DOE/MT/92017--T3

PROGRESS REPORT

1. GRANT NUMBER: DE-FG22-92MT92017

2. PERIOD COVERED BY REPORT: October 1, 1994 - December 31, 1994

3. TITLE OF PROPOSAL: SIMULTANEOUS SO_2/NO_X ABATEMENT USING ZEOLITE-SUPPORTED COPPER.

4. NAME OF INSTITUTION: Clark Atlanta University

5. AUTHOR(S) OF REPORT: Drs. Mark B. Mitchell and Mark G. White

RECEIVED
USDOE/PETC
95 MAR 30 AM 11:24
ACQUISITION & ASSISTANCE DIV.

US/DOE Patent Clearance is <u>not</u> required prior to the publication of this document.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DLC

ABSTRACT

We have made progress in characterizing a Cu-exchanged ZSM-5 for NO decomposition activity. Additionally, we are pursuing the impregnation of alumina with vanadium and copper and studying the adsorption and reaction of SO_2 on these catalysts.

RESULTS

Reactivity of Cu-ZSM-5. We prepared a sample according to the technique of Li and Hall [Li, Y.; Hall, W. K. *J. Catal.*, **1991**, *129*, 202]. We prepared a catalyst by their preparation to show about 2 wt/wt% Cu (0.32 mmole Cu/g). Shown in Figure 1 are the data from our attempts to synthesize the Li and Hall catalyst (denoted here as Cu L-H) and reproduce the data from the literature (denoted here as L-H data). The coppper loading of the catalyst reported in the literature is 0.49 mmole Cu/g. The results in this figure suggest that the data collected in our lab may fit onto a line extending through the literature data. From this we conclude that we are able to reproduce the Li and Hall catalyst in our labs to be used as a standard for comparison to new catalysts.

Also shown in the same figure are the results of a catalyst prepared by ion exchanging $Cu(en)^{2+}$ into the same type of zeolite for which the loading of Cu is 1 wt/wt% (0.16 mmole Cu/g). This catalyst is considerably less active (initial slope about 1/7 that of the Cu L-H catalyst) than the comparison catalyst (Cu L-H) prepared in our labs.

Modeling of the Cu/zeolite catalyst. We have medeled the ion exchange complex of the $Cu(en)^{2+}$ in ZSM-5 (Figures 2 and 3). One view of the zeolite (Figure 2) shows an end view of the cation sited along the main axis of a channel in the zeolite. Two channels orthogonal to this channel show the cations in locations above and below the cation in the main axis. From a detailed analysis of these figures we will be able to predict the fraction of Cu ions which will be located proximally to form Cu ensembles containing two or more atoms upon decomposition of the complex. We are in the process of analyzing these figures to determine whether or not they allow a rationalization of the observed behavior.

Copper and Vanadium Impregnation of Alumina.

We have investigated the impregnation of alumina surfaces using acetylacetonate ligands, specifically Cu(II) acetylacetonate [$Cu(acac)_2$] and vanadyl (IV) acetylacetonate [$V(O)(acac)_2$]. We reported earlier on the results of the impregnation of vanadyl acetylacetonate on alumina [Mitchell, M. B.; White, M. W. Second Yearly Progress Report (10/1/93 - 9/31/94), Submitted to Pittsburgh Energy Technology Center]. The results were not promising with regard to our ability to evaluate the loading or dispersion of the vanadium complex on the surface using FT-IR techniques as we had done with $Cu(acac)_2$ on silica [Mitchell, M. B.; Chakravarthy, V. R.; White, M. G. *Langmuir*, **1994**, *10*, 4523]. The copper impregnation was carried out by mixing 5g of alumina (Goodfellow, 99.9%, 45µm average particle size) in 75 ml acetonitrile (Aldrich, dried over molecular seives). Appropriate amounts of copper acetylacetonate (Aldrich) were added to 25 ml acetonitrile and dissolved. The acetylacetonate solution was added to the solution containing the alumina, and the resultant solution was stirred for 24 hours at room temperature.

Following this, the solid was vacuum filtered and dried under vacuum for 24 hours. For FT-IR analysis, the samples were sieved (63μm average hole width) and mixed with KBr 5% by weight.

The results of the copper acetylacetonate impregnation are shown in Figure 4. Figure 4 is the adsorption isotherm calculated from the atomic analyses on the supported samples (Galbraith Laboratories, Knoxville, TN) and the known impregnation solution concentration. The line A on the plot is a linear regression best fit to the four points shown on the graph, line B on the plot is a fit which ignores the lowest data point, which appears to be in error. Even the highest line, however, represents only a 4% uptake of vanadium from solution onto the alumina surface. Also, we do not appear to be anywhere near saturation for the adsorption of vanadium onto the alumina surface. Only more data points will provide the necessary information.

Both the copper and the vanadyl acetylacetonate impregnations give FT-IR diffuse reflectance spectra which do not correlate well with metal loading, which indicates that the complex is probably decomposing on the surface to give a surface-bound metal oxide while the ligand is released in a protonated form to solution. This observation has been reported by others [Van Veen, J. A. R. *J. Coll. Interface. Sci.*, **1988**, *121*, 214].

Infrared diffuse reflectance spectra of the supported vanadyl acetylacetonate complex were presented earlier. Spectra of the supported copper complex at different weight loadings are shown in Figures 5 - 8, in order of increasing solution concentration. For example, Figure 7 is the diffuse reflectance spectrum from the sample with the lowest surface vanadium concentration, yet the absorption intensity in the region 1800 - 1200 cm^{-1} is the highest of any of the samples prepared. This indicates that species other than vanadyl acetylacetonate are present on the surface or contributing to the spectra.

Given these rather unsatisfactory results, we cannot use infrared diffuse reflectance spectroscopy to characterize the nature of the metal content and dispersion. We have had great success, however, in using infrared diffuse reflectance spectroscopy to characterize the adsorption and reaction of sulfur dioxide on alumina and alkalized aluminas [Mitchell, M. B.; Sheinker, V. R.; White, M. G. "Adsorption and Reaction of Sulfur Dioxide on Alumina and Alkalized Aluminas - DRIFTS and TGA Results," to be submitted to *Langmuir*]. Therefore, the next progress report will contain the results of our initial studies of the adsorbed SO_2 and NO/NO_2 on these materials.

Figure 1 Comparison of Catalytic Activity for NO Decomposition

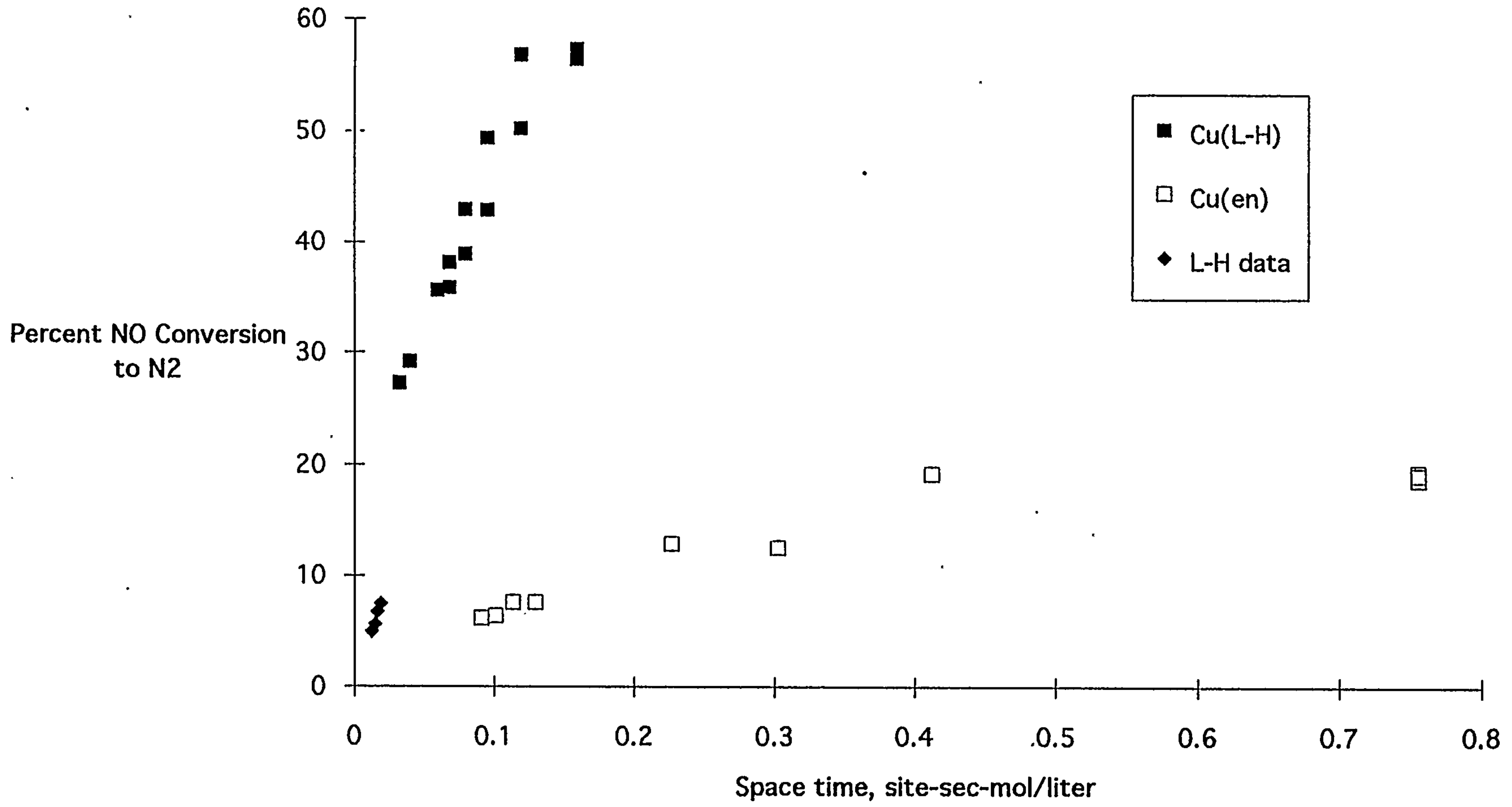


Figure 2 Simulation of Cu(en)2+ Cation Residing in Major Channels of ZSM-5

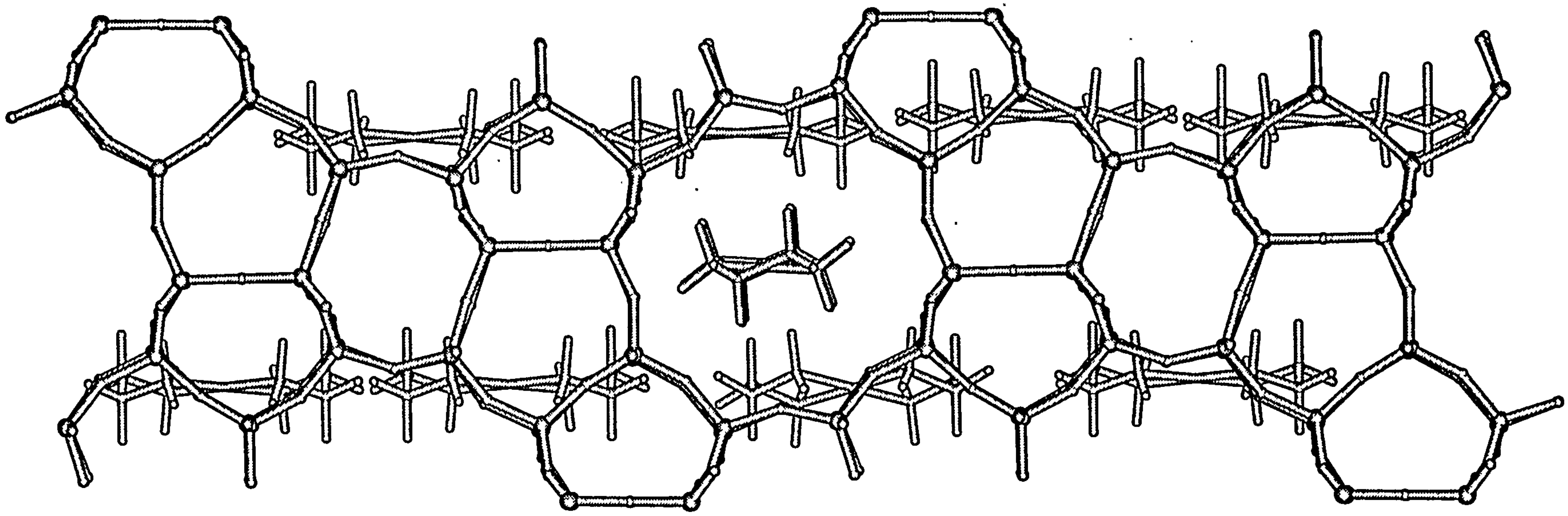
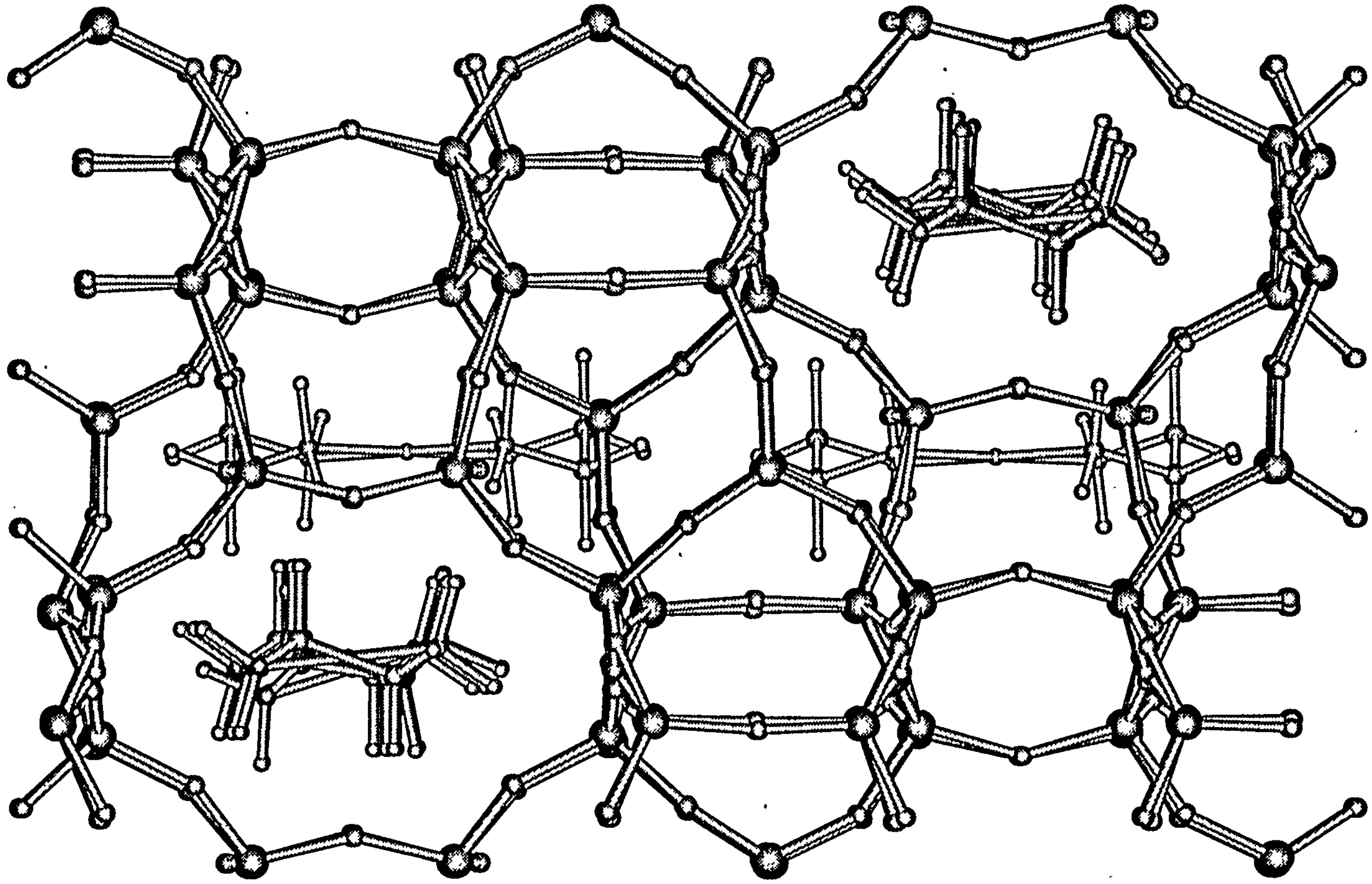


Figure 3 Simulation of Cu(en)2+ Cation
Residing in Major Channels of ZSM-5



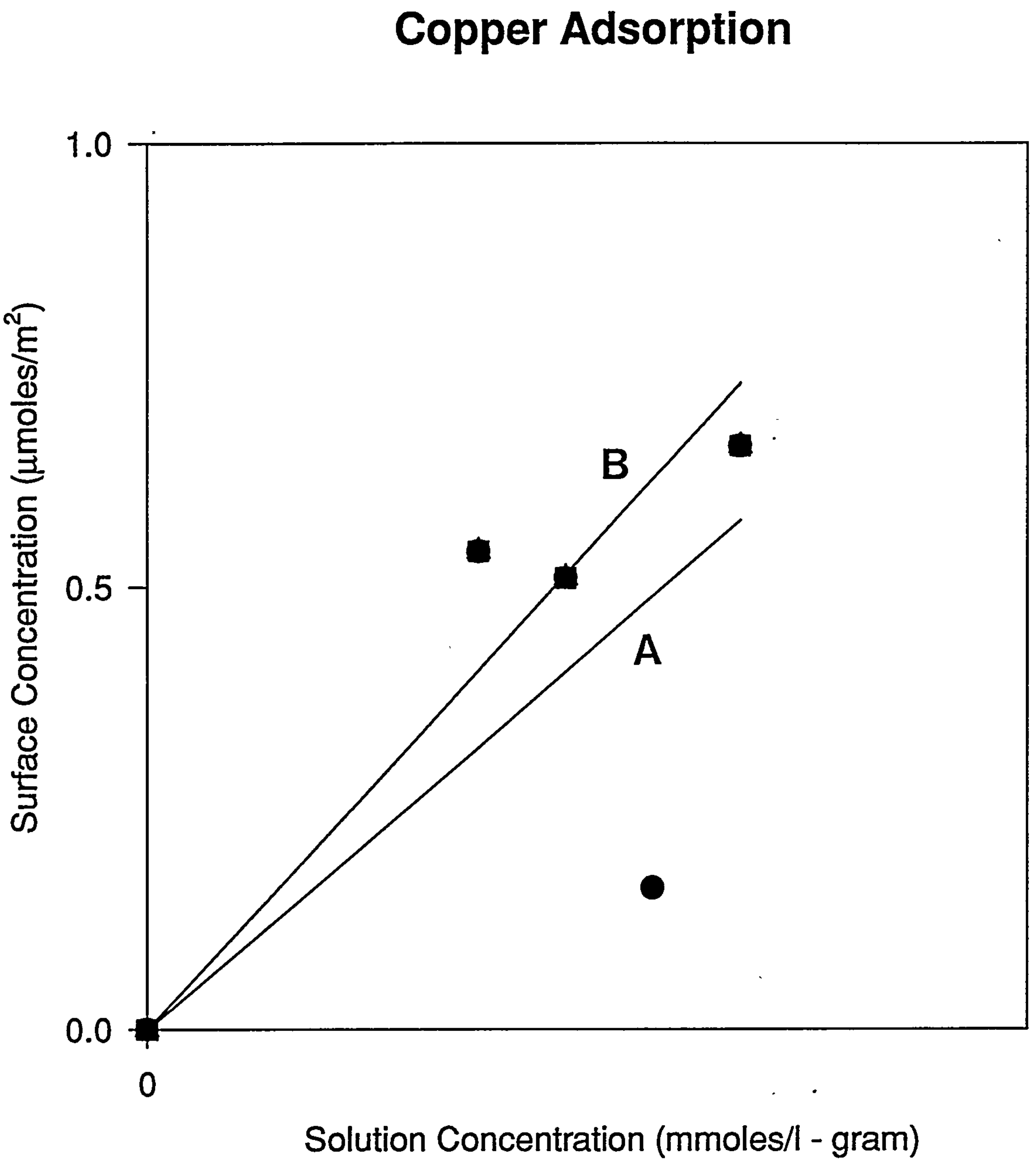


Figure 4. Adsorption Isotherm for Copper Acetylacetonate on Alumina from Acetonitrile Solution.

Figure 5. Infrared diffuse reflectance spectrum of sample containing 0.54μmoles Cu/m^2.

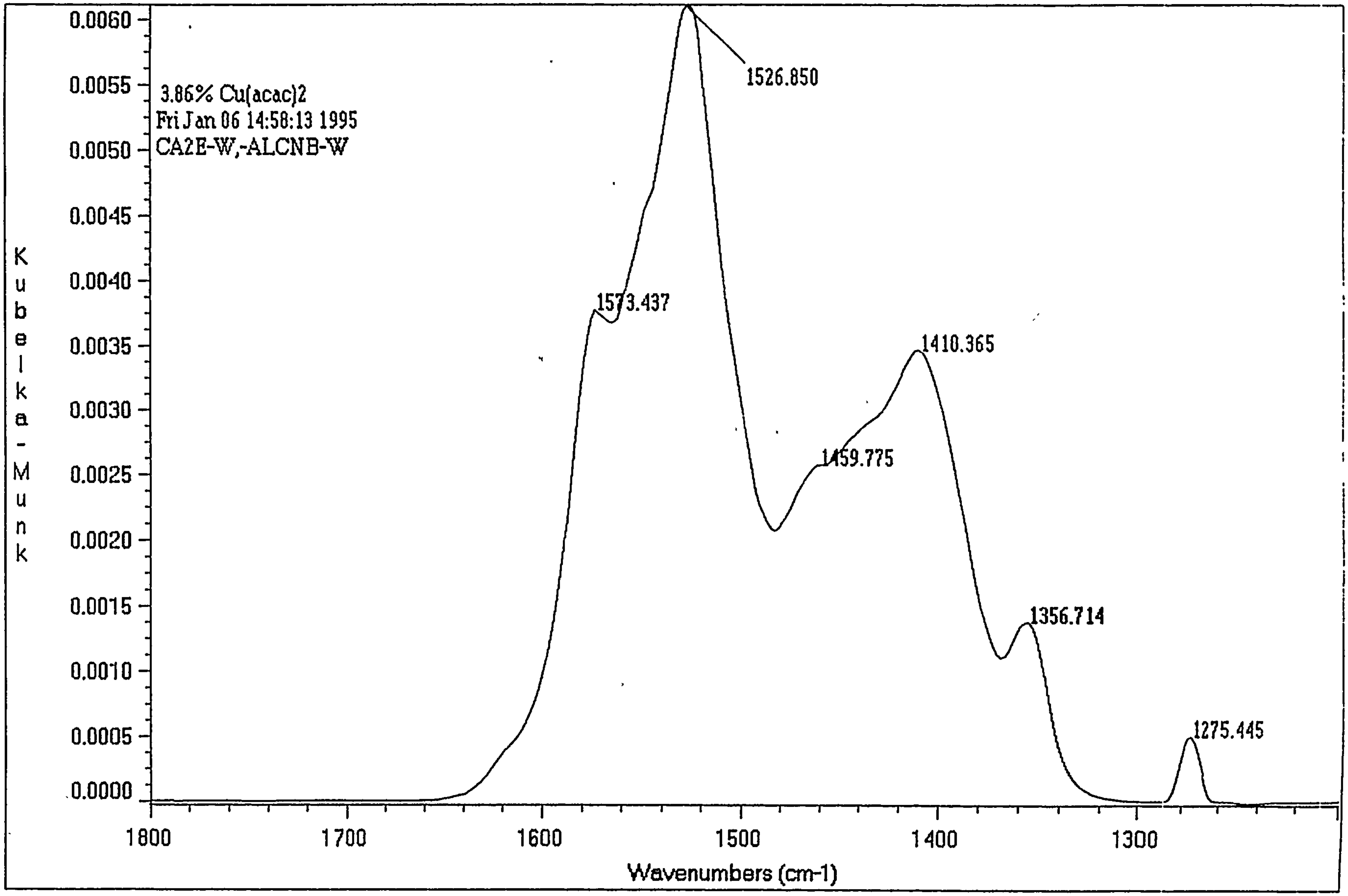


Figure 6. Infrared diffuse reflectance spectrum of sample containing 0.51µmoles Cu/m^2.

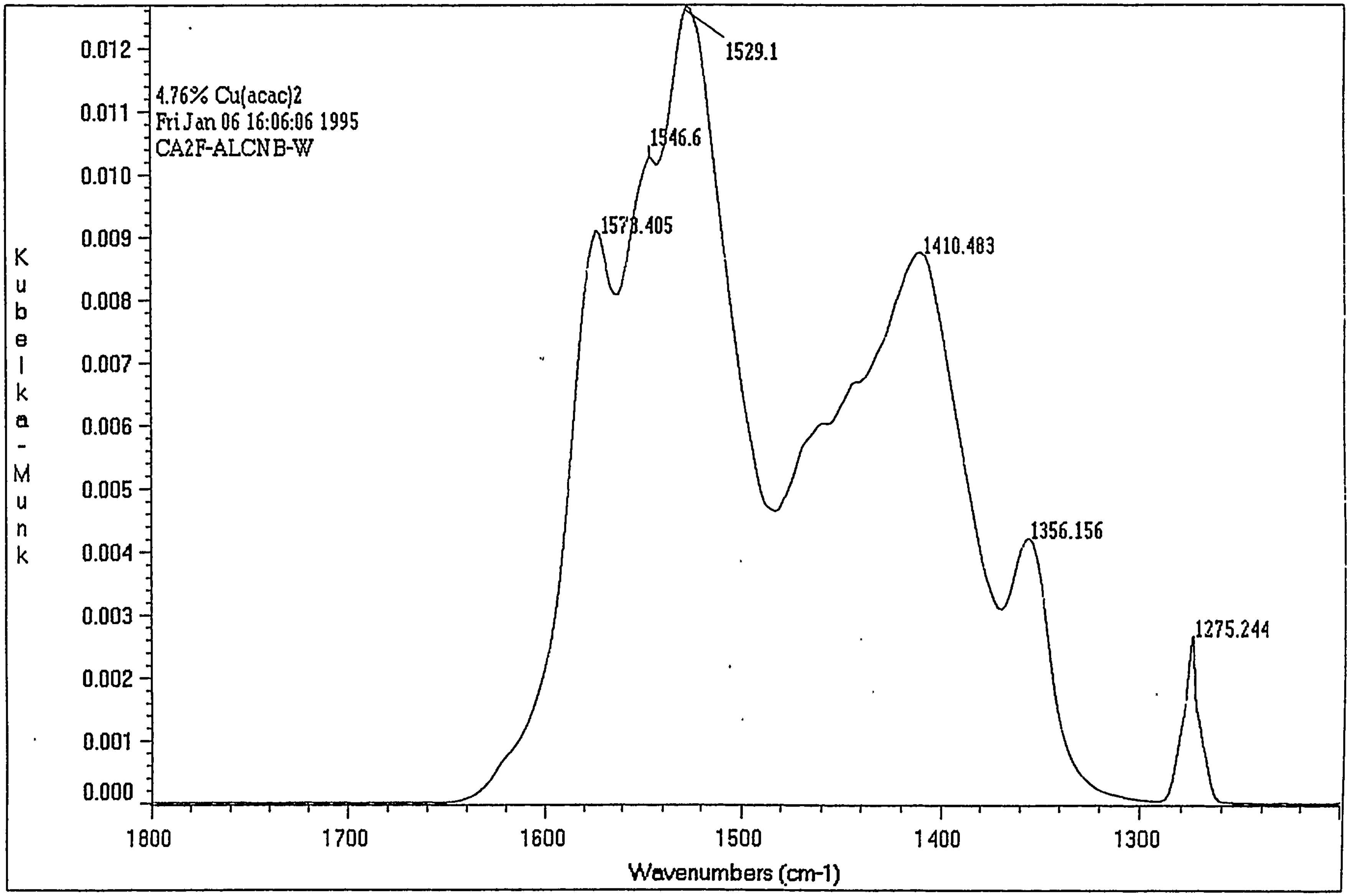
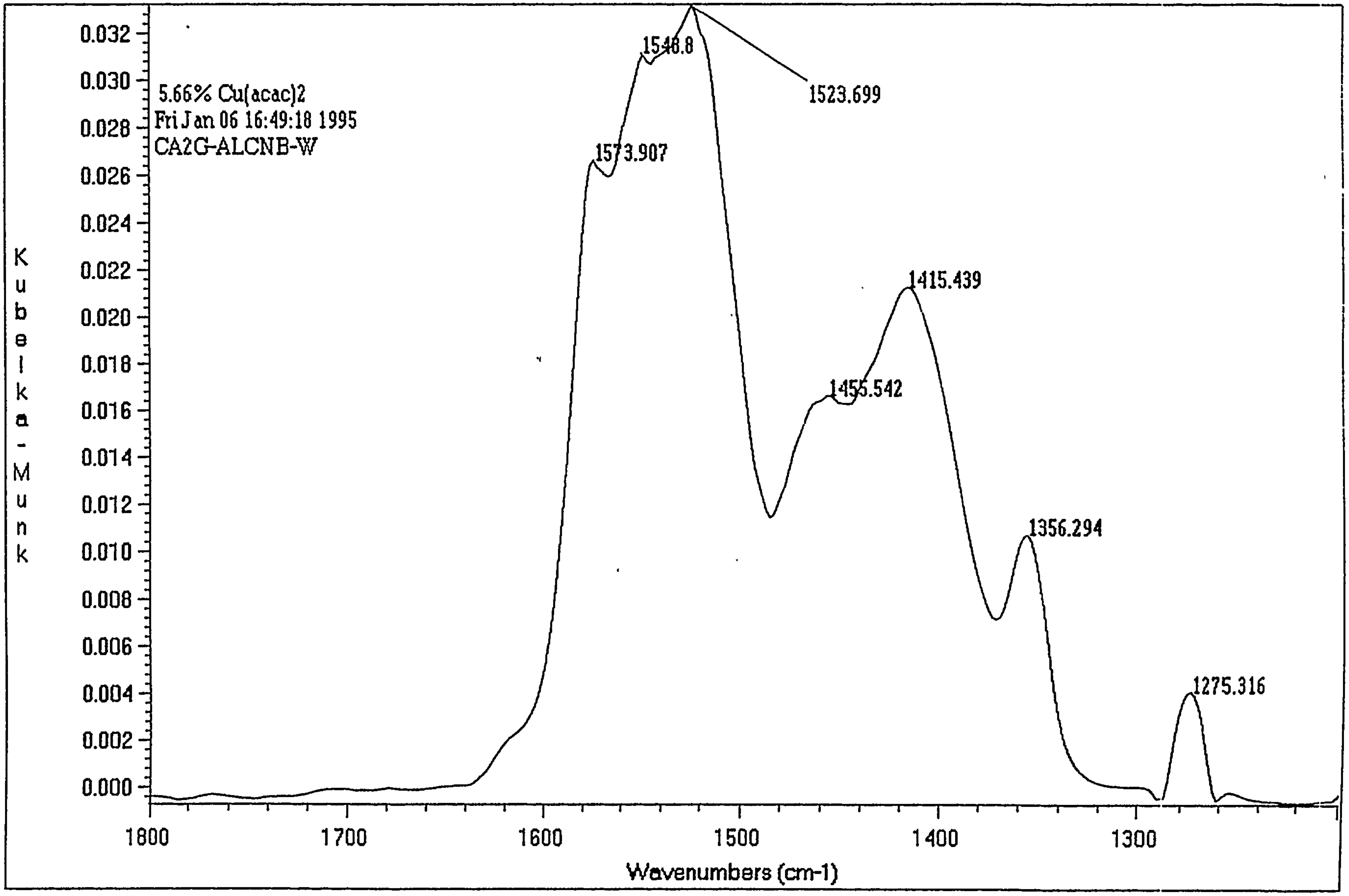


Figure 7. Infrared diffuse reflectance spectrum of sample containing 0.16μmoles Cu/m^2.



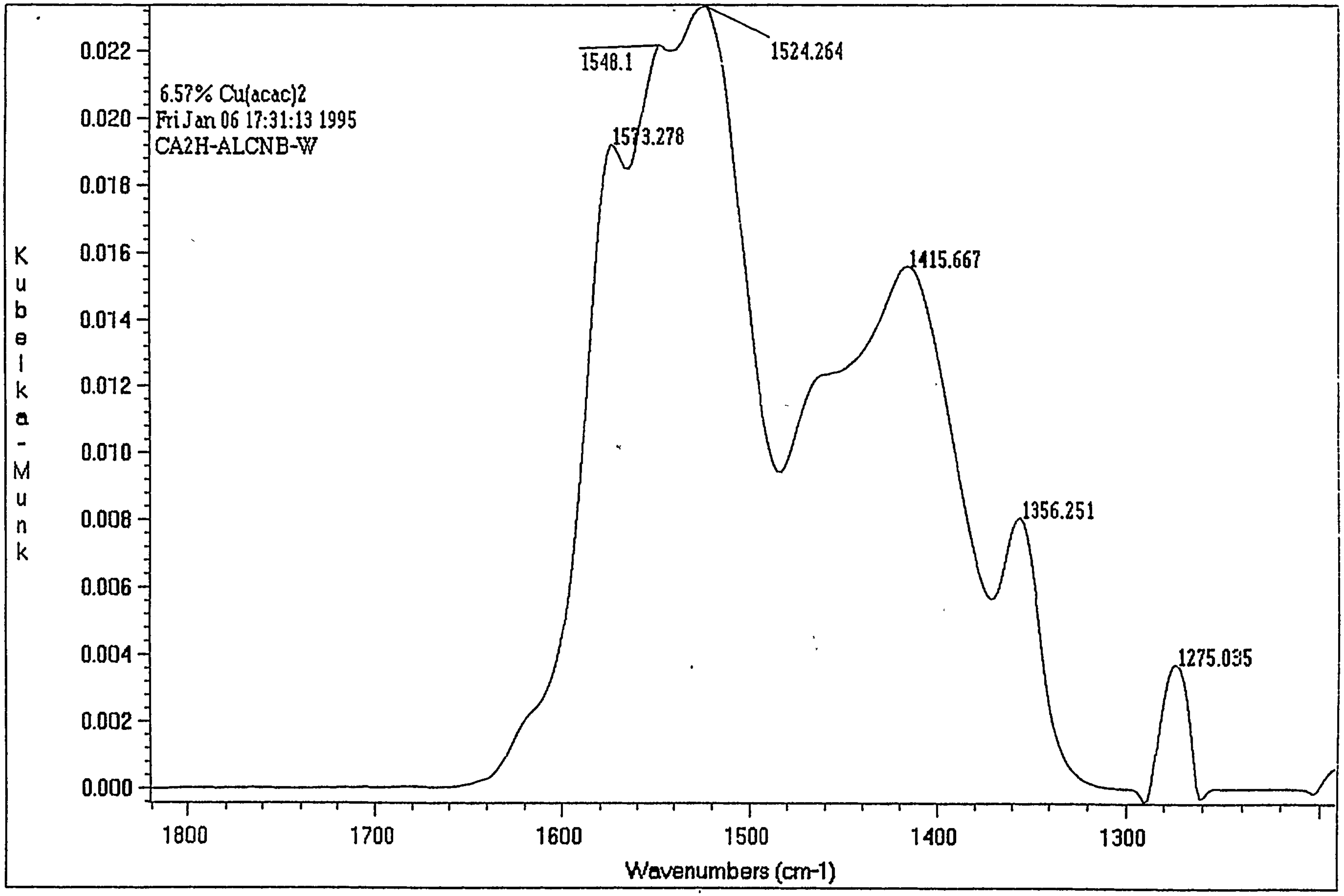


Figure 8. Infrared diffuse reflectance spectrum of sample containing 0.66μmoles Cu/m^2.