The CIRCLE
Cylindrical Internal Reflection Accessory
Instructions

I. INTRODUCTION

The CIRCLE, used in conjunction with your FTIR is a highly sensitive accessory. Unique optics and innovative design have been combined to widen the realm of FTIR analysis to include the routine analysis of aqueous and other IR opaque solutions. Even though we have pre-aligned the accessory, further critical alignment in your FTIR is necessary to insure satisfactory performance. Refer to section III for set-up and alignment instructions.

Cylindrical Internal Reflection (CIR) is a relatively low throughput technique. The percent of the energy getting through the accessory without sample present is usually between 15% and 20% of the open beam throughput. This is due to the high index of refraction of internal reflection materials and the long pathlength of the beam through the crystal (multiple bounces) and aperture losses. For commercial FTIR's currently on the market, excellent signal-to-noise ratios are achieved using standard TGS detectors. Improved ratios are further achieved with MCT detectors.

Aqueous analysis using FTIR has in the past been very difficult due to the highly absorbing nature of water as a solvent. The commercial application of the CIR technique to aqueous analysis is new enough that a large body of data regarding detection limits is not available. Detectability largely depends upon concentration, absorptivity, and pathlength (i.e., Beer-Lambert Law). However, the presence of highly absorbing bands such as the O-H stretch of water tend to obscure weaker, more interesting bands at long pathlengths. These two facts tend to specify an optimal range of pathlengths for much aqueous solution analysis, and the pathlength of the CIRCLE falls within this range. The pathlength of the CIRCLE is not variable, except as caused by changes in the index of refraction of the sample or by use of different internal reflection materials. At the CIRCLE's pathlength, concentrations of 0.5% of moderately absorptive samples typically are detectable, and yield highly reliable qualitative and quantitative information in the 3200 to 750 wave number region (using a ZnSe crystal). Using a MCT detector, the lower limit of detection appears to be from 0.05% to 0.1%.

II. DESCRIPTION

The CIRCLE accessory consists of an assembled flow-thru cell (with crystal), a second cell ("open boat" type), the optical bench, and the base plate assembly.

The CIRCLE is available in either a macro or a micro configuration. The macro version is supplied with a 1/4" diameter zinc selenide internal

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NOTE: Regarding use in the Nicolet 60-SX, some machines are in existance with the beam height 1/2" higher than others. In this case, the accessory as received will not align properly. 2" standoffs are included to replace the 1 1/2" ones if you have this situation.

reflection crystal and two cells, one glass body flow-thru cell with a 3ml cell volume and one stainless steel "open boat" cell with a volume of 5ml The crystal can be used in either cell. Section IV gives instructions on changing the crystal. Other crystal materials are available as special order items.

The micro-CIRCLE is supplied with a 1/8" diameter sampling crystal and two cells, a stainless steel high pressure flow-thru cell with a 25 microliter volume and a stainless steel "open boat" cell with a 1ml volume. Again, the crystal can be used in either cell.

The CIRCLE is easily converted from macro to micro operation and vise-versa. The optical bench is identical, and requires only the movement of the mirror assemblies. A second cell and crystal must be purchased. Sections V details the conversion.

The CIRCLE accessory is mounted to the sample chamber floor plate of your FTIR. Refer to Figure 2 which shows the locations of the screw holes and/or alignment pins for each FTIR.

III. SET UP AND ALIGNMENT INSTRUCTIONS

The CIRCLE accessory should first be set at the proper height by setting the three height adjustment screws so that the bottom of the swivel pad is 1/8" below the base plate (see figure 1).

Prior to inserting the accessory into the compartment, run an open compartment throughput check. Note the throughput for future reference.

Place the assembled accessory onto the compartment floor, insert the base plate locking screws and/or alignment pins but do not tighten down on the screws. Then proceed with the following:

1. Rotate or otherwise move the accessory (to the extent possible) to provide gross alignment of the accessory with the FTIR beam. (i.e., maximize the throughput measure).

2. Place a small white card (e.g., a business card) in front of the input lens. The open laser beam should be approximately centered on the hole of the input lens. If it is grossly off center check Figure 1 and 2 to assure proper setup.

3. Carefully place the card between the input lens and the end of the crystal. You should be able to observe the laser light converging on the input face of the crystal. If necessary loosen the socket head screw holding the input lens in the bracket so that the lens can be moved to provide a better input focus.

4. Loosen the socket head screw on the output lens bracket. Carefully (and slowly) slide the output lens in and/or out to maximize throughput (Do not spend a great deal of time trying to maximize before proceding to the next step).

5. At this point the lenses should be approximately in position, however, it is critical that the accessory center line be concentric with the center line of the energy beam.

Concentricity is achieved by using the three height adjustment screws on the base plate of the accessory(a ball head socket driver is supplied to make this adjustment).

HINT: Make slight rotations of a screw, observing the throughput before proceding to another screw. Then repeat the process as necessary since the three height adjustments <u>are not</u> orthogonal, but instead affect each other.

6. Make final adjustments to the output and input lenses to maximize the throughput.

7. If throughput is below 15% for a ZnSe crystal with no sample check the following:

   a) Remove the cell to assure that the crystal is clean, especially on the input and output faces of the crystals. If not, clean the crystal carefully with water and a soft tissue (lens tissue or soft facial tissue e.g. Kleenex).

   b) Replace the cell, assuring that it is properly seated and aligned with the lenses. (Replace the cell oriented the same way it was removed from the accessory). The cell clamp must be tightened down.

   c) Repeat Step 1.

8. Tighten the base "lock-down screws"-----These usually only need to be finger tight. If a balldriver is used <u>do not</u> apply a great deal of pressure....only a slight torque is required to secure the accessory.

9. Open the instrument aperture to the fully open position if an MCT detector is being used.

<u>IV. CHANGING CRYSTALS</u>

The crystal element is removable for use in other cell types, or for cleaning. It is, however, not always necessary to remove the crystal from it's cell for cleaning. Often the cell may be cleaned by washing through with water or appropriate solvent. Acetone, methyl ethyl ketone, or hexane make good solvents for use with zinc selenide. When a crystal has been removed from it's cell, the CIRCLE will require realignment for optimum throughput, so as a general rule, avoid removing the crystal from the cell.

When it becomes necessary to remove a crystal, follow these steps:

1. Loosen the three screws holding the end pressure cap onto the cell body, a quarter turn at a time, to release the pressure evenly from the crystal. Remove both end caps. The glass body cell has only one end cap to remove. The crystal is now held in the cell only by the o-rings.

2. Glass body cell only: Slide the glass body and crystal out of the aluminum protective housing.

3. Using a Kleenex or lens tissue, push on the crystal endface to release the crystal from one of the o-rings. Do not touch the crystal with anything except soft tissue!

4. Remove the second o-ring from the crystal. The cell is now completely disassembled.

5. Replacement is a reversal of these steps, except that before tightening down on the end cap screws, the crystal should be centered by eye, so that it protrudes an equal amount from both ends of the cell. Tighten the end caps to produce a leak-free seal. Replace the cell on the optical bench and realign. It will usually only be necessary to focus the lenses, i.e. move the lens assemblies in or out, to peak up the throughput.

NOTE: O-rings can be prestreched over a pen or similiar rod slightly larger than 1/4" dia. (1/8" dia. for micro crystal). This will help you slide O-rings over crystal without having to exert excessive pressure onto crystal.

V. MICRO/MACRO CONVERSION

The CIRCLE is sold in both a macro and a micro configuration, but the two forms are interchangeable, at the expense of having to realign the attachment after conversion. The cell and crystal assembly is the only unique part, and the proper size cell and crystal must be obtained if interconversion is desired. Refer to Figure 1 and follow the instructions below to convert your CIRCLE:

1. Remove the cell from the optical bench and set aside. The cell base is the same for either version and should be left in place.

2. Loosen the 2 screws which hold each lens assembly to the baseplate and move the lens assembly in or out to the new micro or macro position. Leave the screws loose.

3. Install the new cell and crystal assembly and observe the throughput. Move the lens assembles to the best position for maximum throughput, then tighten down. The cell is now converted. Follow Section III to optimize the energy.

VI. USING THE CIRCLE

The CIRCLE is designed to be highly repeatable and easy to use. A typical procedure for using the CIRCLE might be as follows:

1) Align the CIRCLE, noting the final throughput at the end of the alignment procedure (Section III).

2) Run a "background" with the empty cell (as just aligned). Save in a background file.

3) Fill the cell with a "reference" or "blank". Scan and save in a reference file, and plot.

4) Clean the cell by either removing the cell, emptying the contents and flushing with appropriate solvent (and drying with dry air) or simply flushing the cell with the sample. (If the cell must be disassembled for cleaning, refocussing of the lenses might be required unless the crystal is replaced to the identical location in the cell).

5) If the cell has been removed, replace and check the throughput of the empty cell to assure that the cell has been orientated properly in the accessory. (The throughput should be the same as that noted in Step 1).

6) Fill the cell with sample, scan and save in a sample file. Plot versus the background.

7) Select a difference factor and display or plot the difference as (sample) minus (factor)x(reference). The difference factor is multiplied by the reference file before subtraction to vary the amount of reference to be subtracted from the sample file. When an appropriate difference factor has been chosen, plot the result.

At this point the resulting spectrum can be "cleaned up" or information extracted as required for identification and/or use in QC or other procedures.

As part of our pre-alignment and check-out procedures we have scanned the cell vs. the open beam "background" (Figure 3). This spectrum shows percent transmission vs. frequency (wavenumbers).

We next filled the cell with distilled water, scanned and plotted the results, which are shown as Figure 4. Figure 5 shows the difference of the cell filled with water and the empty cell. As you would expect, the result is the ATR spectrum of distilled water. As a check-out procedure, we suggest that you duplicate the results shown in Figures 3, 4, and 5.

SPARE PARTS AND ACCESSORIES

MACRO CIRCLE ATTACHMENT

ITEM	PART NUMBER
Internal Reflection Crystals	
Zinc selenide	7005-000
Germanium	7005-010
Silicon	7005-020
Cells	
Glass body flow-thru	0005-200
Glass body (glass part only)	3000-370
Open boat	0005-201
Stainless steel flow-thru	0005-202

MICRO CIRCLE ATTACHMENT

ITEM	PART NUMBER
Internal Reflection Crystals	
Zinc selenide	7005-100
Germanium	7005-110
Silicon	7005-120
Cells	
Glass body flow-thru	0005-300
Glass body (glass part only)	3000-395
Open boat	0005-301
Stainless steel flow-thru	0005-302

MISCELLANEOUS

ITEM	PART NUMBER
Swivel pad ball driver	870-332
Mounting screw ball driver	870-964

Figure 1. ACCESSORY SIDE VIEW

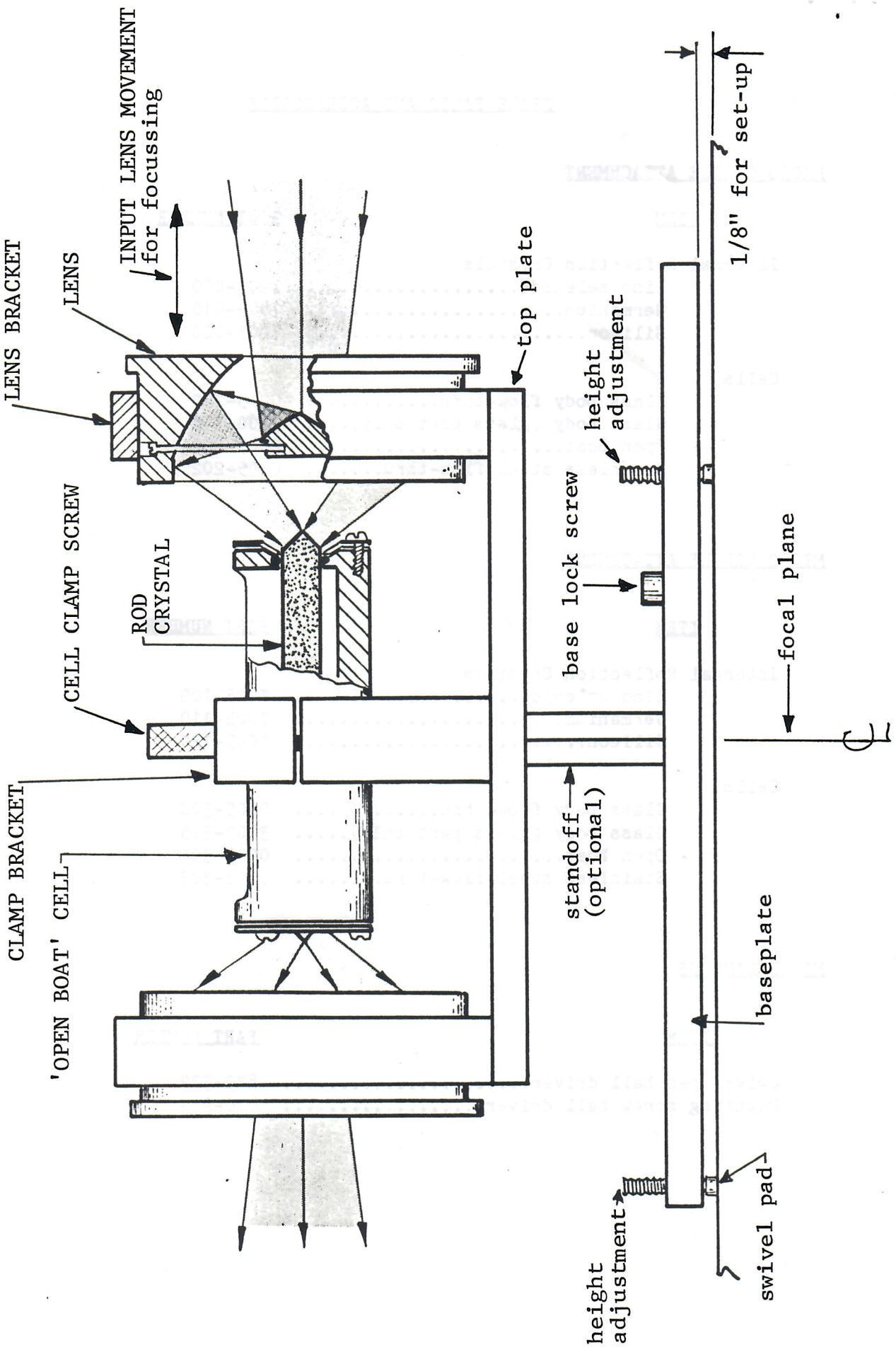
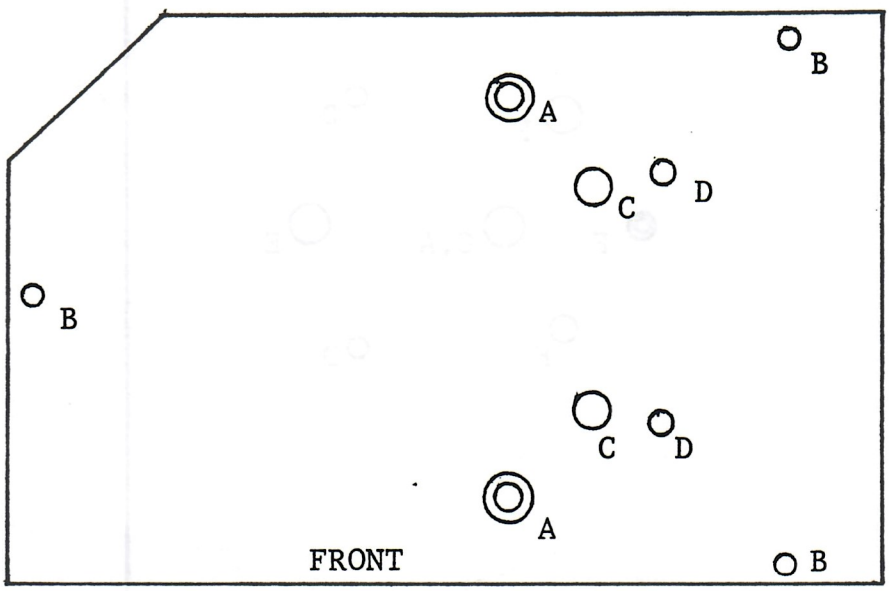


Figure 2.
CIRCLE Baseplate
hole locations



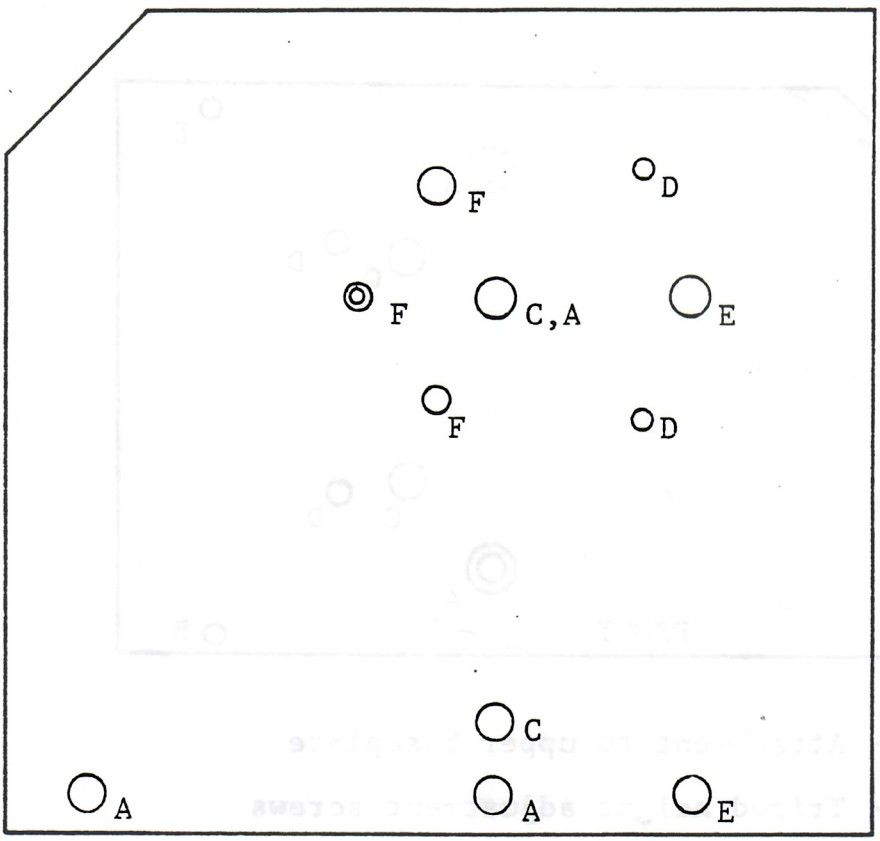
A - Attachment to upper baseplate

B - Tripod height adjustment screws

C - IBM mounting holes. Attach to IBM Kinematic plate with IBM M6 sockethead screws

D - Nicolet, Digilab, Analect, Perkin-Elmer mounting holes. For Nicolet, attach directly to optical bench. For others, first install the mating baseplate shown in Figure 2A on next page

Figure 2A.
CIRCLE Mating Baseplate
Used only with Digilab, Analect,
Perkin-Elmer spectrometers



Install plate into spectrometer compartment as described, then mount CIRCLE onto mating plate through (D) holes

A - Digilab FTS 14, 15, 20P mounting pins and hold-down screw. Mounts in front beam. Flip mating plate over and install position pins from other side to use the back beam.

C - Digilab Qualimatic mounting pins

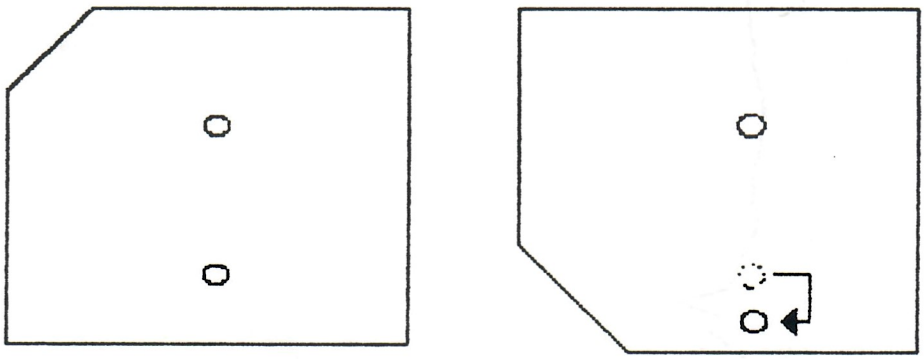
D - CIRCLE mounting holes

E - Digilab FTS 10, 11 mounting pins

F - Analect and Perkin-Elmer 1500 mounting pins and hold-down screw. MOUNTS IN FRONT BEAM ONLY

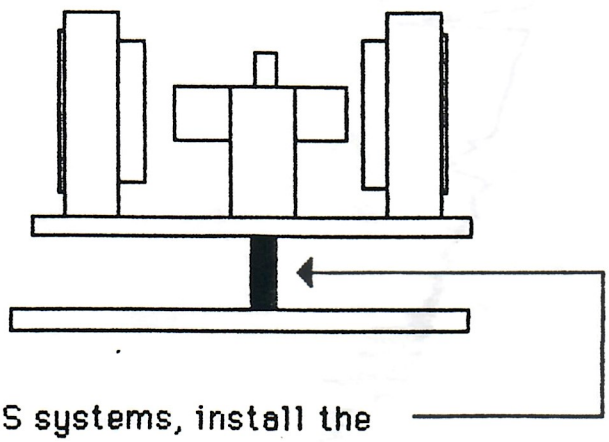
CONVERTING THE CIRCLE BETWEEN FTS 15 AND QUALIMATIC VERSIONS

Two changes must be implemented to convert the CIRCLE BETWEEN THE QUALIMATIC AND THE FTS 15. The removeable dowel pins in the bottom baseplate must be moved, and the stand-off height must be changed.



MATING BASEPLATE

To convert to the FTS version, refer to the above diagram. Flip the mating plate over, and install the dowel pins from the opposite side, moving one of them to the new position, as shown. The CIRCLE will now fit in the front beam of the FTS 15.



Next, for FTS systems, install the 1" tall standoffs as shown above.

Figure 3.

Crystal spectrum
open beam background
1 minute signal averaging

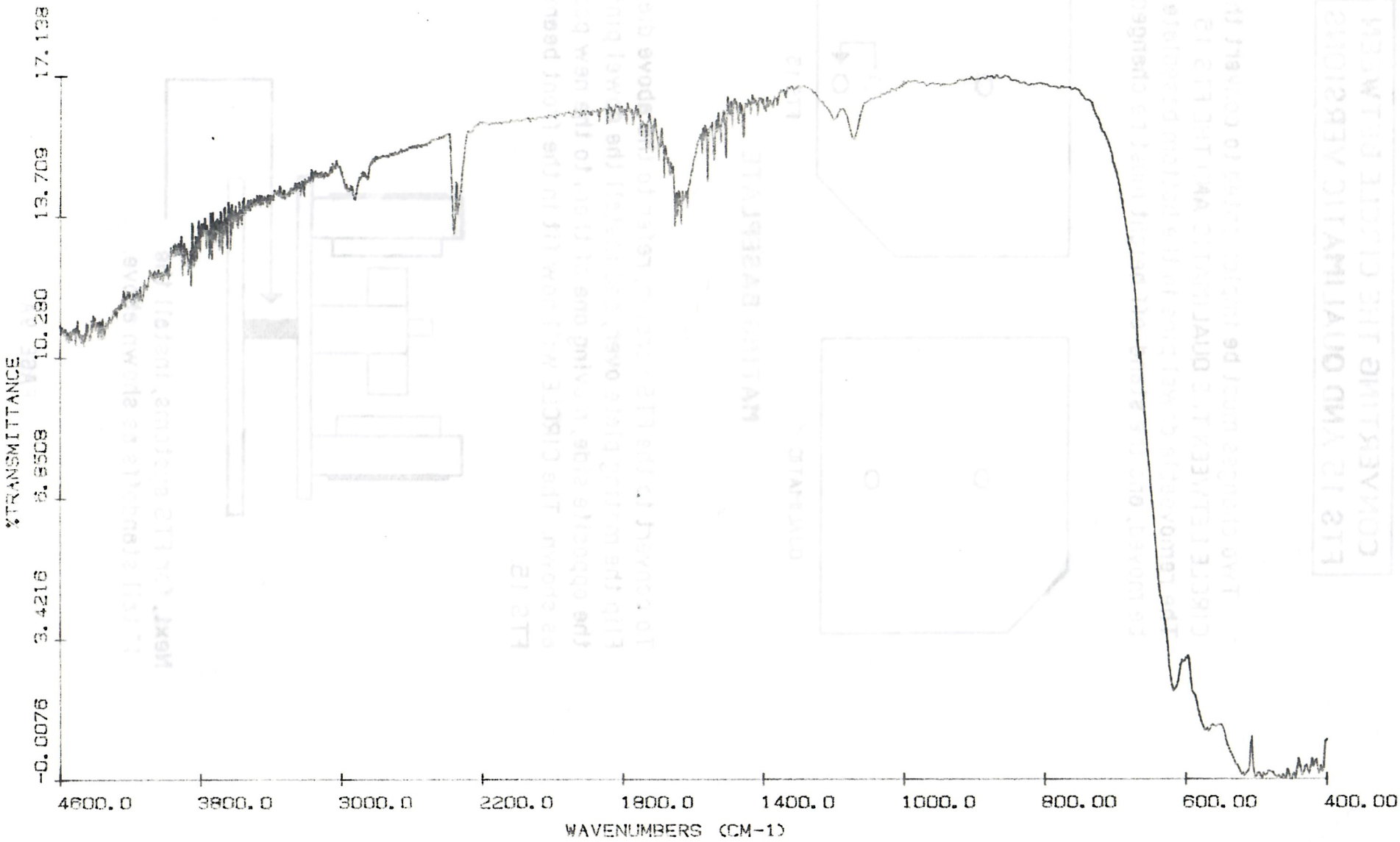


Figure 4.

CIRCLE ATR spectrum of distilled water
open beam background
5 minute signal averaging

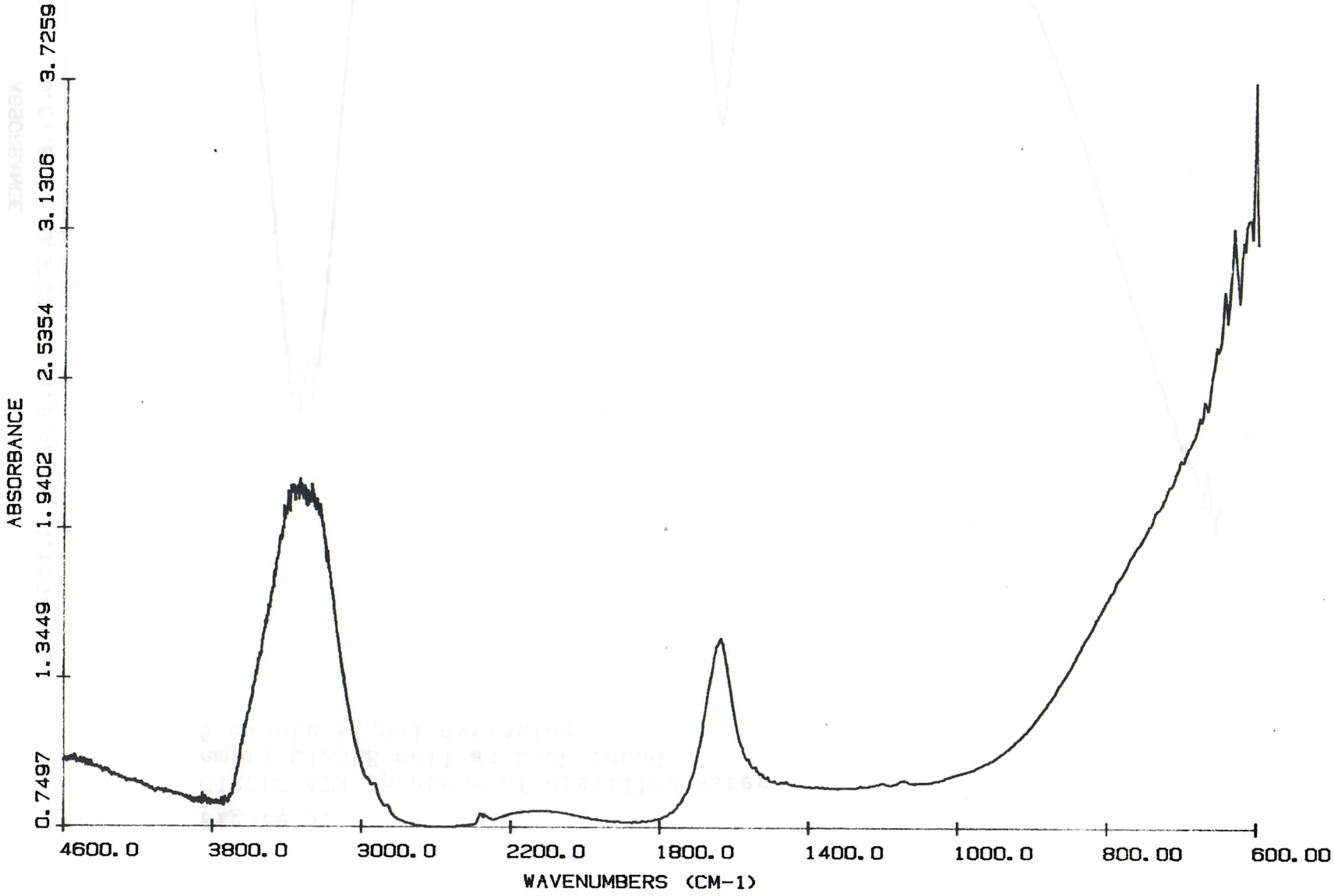


Figure 5.

CIRCLE ATR spectrum of distilled water
empty CIRCLE cell as background
5 minute signal averaging

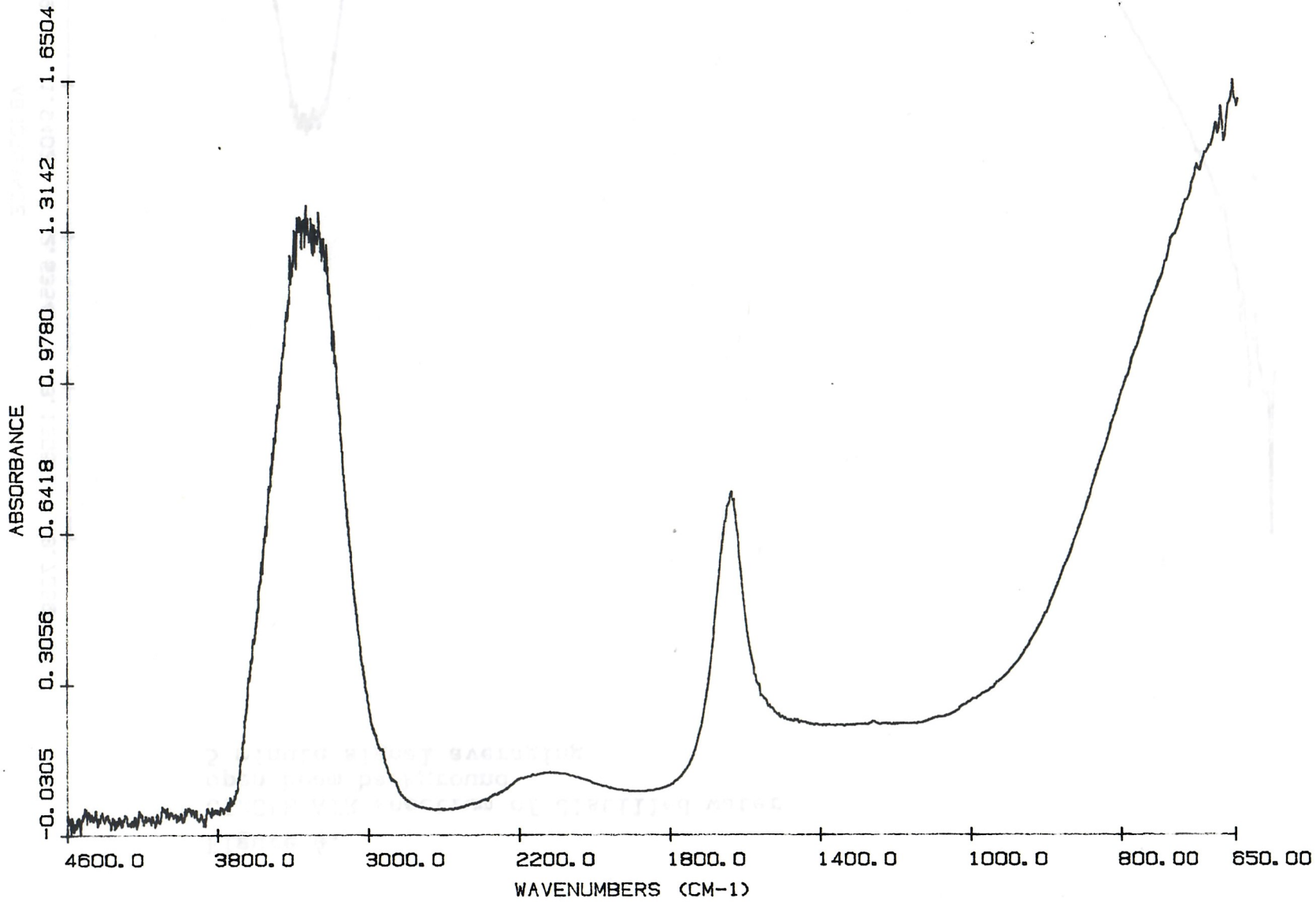


Figure 6.
CIRCLE ATR spectrum of water with 10% isopropyl alcohol
empty CIRCLE cell as background
2 minute signal averaging

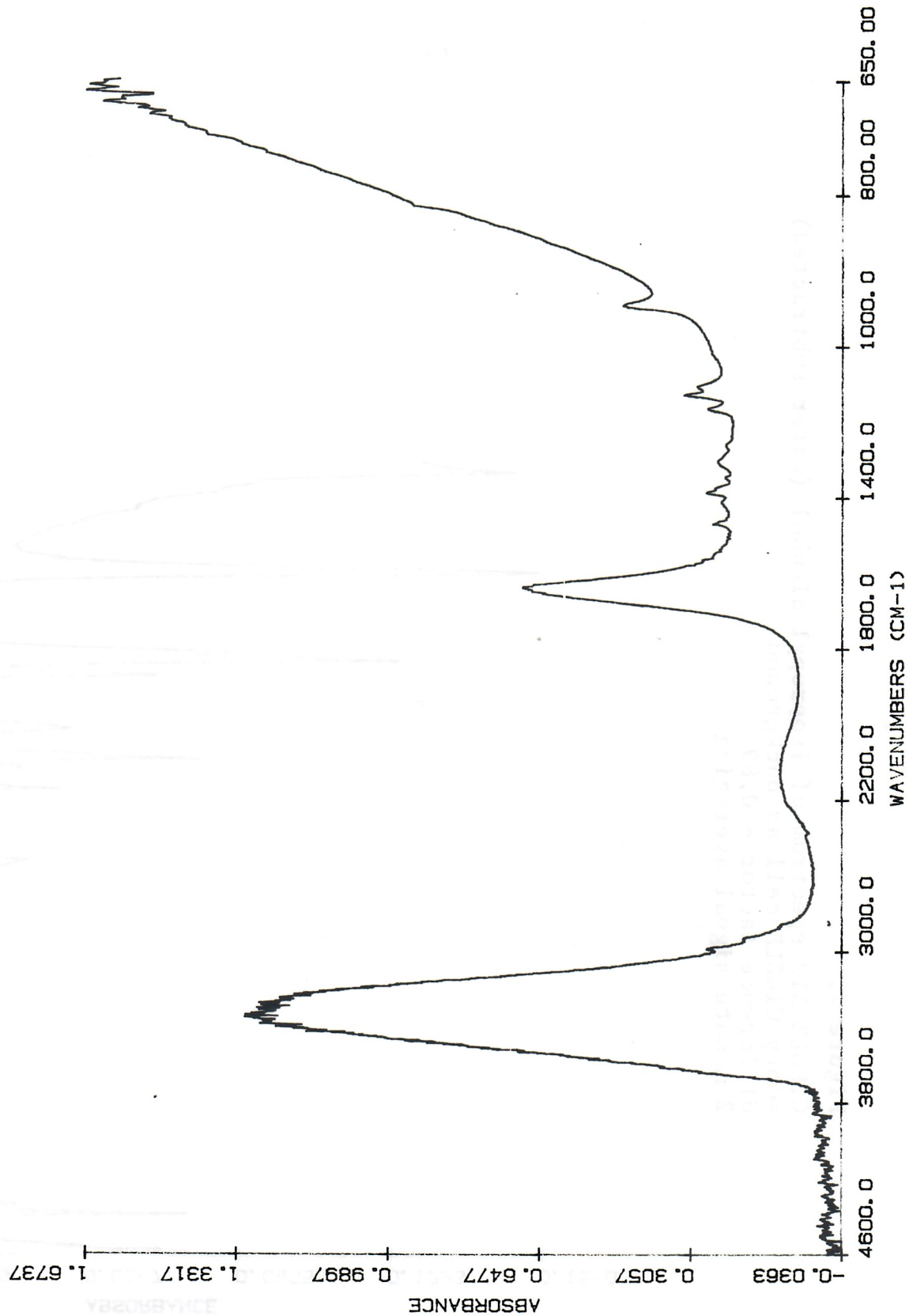
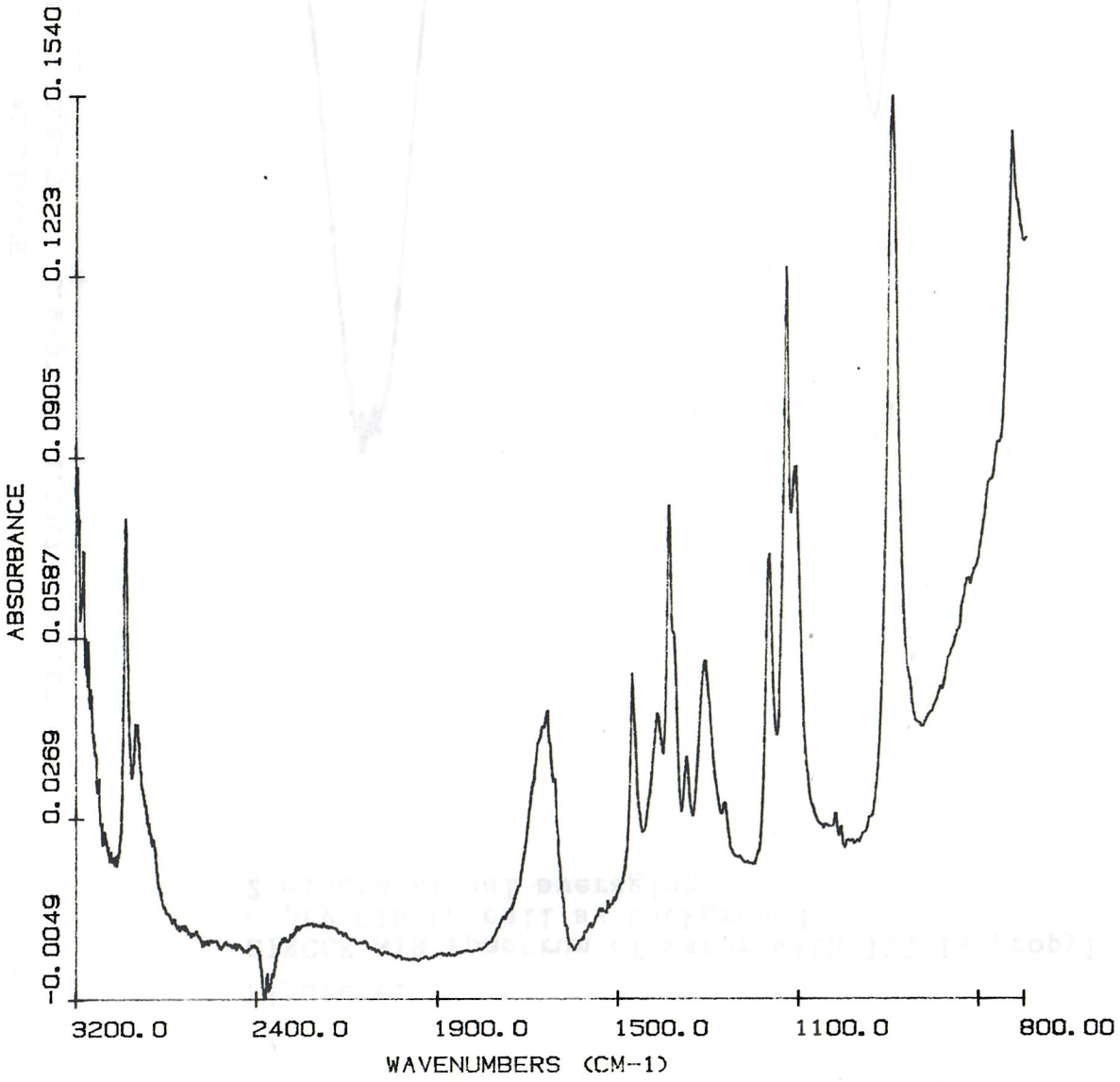
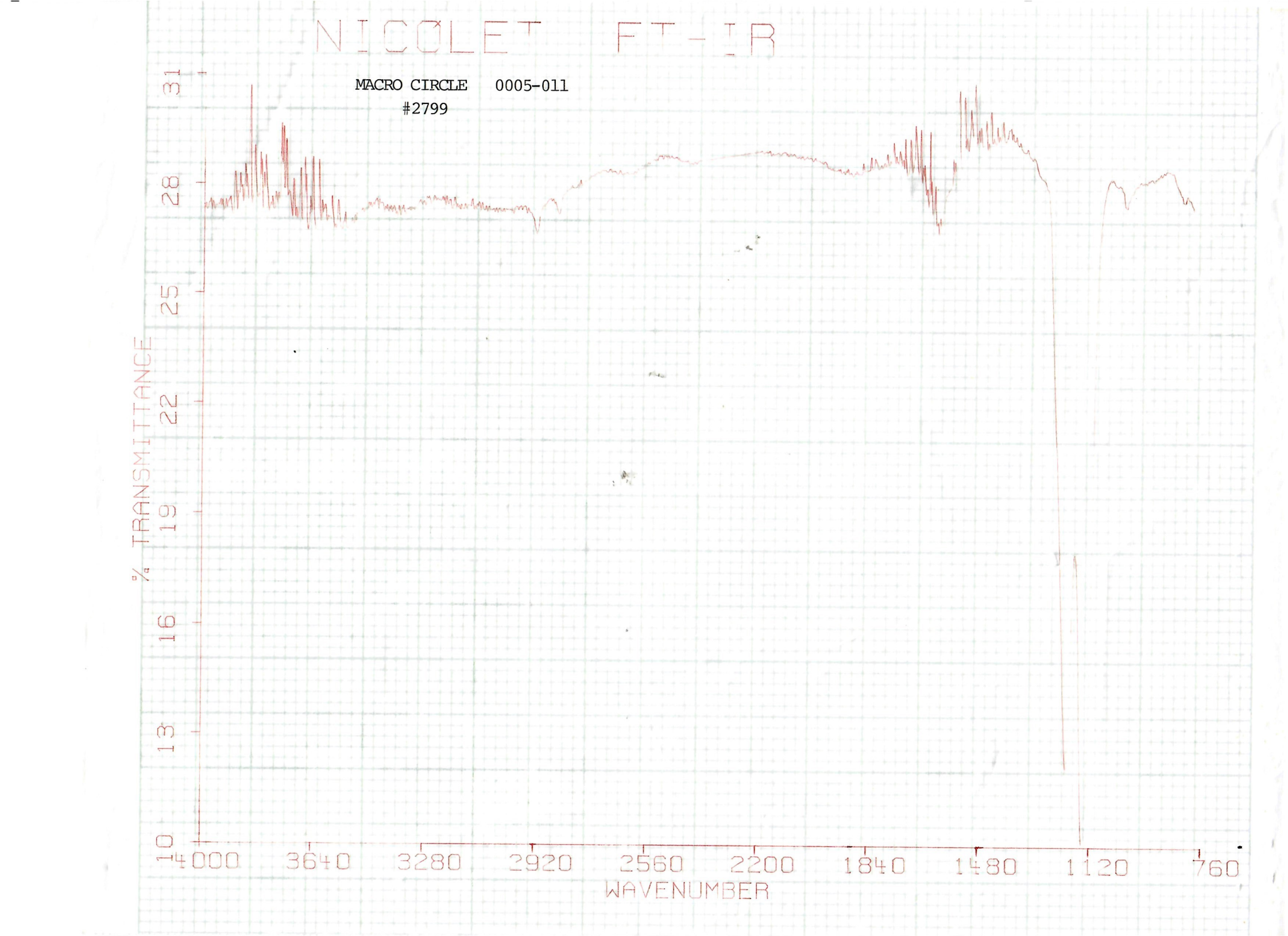


Figure 7.

CIRCLE ATR spectrum of isopropyl alcohol (water subtracted)
empty CIRCLE cell as background
difference factor = 0.89
2 minute signal averaging




NICOLET FT-IR
MACRO CIRCLE 0005-011
#2799
% TRANSMITTANCE
31
28
25
22
19
16
13
10
4000
3640
3280
2920
2560
2200
1840
1480
1120
760
WAVENUMBER