluminas used for flue gas cleanup.

Regeneration of the catalyst is typically carried out with the aid of a reducing gas, since thermal decomposition requires temperatures which are too high to be useful as a commercial method of regeneration.[12] Regeneration can be accomplished with CO, H_2, H_2S, CH_4, or other saturated hydrocarbons. The products of regeneration are distributed among a variety of species depending on the reducing gas, its partial pressure, and the temperature.[11] SO_2 is typically the first regeneration product observed, presumably resulting from the desorption of chemisorbed SO_2. The next products seen depend on the reducing gas used but include COS, H_2S, and elemental sulfur. Surface sulfide, Na_2S, formed during the regeneration is hydrolyzed to Na_2O and H_2S by exposure of the sorbent to steam.

SO_2 Adsorption

Alumina sorbents doped with alkali metal are thought to adsorb SO_2 through interaction of SO_2 with a surface aluminate or surface oxide. Bare alumina will absorb SO_2 but it has been shown that the capacity is increased with the addition of alkali.[8-11,13] These sorbents will also scrub NO_x from the flue gas as well, making them very attractive flue gas cleanup catalysts.

Adsorption of SO_2 on bare alumina has been proposed to occur through adsorption at a variety of different sites, including adsorption at both Lewis base and Bronsted base sites.[3-6,14,15] Infrared spectroscopy has been used in all of these studies to develop a mechanism for adsorption of SO_2 at the various sites. These experiments involved both pulsed addition of SO_2 and desorption of the various adsorbed species under vacuum as a function of temperature. The most popular mechanism for the interaction involves the initial chemisorption of SO_2 at Lewis base sites with the eventual oxidation at high temperature (400°C) to sulfate.[5,6]

Alkali Impregnation

Studies by Hombek et al.[16] indicate that the larger alkali cations, K^+ and Cs^+, deposited from non-aqueous solution as ethoxides, do give rise to a more strongly basic alumina surface with a higher concentration of basic sites than does doping with Na^+. They found that the OH group concentration, the concentration of Bronsted base sites on the alumina surface, was greater on bare alumina than on any of the impregnated samples, with the cesium-doped sample giving values closest to those found for the bare substrate. These results imply that the increase in surface basicity on alkali-doped aluminas versus bare alumina results from a greater number of Lewis base sites. The researchers also observed that it required less potassium or cesium than sodium or lithium to generate a particular level of basicity.

Regeneration

The choice of a suitable desulfurization agent must include not only the adsorption

kinetics but also the regeneration kinetics. The regeneration of the adsorbent proceeds with a reducing agent. The desorbed products can be varied with the choice of reducing agent: hydrogen yields SO_2 as the major product, whereas reduction with CO gives H_2S as the major species. The kinetics of the regeneration are also affected by the choice of reducing agent. Regeneration is 60% faster with hydrogen as the reducing agent than CO.[11] Thus, the choice of reducing agent depends upon the kinetics, the desired product distribution, as well as the cost of the reducing agent.

Non-Aqueous Impregnation -- Metal Acetylacetonates

Metal acetylacetonates are prepared easily from the metal salt[17] and beta-diketones for most of the elements in the Periodic Table up to and including Group III (B, Al, Ga, In, & Tl). This synthetic flexibility makes the metal acetylacetonates very attractive precursors for supported catalysts. The ligands to the metal can be substituted on the ring such that the size of the ligands can be very large. The advantage of this substitution is that the ligands can act to limit the nearest approach of another metal acetylacetonate. On the surface of a support, this "buffer" zone occludes an area around the metal such that the metal ions can be separated by a minimum distance. In the case of copper acetylacetonate on silica, the acetylacetonate ring prevents the coppers from reacting with half of the available sites on the silica; thus, providing some spacing between the coppers. This spacing between the metal ions is useful in preventing sintering of the metal at high temperatures.

The chemistry of the acetylacetonates also merits interest. The conjugated rings are electron rich and thus are susceptible to electrophiles such as the protons of surface-bond hydroxyl groups. We have exploited this chemistry to attach copper acetylacetonate to the surface of silica as a thin film.[18-20] Others have attached iron acetylacetonate to titania as a monolayer film.[21] We believe this technique may be generally applied to all metal acetylacetonates. After attachment, we have removed in a controlled manner the ligands to expose the reactive sites attendant to the copper metal ion. We hope to explore this technique as a means to place the alkali/alkaline metal earths on alumina and render them active by ligand removal.

We have shown[20,22] that infrared diffuse reflectance spectroscopy, discussed in more detail below, can be used to determine the relative degree of dispersion of $Cu(acac)_2$ supported on silica.

Infrared Spectroscopy

Infrared spectroscopy provides critical information toward the elucidation of structures formed on adsorption of species on alumina. Virtually all of the assignments made regarding the structure of the more complex oxygenated species (SO_2, SO_3, SO_3^{2-}, HSO_3^-, SO_4^{2-}, HSO_4^-, NO_2, NO_2^-, NO_3^-, CO_2, HCO_2^-, CO_3^{2-}, HCO_3^-) on surfaces are carried out by comparison of

the infrared spectra of the surface-adsorbed species with those determined for metal coordination compounds, inorganic salts, and gas-phase species.[23-25] In the proposed study, the nature of the surface complexes formed is a key parameter. Knowledge of the types and relative amounts of the different surface complexes formed as a function of the identity of the alkali/alkaline earth additive or the impregnation method will allow us to manipulate the relative amounts of the surface species formed during adsorption in an intelligent way, thus maximizing the performance of the catalyst in terms of sorbent capacity and regeneration ability.

A significant data base exists on the infrared absorption spectroscopy of SO_2[3-6,14,15] adsorbed on bare alumina. An infrared investigation has been carried out on the interaction of SO_2 with NaOH-doped alumina[3] but the results were inconsistent with other studies. In addition, there are some disagreements regarding the assignment of the adsorbed SO_2 infrared absorptions to particular surface species which would require a significant amount of space to discuss. These inconsistencies appear to be related to the nature of the alumina used, catalyst pretreatment, and details of the experimental procedure used in the investigations. We will address these problems by using several different well-characterized supports with known but distinct degrees of crystallinity and impurity concentration, and by using isotopically labelled adsorbent and adsorbate where appropriate to aid the elucidation of the surface structure.

The technique of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been in use for several years, and has been shown to be particularly useful for the study of nitrate, carbonate, and sulfate species on supported catalysts.[26,27] The conversion of the diffuse reflectance data into spectra which vary in a linear way with concentration is accomplished via the Kubelka-Munk transform.[28] A idealized sketch of the DRIFTS interaction and a diagram of the controlled environment cell are shown in Figure 1.

All of the previous infrared studies of SO_2 on alumina have used the sampling technique of pressing self-supporting pellets of the sample under high pressure.[3-6] However, when using this type of sample, the interaction of reactant gases with the sorbent is very limited with respect to the bulk of the sample. Interaction occurs primarily at the faces of the pellet, with very slow diffusional processes controlling access of reactant gases to the bulk of the sample. This means that evolution of the surface species occuring as a result of the catalytic reaction take place at different observed rates as a function of distance through the pellet. Thus, unless experiments are very carefully carried out, transmission infrared spectroscopy of pressed pellets cannot be relied upon to give accurate kinetic information for rapidly changing surface species. Another major disadvantage of using pressed pellets in this type of study is that the process of preparing the pellet can change the nature of the support phase and the surface species themselves.[29]

With the DRIFTS technique, the sample is a powder and is not pressed under high pressure, maintaining the integrity of the support phase and the surface species. In addition,

reactant gases can flow through the sample, resulting in equal access of the reactant gases to all parts of the sample. Spectroscopic changes which are observed are occuring throughout the catalyst sample at the same time and at the same rate. Experiments carried out in this fashion have been shown to result in an order or magnitude improvement in reproducibility compared to static DRIFTS measurements.[30] DRIFTS has also been shown to have much greater sensitivity for supported species than normal transmission spectroscopy.[31] This increase in sensitivity is a result of multiple interactions of the infrared radiation with the supported surface species.

Experimental Method

Our approach involves obtaining two different types of information: 1) gravimetric data on the amount of SO_2 and NO_x adsorbed by the various solid materials investigated and the relative recovery of those materials upon heating and/or exposure to gas-phase reagents, and 2) infrared spectra of the solid before, during, and after exposure to SO_2 and NO_x, and during regeneration. The gravimetric data provides the key information regarding the physical adsorption capacity and regenerability of the materials as a function of time, temperature, gas composition, solid formulation, etc. The infrared data provides detailed information on the mode of adsorption of the gas-phase adsorbates and the ways in which various additives affect the distribution of suface species and their modes of decomposition. The coupling of these two types of information allows the optimization of the sorbent formulation for both of the critical processes which determine the utility of a regenerable adsorbant: 1) the adsorption of SO_2 and NO_x from flue gases and their conversion to stable surface species, and 2) the regeneration of the adsorbant to a capacity similar to its capacity before exposure to flue gases with only modest effort.

EXPERIMENTAL

We purchased the infrared diffuse reflectance optical equipment and the associated controlled environment cell from Harrick Scientific Corporation. We coupled this cell to vacuum pumps and a gas delivery system and checked the entire system for vacuum integrity and optical throughput. These interfaces include tubing and couplings to connect the pump to the cell, with integral valves for isolation of the cell from the pumping station as well as the gas delivery system. The combined roughing pump/diffusion pump system pumps the cell down to the limit of our current pressure gauge, < 1 mTorr. We designed, purchased, assembled, and checked out the temperature control system, and we have good control under vacuum, where thermal losses are confined to the sample support. A schematic diagram of the controlled environment cell and associated gas and temperature control system is shown in Figure 2.

Design work was completed to reconfigure the thermal gravimetric analyzer (TGA) in Dr. White's laboratory for this new project. The design involved the re-piping of a gas handling system and the installation of electronic mass flow meters and flow controllers. The Perkin-

Elmer TGA was repaired and refitted by Perkin-Elmer so that the extreme conditions of the adsorption experiments could be accommodated.

Both α– and γ–alumina have been used as sorbents.[3-6,8-15] Because of its inherently higher surface area, we have chosen to use γ–alumina as the support. Initially, four γ–aluminum oxides or γ–aluminas (γ–Al_2O_3) were studied to determine which ones would be appropriate for use as supports. Three of these materials are available in industrial-scale amounts and are of varying purities. One of these was obtained from Harshaw Chemical Company, and two others from the Alcoa Company (S-100 and F-100). These materials were analyzed by XPS to determine to determine their surface alkali content. We purchased an additional, high-purity γ-alumina (99.995%) from Goodfellow to establish a baseline for the commercial and doped alumina adsorption studies.

The infrared diffuse reflectance spectra are generated using a Nicolet 60-SXR FT-IR. Typically we use 2 cm^{-1} resolution and collect 1000 scans. Triangular apodization is used during the transformation of the spectra. The spectra of the samples are ratioed to a diffuse reflectance spectum of KBr, any residual water vapor is subtracted from the spectra after converting to absorbance, and the spectra are transformed using the Kubelka-Munk transform as discussed earlier.

RESULTS

Analyses of Aluminas

The Harshaw alumina and the two aluminas from Alcoa were studied by x-ray photoelectron spectroscopy (XPS) to determine the qualitative chemical composition of the surface region. These analyses are necessary to establish a standard alumina which contains no alkali so that the incremental benefit for adding alkali can be documented.

Bulk Analyses

Elemental analyses and physical properties for the aluminas are reported in the vendor's literature for the Alcoa products. These data are presented in Table 1.

Surface Analysis

The fresh aluminas were ground to fine powders and submitted for XPS analysis. The materials were not heated but simply evacuated at room temperature to ultrahigh vacuum conditions (1×10^{-10} torr). Surveys were conducted with 10-20 scans to affect signal averaging. The spectra are given in Figures 3-5. The Alcoa S-100 alumina (Fig. 3) Shows XPS signals from Al, O, C, No, K, Br, and Cl. Semi-quantitative surface analysis of this sample (Table 2) shows alkali present on the surface in minor but significant amounts (0.12 and 0.33 atom % for Na and K, respectively). Also, halogens are present in small amounts (0.41 and 0.10 atom % for

Br and Cl, respectively). The atom ratio of Al to O in this sample (42.3/54.6) is near that expected for stoichiometric alumina (40/60).

Table 1. Physical Properties and Analyses for Alcoa Aluminas

	Percent Composition	
Species	S-100	F-100
Al_2O_3	94.6	93.1
SiO_2	0.03	0.02
Fe_2O_3	0.05	0.02
CaO	---	0.02
TiO_2	---	0.005
Na_2O	0.35	0.35
Loss on Ignition	5.0	6.5
Surface area by BET method (m^2/g)	300	325

Table 2. Surface Elemental Analyses for Alcoa S-100.

Element	Percent Composition
Al	42.28
O	54.63
K	0.33
Na	0.12
Br	0.41
Cl	0.10
C*	2.13

*The source of carbon is adventitious carbon in the spectrometer.

The XPS analysis did not reveal any silica or iron oxide which appeared in the bulk elemental analysis. Moreover, sodium and the halogens detected in the XPS spectrum were not assayed in the bulk elemental analysis.

The XPS of the Harshaw and F-100 aluminas are very similar in that only Al, O, and C are found in the surface analysis. No alkali or halogens are present on these samples. However, these surface analyses do not show the sodium, silica, iron oxide, calcium oxide, and titania which are reported in the bulk elemental analysis of the Alcoa F-100.

XRD Analysis.

In order to determine the phase(s) of the alumina present in the Harshaw material, a sample of this material was submitted for powder, XRD analysis. (The Alcoa samples are reported in the sales literature as mixtures of Boehmite (AlOOH) and γ–alumina.) The sample was scanned for angles (27) between 0 and 80^0 (Figure 6). The small, broad peaks suggest that the crystallite size is small. The best match with a known sample occurs with Boehmite.

We have also purchased an ultra-high purity alumina from Goodfellow with the specifications shown in Table 3.

Table 3. Analysis and Physical Properties of the Goodfellow Alumina

Species	Bulk Analysis
Al_2O_3	99.995%
Si	8 ppm
Na	3 ppm
Mg	3 ppm
Cu	3 ppm
Fe	8 ppm

Specific Surface Area: 110-150 m^2/g

Crystalline Phase: γ-alumina

These surface and bulk analyses may be used to select an alumina as the commercial standard in these studies. (The Goodfellow Alumina will be used as a pure γ-alumina standard). Since alkali is a known promoter for the adsorption of SO_2 by alumina, it is desirable for the standard to have little or no surface alkali. A high surface area is also desirable. Since the Harshaw alumina has a surface area of 200 m^2/g, compared to the Alcoa F-100 surface area of 325 m^2/g; and the Alcoa S-100 shows considerable surface alkali compared to the absence of alkali for the Alcoa F-100, we choose the Alcoa F-100 as the commercial standard, to be compared to the Goodfellow alumina as the pure γ-alumina material.

DRIFTS Studies

As initial studies using the new diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) controlled environment cell and optical configuration, we have carried out experiments which involve the characterization of $Cu(acac)_2$ on Cabosil (a non-porous silica), a system which we had previously studied, and which we will use as a model system to compare the non-aqueous impregnation results with. The experiments have studied the behavior, as a function of temperature, of the supported complex under vacuum. In an oxygen-rich

atmosphere, the supported complex has been shown to decompose in two steps, involving the sequential loss of the two acetylacetonate ligands. The first loss is in the temperature range 180-300°C, the second is in the range 300-400°C. The DRIFT spectra in the 1800 - 1300 cm^{-1} region, the region which we have used to characterize the coverage of the complex on Cabosil, as a function of temperature are shown in Figure 7. Three different spectra are shown, all on the same scale. The lowest intensity spectrum was taken at 25°C, the middle spectrum was taken at 100°C, the most intense spectrum was obtained at 250°C. From previous studies,[20,22] we know that the particular weight loading of the complex on Cabosil in this sample leads to the formation of less than a complete monolayer. We also know that the presence of the peak at 1552 cm^{-1} indicates the presence of multiple layers. The explanation for the curious increase in overall intensity and formation of multiple layers is that we are observing a sublimation process. As can be seen from Figure 1, the sample powder is heated from the bottom and the infrared radiation is incident at the top. As the $Cu(acac)_2$ near the bottom of the sample sublimes and condenses on cooler sample grains higher in the sample powder, it forms multiple layers. The sublimed complexes also contribute more to the observed absorbance when they are near the top of the sample than near the bottom, due to the nature of the diffuse reflectance technique. This is an important observation since it points out that when the sample is under vacuum, and there is little net flow through the sample to the pumps, that there is very little driving force removing evolved species from the sample. It will be a critical observation to keep in mind when evaluating the results from thermal desorption experiments.

Dehydration of Aluminas: TGA and DRIFTS Results

We have examined the dehydration behavior of the two particular aluminas which we have chosen to use as "standard" materials, a 99.995% pure γ-alumina from Goodfellow with a surface area of 110 -150 m^2/g and a "commercial" alumina from Alcoa, containing significant amounts of Boehmite, with a surface area of 325 m^2/g.[32] Figures 8 through 11 are the thermogravimetric analysis (TGA) results from the two different materials. Figures 8 and 9 show the percent weight losses as a function of temperature for the Goodfellow and Alcoa aluminas, respectively. The Goodfellow alumina loses approximately 7% of its total weight on heating to 800°C, while the Alcoa alumina loses 18.75%.

Figures 10 and 11 show the absolute weight losses as a function of temperature (trace A in the two figures) as well as the differential weight loss with temperature, dW/dT, (trace B in the two figures) for the Goodfellow and Alcoa aluminas, respectively. Peaks in the dW/dT traces correspond to losses of chemically distinct species. For example, a peak occurs in the dW/dT traces for both materials between 50°C and 100°C. This peak corresponds to the loss of physisorbed water. This is the only peak seen in the Goodfellow dW/dT trace has a maximum at 52°C. The gradual weight loss with increasing temperature above 100°C for this material

corresponds to gradual condensation of neighboring surface OH groups to form water which then escapes.

The Alcoa material behaves significantly differently. Like the Goodfellow alumina, it has as its major weight loss the escape of physisorbed water. Compared to the corresponding peak for the Goodfellow alumina, however, this peak for the Alcoa alumina is slightly broader and shifted to higher temperature, with a maximum at 73°C. These results indicate a greater variety of adsorption sites, which, on the average, interact more strongly with water than those found on the pure γ-alumina. The peak in the dW/dT spectrum at approximately 450°C is entirely consistent with our earlier results from this material showing significant amounts of Boehmite.[32] Boehmite is known[33] to decompose over the range 450 -500°C:

$$2\ Al(OOH)\ H \rightarrow Al_2O_3 + H_2O.$$

Based on stoichiometry, pure Boehmite should lose 15% of its initial weight via this route.

Figures 12 and 13 are diffuse reflectance infrared spectra of the neat Goodfellow and Alcoa alumina powders, respectively, at room temperature. No dehydration has been carried out on these materials. What is interesting in these spectra is that even before dehydration, the Alcoa alumina still contains some "free" OH groups, indicated by the 3750cm^{-1} absorption, whereas the Goodfellow γ–alumina does not. This, again, is consistent with the identification of significant amounts of Boehmite in the Alcoa material.

We anticipate that the nature of the sorbent support used for the overall sorbent development study will have significant effects on the ability of the sorbent to selectively adsorb SO_2 and then release the adsorbed species at a "reasonable" temperature. The studies described here establish the properties of the undoped aluminas and will be used when comparing the properties of the aluminas which have been doped with alkali to define the level of improvement offered by the alkali and the different impregnation methods.

PROBLEMS

Students

An Hispanic Clark Atlanta University student, Willer Pos, agreed to begin work on the project in May, and performed very well through the summer. At the beginning of September, however, he informed one of the principal investigators, MBM, that he was leaving graduate school. The next day he left, and would not say what he was going to do, except that he was going to try to attend graduate school elsewhere. He cited personal reasons as his motivation for this change, and would not discuss staying to finish at least a Master's degree.

FT-IR Detectors

One of the results from the initial DRIFTS studies was that, in order to be able to distinguish different forms of chemisorbed SO_2 on the surface of the alumina, we would need to use a more sensitive detector than the one used to obtain the dehydration results. The alumina infrared absorption at approximately $1000cm^{-1}$ was simply too strong for that detector to see any differences when SO_2 was adsorbed on the surface. We have another detector which is significantly more sensitive, but that detector was not functioning. We were able, finally, to fix that detector, but have not been able to obtain the SO_2 adsorption results yet.

DRIFTS Controlled Environment Cell

In order to protect the controlled environment cell from corrosion by SO_2, we sent the cell back to the manufacturer, Harrick Scientific Corporation, to be gold coated. That process has taken *much* longer than initially anticipated. After approximately two months and several telephone calls, Harrick Scientific sent the cell back, but the gold coating was flaking off in several places and, after some discussion with the engineer in charge, we sent it back to be re-coated. Harrick Scientific does not perform the gold-coating themselves, but send it to an outside contractor. The re-coating was supposed to be accomplished within about two weeks. After two months without hearing from Harrick Scientific, we found out that nothing had been accomplished. The initial contractor claimed he could do no better and other contractors that could be found wanted significantly more money for the job. However, no one had communicated any of that to us. Needless to say, we are very disappointed with Harrick Scientific. They have agreed to send the cell back with the original gold coating.

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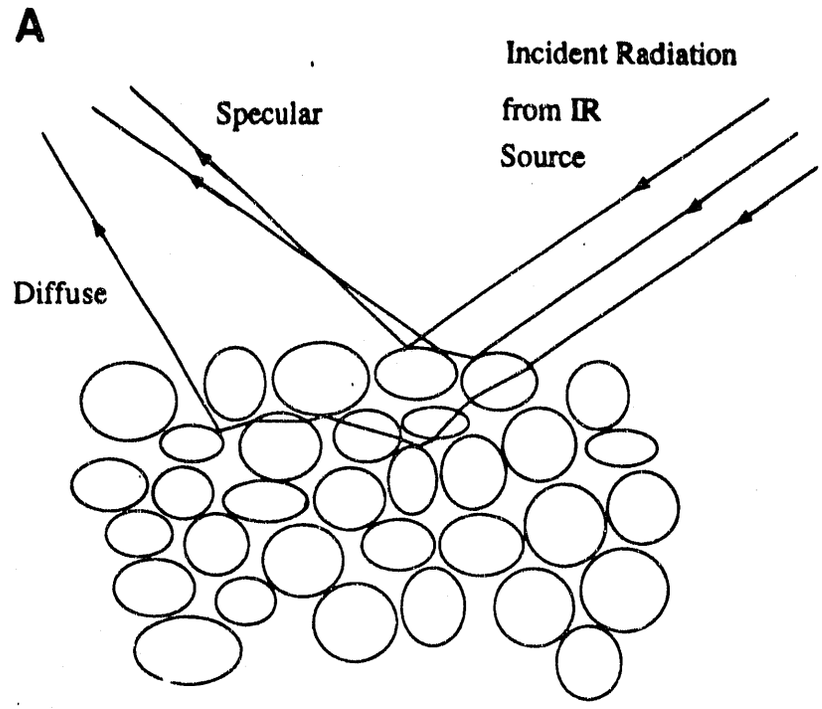

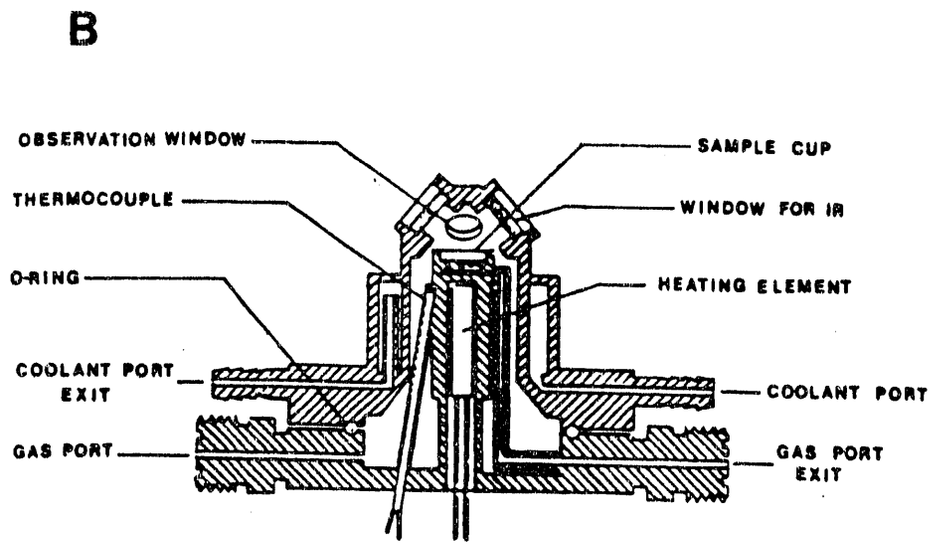

Figure 1. A) Visualization of the interaction of electromagnetic radiation with a powdered sample in the diffuse reflectance experiment. B) Drawing of the Harrick Scientific controlled environment cell for DRIFTS studies.

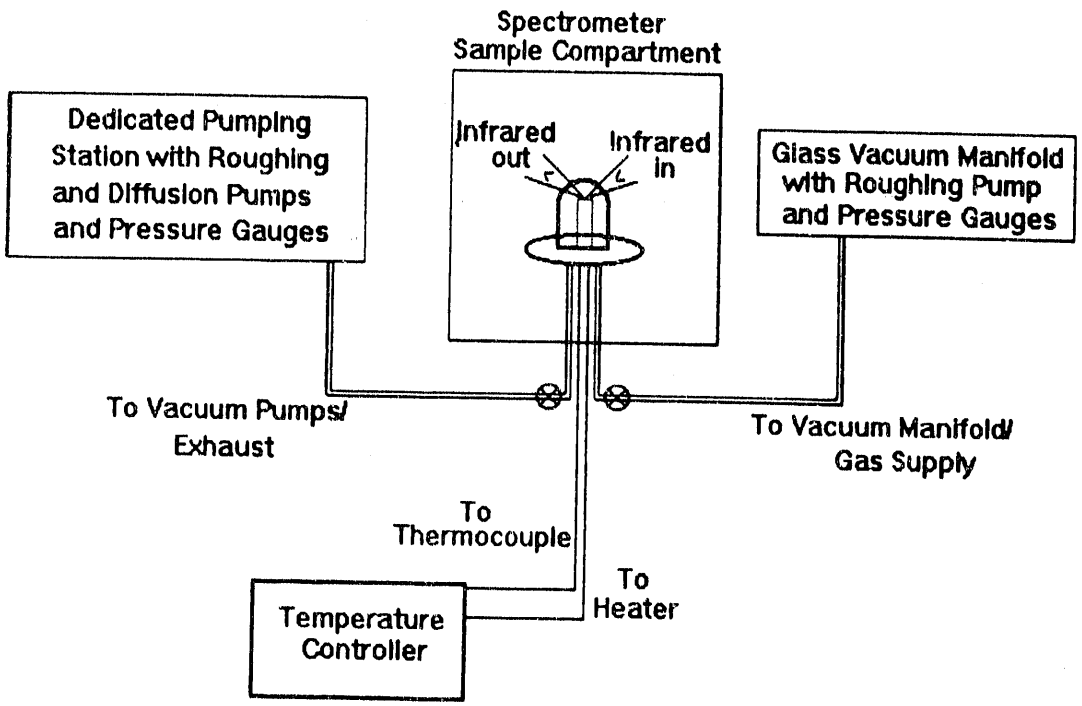

Figure 2. Schematic diagram of the DRIFTS experimental set-up. The DRIFTS controlled environment cell is shown inside the dry air-purged sample compartment of the Nicolet FT-IR. "Infrared in" and "Infrared out" refer to electromagnetic radiaiton being transmitted through the infrared-transparent windows to and from the sample powder.

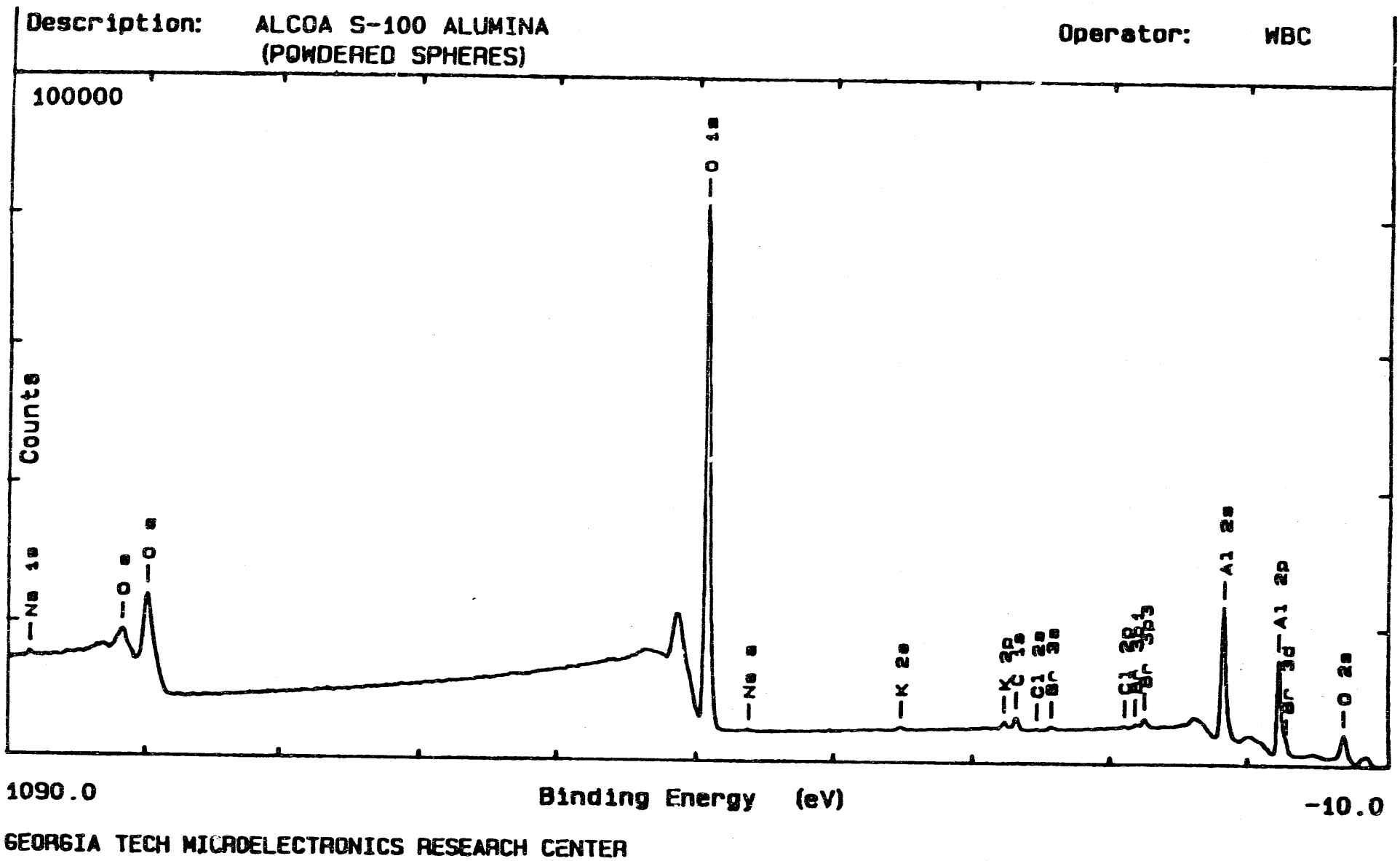

Figure 3. XPS of Alcoa Alumina S-100.

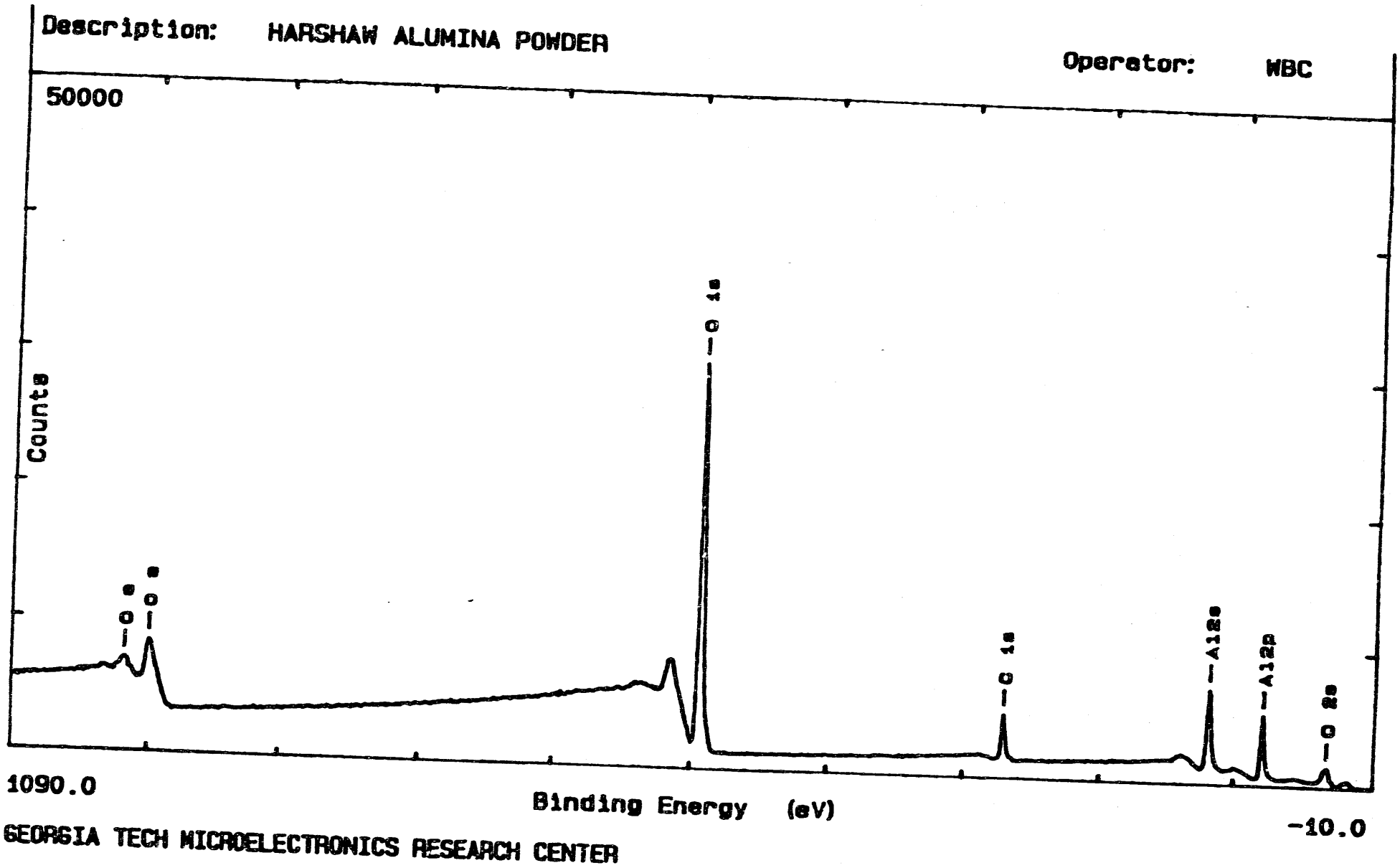

Figure 4. XPS of Harshaw Alumina.

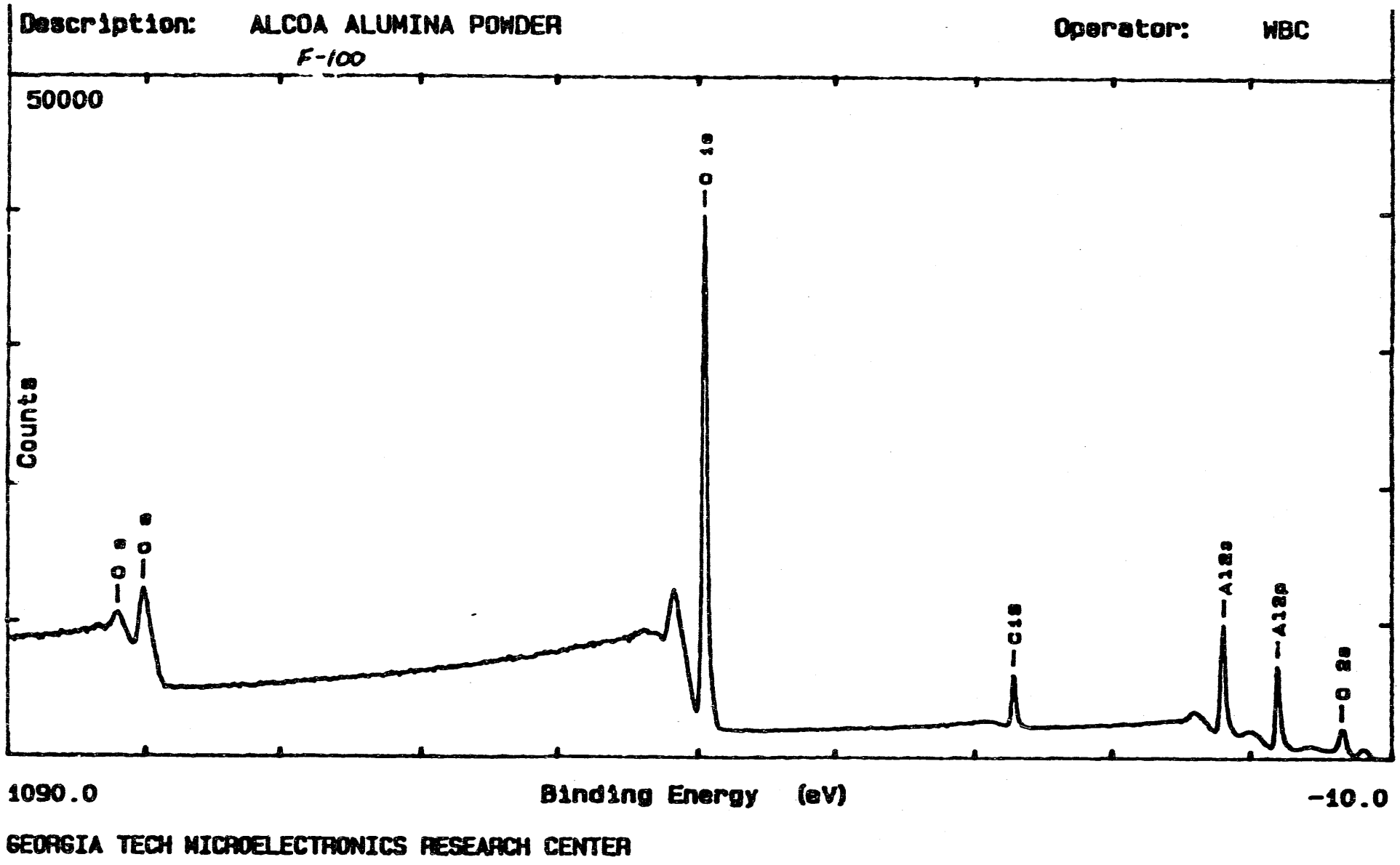

Figure 5. XPS of Alcoa Alumina F-100.

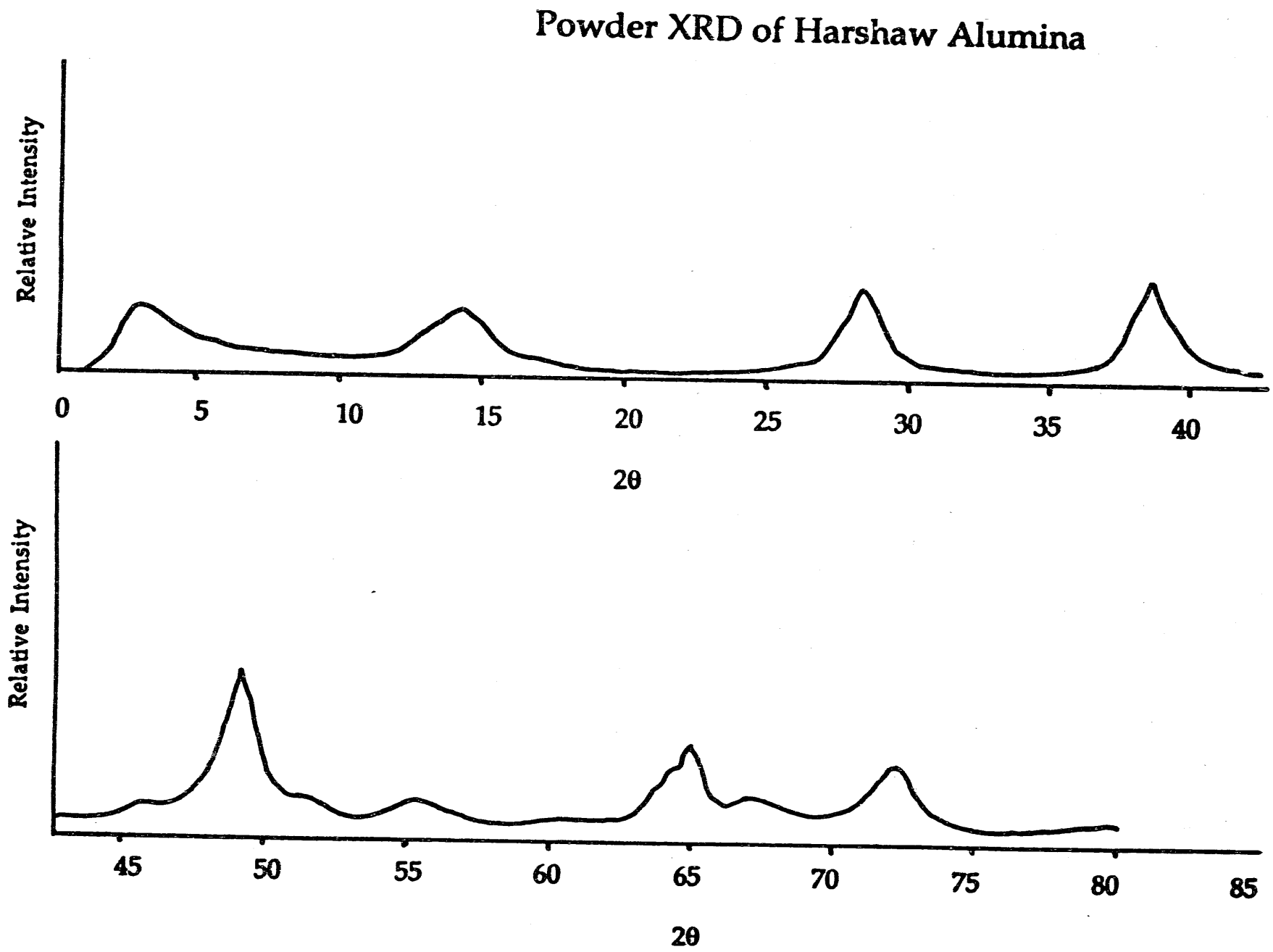

Figure 6. Powder XRD of Harshaw Alumina.

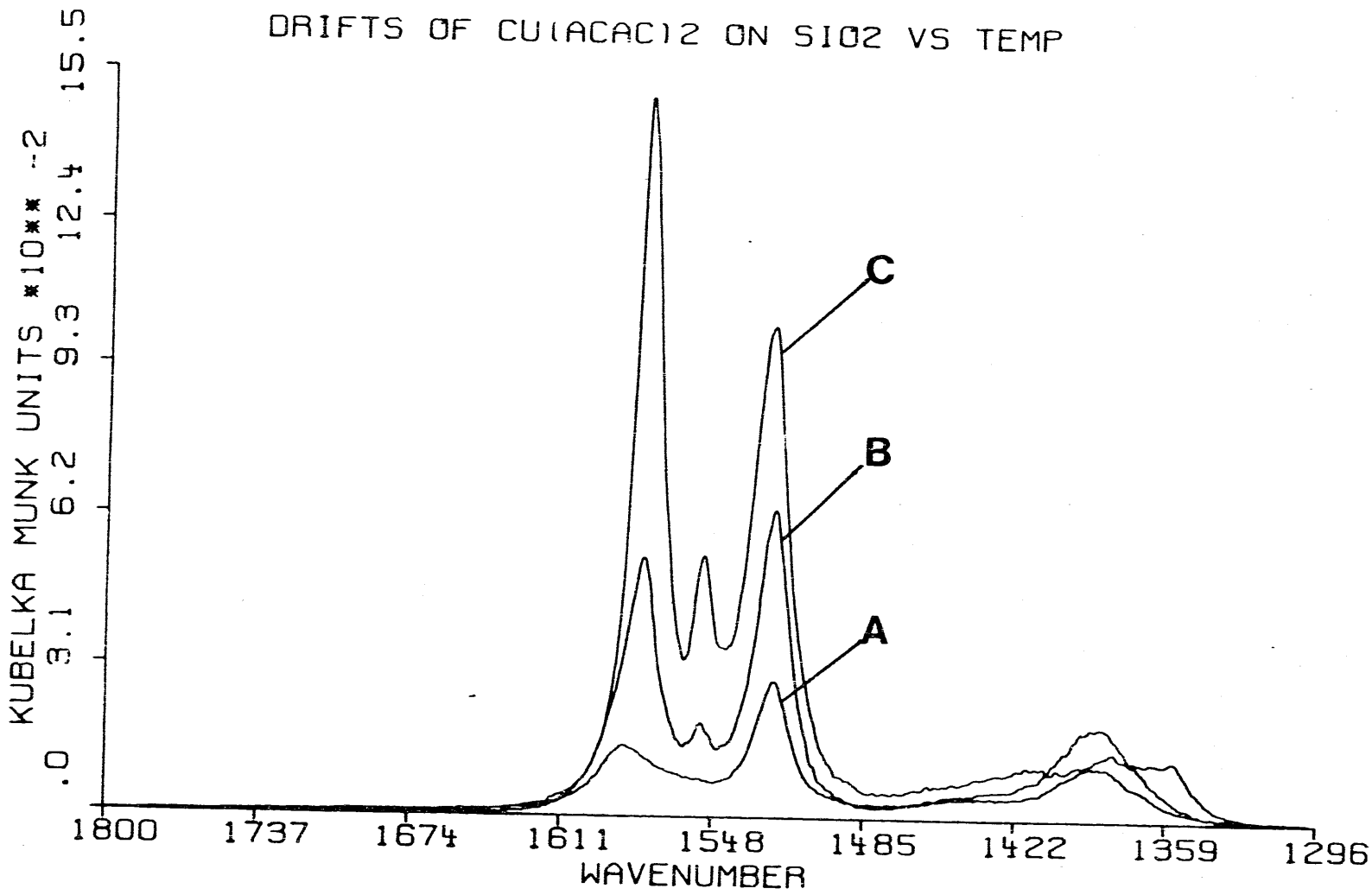

Figure 7. DRIFT spectra of a 2.5% by weight Cu (as $Cu(acac)_2$) on Cabosil. Spectrum A was taken at 25°C, spectrum B at 100°C and spectrum C at 250°C. The true relative intensities are shown.

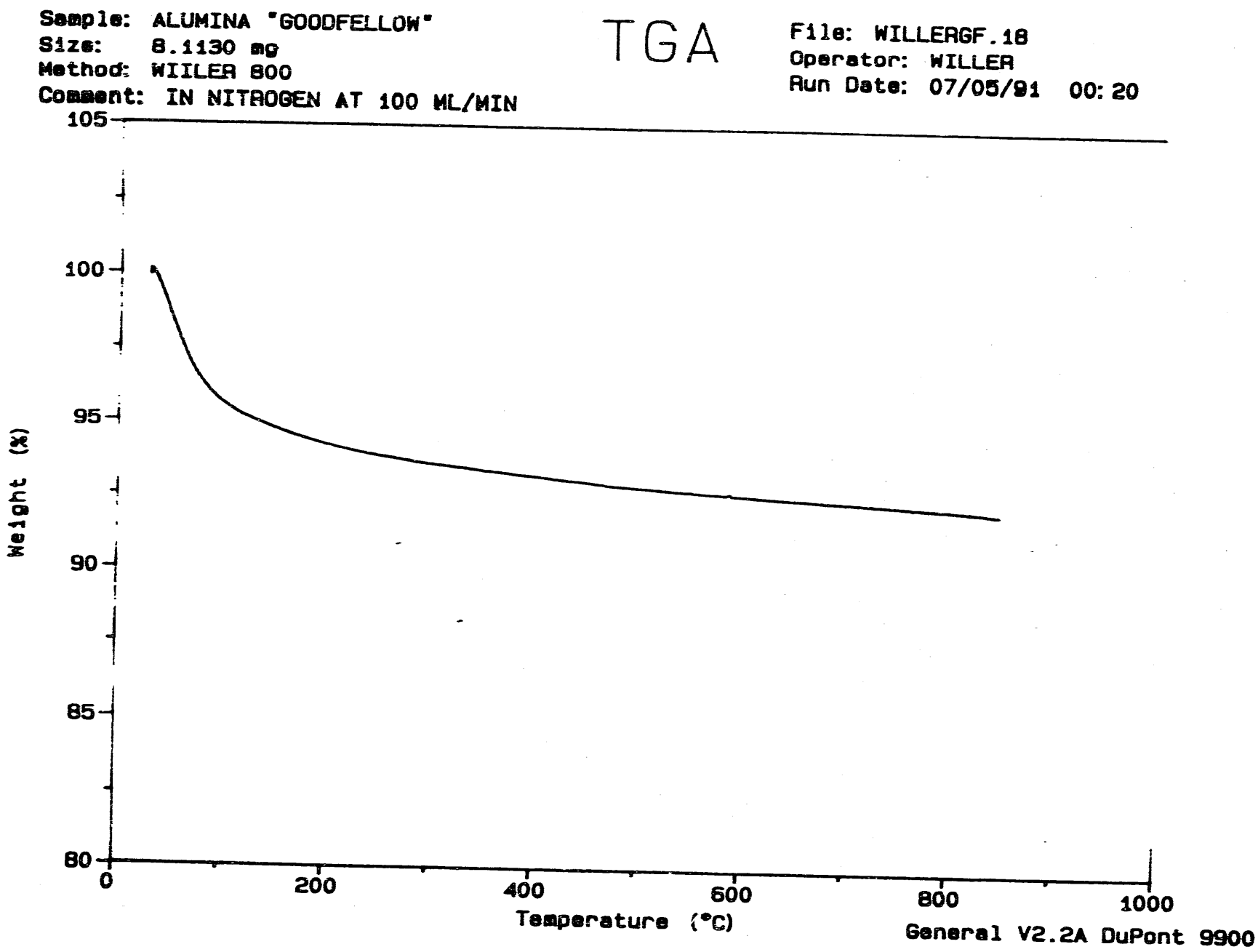

Figure 8. TGA of Goodfellow Alumina - Percent Weight Loss.

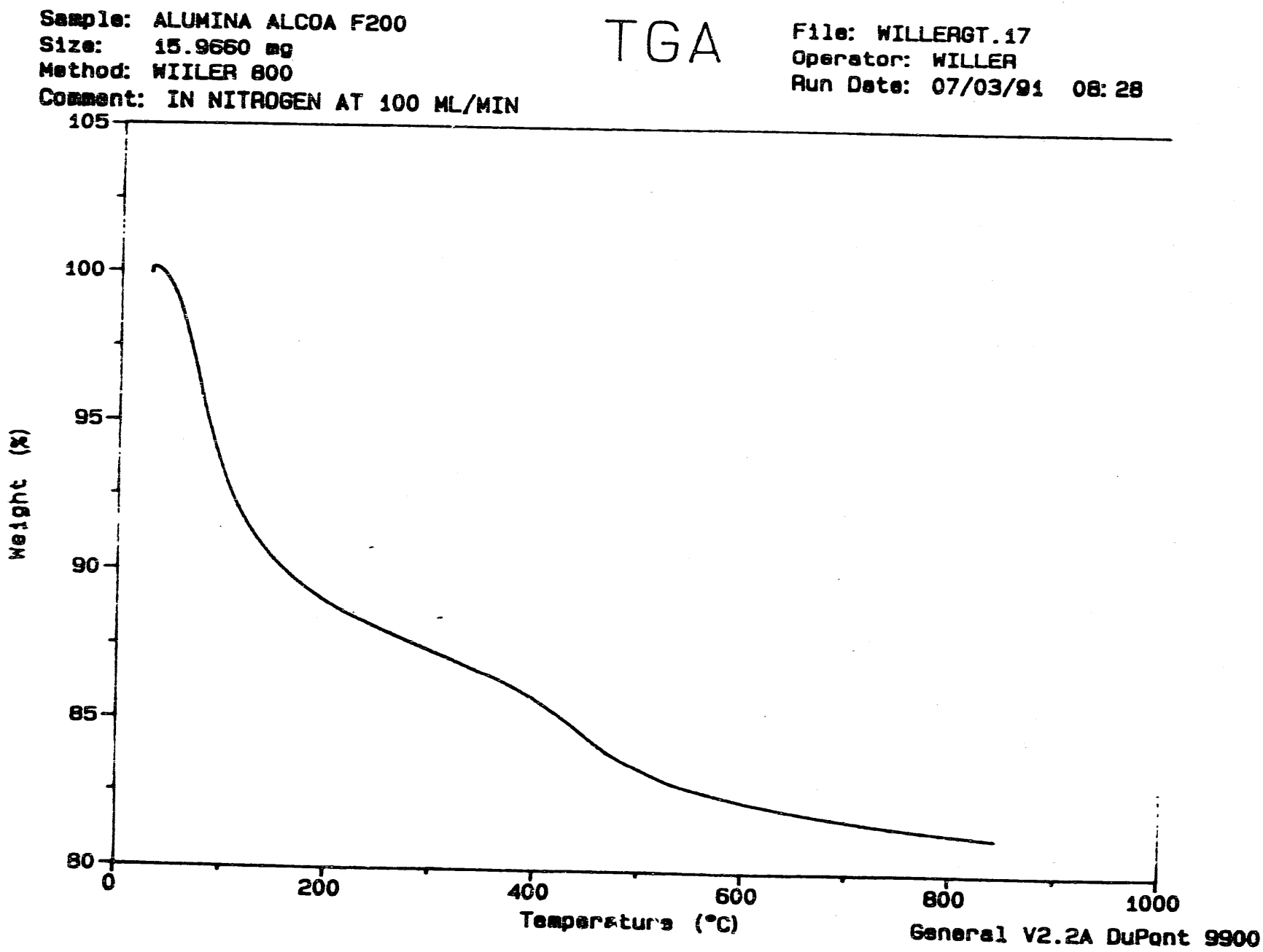

Figure 9. TGA of Alcoa Alumina - Percent Weight Loss.

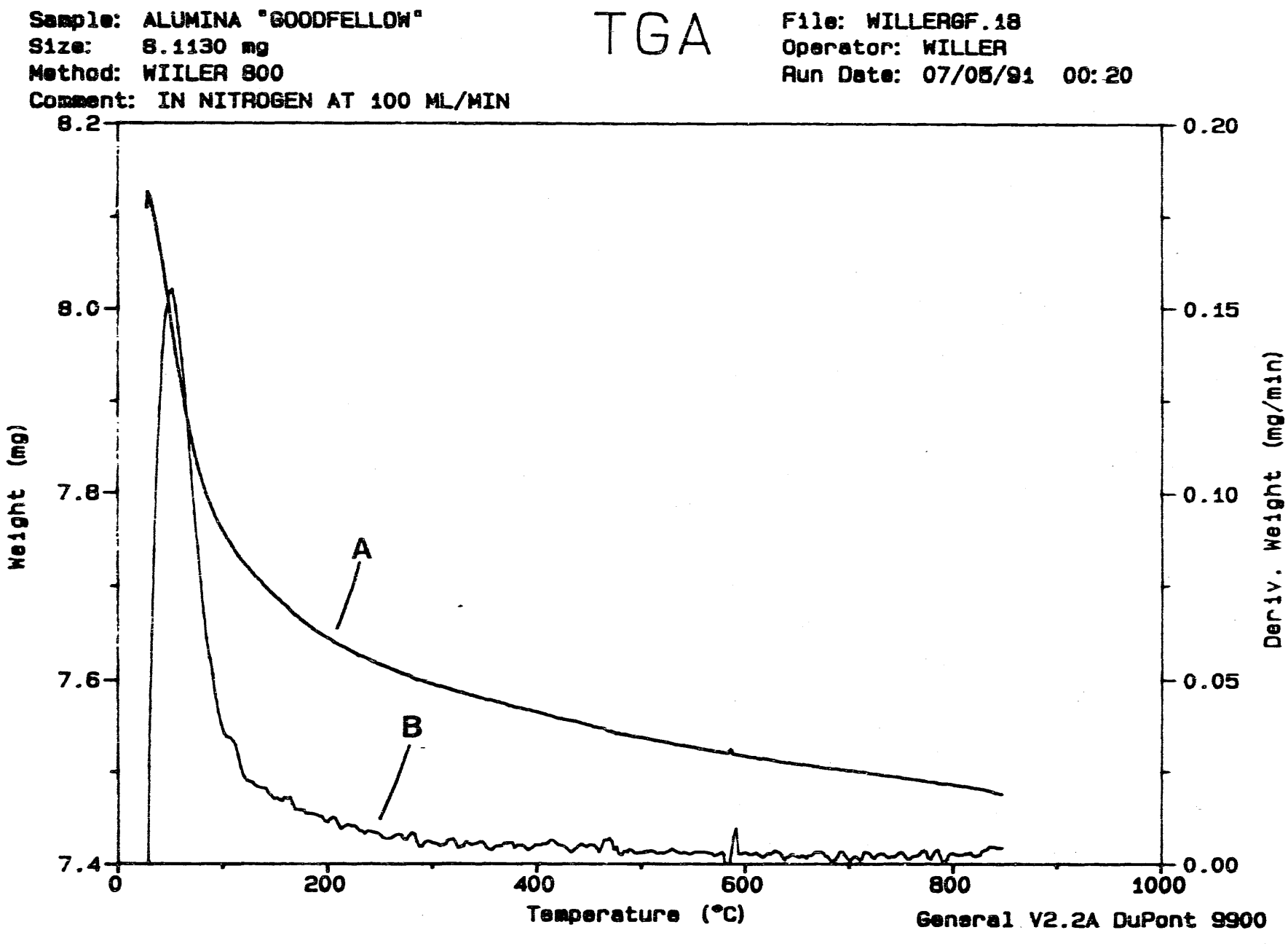

Figure 10. TGA of Goodfellow Alumina: a) Absolute weight loss; b) dW/dT plot.

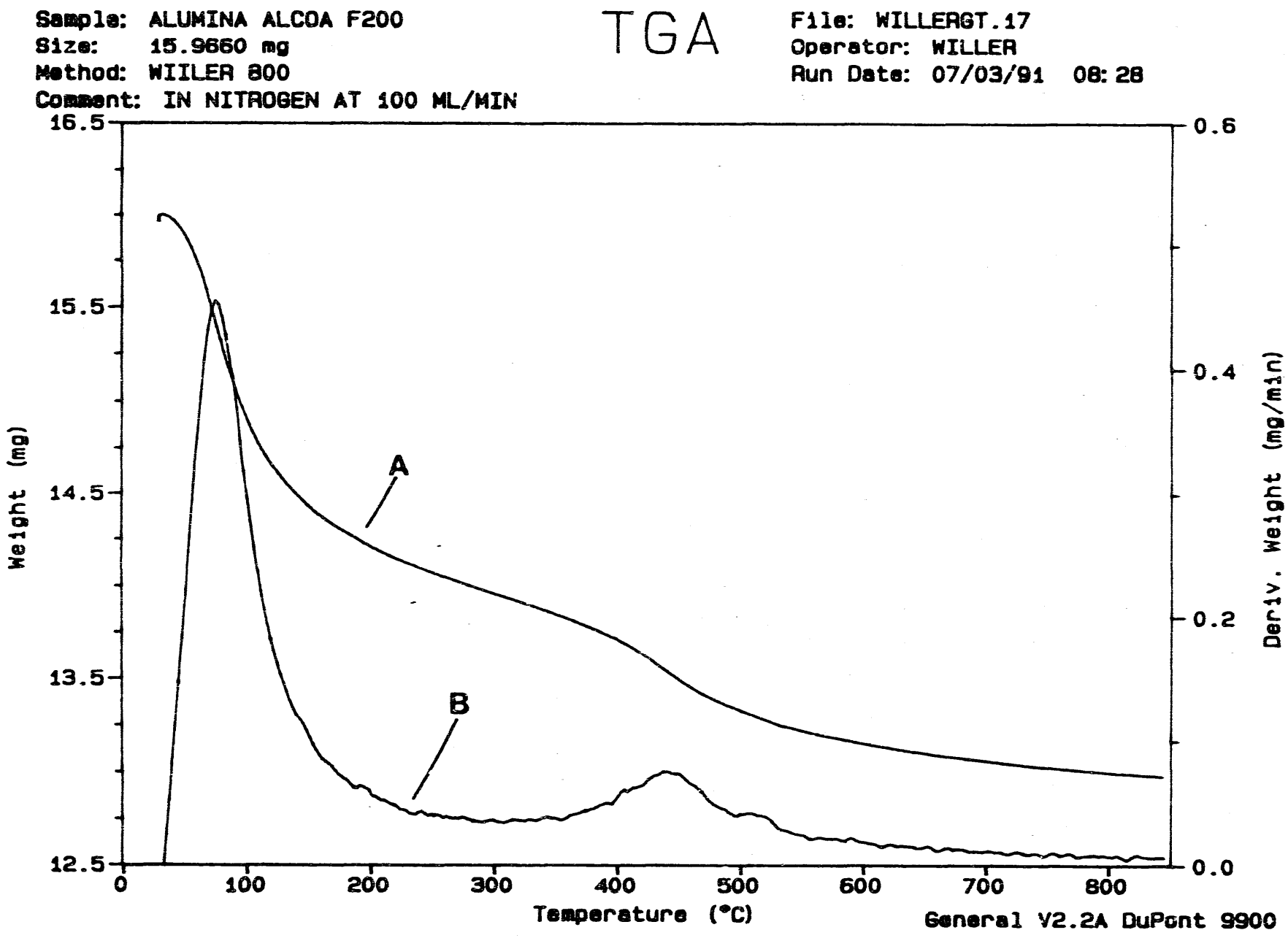

Figure 11. TGA of Alcoa Alumina: a) Absolute weight loss; b) dW/dT plot.

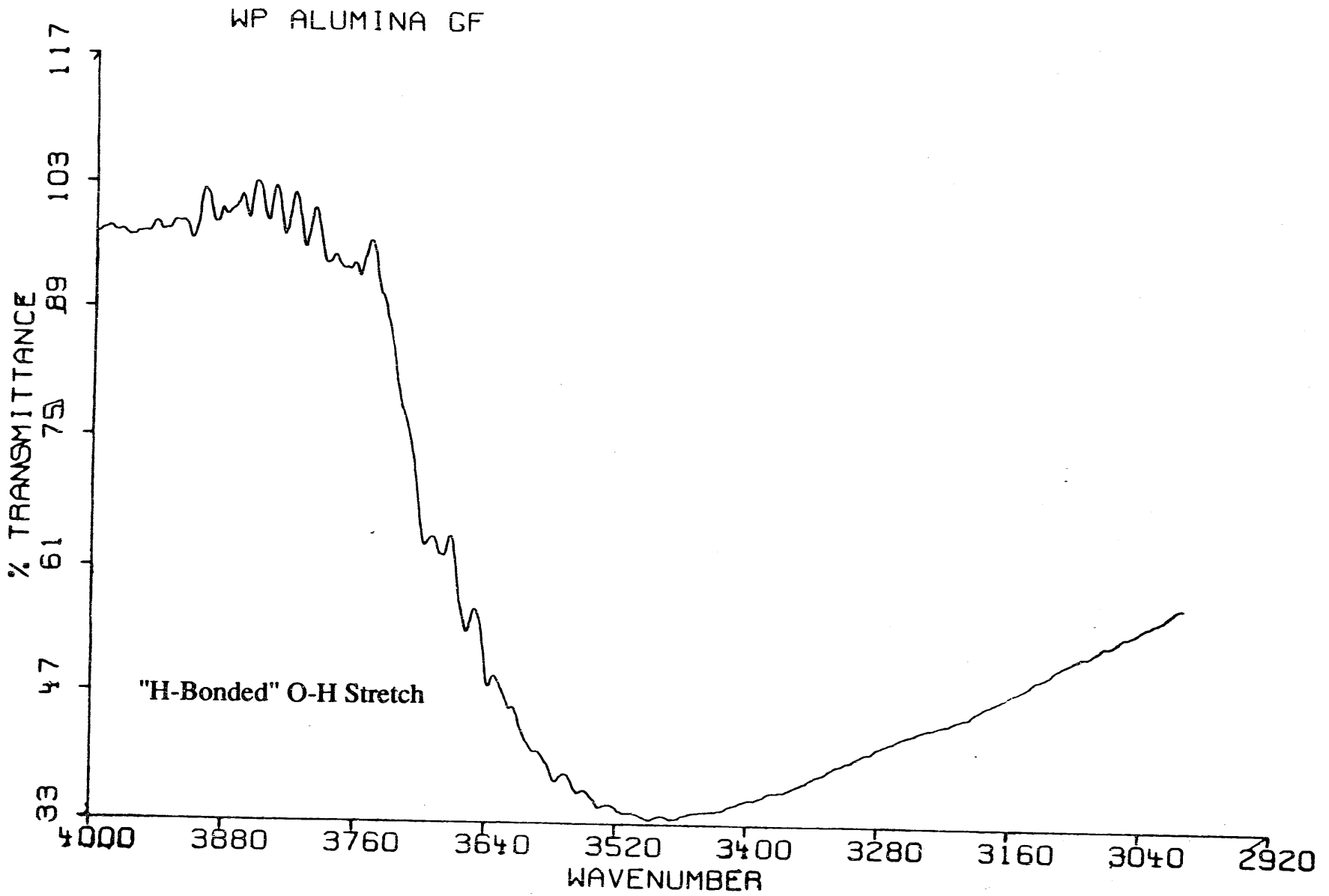

Figure 12. DRIFT spectrum of Goodfellow Alumina. (Spectrum plotted as Transmittance).

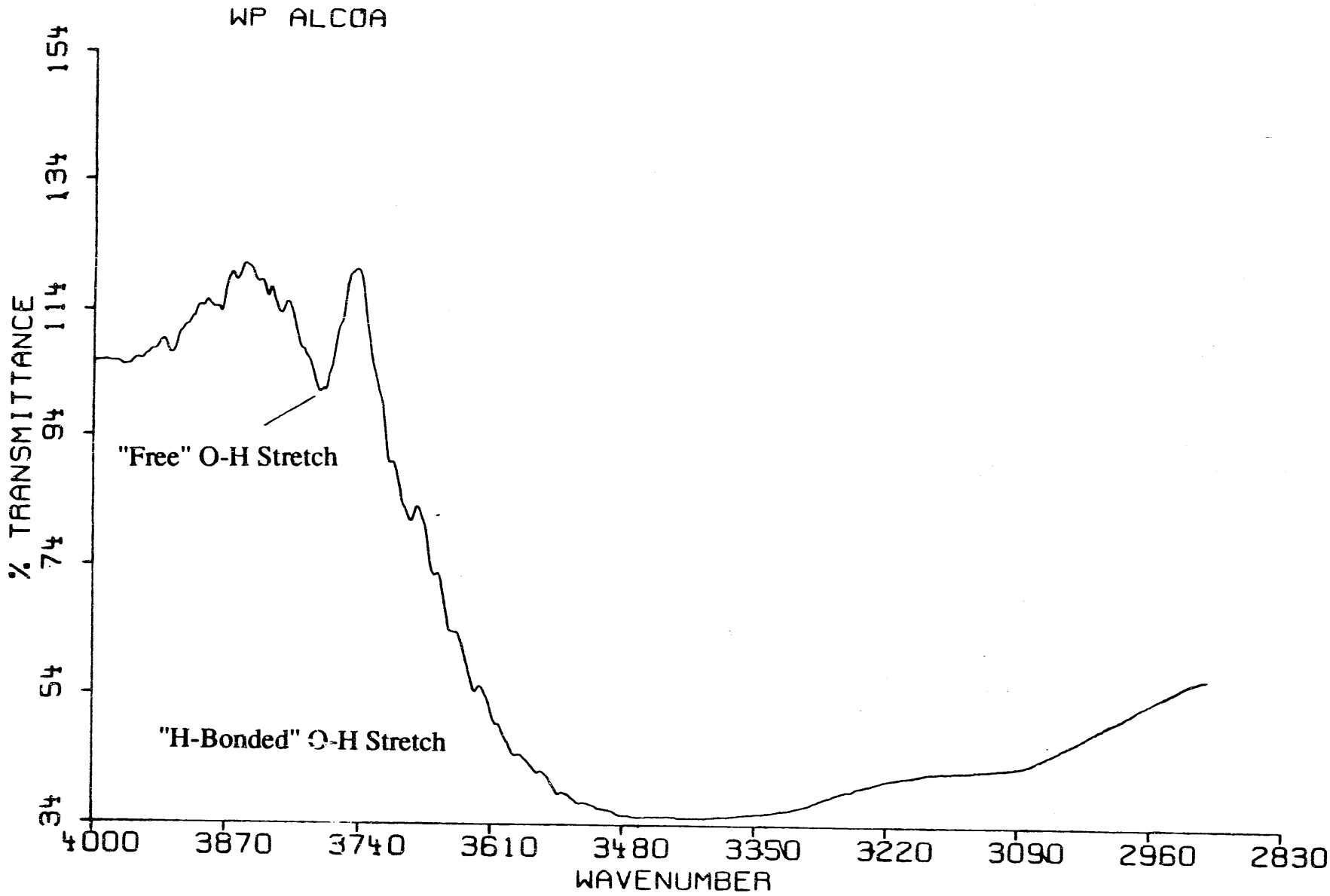

Figure 13. DRIFT spectrum of Alcoa Alumina. (Spectrum plotted as Transmittance).

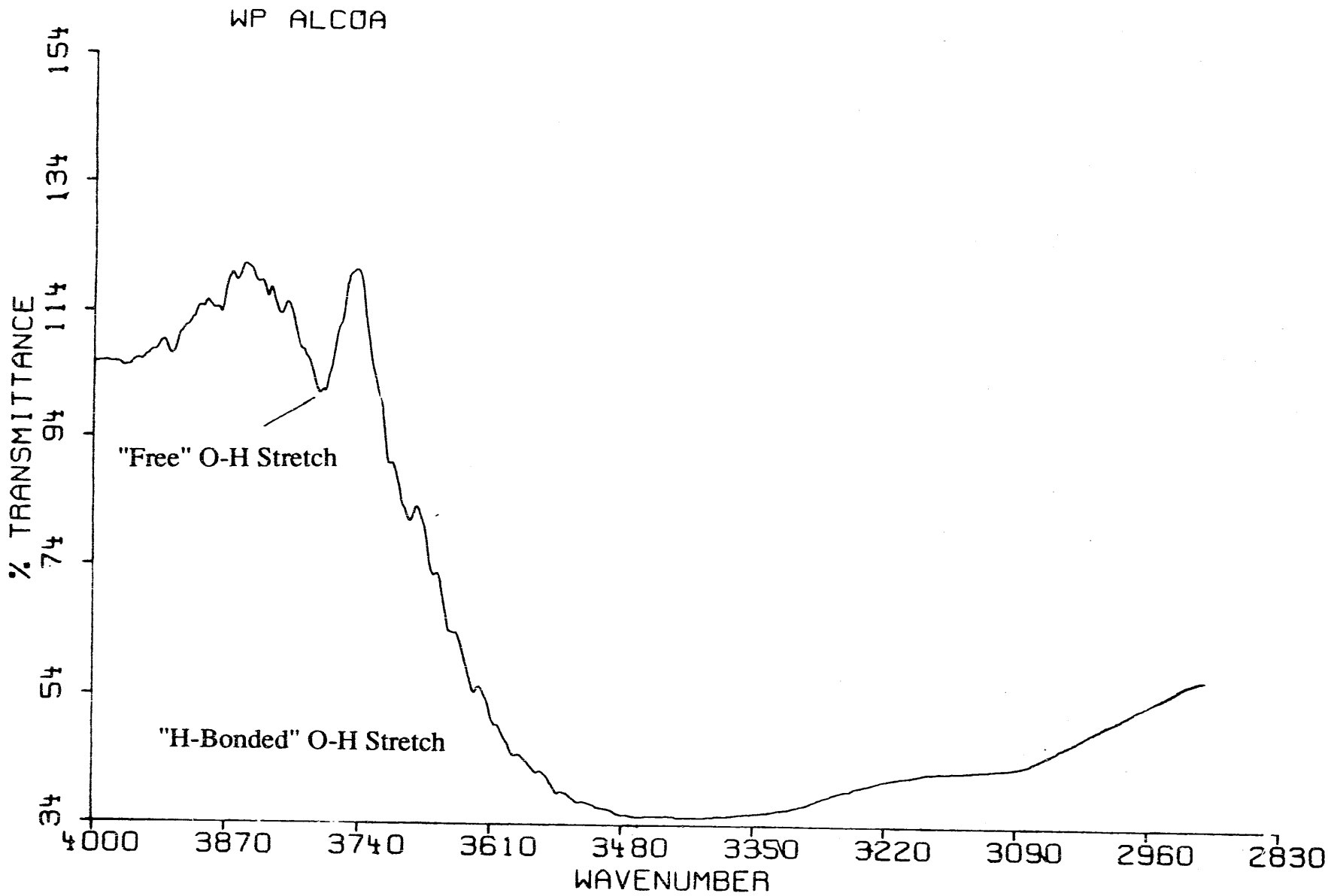

Figure 13. DRIFT spectrum of Alcoa Alumina. (Spectrum plotted as Transmittance).

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