SEMI-ANNUAL TECHNICAL REPORT

February 1 - July 31, 1971

CONTRACT DAAH 01-71-C-0639

Sponsored by:

Advanced Research Projects Agency

ARPA Order No. 1463

August 1971

23

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

University of Maryland
Center of Materials Research
College Park, Maryland 20742

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

ANOMALOUS WATER AND OTHER POLYMERIC MATERIALS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Semi-annual Report February 1 - July 31, 1971

5. AUTHOR(S) *(First name, middle initial, last name)*

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6. REPORT DATE

August 1971

7a. TOTAL NO. OF PAGES

16

7b. NO. OF REFS

0

8a. CONTRACT OR GRANT NO.

DAAH01-71-C-0639

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

U. S. Army Missile Command
ATTN: AMSMI-RND
Redstone Arsenal, Alabama 35809

13. ABSTRACT

The first six months after the start of the project has been completed. Various materials have been isolated by several procedures and partially characterized. Spectroscopic data are reported and conclusions are drawn regarding probable structures of these materials.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Unclassified

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared, anomalous water, polywater, glass wool, sodium carbonate, sodium bicarbonate.						

Semi-Annual Technical Report

on

Anomalous Water and Other Polymeric Materials

ARPA Order No. 1463
Program Code No. N66109
Contractor: University of Maryland
Amount of Contract: $103,340
Contract No. DAAH01-71-C-0639
Effective Date: 2/1/71
Contract Expiration: 2/28/72
Project Scientist: Ellis R. Lippincott
Phone No. (301) 454-4126

I. BACKGROUND

Over the past decade the behavior of the products of condensation of water vapor in thin glass and quartz capillaries have been studied extensively by Prof. Deryagin and associates in Moscow. The properties of these materials differ from those of ordinary water, and significant evidence has been submitted to support the hypothesis that these "anomalous waters" consist of a solution of a hitherto unknown molecular form of water in the ordinary compound (see, for example, B. V. Deryagin, Scientific American, 223, #5, p. 52, November 1970, whose work has been repeated in this country by G. Swinzow, "Anomalous Water: Nucleation, Growth & Properties," Cold Regions Research Lab, SR 156, May 1971).

A number of measurements on physical properties have been carried out on this supposed new form of water, but because of the minute amounts in which it has been made thus far, no complete chemical analyses have been reported by the Russian workers, who base their opinion that the solute in "anomalous water" is also a form of H_2O on:

1) The insolubility of quartz under their experimental conditions;
2) The extreme cleanliness and care of the experimental arrangements, which render it highly improbable that their water and apparatus could have been contaminated;
3) Their inability to account for the properties of "anomalous water" by admixtures of impurities in the samples;
4) The apparent conversion of all of the "anomalous water" into ordinary water by distillation through a zone heated to 700 C.

In addition to anomalous water, these workers also report similar solutions prepared from hydrogen-bonded organic liquids, such as alcohols and acids.

In 1969 attempts were made in these laboratories and at the National Bureau of Standards to confirm this work by means of infrared spectroscopy and microanalyses. A unique IR spectrum was obtained, not associated with any single known compound, the chief bands of which occurred at 1595, 1410 and 1360 cm^{-1}. No major impurities could be detected by analysis, supporting the hypothesis that we were indeed concerned here with a new form of water, synthesized as a result of an interaction between water vapor and silica surfaces. (E. R. Lippincott _et al_., _Science_, _164_, 1482 (1969)).

Subsequently, however, serious problems were encountered with this interpretation:

1) The extreme difficulty of reproducing the experiments by which even tiny quantities of "anomalous water" are made (G. Cessac, Dissertation, University of Maryland (1970)).

2) The strong likelihood that all of the structural interpretations advanced theoretically thus far for a new form of water, in accord with the published physical properties, are seriously dificient. (B. Kamb, _Science_, _172_, 231 (1971)).

3) The apparent ability of even non-hydrogen bonded liquids to form anomalous residues after prolonged exposure of silica surfaces to their vapors. (P. A. Christian and L. H. Berka, Chem. Comm. 487 (1971)). This seems to be outside of all plausible structural interpretations of polymeric liquids.

4) The formation of "anomalous water" itself on silica-free surfaces. (J. Middlehurst & L. R. Fisher, Nature, 230, 575 (1971)).

5) The presence of a wide variety of impurities in materials made under conditions similar or identical to those reported by Deryagin, and which yield spectra that are the same as or closely resemble that of our original work (e.g., P. Barnes et all, Nature, 230, 31 (1971)); W. A. Adams et al., Nature Phys. Sc., 230, 39 (1971); R. E. Davis et al., Science, 171, 167 (1971); D. L. Rousseau, Science, 171, 170 (1971); S. W. Rabideau and A. E. Florin, Science, 169, 48 (1970); W. D. Bascom et al., NRL Report 7115, April 21, 1970). The identity of the compound or compounds responsible for the IR spectrum of "polywater", however, has not yet been established convincingly.

6) The invariability of the IR spectrum of "polywater" to isotopic substitution with deuterium. (S. B. Brummer and G. Entine, Tyco Laboratories, "Anomalous Water", May 1971).

II. OBJECTIVES

The greater part of the experimental work reported so far on "anomalous water" has been carried out by allowing the vapors of water (or, occasionally, other liquids) to condense slowly in Pyrex or quartz capillary tubes of various kinds, shapes and diameters, under a wide range of temperatures and pressures. This sometimes leads to the formation of a water-like condensate that shows properties different from those of water and which, upon evaporation, leaves a solid residue the infrared spectrum of which is very often similar or identical to that of "polywater" (Science, 164, 1482 (1969)).

Our approaches to the problem of the nature and synthesis of "anomalous water" were this time directed to the following objectives:

1) To determine the properties of the products of the interaction of high-surface area forms of silica (Pyrex wool and quartz wool) with hydrogen-bonded liquids (mainly water and methanol). If silica does catalyze the formation of "anomalous water", we would expect that suitable treatment of silica wools would lead to particularly abundant amounts of product.
2) To determine whether or not the low and erratic yields of "anomalous water" attained in most laboratories by use of the standard methods, could be remedied by applying higher temperatures, privately reported to lead repetitively to a product of constant infrared spectrum, in better than the normal quantities.

III. EXPERIMENTAL

A. Glass Wool

A batch of Corning Pyrex wool, free of coatings, was treated in the following way:

a. Heated on a steam bath for two hours in concentrated nitric acid.

b. Washed with deionized water until neutral and then rinsed six more times.

c. Boiled in deionized water for ten minutes.

d. Dried in air for twelve hours at 110 C.

e. Suspended over deionized water in a grease-free vacuum desiccator for two days.

1. Water

A portion of the glass wool (5 g dry weight) treated above was placed in a Buchner funnel and extracted by suction. Since only a few drops of liquid could be obtained, the wool was rinsed with 10 ml of deionized water, and this was also collected. The filtrate, when allowed to evaporate onto a ZnS plate, left a clear glassy residue, which on long standing or upon heating changed to small white crystals. The main absorption bands were at 1685, 1575, 1420 and 1100 cm^{-1}, as shown in Figure 1.

The following qualitative tests were carried out on the filtrate:

Chloride test with $AgNO_3$ ----- negative
Sulfuric acid test for charrable material---- negative
Acidified $BaCl_2$ test for sulfate ion ----- positive
HCl test for carbonate or bicarbonate ----- positive

After treatment of the glassy film on the plate with hydrochloric acid, all of the IR absorption bands disappeared, except for the one at 1100 cm^{-1}.

2. Methanol

A portion of the cleaned Pyrex wool was removed from the moist atmosphere and stuffed into a glass column 60 cm x 2 cm i.d. A space approximately 20 cm long was left above the wool. The bottom of the column was equipped with a sintered glass plate and a Teflon stopcock. Care was taken to handle the wool only with plastic gloves or a glass stirring rod. The wool was rinsed with about 20 ml of spectral-grade absolute methanol. The rinsings were collected and poured through the glass wool about ten times. In most cases the filtrate was quite clear and no further filtration was needed before a sample could be placed on an infrared plate. The filtrates were concentrated by putting them in an evacuated desiccator over drierite and calcium chloride. It was observed that when the preparation went to dryness, it was not possible to get all of the solid back into solution in the original volume of alcohol.

The IR spectrum of the residue, taken on an Irtran (ZnS) plate, is shown in Figure 2. It bears some resemblance both to those published for polywater, and to that of sodium bicarbonate In the latter compound, however, the OH stretching mode, which is absent in Figure 2, is seen. The bands around 2900 cm^{-1}, commonly associated with CH stretching, probably reflects the presence of methanol in our samples.

The residue of Figure 2 was placed in a dry atmosphere, in the purged sample compartment of a Perkin-Elmer 225 spectrometer, under a continuous stream of dry air. The bands at 1425 and 875 cm^{-1} increased in intensity, while those at 1625, 1085, and 820 decreased correspondingly. This is the behavior to be expected of a bicarbonate salt under these conditions. In a similar way, when 5% sodium hydroxide solution is added to the dry residue (as in Figure 1), the 1425 and 875 bands become much stronger, showing the $NaHCO_3 \longrightarrow Na_2CO_3$ conversion.

The IR spectrum of the methanol extract of glass wool (Fig. 2) is compared with those of sodium bicarbonate and sodium carbonate in Table I.

TABLE I

Absorptions, cm^{-1}

Presumed $NaHCO_3$ Complex with Methanol	$NaHCO_3$	Na_2CO_3 (1)
	3320 W	3000 M, br
2980 VW		
2950 W		
	2920 W	
2850 VW		
	2620 VW	
	2550 M	2500 M
	1910 M	
	1730 M	1755 M
	1690 S	
	1665 S	
1625 VS	1625 S	
1610 VS		
1520 VW		
1470 M		
1460 M	1460 W	1440 VS
1425 W		
1380 M		
1315 VW		
	1300 VS	
1180 VW		
1085 S		
	1040 W	
	1030 VW	
	985 M	
930 W		
920 W		
875 W	875 S	
820 S	820 S	855 VW
		705 M
		700 M

Intensities. VW = very weak W = weak M = medium
S = strong VS = very strong br - broad

(1) Foil A. Miller & Charles H. Wilkens, Anal. Chem. 24, 1253 (1952).

3. Sodium Bicarbonate Crystallized from Methanol

Some time was spent in determining properties of the compound of Figure 2, an apparently hitherto unreported form of sodium bicarbonate, synthesized by the interaction of sodium (extracted from glass by methanol) with carbon dioxide in the air. In particular we wanted to ascertain whether or not such a compound, characterized primarily by the IR spectrum of Figure 2 could be prepared without the presence of glass wool.

A synthesis of this compound was devised by allowing a saturated solution of $NaHCO_3$ in methanol to evaporate until a solute precipitates.

We found that the spectrum of Figure 2 is independent of the plate used to measure the absorptions; both zinc sulfide (Irtran) and silver chloride were used, with identical results. Pure sodium bicarbonate and pure methanol give clear Raman spectra; however, when the two are mixed in the manner just described, the resulting residue gives a high fluorescent background identical to that found for the methanol extract of glass wool. Even in very dilute solution, this background was strong enough to obscure the Raman absorptions completely. The nature of the alcohol - bicarbonate interaction that produces fluorescence is under study.

Additional evidence that we are dealing with a complex of bicarbonate and methanol was obtained from three other experiments: weight loss, gas chromatography, and spectral shifts with other alcohols.

Sodium bicarbonate was stirred for several hours in warm methanol, filtered, and the filtrate evaporated to dryness at 40 C. When the temperature was raised to 50 C, no weight loss was observed, but at 100 C., 27% of the sample evaporated, which corresponds to the weight loss of methanol from the hypothetical complex $NaHCO_3 \cdot CH_3OH$. (Theoretical, 27.6%. The weight loss for the conversion of bicarbonate to carbonate is 37%).

A gas chromatographic analysis of the dry residue from the methanol extraction of glass wool (i.e., the material of Figure 2) showed peaks for carbon dioxide, water and methanol.

Saturated solutions of sodium bicarbonate were also prepared in ethanol and in isopropanol. The IR spectra obtained with these solvents were less intense than those typically found with methanol, reflecting the lower solubility of sodium bicarbonate in these other alcohols. However, the same type of spectrum is found, although with some changes. The most important shift is that the 1625 band in methanol and ethanol extracts is at 1750 cm^{-1} in isopropanol. The three are compared in Figure 3.

However, when the residue from a methanol - sodium bicarbonate residue was ground to form a Nujol mull, the resulting IR spectrum is that of standard $NaHCO_3$. The powder x-ray diffraction spectrum of the material that gave the IR of Figure 2 showed a mixture of trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) and an unidentified species.

4. Contamination

For a time during the course of these experiments we were puzzled by the transformation of the IR spectrum of Figure 2 into that of Figure 4. This occurred in samples that were allowed to stand in dessicators for a long time (one to two weeks); or that had been obtained from Pyrex wool that had been extracted repeatedly and had thus been exposed to the air for at least several hours. A search carried out at Sadtler's of their infrared spectral files showed that this compound was sodium trifluoroacetate, a fairly volatile and very water-soluble salt with which some parts of our laboratory are apparently contaminated. Trifluoroacetic acid had been used by us in the course of entirely different work two years before, and amounts sufficient to give very clear and distinct IR spectra can still, surprisingly enough be obtained by prolonged exposure of certain materials - such as glass wool - to the air.

These experiments, although in the end they proved not to be significant from the standpoint of our research objectives, pointed out the very serious danger of contamination when trying to reduce a large quantity of material to small residues, even when all of the necessary precautions appeared to have been taken to ensure cleanliness. In fact, we were able to crystallize sodium trifluoroacetate several times (but not at will) by dissolving sodium bicarbonate in methanol, filtering the solution, and placing a shallow layer of it in a beaker, which was then stored in a dessicator over Drierite for twenty-four hours. After evaporation, the hygroscopic needles of $F_3CCOONa$ were found; they gave the IR spectrum of Figure 4.

We have satisfied ourselves that the starting methanol and sodium bicarbonate were free of trifluoroacetic acid or its salts.

B. Quartz Wool

We did little work on quartz wool, and no conclusions can be drawn from it. When a column packed with quartz wool was rinsed either with water or methanol, a filtrate was obtained, the residue of which was a white, crystalline material.

C. Anomalous Residues from Capillary Tubes

1. Thin Tubes

The object of these experiments was to determine whether the composition (H_2O, CO_2, CO and HNO_3) and pressure of the gas in the dessicator employed as a closed chamber to prepare anomalous water, influenced the amount of material formed.

The thin Pyrex tubes used in this work had an outer diameter between 75 and 150µ , and a bore of from 1 to 30µ. It was known that when placed in a dessicator under a saturated vapor pressure of water, practically all of these capillaries would develop some condensate.

Four dessicators were used, equipped with o-rings and Teflon stopcocks. They were washed in hot soapy water, carefully rinsed in hot water and then with distilled water, and dried in an oven at 70 C. The pyrex dishes used to hold the capillaries were similarly washed, but with the addition of a final rinse in 30% hydrogen peroxide. Plastic gloves or tongs were used for all handling. About 200 ml of distilled water were poured into the bottom of each dessicator and a covered dish containing several hundred of the thin capillaries placed on the shelf above. In one of the dessicators, an erlenmeyer with concentrated nitric acid was put on the shelf beside the dish with the capillaries. All dessicators were pumped down with a water aspirator to about 40 mm of Hg; no additional gases were added to the first dessicator; pure dry CO_2 was placed in the second, 0.5% CO in helium in the third, and pure CO in the fourth (the one containing nitric acid). Every day about ten capillaries were removed from each dessicator and examined under a microscope; the dessicators were again pumped down and gases added as before.

A study of the results shows that:

1) The total pressure of gas over the capillaries had no effect on the results;
2) The composition of the gas in contact with the capillaries likewise had no effect on the number of filled tubes, nor in the time needed to remove the liquid columns from the tubes.

About 10,000 capillaries were placed in a dessicator over water, removed, and then heated while they were being pumped into a cold trap. A number of drops of liquid were collected, but all of it evaporated within a few hours at room temperature. No anomalous behavior could, therefore, be observed.

2. Higher Temperatures

A process in which acid-treated Pyrex or quartz capillary tubes are kept at slightly higher than normal temperatures, in an evacuated container, in the presence of water and water vapor, was privately reported to us to yield material repeatedly and in fair amounts, which material consistently showed the IR spectrum of "polywater". In this procedure, water is allowed to enter the tubes in the liquid phase. More difficulties were experienced with it than had been anticipated. The problem seems to lie in that if the tubes are shielded from the water droplets, no condensate appears in them, and consequently, no "anomalous" material. But if the tubes are insufficiently shielded, too much liquid accumulates, and the "anomalous" material, if any, is too dilute to be detected. Out of twelve experiments, three gave low but distinct yields of a "polywater-like" substance; the amounts were not enough for further determinations.

IV. CONCLUSIONS

A. Sodium bicarbonate is formed from glass wool when the latter is extracted with methanol and with water, as a result of a reaction with carbon dioxide in the air. Although the sodium bicarbonate when extracted with methanol could be called "anomalous" in some ways, no material that gives the exact spectrum of "polywater" could be found. However, if any had formed in this procedure, it would have been overwhelmed by the relatively large amounts of common salts extracted from the glass, and gone undetected.

B. An interesting and previously unreported form of sodium carbonate is formed when this compound crystallizes from methanol.

C. Yields of the "polywater-like" material seem to vary greatly from laboratory to laboratory, even when simple procedures that are seen to work in one are tried in another.

D. "Polywater-like" material can be formed from tubes in contact with bulk liquid water, which renders it extremely unlikely that we are dealing with the formation of a polymeric form of water.

V. Manpower and/or Fiscal Status

1. Fiscal Status

a.	Total costs authorized by contract:	$103,340.00
b.	Total funds expended and/or obligated during month	$ 8,154.20
c.	Total funds expended and/or obligated	$ 77,537.18
d.	Unexpended balance	$ 25,802.82

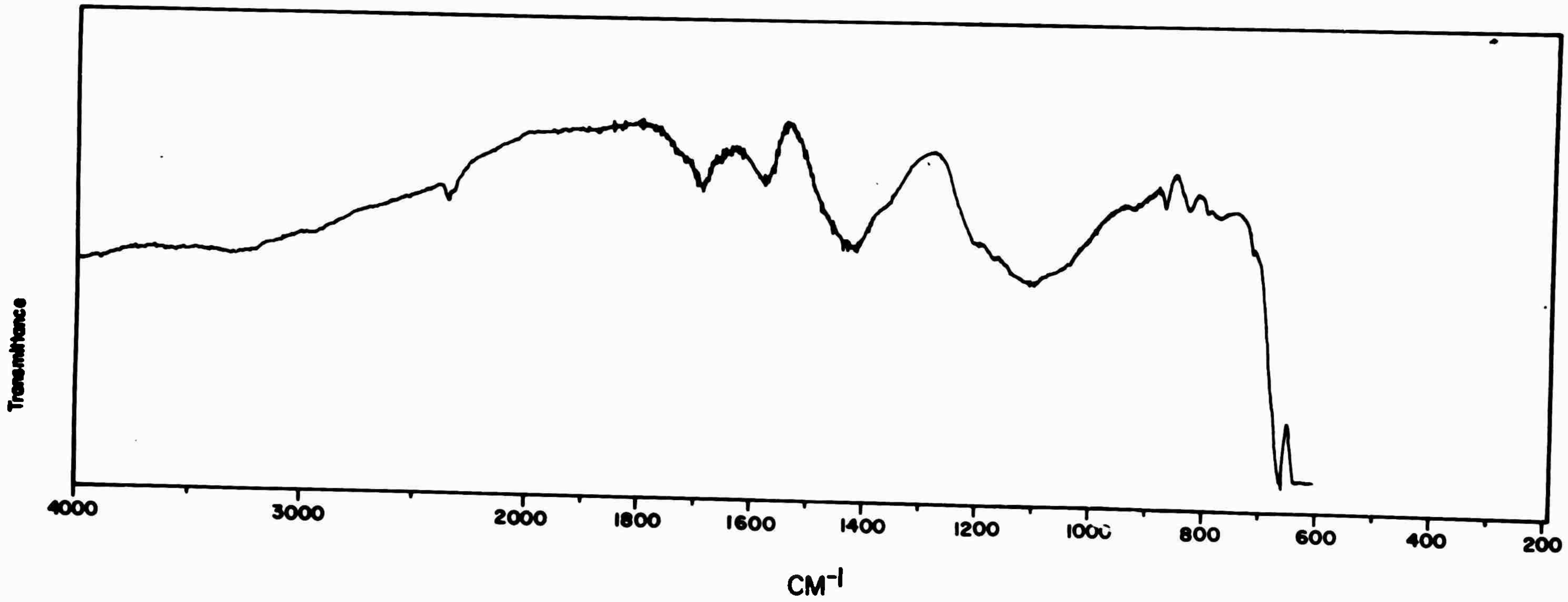


Figure 1. Water extract of pyrex wool.

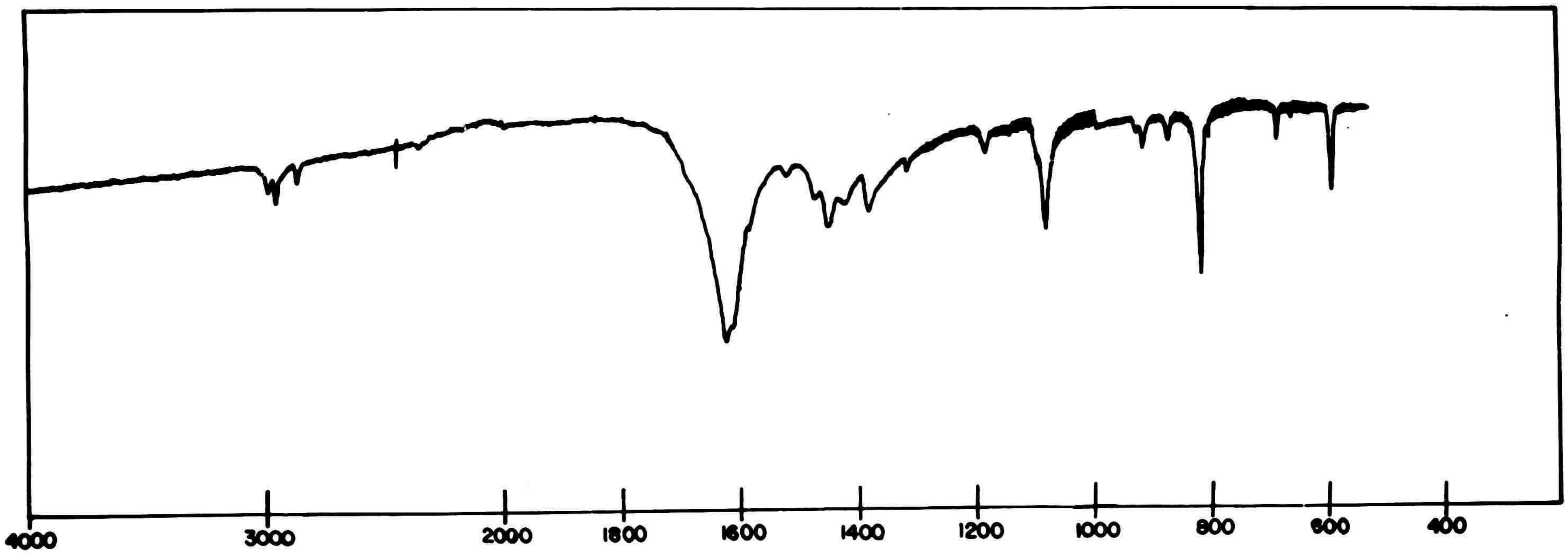
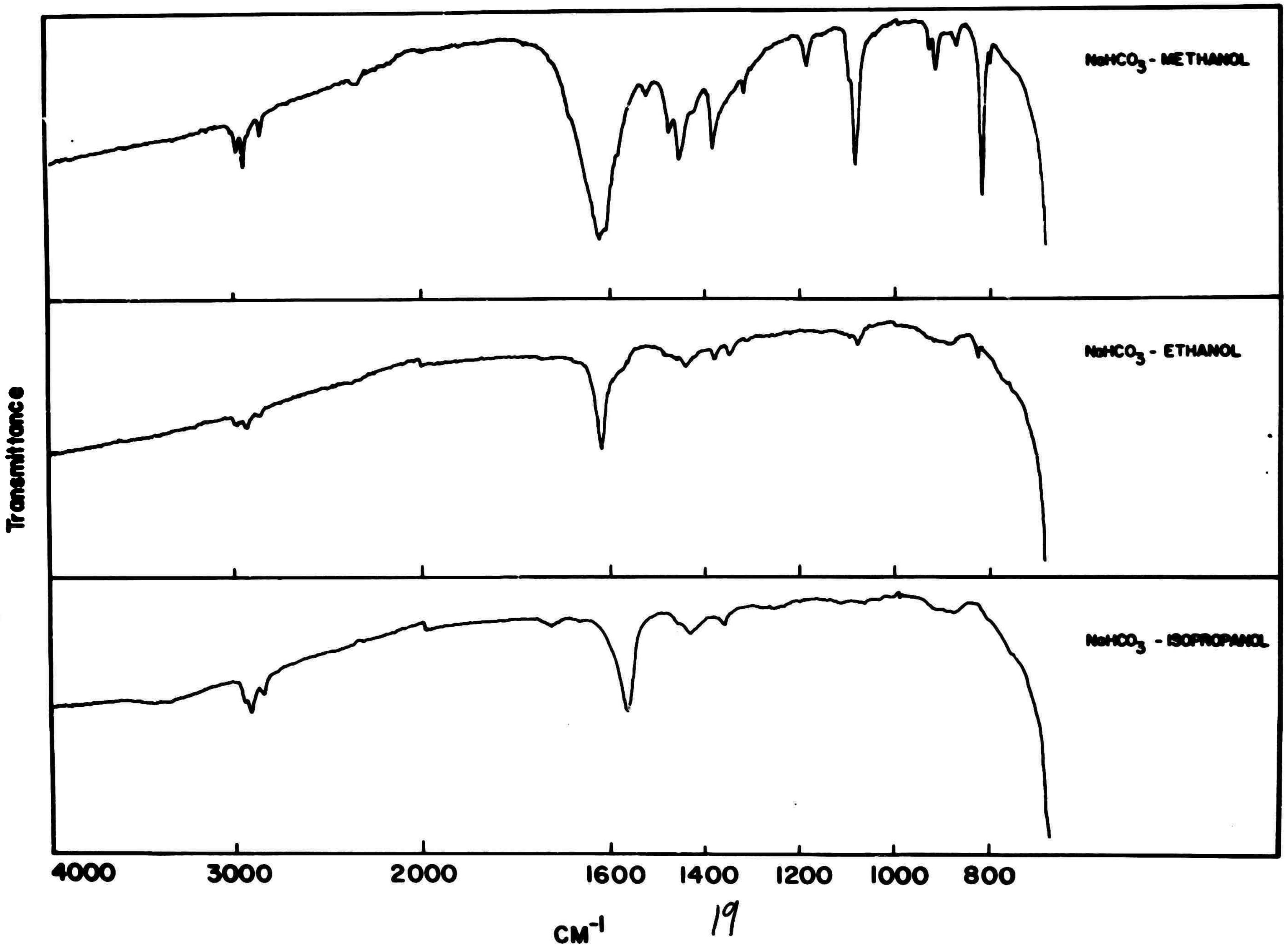


Figure 2. Methanol extract of pyrex wool.

Figure 3. IR Spectra of sodium bicarbonate in methanol, ethanol and isopropanol.



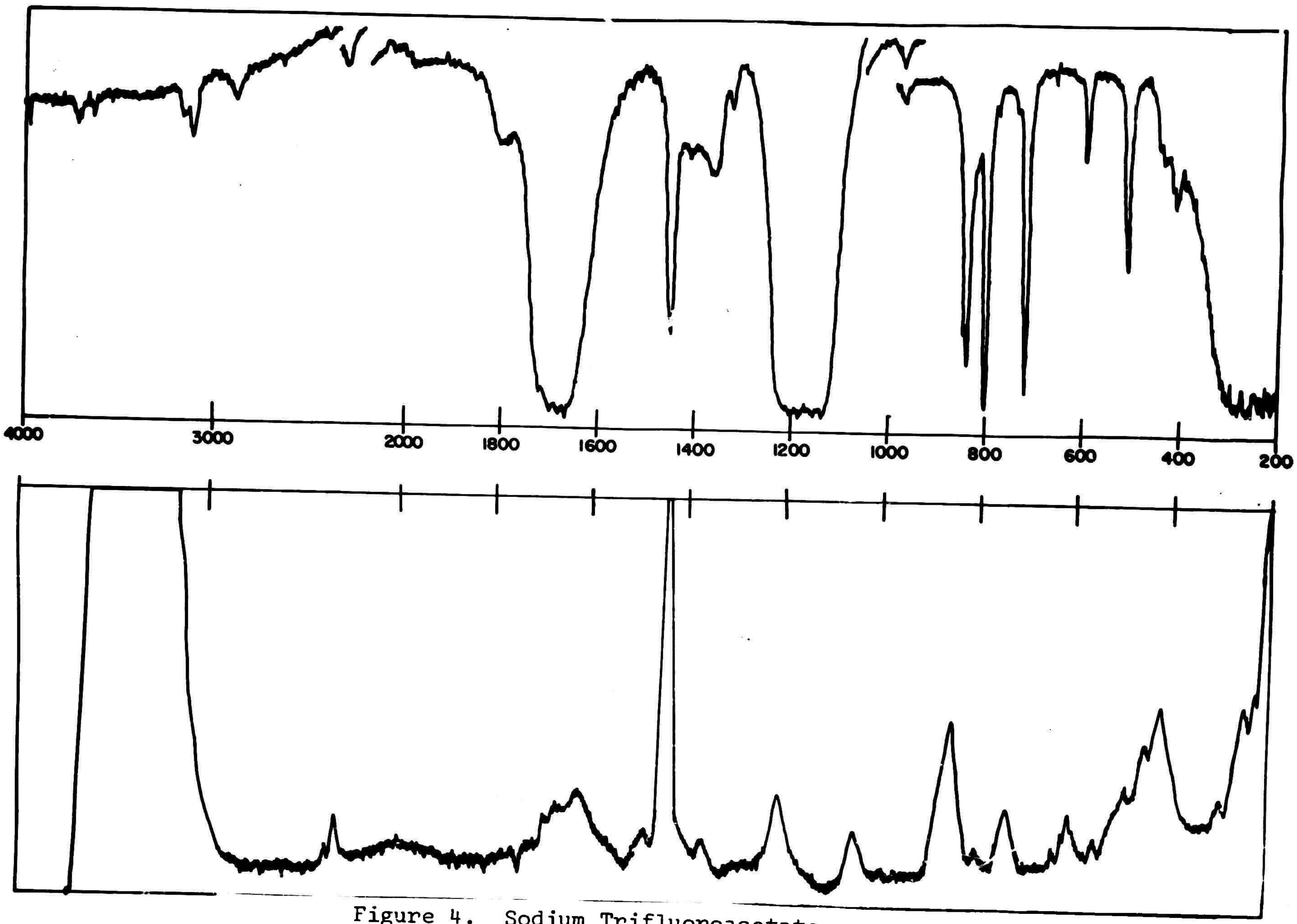


Figure 4. Sodium Trifluoroacetate.

Upper: Infrared Spectrum.