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SEMIANNUAL TECHNICAL REPORT*

on

ANOMALOUS WATER AND OTHER POLYMERIC MATERIALS

SPONSORED BY
ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 1463

to

U. S. ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA

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July 16, 1971

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Attention AMSMI-RND

Dear Sir:

Enclosed are 46 copies of the Semiannual Technical Report on "Anomalous Water and Other Polymeric Materials". This research is being carried out under Contract No. DAAH01-71-C-0491. This report covers the period from December 15, 1970 to June 15, 1971.

Please do not hesitate to call us if you have any questions concerning this report.

Very truly yours,

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SYNOPSIS

During the preparation of anomalous material from water, a residue is found in the capillary tubes even though the tubes themselves had been cleaned prior to the preparation; i.e., the capillary tubes were washed 15 times with water at which time no measurable residue could be extracted. The total quantity of elements other than H and O is smaller for the preparations from cleaned tubes than either the first tube washings with water or the preparations from uncleaned tubes. All of the elements found to be present in either the water washings of capillary tubes or in preparations from uncleaned tubes were detected in the preparations from cleaned tubes. All tube washings and preparations give roughly equivalent infrared spectra; i.e., three broad bands near 1600 cm^{-1}, 1400 cm^{-1}, and 1100 cm^{-1}. However, there are distinct and consistent differences in the exact frequencies of these absorption bands between the spectra of liquid water tube washings and the spectra of anomalous material preparation, whether from cleaned or uncleaned tubes. These spectral differences cannot be explained by changes in the amounts of the elements thus far detected. The frequency differences definitely show changes in chemical composition between preparations and washings and strongly indicate that the preparation of anomalous materials from water cannot be accounted for solely on the basis of extraction by liquid water of elements from the glass of which the capillary tubes are made.

Preparation of anomalous material from 3 percent H_2O_2 solutions gave a material with an infrared spectrum which differed in some frequencies from the spectrum of preparations from 100 percent H_2O. Upon heating, the frequencies of the H_2O_2 preparation in the 1600 cm^{-1} and 1400 cm^{-1} range decreased in intensity, but shifted to the frequencies found for H_2O preparations. These frequency shifts could not be correlated with a change in elemental composition.

The residues from water extraction of seven types of crushed glass can be divided into three groups, each of which can be classified by spectral characteristics, by elemental composition, and by amount of material extracted. Unlike the tube washings and preparation with water, the three groups of water extractions of crushed glass give spectral differences which are reflected by changes in elemental composition.

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from

BATTELLE
Columbus Laboratories

July 16, 1971

INTRODUCTION AND BACKGROUND

Few scientific reports in the last decade have attracted such widespread interest as has that of anomalous water. One result of this interest has been the experimental and theoretical investigations of anomalous materials by researchers who are expert in a wide range of technical disciplines. Yet even after these investigations, a number of basic questions concerning anomalous water remain either unanswered or incompletely answered.

Probably the most important of the unanswered questions is "Does water alone or water combined with another chemical moiety account for the anomalous water phenomenon?" From the experimental results obtained from samples of a new micrograms of anomalous water, one cannot answer this question unambiguously.

Chemical analyses by a number of laboratories strongly indicate that elements other than H and O have been present to varying degrees in the anomalous water samples. It is important to note, however, that excluding H and O, no combination of the elements detected to be present by chemical analysis of microgram samples has been conceived which will explain all of the experimental observations for anomalous water -especially the infrared spectrum.

The purpose of this research is the production of anomalous material prepared from water and anomalous materials prepared from selected organic compounds in amounts sufficiently large to enable their characterization, and to permit an assessment of the technological utility of the anomalous materials to be made.

It is believed that a knowledge of the impurities present and the role such impurities play, if any, in the anomalous water phenomenon is critical for an accurate evaluation of data obtained by chemical analysis and for optimization of synthesis techniques to be made. Therefore, the initial experimental work was designed to establish qualitatively and, where possible, quantitatively, the impurities which could be introduced during the preparation of anomalous materials.

It has been demonstrated that freshly drawn pyrex and quartz capillaries like those used for anomalous water preparations yield a water-soluble residue when they are washed with quadruply distilled water.(1) While the exact nature of this water-soluble residue was not characterized, it was shown that this residue from the water-soluble fraction appeared to be different from anomalous material prepared in the same capillaries. Also, as the number of washes of a group of capillaries was increased, it was observed that the amount of the residue from the water soluble fraction significantly decreased. However, after four washings, some water-soluble components were still being extracted.(1)

Therefore, an integral part of the present research program is to determine the nature of the water-soluble fraction and to test if all detectable water-soluble material could be removed from the capillaries*. Experiments were conducted in which a group of pyrex capillaries was washed until no detectable water-soluble component was removed.

The residue from the water used for each wash was retained separately for analysis to determine the elemental composition of each residue and to approximate the relative rate at which each element was removed. These same "cleaned" capillaries were then used to prepare anomalous material and to investigate if additional components of the pyrex were extracted.

Exactly analogous experiments were performed using propanol-1 instead of water in the initial investigation of anomalous organics.

It has been observed by a number of researchers that anomalous water forms detectably only from water vapor.(2) Also, it has been reported that in some cases solubility can be increased by as much as 9 orders of magnitude in a thin layer of solvent, as opposed to the bulk solvent.(3) Research in this report period included experiments to test if such an abnormal solubility effect is involved in the formation of anomalous materials. Accordingly, capillaries were washed with water vapor in a pressure cooker.

It has been proposed that the anomalous character of anomalous water is due to the extraction of some unspecified component of the glass from which the capillaries are made.(4) Such an extract, like anomalous water, would have a density and index of refraction greater than those of water.

(*) In this report, the terms capillary and tube are used interchangeably.

To investigate if some water-soluble fraction of a glass could account for the reported infrared spectrum of anomalous water, experiments were started to determine what kind and how much material can be extracted from various glasses. Crushed portions of seven different glasses were extracted with water. In addition to recording their infrared spectra, the water-soluble fraction of each glass was analyzed by emission spectrography to determine the metallic composition of the residues.

Early anomalous water research at Battelle's Columbus Laboratories suggested that oxygen could play a key role in the formation of anomalous water.(4) In an attempt to test this hypothesis, the preparation of anomalous material from 3 percent aqueous H_2O_2 instead of H_2O was attempted. The preparation of anomalous material from 30 percent H_2O_2 is in progress.

EXPERIMENTAL

Liquid Water Cleaning of Capillary Tubes

For the liquid water cleaning experiments, about 500 freshly pulled pyrex capillary tubes were placed in a pyrex baking dish and the tubes were covered with 500 ml of demineralized water. The baking dish was then covered with Saran wrap and allowed to stand (with occasional shaking) for seven days. On the seventh day, the water was poured off into a round-bottomed pyrex flask. The baking dish and tubes were dried in an oven at 100 C and then a second cleaning was started by adding another 500 ml of demineralized water to the dish. This weekly cleaning cycle was repeated until the 500 tubes had been washed 15 times.

The flask containing a single washing was then placed on a rotary evaporator where most of the water was removed. At the point where a few ml of water remained in the flask, the evaporation was stopped and the water was transferred to a weighed pyrex vial. The remaining water was removed by evaporation with N_2 and the weight of the dry residue was obtained. A few drops of water were then added to the vial and aliquots of the solution were removed for infrared, emission, and electron microprobe analysis.

The washing was halted and the tubes were considered "cleaned" when the barely perceivable residue from the 15th washing gave no detectable weight (less than 0.1 mg) and no infrared spectrum could be obtained from the residue by the techniques used for the other washings. These samples of washings are designated LW-H_2O-1*, LW-H_2O-2, etc. The letters stand for liquid wash with water and the numbers indicate which washing.

In addition, several standards or blanks were obtained. LW-H_2O-00 is the residue obtained from the water used in these experiments. LW-H_2O-01 and LW-H_2O-02 are the first and second system blanks, respectively. A system blank is a duplicate of the washing experiments without the tubes being present. Thus the sample under consideration is the residue obtainable from a water wash of the baking dish, round-bottomed flask, and vial.

Preparation of Anomalous Materials from Water

The technique used in our laboratory for preparation of anomalous material has been described in detail(1) and will be only briefly described here. The capillary tubes are placed on pyrex Petri dishes resting on a porcelain plate in a greaseless desiccator. A pyrex evaporating dish containing demineralized water is placed below the porcelain plate and the desiccator is sealed with a vacuum of about 5 millimeters of pressure of mercury. After seven days the capillaries are removed from the desiccator

(*) A complete list of sample notations is given in Appendix A.

and the anomalous material is removed from the tubes by washing with demineralized water. This wash water is then placed in a round-bottomed flask and the residue is obtained by the same procedure as used in the liquid washing experiments.

Two types of preparation were attempted. In one the pyrex tubes which had been washed 15 times (and designated "cleaned") were used for preparation of the anomalous material. This preparation is labeled H_2O-CP-1. The same tubes were then dried and placed in the desiccator for a second preparation. The sample resulting from this is labeled H_2O-CP-2. (CP stands for cleaned pyrex). In the second type of experiment, pyrex tubes which had not been washed or "cleaned" were used for the preparation. This sample is labeled H_2O-UP-1. (UP stands for uncleaned pyrex).

A system blank for the anomalous material preparation (H_2O-P-01) has just been completed, but the analyses will not be available for this report. This blank is a duplication of the preparation, but without any capillaries, and thus will represent the residue obtainable from a water wash of the desiccator, petri dishes, porcelain plate, round-bottomed flask, and vial.

Preparation of Anomalous Material from H_2O_2 Solutions

To test the role played by oxygen in the formation of anomalous material, two preparations were initiated using 3 percent aqueous H_2O_2 solutions and 30 percent aqueous H_2O_2 solutions, respectively, instead of H_2O. The method of preparation used was identical to that described above except the pyrex tubes were washed several times with water and several times with ethanol prior to being placed in the desiccator.

Upon removal from the desiccator the tubes were washed with quadruply distilled water. The major portion of the wash water (~80 ml total) was removed by evaporation under reduced pressure (~5 mm Hg). A water bath maintained at 40 C was used to warm the round-bottom flask containing the sample. Aliquots of the resulting concentrated solution (~4 ml) were used for analysis. The residue remaining after evaporation of the water from the 3 percent H_2O_2 preparation is labeled H_2O_2-P-1. After casting a film on an Irtran plate from an aliquot of concentrated solution for infrared analyses, the plate and sample were heated for 60 minutes at 400 C in air. This sample is designated H_2O_2-P-1H. The preparation involving the 30 percent aqueous H_2O_2 is still in progress.

Vapor Water Cleaning of Capillary Tubes

Experiments to clean capillary tubes with water vapor to test the possibility that vapor water has a greater solvent power for glass than does liquid water were carried out. In this experiment a pressure cooker was used to generate the water vapor as steam. About 500 pyrex tubes were heated in the pressure cooker for periods up to eight hours. The residual water was poured off and the residue worked up via a rotary evaporator as in the liquid water wash experiments. These samples were labeled VW-H_2O-1, VW-H_2O-2, etc. The letters stand for vapor washing with water and the numbers indicate which washing.

Liquid Propanol Cleaning of Capillary Tubes

Prior to the preparation of other anomalous materials (such as from propanol instead of water), capillary tubes were repeatedly washed with liquid propanol. The procedure and experimental arrangement was identical to that described for the liquid water, except that 99 percent plus propanol was used for the washing instead of demineralized water. These samples are designated LW-Pr-1, LW-Pr-2, etc.

Sample LW-Pr-00 is the residue obtained from the propanol used in the washings. LW-Pr-01 is the residue from a propanol extraction of the Saran wrap used to cover the baking dish.

In addition, sample LW-Pr-2 was cross-extracted with CCl_4 and infrared spectra obtained on both the CCl_4 solubles and the CCl_4 insolubles.

Liquid Water Extraction of Crushed Glasses

Experiments were designed to determine the composition of extractable material from various glasses. About 150 grams each of seven types of glass were crushed with a mortar and pestle and transferred rapidly into a new round-bottom flask containing about 150 grams of quadruply distilled water. The crushing was done on 30 to 50-g portions of glass. Each portion was transferred rapidly into the water to optimize contact of the freshly formed glass surfaces with the water. The glass was finely crushed, but no attempt to control particle size was made. Each crushed glass remained in contact with H_2O for 10 days. The samples were periodically agitated. The water was decanted and filtered through a Gooch crucible, using a slurry of Whatman #1 filter paper to remove the fines. After filtration, the volume of the water was reduced to ~4 ml by the method described above for H_2O_2.

These samples are designated CG-V-1, CG-Q-1, etc. CG stands for crushed glass extraction and 1 signifies the first extraction. The middle letter indicates the type of glass: V=Vycor, Q=quartz, P=pyrex, N=Nonex, C=cobalt, U=uranium, and 7052=7052 glass. CG-H_2O-01 is a system blank.

The blank was a 150-g aliquot of the same water used for extracting crushed glass. The blank was carried through all operations described above except that it was never exposed to a crushed glass.

Analyses

Infrared Spectroscopy

The infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer. Samples were run as films from water on Irtran plates or films from propanol on NaCl plates. It is quite significant that all samples were large enough so that spectra could be obtained without a beam condenser or the use of scale expansion.

Electron Microprobe

The microprobe analyses were done on a Model 400S Scanning Electron Microprobe manufactured by the Materials Analysis Company. The samples were prepared for the electron microprobe by laying films (from water or propanol) on high purity aluminum plates. X-ray images of the element distributions are shown in various figures throughout this report. The numerical value of the relative intensity counts for all elements and samples studied are given in Appendix B. These relative count values cover the range observed under the area of the electron beam. Two points of caution in the interpretation of results must be mentioned here. All samples showed varying amounts of browning or darkening under the electron beam. This coupled with the high vacuum used in the electron microprobe suggests that the electron microprobe sample might not be equivalent in composition to the samples used for other techniques of analysis. Secondly, the area shown in the photographs in the figures represents only a small portion of the total sample. As will be seen later, all elements are not distributed evenly throughout the sample, and thus the electron microprobe analysis might not be representative of the entire sample.

Emission Spectrography

The emission analysis was performed on an ARL 1.5 meter; 25,000 line/inch grating instrument. The spectra were recorded on photographic film in the region 2200A to 9400A.

Partial results of the emission analyses are listed in several tables throughout this report. The total emission results are listed in Appendix C. All values are expressed in micrograms with an accuracy of ±50 percent. The weights of the samples used for emission analysis are not known; therefore some measure of sample amount is needed in order to be able to compare samples realistically. The next to last column of Appendix B gives the total weight of the elements detected. Values reported as <0.1, <1.0, <50.0, etc. are included in the total as 0.1, 1.0, 50.0, respectively. For some samples, a camera was used which did not give precise values for K (only reported as <50.0). For the same samples, no values are reported for Co, Sb, and As. Thus the last column of Appendix B gives the total weight of the elements detected minus the weight of K. Using the weights reported in this last column does not guarantee direct comparison of samples, but does give a better means of evaluating large scale changes in elemental composition; especially for samples containing equivalent amounts of K.

Other Analyses

Conventional wet chemical C, H, and N analyses were done whenever the samples were large enough. These results are listed in Table 3. The weights of the residues obtained from the various washings and preparations are listed in Table 1.

RESULTS

Liquid Water Cleaning of Capillary Tubes and Preparation of Anomalous Materials from Water

Infrared Spectra

The infrared spectra of the samples obtained from the liquid water cleaning of capillary tubes are shown in Figures 1 and 2. The infrared spectra of the preparation of anomalous materials from water utilizing these cleaned tubes are also shown in Figure 2.

All of these samples show some infrared absorption in the conventional OH stretching region from 3350 to 3500 cm^{-1}. This appears to be quite typical of an anomalous water prepared in pyrex tubes. This, however, is a very, very small amount of OH absorption when compared to the OH band of water.

In addition all of these samples show a very weak CH absorption between 2850 and 3000 cm^{-1}. This might indicate some fingerprint contamination (although gloves are always used) or absorption of organic vapors which are only slightly washed off each time because water is not a good solvent for many organics. On going from LW-H_2O-1 through to LW-H_2O-15 the amount of CH material appears to be decreasing, but then it increases again, especially in H_2O-CP-2. This indicates a need to wash the tubes with an organic solvent prior to any water washing or preparation. In sample H_2O-CP-2 there is a weak 1730 cm^{-1} absorption in addition to the CH absorption. A CCL_4 extraction of H_2O-CP-2 gave a residue whose spectrum showed only 2850-3000 cm^{-1} absorption and 1730 cm^{-1} absorption of about the correct relative intensity to account for all the absorptions

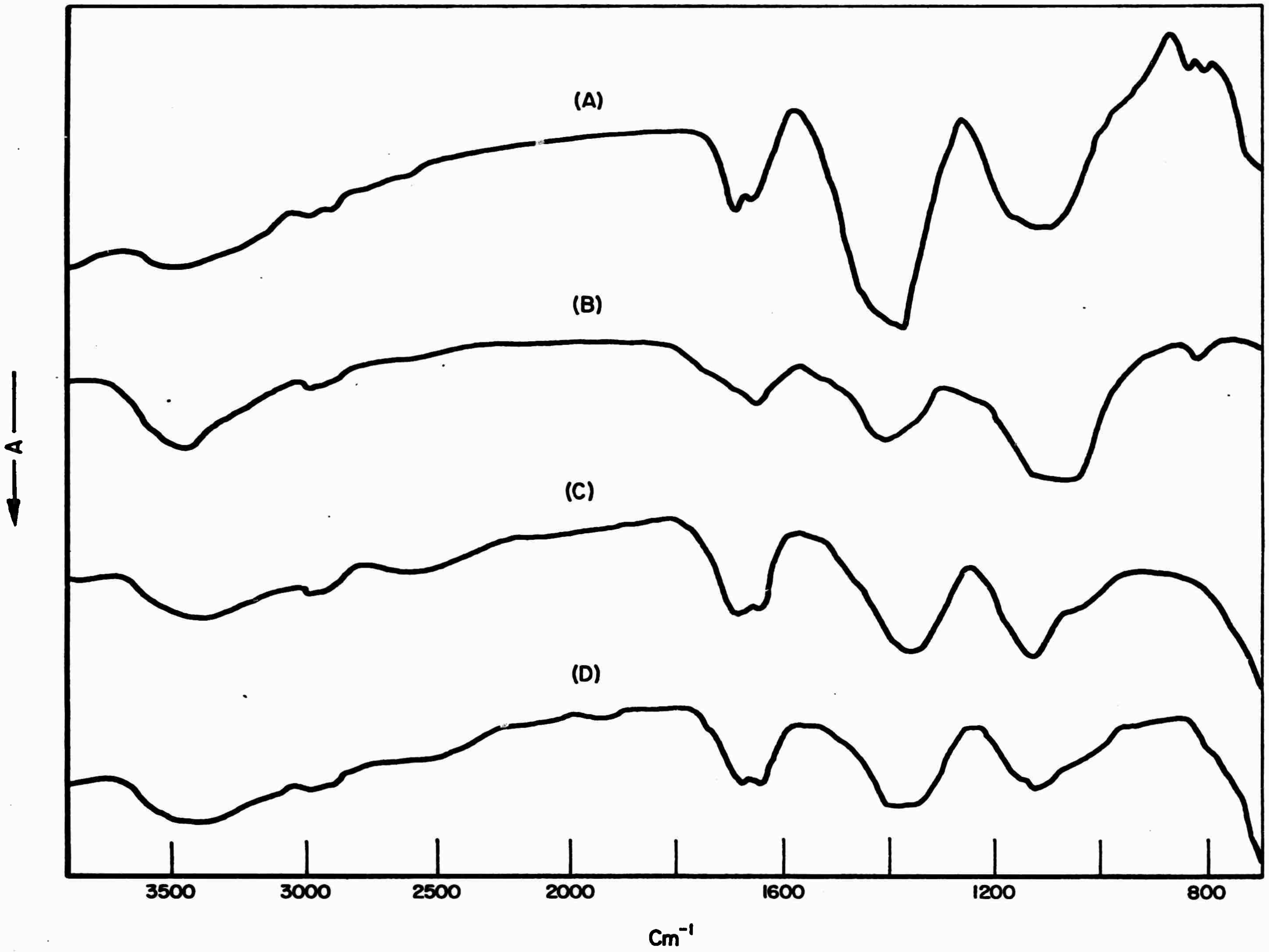


FIGURE 1. INFRARED SPECTRA OF (A) LW-H_2O-1, (B) LW-H_2O-2, (C) LW-H_2O-12, AND (D) LW-H_2O-13

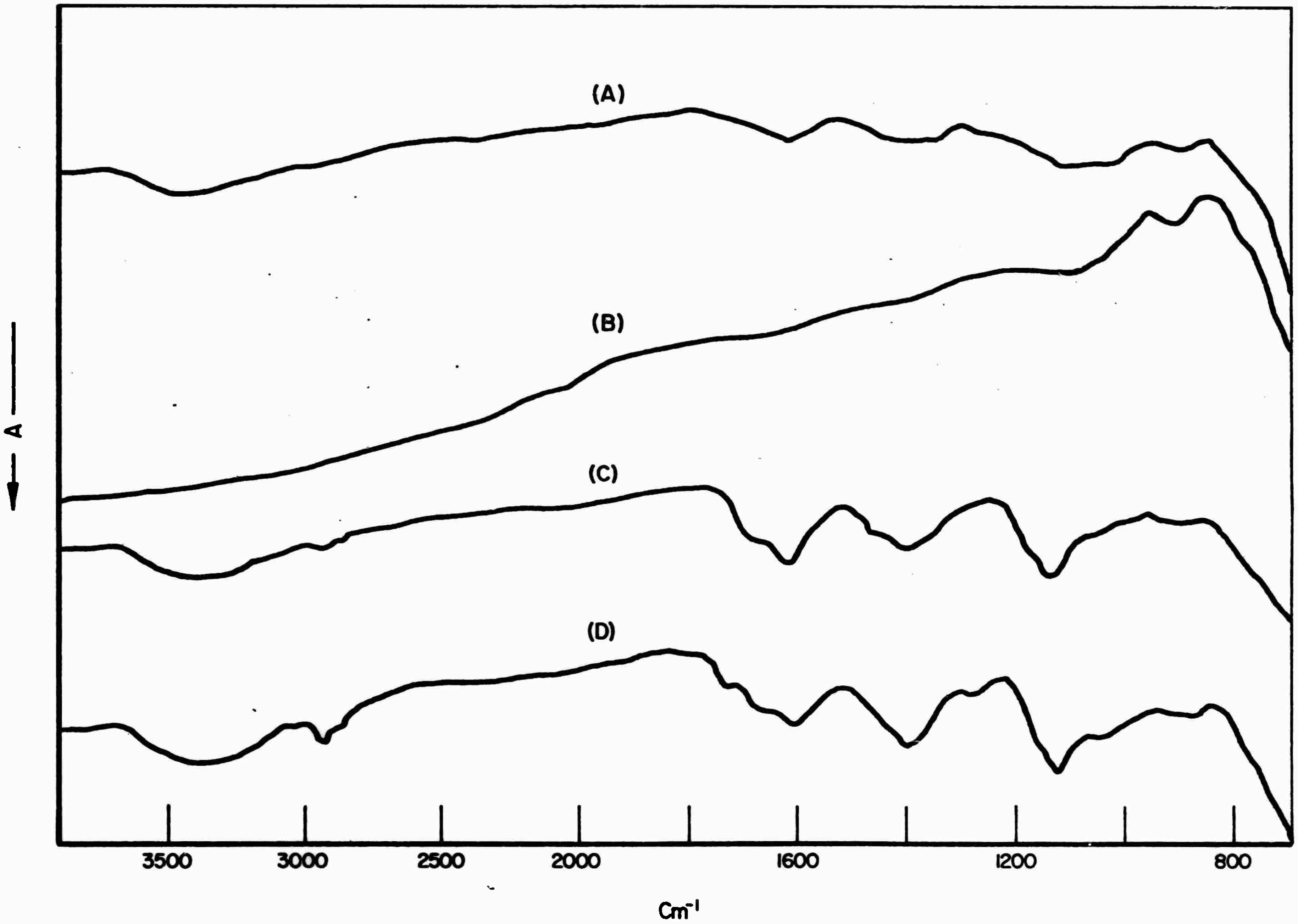


FIGURE 2. INFRARED SPECTRA OF (A) LW-H_2O-14, (B) LW-H_2O-15, (C) H_2O-CP-1, AND (D) H_2O-CP-2

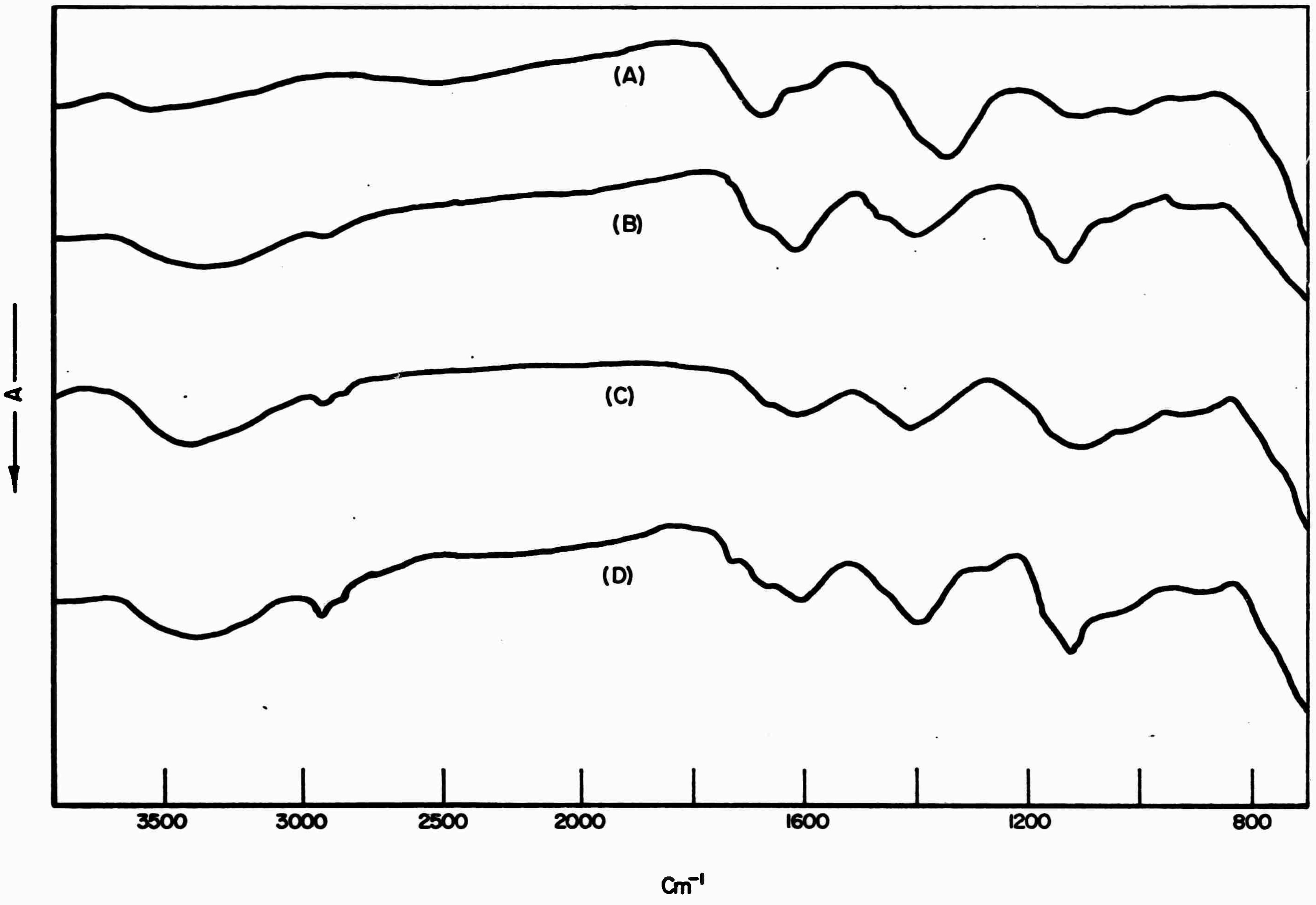


FIGURE 3. INFRARED SPECTRA OF (A) LW-H_2O-02, (B) H_2O-CP-1, (C) H_2O-UP-1, AND (D) H_2O-CP-2

at these frequencies which are seen in the spectrum of H_2O-CP-2. Thus the organics can be removed without affecting the rest of the spectrum of anomalous water samples.

Most of the spectra of the liquid water washings show two absorption bands in the 1600 cm^{-1} region. One is at 1640 cm^{-1} and the other is at 1680 cm^{-1}, with the 1680 cm^{-1} band being, generally, the stronger absorption. It is interesting to note (although difficult to see in the figures) that the spectra of the anomalous water preparations also show two bands in this region. One is at 1680 cm^{-1}, but the other is shifted to 1620 cm^{-1}. In addition the 1620 cm^{-1} band is always the stronger absorption in the spectra of the preparations. This observation strongly suggests that a different chemical species is present in the preparations than in the washings. All washings (LW-H_2O-1 through LW-H_2O-14) and the system blank (LW-H_2O-02, Figure 3) show the absorption at 1640 cm^{-1}. All preparations including H_2O-UP-1 (Figure 3) have this absorption at 1620 cm^{-1}. This shift is quite consistent and is believed to be significant.

In the 1400 cm^{-1} region, the infrared spectra of the liquid washings give very broad absorption which shows two peaks; one at 1350-1360 cm^{-1} and one near 1410 cm^{-1}. The peak near 1350 cm^{-1} is generally the stronger absorption although occasionally the peaks are nearly equal in intensity. On the other hand, the spectra of the anomalous water preparations show a strong 1410 cm^{-1} absorption with, at best, a weak 1350 cm^{-1} absorption (the width of the 1410 cm^{-1} band makes it difficult to determine if a 1350 cm^{-1} absorption is present). This shift between washings and preparations is best seen in Figure 3. The system blank or washing (LW-H_2O-02) clearly shows strong absorption at 1350 cm^{-1}

while the preparations (H_2O-CP-1, H_2O-UP-1, and H_2O-CP-2) show strong 1410 cm^{-1} absorption. Thus the 1400 cm^{-1} spectral region also clearly shows differences between the liquid water washings and the preparations.

Spectral differences are also seen in the 1100 cm^{-1} region. However, these are not differences between washings and preparations. For purposes of discussion consider two areas of infrared absorption in this spectral region; one from 1040 to 1090 cm^{-1} and one from 1120 to 1140 cm^{-1}. In Figure 1 it can be seen that LW-H_2O-1 and LW-H_2O-2 show stronger absorption in the 1040 to 1090 cm^{-1} range while LW-H_2O-12 and LW-H_2O-13 show a stronger band at 1120-1140 cm^{-1}. This would seem to indicate that continual washing was removing the species giving rise to the 1040-90 cm^{-1} absorption more than the species giving rise to the 1120-40 cm^{-1} component. However in LW-H_2O-14 (Figure 2) these bands are nearly of equal intensity again. From Figure 3 it can be seen that the preparations in cleaned tubes (H_2O-CP-1 and H_2O-CP-2) give a stronger 1120-40 cm^{-1} peak. However, while H_2O-UP-1 gives a stronger 1120-1140 cm^{-1} absorption there is definitely some 1040-90 cm^{-1} absorption also. The system blank or washing LW-H_2O-02 gives mainly 1040-1090 cm^{-1} absorption.

The effectiveness of the washing procedure can be judged from the spectra of Figures 1 and 2. More than adequate residue was obtained to record the spectra of LW-H_2O-1 and LW-H_2O-2 (Figures 1A and -B). There was a significant decrease in the amount of residue available to obtain spectra of LW-H_2O-12 and LW-H_2O-13 (Figures 1C and -D). The sample LW-H_2O-14 was very small (Figure 2A). The resulting spectrum (Figure 2A) showed only weak bands. The residue LW-H_2O-15 was barely perceivable and no spectrum (Figure 2B) could be obtained. The total weights of these residues and preparations are given in Table 1, and the weights give clearer indications of the above trends due to the washings.

After the 15th wash, the tubes were judged to be "cleaned" and an anomalous material preparation using these tubes was started. Even though these were "cleaned" tubes, material was observed in the tubes after they were used for a preparation. When the material was removed from the tubes and the normal water evaporated, the weight of material from this first preparation was determined to be 0.4 mg. While this is greater than the non-measurable (<0.1 mg) weight of the 15th washing, it is not as much as had been produced in past preparations at Battelle, and is in the range of washings LW-H_2O-10 to LW-H_2O-14. This observation alone may indicate that a new material is formed in the tubes during the preparation process or it may only indicate that the vapor-like washing that goes on during the preparation can leach additional materials from the glass even after the glass tubes had been cleaned by the liquid washings. A second preparation using the same cleaned tubes yielded 0.3 mg of residue while material prepared in uncleaned tubes weighed 1.4 mg.

The preparation in the uncleaned tubes should give a weight in the range of 3.6 mg obtained for the first washing (LW-H_2O-1) if a vapor-like washing is as effective as a liquid washing. Since it did not, the formation of a material in the tubes during the preparation could be supported.

TABLE 1. WEIGHTS OF RESIDUES FROM LIQUID WATER CLEANINGS AND ANOMALOUS MATERIAL PREPARATIONS

Sample	Weight, (mg)
LW-H_2O-02 (blank)	0.4
LW-H_2O-1	3.6
LW-H_2O-2	1.5
LW-H_2O-10	0.5
LW-H_2O-14	0.3
LW-H_2O-15	no measurable weight, <0.1
H_2O-CP-1	0.4
H_2O-CP-2	0.3
H_2O-UP-1	1.4

On the other hand, the spectra of H_2O-CP-1, H_2O-UP-1, and H_2O-CP-2 are qualitatively similar. Thus, the differences in the weights (0.4, 1.4 and 0.3 mg, respectively) of the three preparations may only reflect amounts of available sample and not changes in composition. This will be discussed further in following sections.

The spectra of the washings in Figures 1 and 2 all show the 1600 cm^{-1} band to be weaker than the 1400 cm^{-1} band. The spectrum of the first preparation in these cleaned tubes (H_2O-CP-1) shows an intensity reversal, i.e., the 1600 cm^{-1} band is stronger than the 1400 cm^{-1} band. In the past(1) we have used the latter intensity relationship as one indication of the formation of a new material during the preparation process. At the present time it would appear that the relationship based on the stronger 1600 cm^{-1} versus 1400 cm^{-1} band must be qualified since in Figure 3, it is clearly seen that the spectra of both H_2O-CP-2 and H_2O-UP-1 show the 1600 cm^{-1} band to be weaker than the 1400 cm^{-1} band (as in the H_2O washing samples).

Emission Analysis

Emission spectrographic analyses have been obtained on all the liquid washing samples and on the preparations of anomalous materials from water (except for H_2O-CP-2). Complete emission results on all samples are given in Appendix C. Partial emission results for the washings and preparations are given in Table 2. The elements listed in Table 2 are those which show weight changes on going from sample to sample. With this criterion elements such as Ba, Mn, Fe, Sn, Ni, Cu, Ti, and Cr are not included in Table 2. Note that the numbers

TABLE 2. PARTIAL EMISSION SPECTROGRAPHIC ANALYSES FOR LIQUID WATER CLEANING SAMPLES AND PREPARATIONS OF ANOMALOUS MATERIAL FROM WATER

Sample	Elements (μg)						
	B	Si	Mg	Al	Na	Ca	K
LW-H_2O-00	<0.1	0.1	0.02	<0.1	<1.0	0.1	<50.0
LW-H_2O-01	2.0	5.0	0.5	0.2	1.0	1.0	<50.0
LW-H_2O-02	0.1	1.0	0.2	<0.1	<1.0	0.3	<1.0
LW-H_2O-1	15.0	10.0	2.0	1.0	50.0	5.0	<50.0
LW-H_2O-2	3.0	3.0	0.3	0.2	>100.0	3.0	>100.0
LW-H_2O-12	0.2	2.0	0.3	0.1	<1.0	1.0	<50.0
LW-H_2O-13	0.3	2.0	0.3	<0.1	<0.1	1.0	<50.0
LW-H_2O-14	2.0	5.0	0.5	0.2	10.0	1.0	<50.0
H_2O-CP-1	0.3	2.0	1.0	0.2	20.0	2.0	<50.0
H_2O-UP-1	5.0	10.0	5.0	1.0	30.0	5.0	<50.0

represent the total weight in micrograms of each of the elements observed. Since all of the elements present in the sample (such as C, O, S, Cl) are not observed and since the total weight of the sample is not known, comparisons between samples must be made with some caution.

First, the water (LW-H_2O-00) used in the washings is comparatively clean, i.e., comparatively free of the elements listed in Table 2. Comparing the analysis of the water (LW-H_2O-00) to the analysis of the system blanks or washings (LW-H_2O-01 and LW-H_2O-02) shows that additional elements are being extracted from the system (the baking dish, flask, and vial). Principal among these appear to be B, Si, Mg, and Ca. The differences between the two system blanks (LW-H_2O-01 and LW-H_2O-02), can reasonably be used to indicate the limits of accuracy between any two samples. The analysis of the first tube washing (LW-H_2O-1) shows a large increase in some elements when compared to the analyses of the system blanks. This observation shows that comparatively large amounts of B, Si, Ca, and especially Na are being extracted from the pyrex capillary tubes. In fact, comparison of the analyses of LW-H_2O-01 and LW-H_2O-14 indicates that except for Na the quantity of elements present in LW-H_2O-14, the last listed tube washing, is similar to that of the system blank. However it must be mentioned here that in LW-H_2O-14 some of the material present must still be coming from the tubes since at this point the system has also gone through 14 washings. Therefore the 14th system blank should, in theory, yield less material than LW-H_2O-01.

Some of the numerical values from the emission analyses of the residues from tube washing are not yet understood; for example the exceptionally high Na and K values in LW-H_2O-2, or the low values for all elements in LW-H_2O-12 and LW-H_2O-13. Part, but not all, of the low values can be explained by a much smaller total sample for LW-H_2O-12 and LW-H_2O-13.

The first preparation using the cleaned tubes (H_2O-CP-1) gives emission analysis values that, except for Na, are below the values for the last listed tube washing (LW-H_2O-14). In fact the emission values for the first preparation are within the range (again except for Na) of the elements of the two system blanks (LW-H_2O-01 and LW-H_2O-02) and are distinctly lower than the emission values found for the first preparation in uncleaned tubes (H_2O-UP-1). As would be expected the values found for H_2O-UP-1 are most similar to those found for the first tube washing (LW-H_2O-1).

The values found for the first perparation in cleaned tubes (H_2O-CP-1) are also substantially below the values found for the first washing (LW-H_2O-1). Thus as indicated by infrared, washing the tubes clearly decreases the concentration of certain elements. The principal elements which are definitely being removed by washing are B and Si while Na and Ca are possibly being removed.

Electron Microprobe Analysis

In addition to the metals detected by emission spectroscopy, electron microprobe microanalysis is also capable of detecting many nonmetals. Electron microprobe analyses have been obtained on all the liquid washing samples and on the preparations of anomalous materials from water (again except for H_2O-CP-2). The complete electron microprobe results are listed in Appendix B. These results are given in numerical values which represent the density counts per second for each element studied. In most cases a range is given for the extremes observed over the area covered by the electron beam. Use of these numerical values can often provide a better basis for comparison of the overall composition of samples than X-ray images.

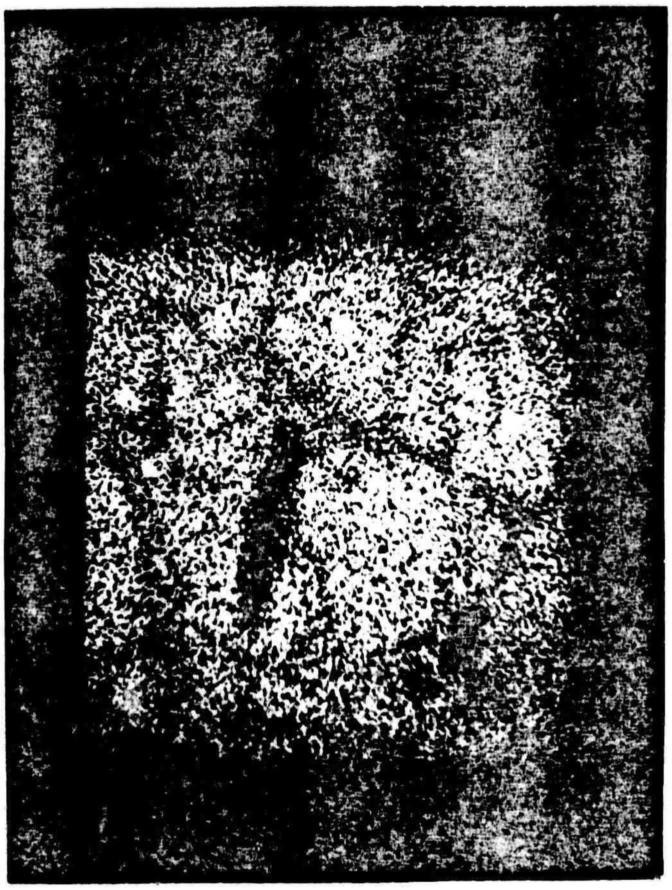
However the X-ray images often provide information on the distribution of elements within a specific sample area. Such X-ray images are shown for two samples in Figures 4 through 9. X-ray images are shown for only two samples since these two are fairly representative of the remainder of the samples.

Figures 4 to 6 are X-ray images of the first system blank, sample LW-H_2O-01. X-ray images of the first preparation from cleaned tubes, sample H_2O-CP-1, are shown in Figures 7 to 9. It was previously stated that based on emission analysis results LW-H_2O-01 and H_2O-CP-1 had similar elemental compositions except for the Na content. The X-ray images and Appendix B support most of the emission results. The B X-ray images in Figures 4 and 7 indicate a slightly higher boron or B content in LW-H_2O-01 than in H_2O-CP-1; consistent with the emission results in Table 2. The X-ray images in Figures 4 to 9 also show roughly equal amounts of C, K, Ca, S, and Mg for the two samples which agrees with the count per second values in Appendix B and with the emission values for K, Ca and Mg in Table 2. The X-ray images (and the numerical values from Appendix B) indicate a higher concentration of both Si and O in the system blank (LW-H_2O-01) than in the residue from the clean tube preparation (H_2O-CP-1); consistent with the emission values for Si. There are no emission values for O.

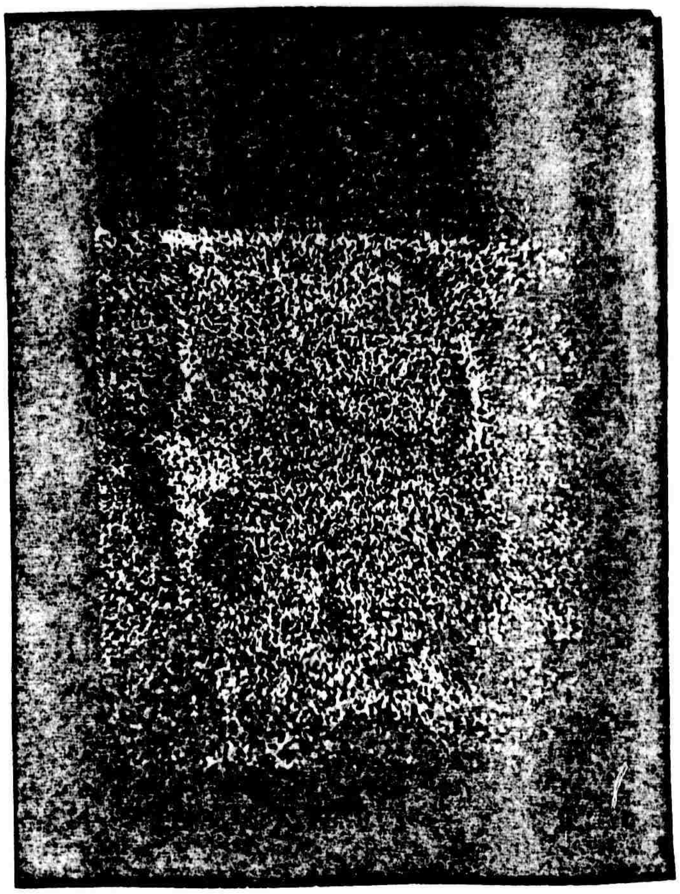
FIGURE 4. ELECTRON MICROPROBE ANALYSES OF LW-H_2O-01 SHOWING THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE AND THE X-RAY DISTRIBUTION IMAGE FOR B, Na, AND C

LW-H_2O-01

B



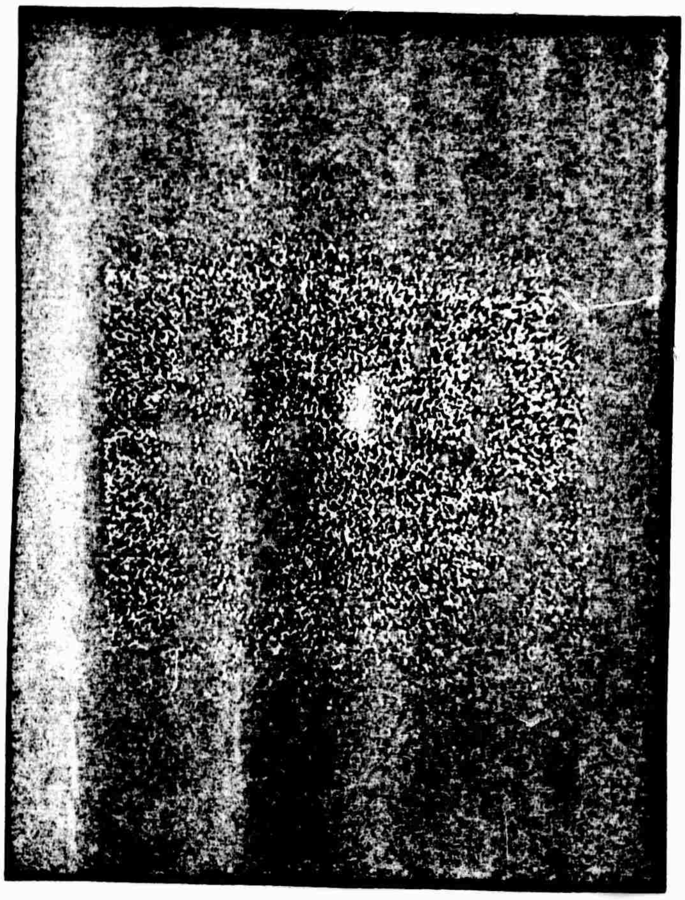
Na



C

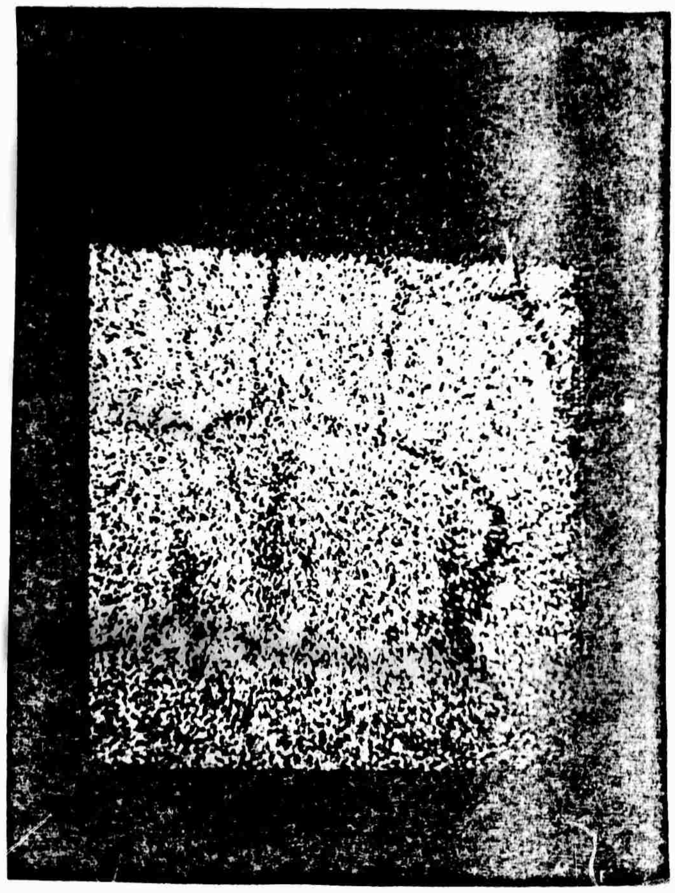
FIGURE 5. ELECTRON MICROPROBE ANALYSES OF LW-H_2O-01 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Mg AND O_2, THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE, AND THE X-RAY DISTRIBUTION IMAGE FOR K

LW-H_2O-01



Mg

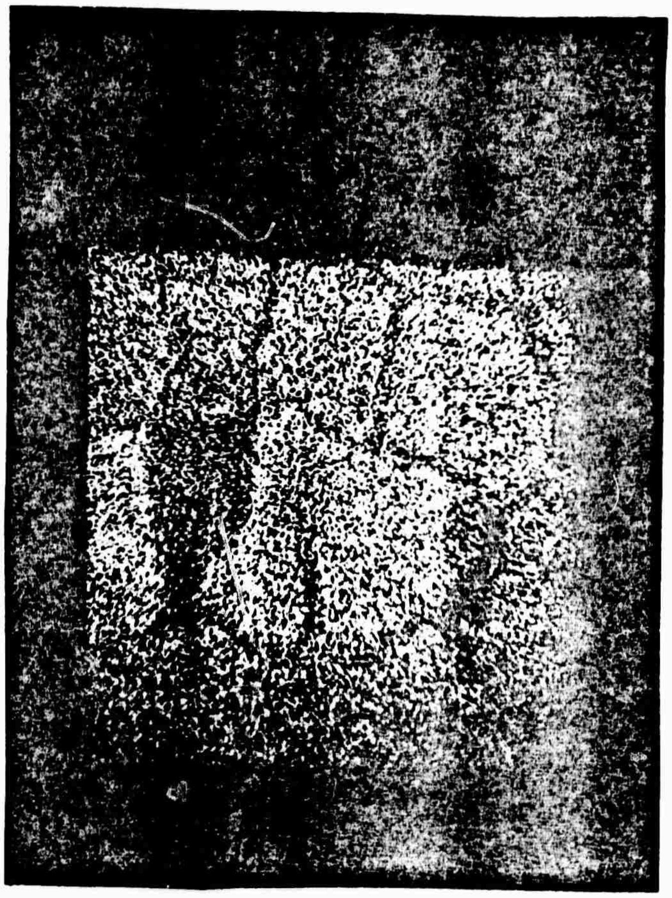
O_2



K

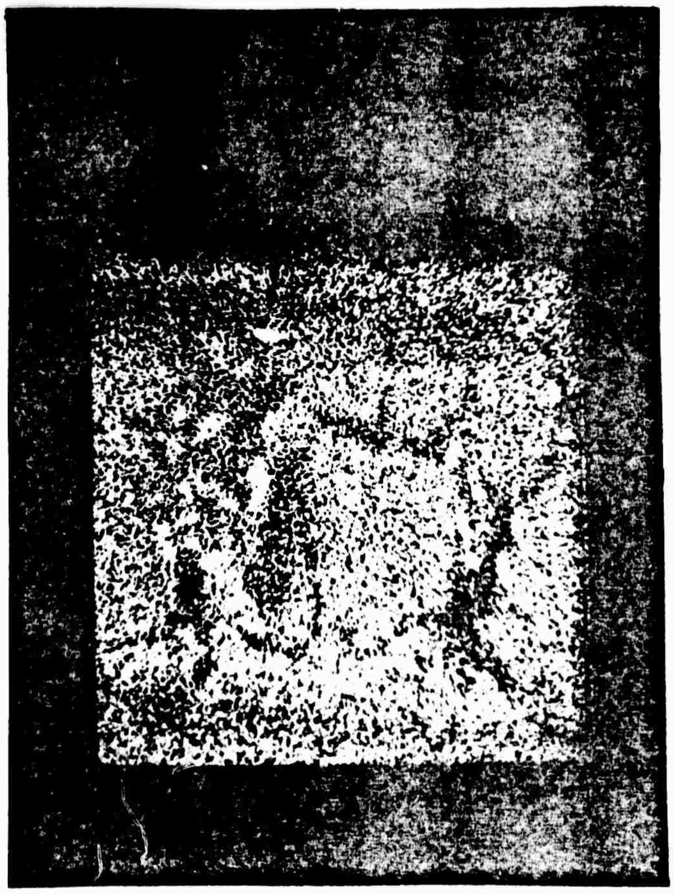
FIGURE 6. ELECTRON MICROPROBE ANALYSES OF LW-H_2O-01 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Ca, Cl, S, AND Si

LW-H_2O-01



Ca

Cl

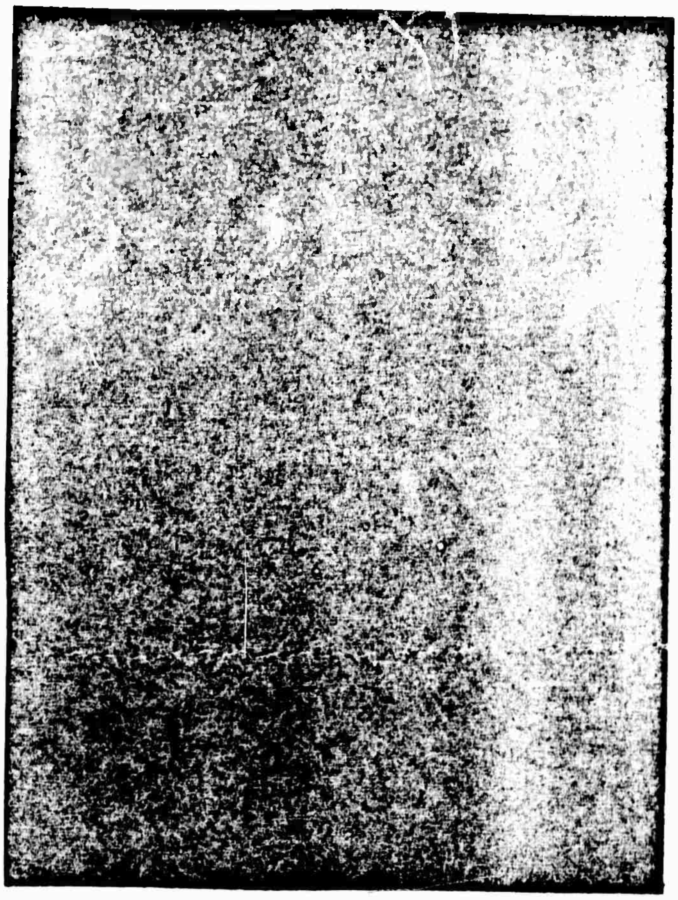


S

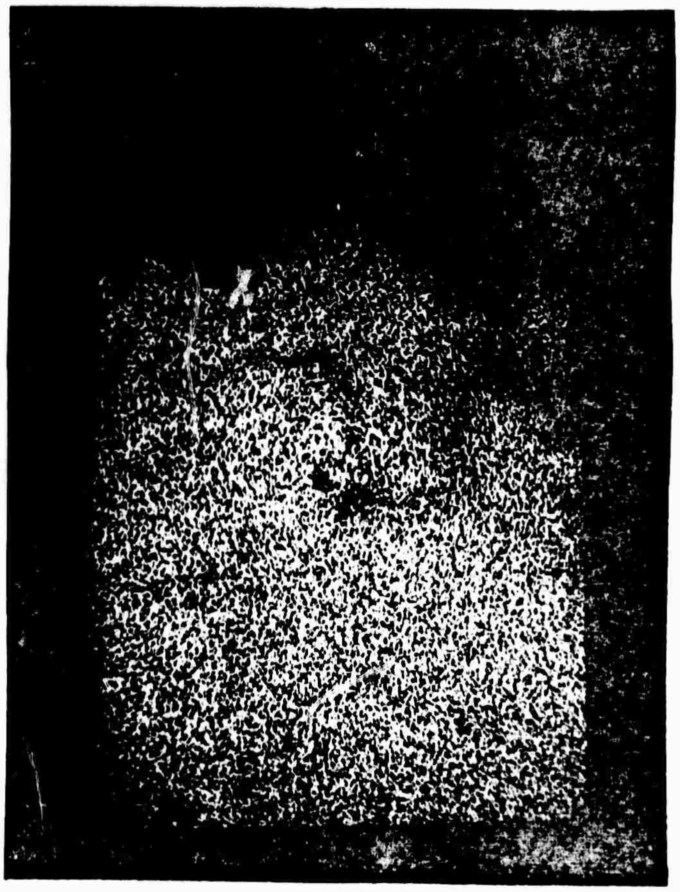
Si

FIGURE 7. ELECTRON MICROPROBE ANALYSES OF H_2O-CP-1 SHOWING THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE AND THE X-RAY DISTRIBUTION IMAGES FOR B, Na, AND C

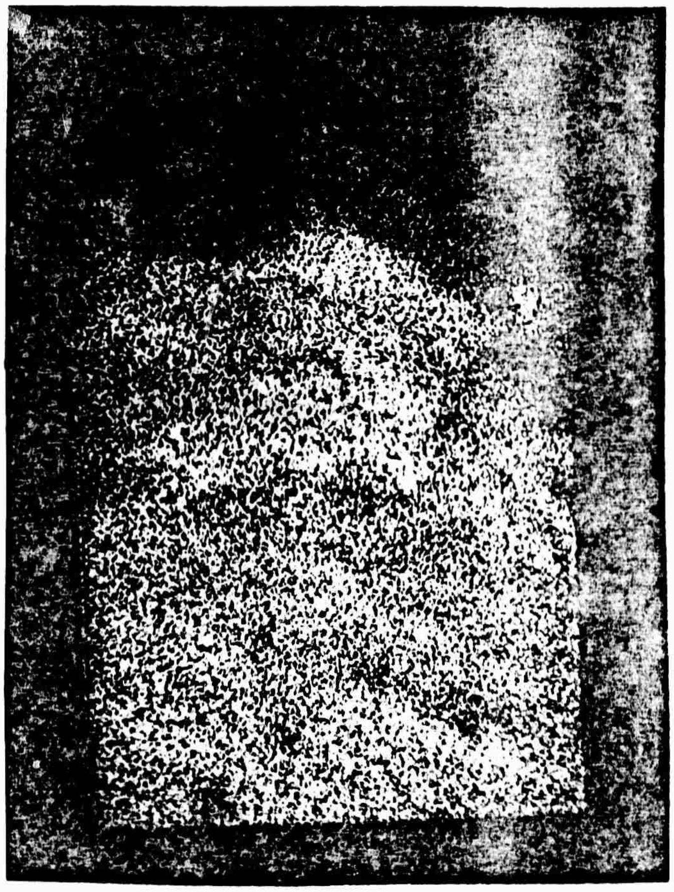
H_2O-CP-1



B



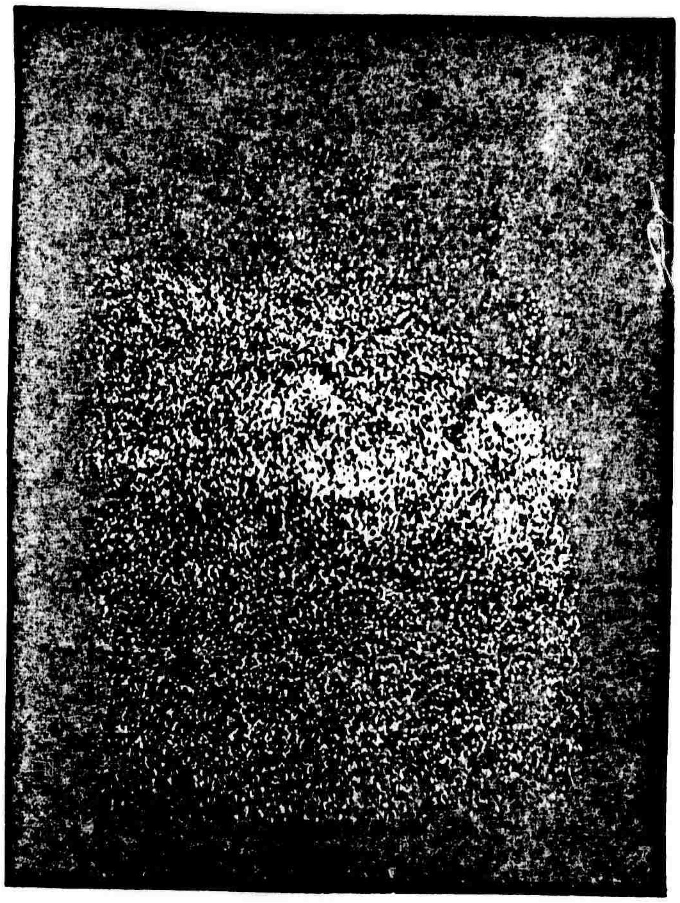
Na



C

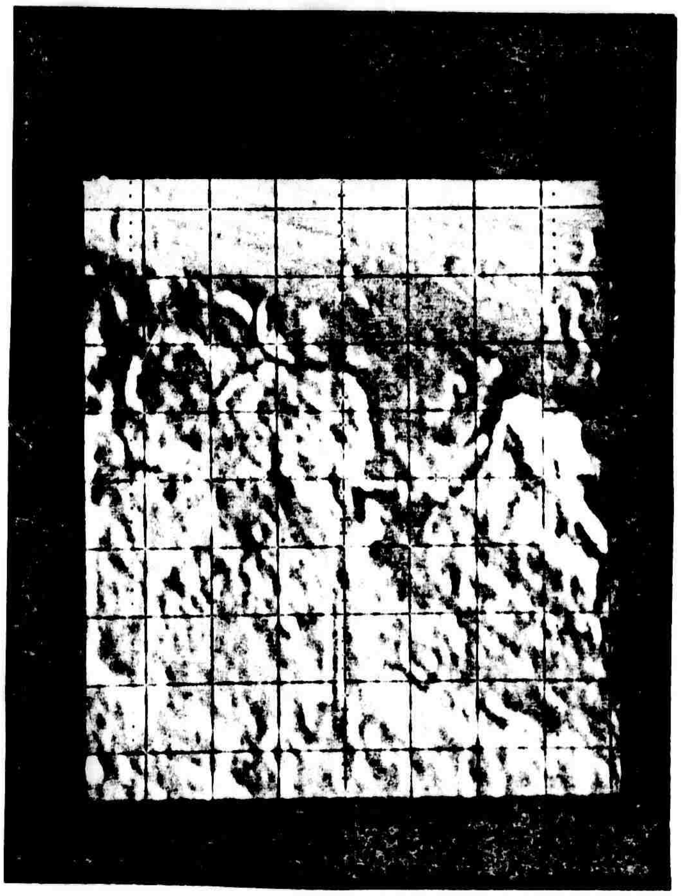
FIGURE 8. ELECTRON MICROPROBE ANALYSIS OF H_2O-CP-1 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Mg AND O, THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE, AND THE X-RAY DISTRIBUTION IMAGE FOR K

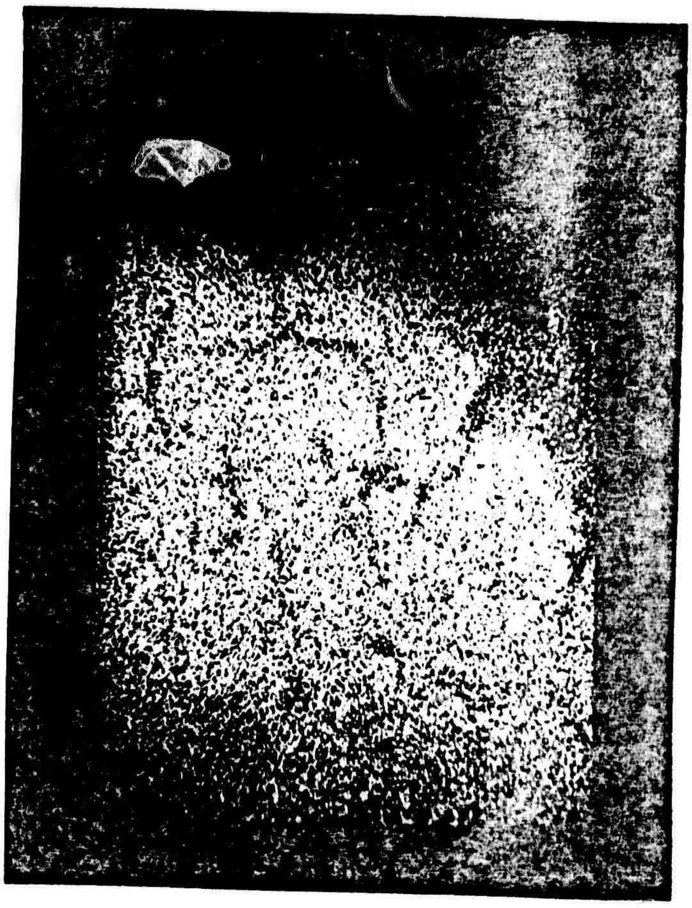
H_2O-CP-1



Mg

O_2



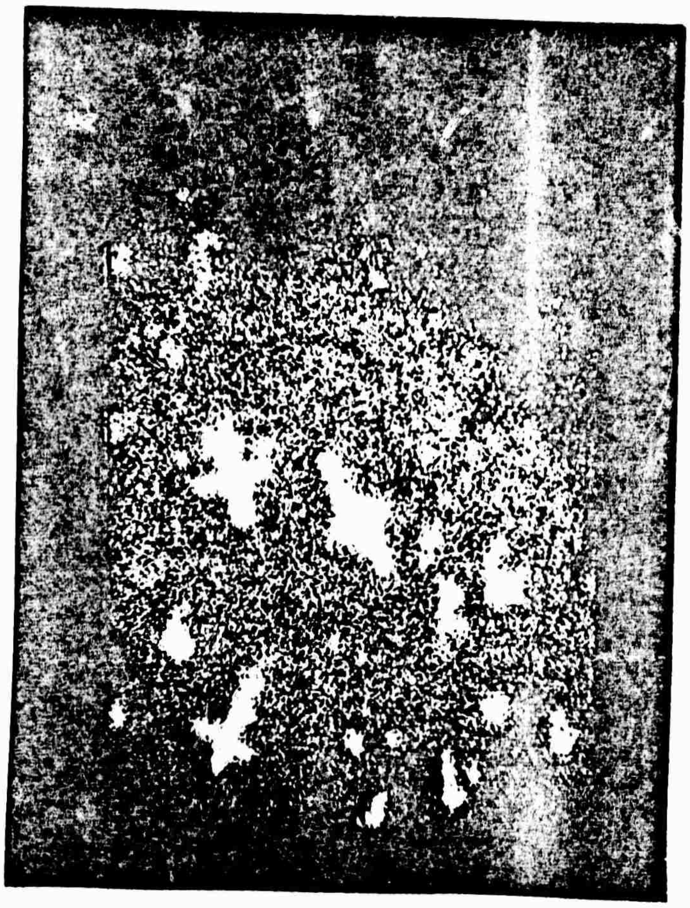


K

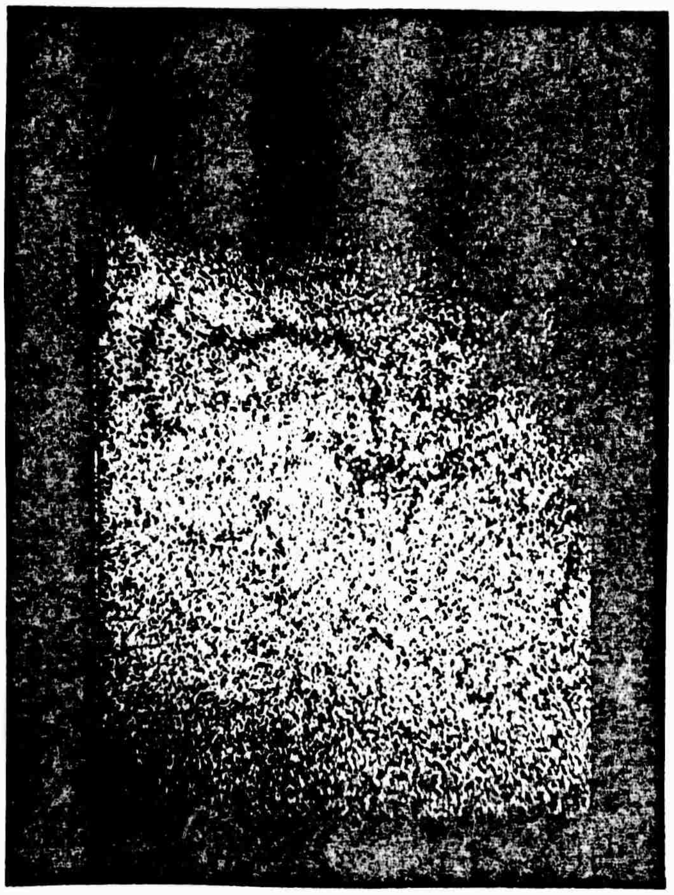
FIGURE 9. ELECTRON MICROPROBE ANALYSES OF H_2O-CP-1 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Ca, Cl, S, AND Si

H_2O-CP-1

Ca



Cl



S

Si

For Cl, the X-ray images indicate approximately equal quantities in the two samples except that H_2O-CP-1 shows a very heavy concentration of Cl in certain spots, some of which are observed as a cross pattern. However for Na, the electron microprobe results do not agree with the emission results. Both the X-ray images and the numerical values in Appendix B indicate a higher concentration of Na in LW-H_2O-01 than in H_2O-CP-1, yet the emission results in Table 2 indicate much more Na in H_2O-CP-1 than in LW-H_2O-01. This discrepancy may result (as noted in the Experimental section) from the fact that the electron microprobe beam covers only part of the sample. Thus if Na is not evenly distributed in one of the samples, it would be possible for the electron microprobe and emission analyses to differ since the emission analysis is a function of the total sample. In fact, it is somewhat surprising that there are not more such differences.

Uneven distribution of elements has been noted in several samples and these can be discerned from the numerical values in Appendix B. Most notable of these is LW-H_2O-2. In this sample large crystals resembling pentagons are observed around the edge of the sample. These large crystals have not been detected in any other sample. The crystals contain a very heavy concentration of K and some Cl, but not nearly enough Cl to satisfy stoichiometry with the K. All the other elements reported were detected in the area away from the large crystals.

As can be seen in Appendix B, Cl was found to be concentrated in spots for most of the samples rather than being evenly distributed. Most of the time (as in the X-ray images of H_2O-CP-1) no cationic element was detected which showed a pattern of spots similar to that found for Cl.

Occasionally, however, some of the Si distribution patterns were similar to that of Cl.

Silicon, like Cl, many times was found to be unevenly distributed, i.e., heavily concentrated, at the edge of the sample.

K and Ca were found in heavier concentrations at the edges for the beginning tube washings (LW-H_2O-1,2, and 12), but noted to be more uniformly distributed for the other samples.

For any given element, the electron microprobe analyses can be used to detect changes in concentration of that specific element among the various samples. However the greatest benefit of the electron microprobe work to this point in the research has come from the detection of the elements that cannot be studied by emission spectroscopy, i.e., C, O, Cl, and S. Quantitative values of the concentration of these elements cannot be obtained. However it is important to note that these elements were detected in all of the system blanks, all of the liquid washings, and all of the preparations from cleaned or uncleaned tubes alike. The only possible exceptions are those of LW-H_2O-2 and LW-H_2O-14 where the S content appears to be near trace quantities.

It is especially important (for purposes of interpreting the infrared spectra) to note that C was detected in every sample. Based on a count per second value of about 2475 for carbon in a graphite standard, it can be estimated that the carbon weight percentage in these samples of residues is in the 5 to 15% range. The total quantity of elements may be decreased with washing, but all elements originally detected in the blanks and first wash (LW-H_2O-1) are present at all stages to varying degrees. Thus no element originally detected was completely removed by washing - even for tubes which had been cleaned 15 times.

C, H, N Analysis

Wet chemical or combustion C, H, N analyses were obtained whenever the sample was large enough. These values are listed in Table 3. Such analyses were obtained for three samples of which only one (LW-H_2O-1) is in the group of samples being presently discussed. Even for these samples, the amount of material was small enough that it is difficult to state accuracy limits for these analyses. However for LW-H_2O-1, the carbon percentage is at the extreme upper limit deduced from the electron microprobe analyses.

It is interesting here to note that N was detected in sample LW-H_2O-1. The C, H, N analyses for the other samples will be discussed in later sections.

Preparation of Anomalous Material From H_2O_2 Solutions

Infrared Spectra

A preparation of anomalous material using 3% aqueous H_2O_2 was completed. In addition a preparation utilizing 30% H_2O_2 in water is in progress. The purpose of these preparations was to learn more about the role oxygen plays in the formation of anomalous material. Some surprising results were obtained. First, the yield from the 3% H_2O_2 preparation was about 5 mg, a fairly large yield. In addition, the infrared spectra (shown in Figure 10) of the residue from the 3% H_2O_2 preparation are similar, yet have distinct differences, when compared to the spectra of anomalous material prepared from 100% water. The film prepared for the infrared analyses was distinctly sticky to the touch, differing from

TABLE 3. C-H-N ANALYTICAL RESULTS OF RESIDUES

Sample	%C	%H	%N
LW-H_2O-1	16.2	2.2	2.5
H_2O_2-P-1	12.1	2.5	4.2
LW-Pr-1	38.9	5.6	2.0

most preparations from 100% water. The top spectrum (A) of Figure 10 shows the residue obtained from the 3% H_2O_2 preparation. Spectrum (B) is that of a much thicker run of the first spectrum. That such intense spectra are easily recorded is an indication of the large quantity of material available. In addition,the absorption bands are sharper and at more distinct frequencies than in any previous spectrum of anomalous material.

Instead of the usual broad OH stretching vibration (seen in preparations from pyrex tubes), the spectrum of this material shows three OH peaks near 3460, 3380, and 3230 cm^{-1}. This observation indicates that three types of OH groups are present in the sample. The two bands in the 1600 cm^{-1} region are very strong and at 1680 and 1640 cm^{-1}; not 1620 cm^{-1} as in the preparations from pure water. In the 1400 cm^{-1} region a band can be seen at 1470 cm^{-1} with shoulder near 1390 or 1400 cm^{-1}. The 1470 cm^{-1} frequency is high compared to 1410 cm^{-1} in the preparations from pure water. A band is observed at 1175 cm^{-1} with some additional absorption on the low frequency side near 1090 cm^{-1}. In addition, a weak band at 787 cm^{-1} is observed in the spectrum of the thicker sample.

Spectrum (C) of Figure 10 shows the results of heating (B) of Figure 10 at 400 C for five minutes. The three OH peaks in the 3400 cm^{-1} region have disappeared and a more normal broad OH band is observed. The intensity of the bands in the 1600 and 1400 cm^{-1} region are diminished compared to the 1100 cm^{-1} band. The 1680 cm^{-1} has disappeared and the 1640 cm^{-1} band has shifted to 1625 cm^{-1}. The 1470 cm^{-1} peak shows a large shift to 1425 cm^{-1} and a peak at 1325 cm^{-1} can now be clearly seen. The appearance of a band near 1425 cm^{-1} could signify carbonate formation,

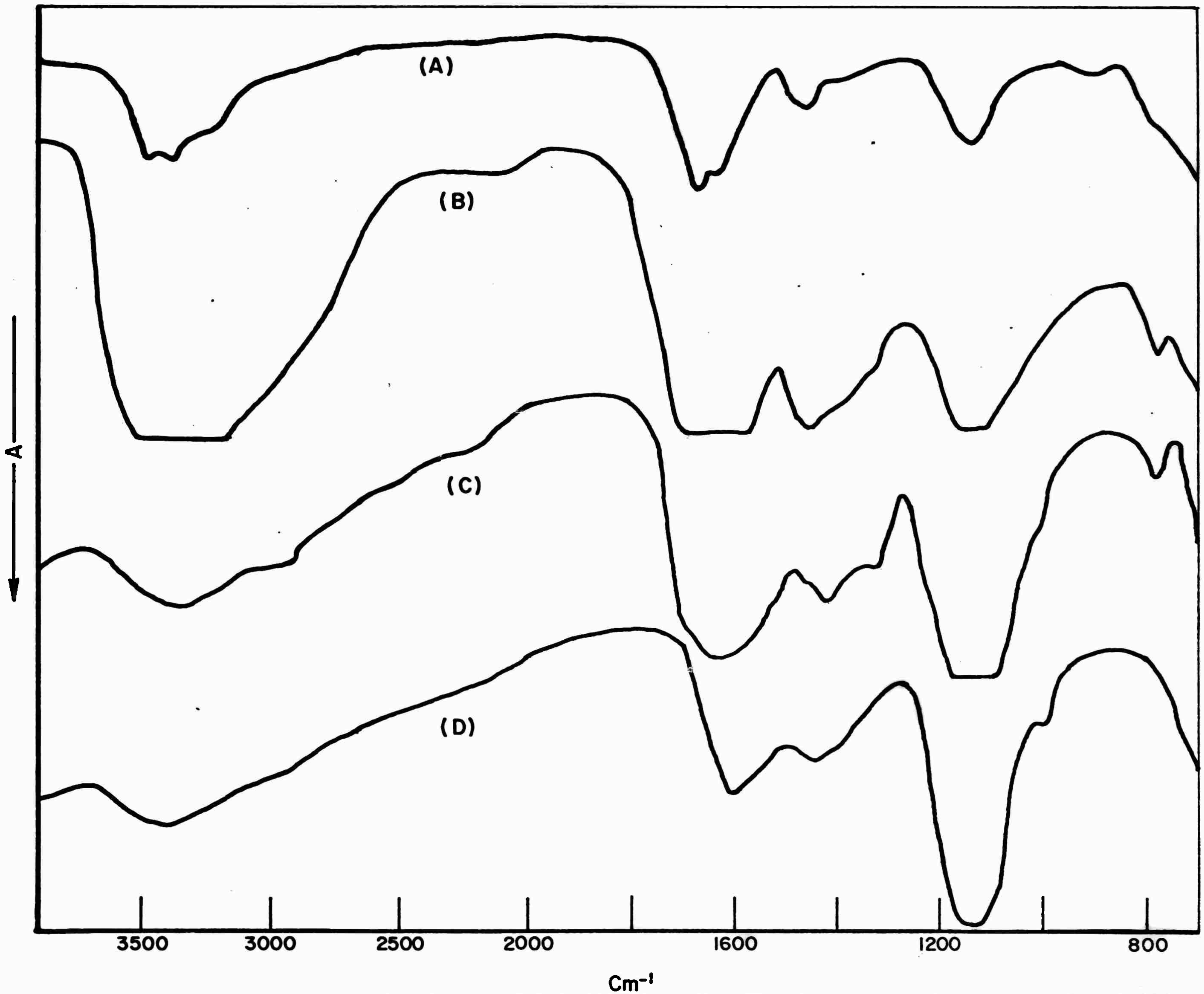


FIGURE 10. INFRARED SPECTRA OF (A) H_2O_2-P-1, (B) A THICKER SAMPLE OF H_2O_2-P-1, (C) H_2O_2-P-1 HEATED AT 400 C FOR 5 MINUTES, AND (D) H_2O_2-P-1H WHICH IS H_2O_2-P-1 HEATED AT 400 C FOR 60 MINUTES

but no confirming band near 880 cm^{-1} can be detected as is the usual case. The 1100 cm^{-1} absorption of (C) appears unchanged.

After heating (C) of Figure 10 at 400 C for an additional 60 minutes, spectrum (D) is obtained (H_2O_2-P-1H). Upon heating, the sample begins to brown and after 60 minutes at 400 C, it appears to be a black powder. The 1640 cm^{-1} absorption of spectrum (B) now appears at 1615 cm^{-1}. The band in the 1400 cm^{-1} range has broadened, reversed the original direction of its shift and now appears near 1450 cm^{-1}. The band at 1325 cm^{-1} can no longer be seen. The 1145 cm^{-1} band has decreased in intensity, but is still very strong. The 787 cm^{-1} band is missing from the spectrum of (D), but a new band appears at 1000 cm^{-1}. The frequency shifts due to heating this sample are summarized in Table 4. From these frequencies it can be seen that even though the frequencies of the unheated sample (H_2O_2-P-1) are somewhat different than those of preparations from pure water the frequencies of the heated sample (H_2O_2-P-1H) are quite similar to those of preparations from water. In fact, the spectrum of H_2O_2-P-1H would compare quite well to spectra of samples such as H_2O_2-CP-1 and H_2O-UP-1, except for the intensity of the 1145 cm^{-1} band.

Emission Analysis

As an aid to interpreting the infrared spectral changes due to heating H_2O_2-P-1, emission analyses of H_2O_2-P-1 and H_2O_2-P-1H were obtained. Partial results of these analyses are given in Table 5 together with the emission values obtained for preparations from pure water (H_2O-CP-1 and H_2O-UP-1) for comparison. Complete emission results are given in Appendix C. Considering the drastic spectral changes between H_2O_2-P-1 and H_2O_2-P-1H,

TABLE 4. FREQUENCY SHIFTS (cm^{-1}) DUE TO HEATING H_2O_2-P-1

H_2O_2-P-1	H_2O_2-P-1 (5 min., 400 C)	H_2O_2-P-1H (60 min., 400 C)
3460		
3380	3360	3400
3230		
1680		
1640	1625	1615
1470	1425	1450
1400 (Sh)		
1325 (Sh)	1325	
1145	1145	1145
1090 (Sh)		
		1000
787	787	

TABLE 5. PARTIAL EMISSION SPECTROGRAPHIC ANALYSES FOR ANOMALOUS MATERIAL PREPARATIONS

Sample	Elements (μg)							
	B	Si	Fe	Mg	Al	Na	Ca	K
H_2O_2-P-1	2.0	3.0	0.1	5.0	0.1	5.0	1.0	5.0
H_2O_2-P-1H	1.0	3.0	0.1	5.0	0.5	2.0	8.0	1.0
H_2O-CP-1	0.3	2.0	0.1	1.0	0.2	20.0	2.0	<50.0
H_2O-UP-1	5.0	10.0	0.5	5.0	1.0	30.0	5.0	<50.0

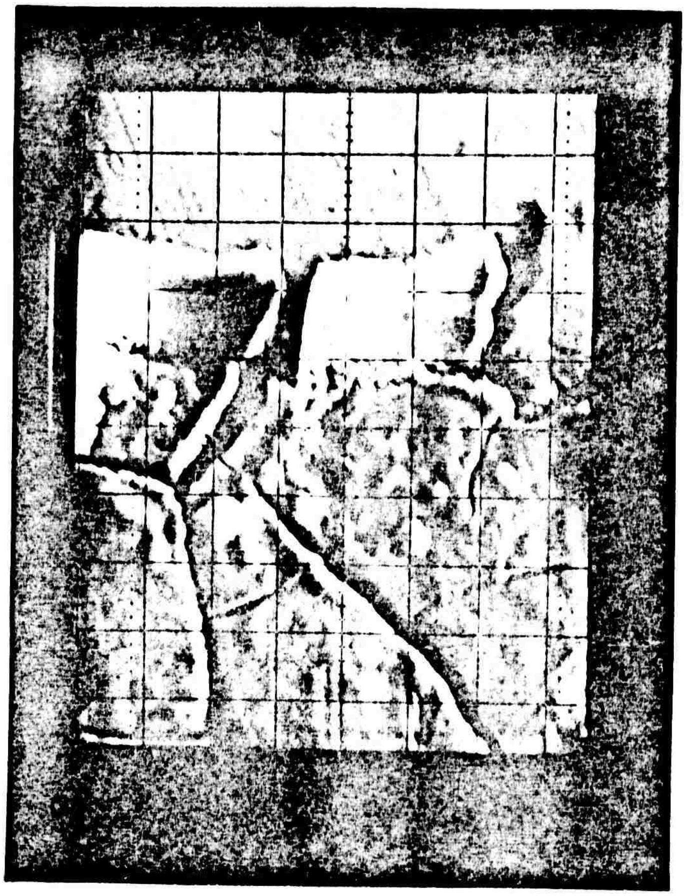
the differences in elemental composition are surprisingly small. Some Na and K are lost by heating the sample, but this is offset by a gain in Ca upon heating. (It is at present difficult to understand how Ca increases by heating a sample.) Comparing the H_2O_2 preparations (H_2O_2-P-1) to the preparations from pure water shows that the H_2O_2 residue contains much less Na than the H_2O residues. For other elements the H_2O_2 residue is closer to H_2O-CP-1 (except for Mg and possibly B) than to H_2O-UP-1. This is somewhat understandable since the pyrex tubes used for the H_2O_2 preparation were washed several times with water and several times with ithanol before the preparation was started. Thus the H_2O_2 tubes are probably nearer the condition of the cleaned tubes used for H_2O-CP-1 rather than the uncleaned tubes used for H_2O-UP-1.

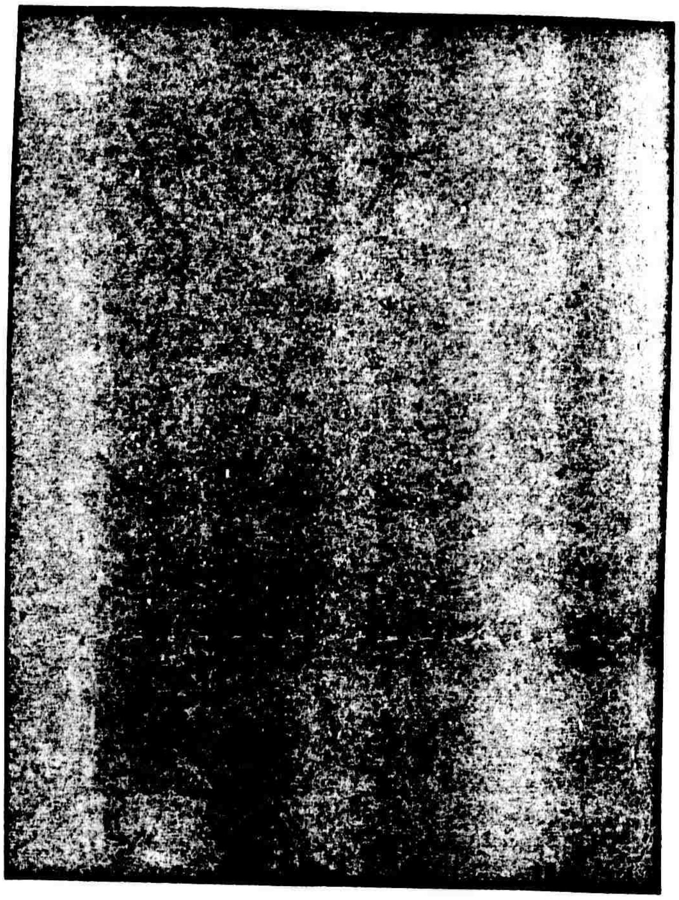
Electron Microprobe Analysis

The electron microprobe results for H_2O_2-P-1 and H_2O_2-P-1H tend to support the emission spectrographic results for these two samples and give information about changes in concentrating of elements not analyzed by emission spectrography. Numerical values of the electron microprobe analyses are given in Appendix B. Figures 11 through 19 show X-ray images of these samples. Figures 11, 12, and 13 are X-ray images of an edge of H_2O_2-P-1. The sample H_2O_2-P-1H was prepared for the electron microprobe study by scraping the black powder off the Irtran plate used for the infrared study onto an Al disc. In anticipation of fixing the black powder to the Al plate, a drop of water was placed on the black powder. The area of the drop of water was many times larger than the area of the black powder. After the water had evaporated, the black powder was observed in approximately its

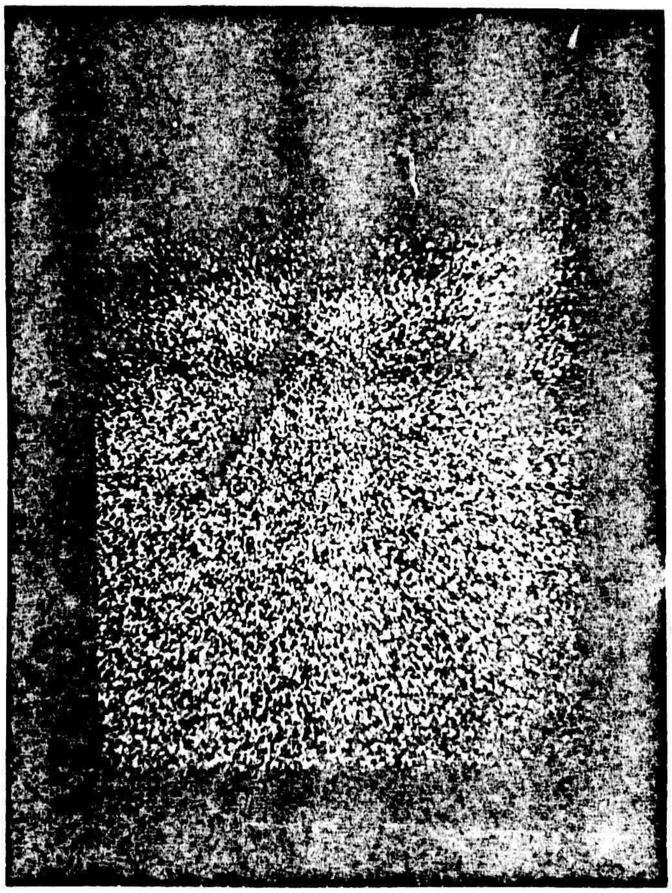
FIGURE 11. ELECTRON MICROPROBE ANALYSES OF H_2O_2-P-1 SHOWING THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE AND THE X-RAY DISTRIBUTION IMAGES FOR B, Na, AND C

H_2O_2-P-1

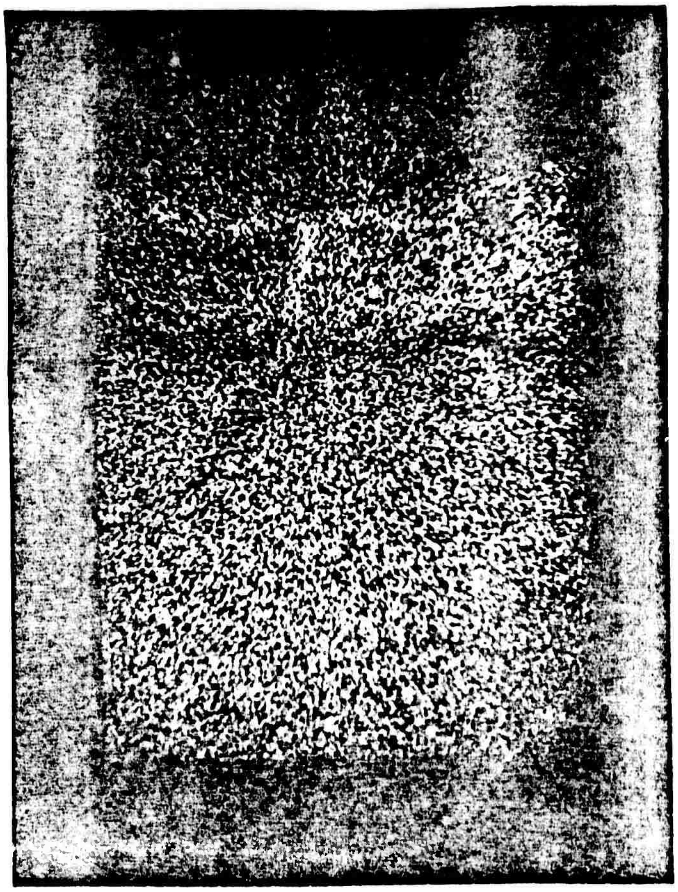




B



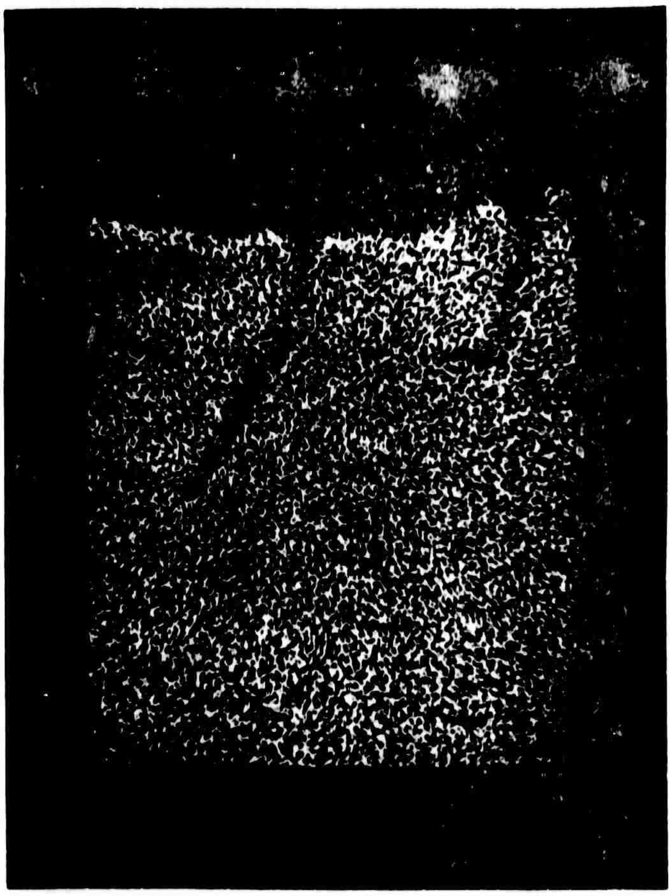
Na



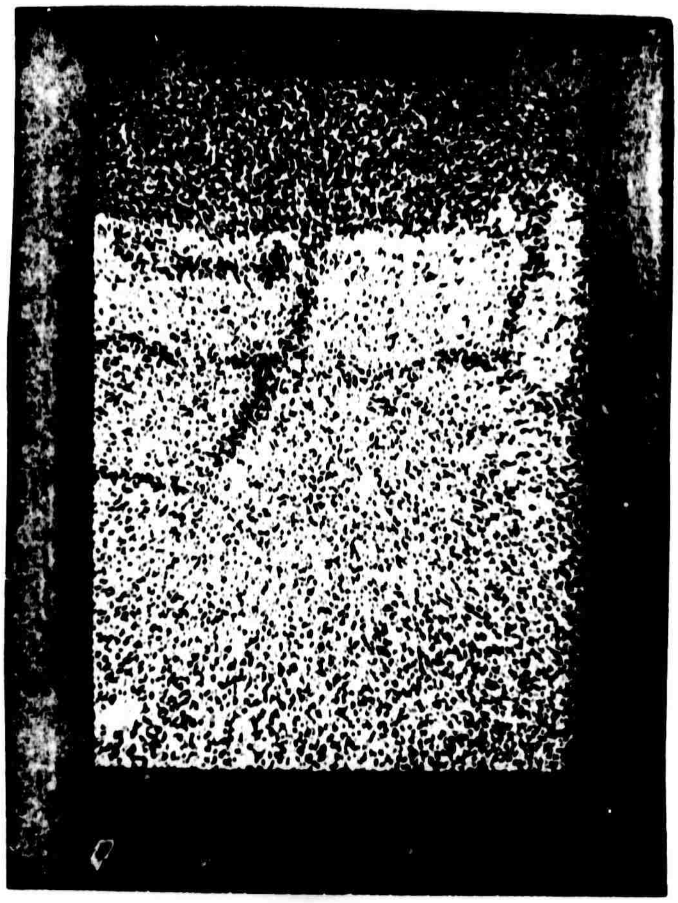
C

FIGURE 12. ELECTRON MICROPROBE ANALYSIS OF H_2O_2-P-1 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Mg AND O, THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE, AND THE X-RAY DISTRIBUTION IMAGE FOR K

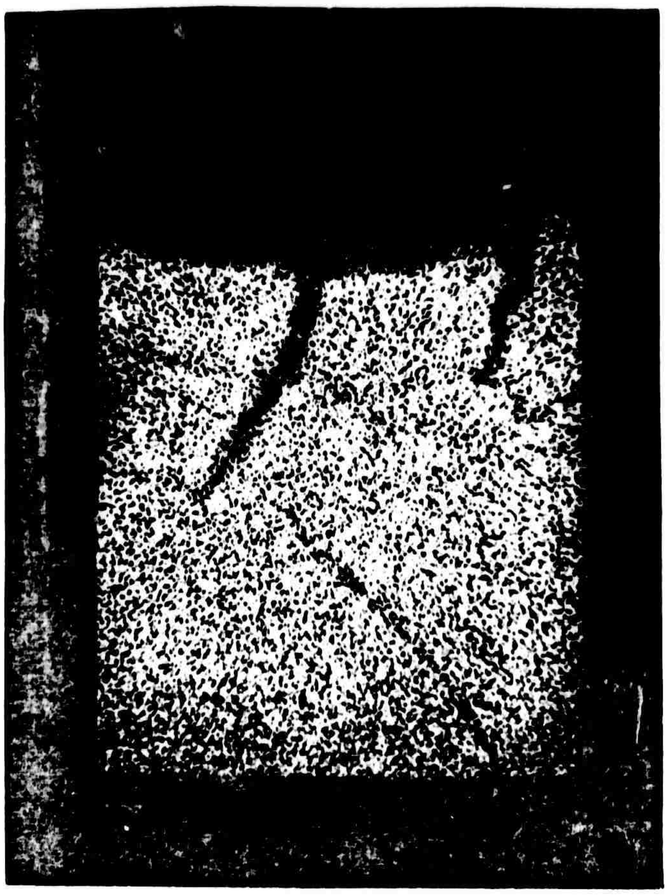
H_2O_2-P-1



Mg



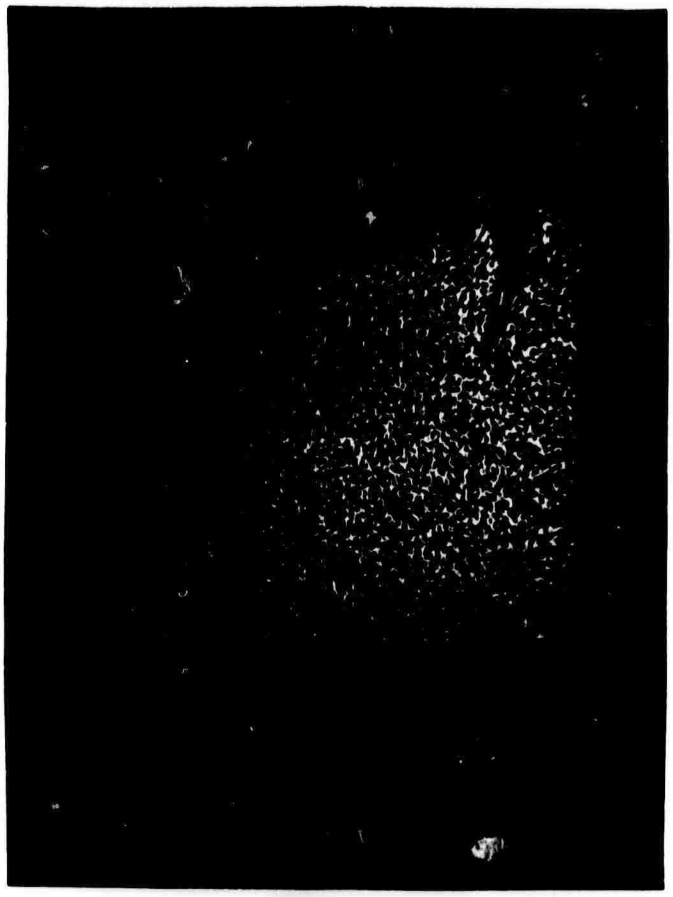
O_2



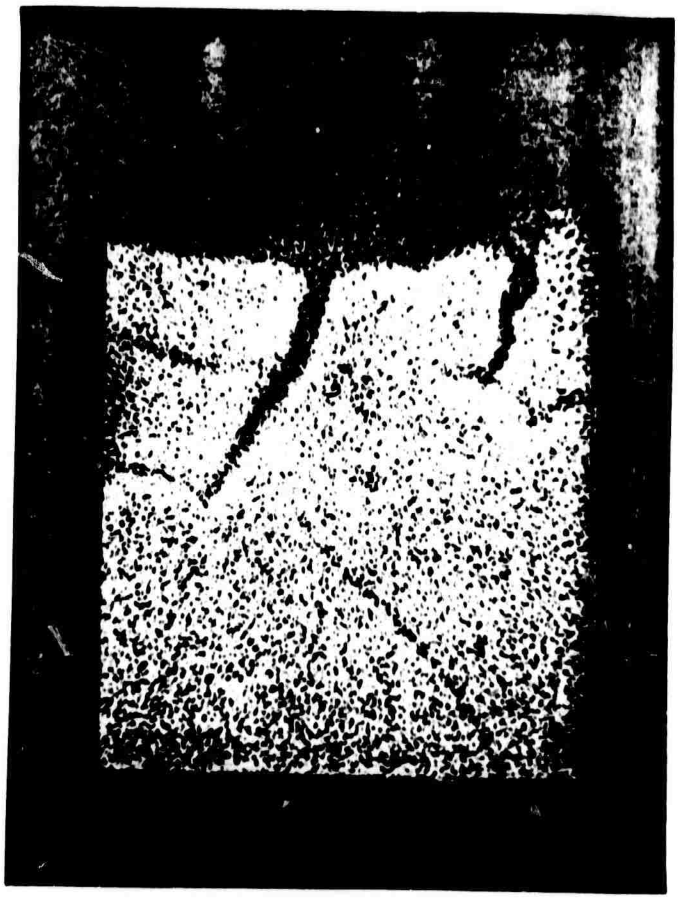
K

FIGURE 13. ELECTRON MICROPROBE ANALYSIS OF H_2O_2-P-1 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Ca, Cl, S, AND Si

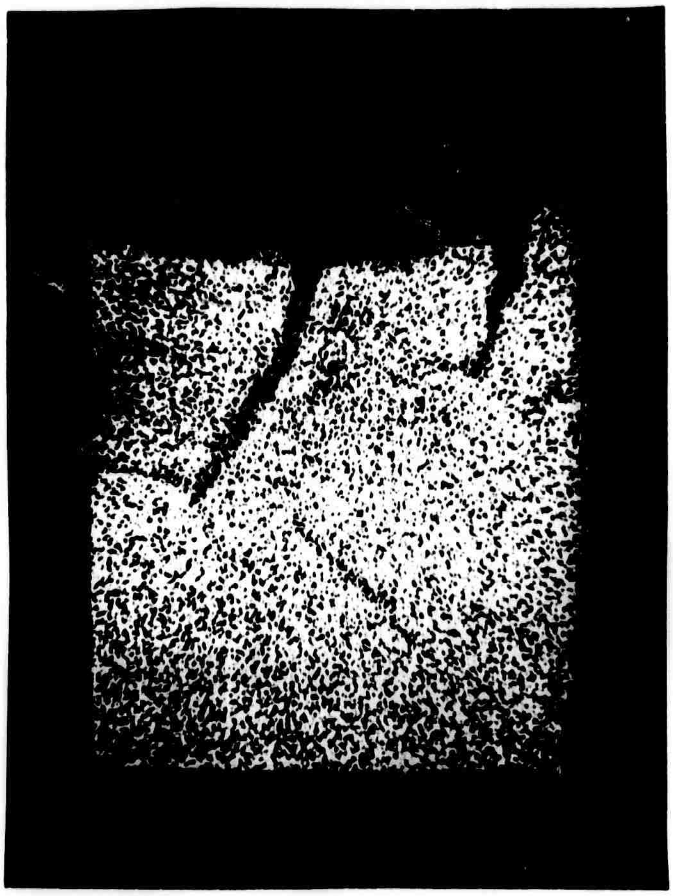
H_2O_2-P-1



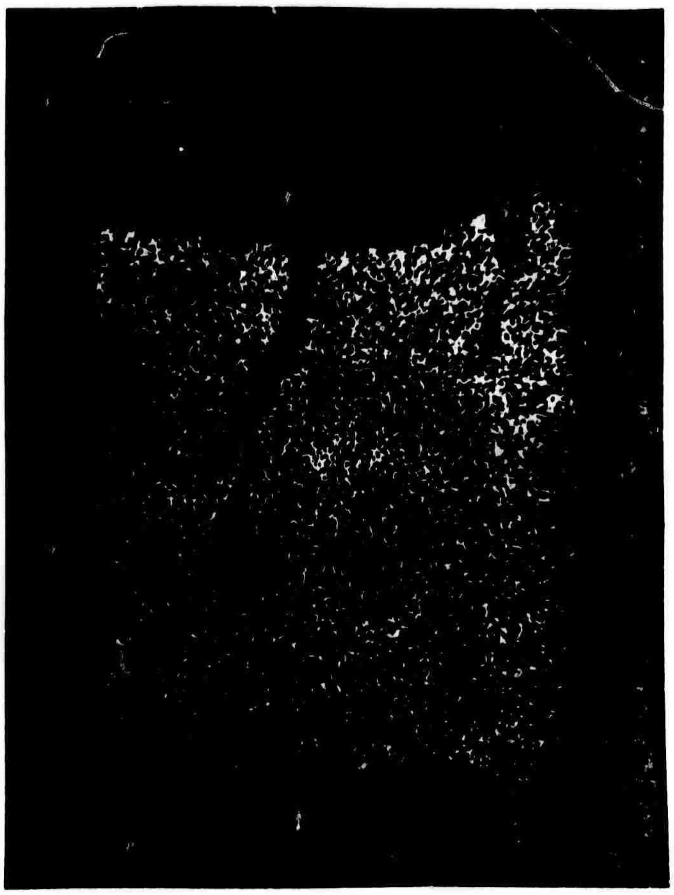
Ca



Cl



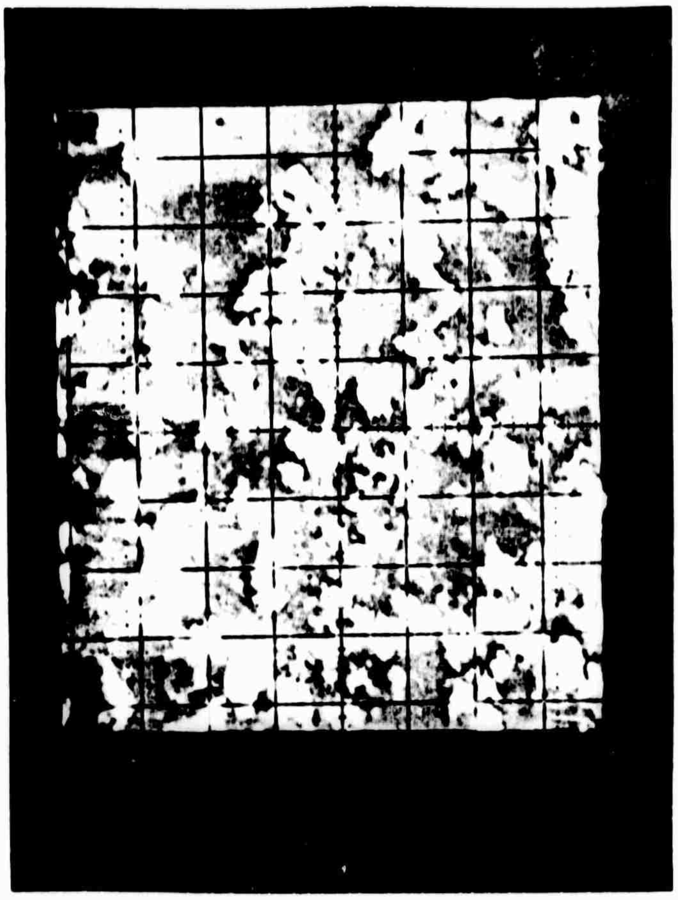
S

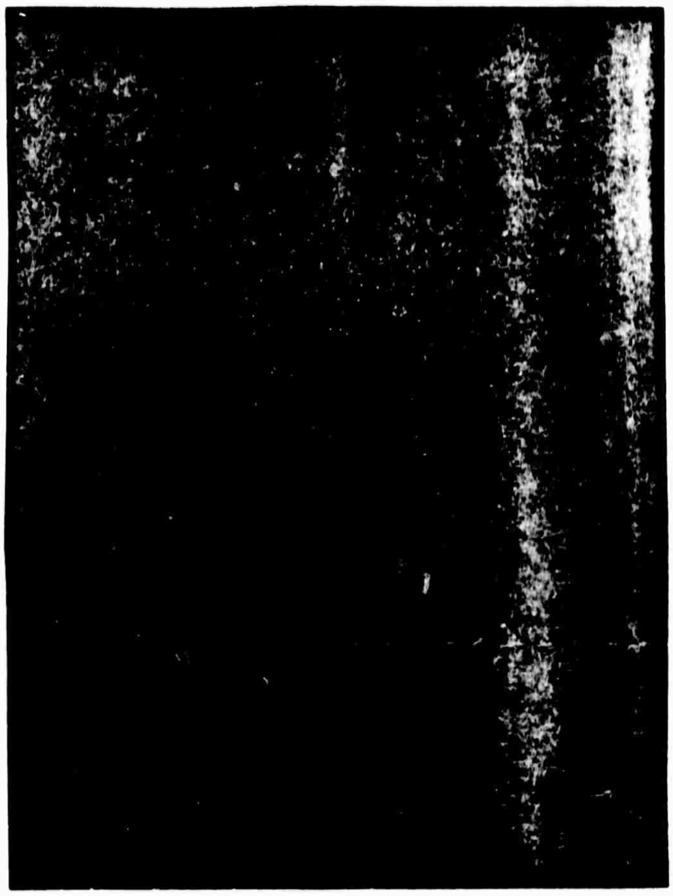


Si

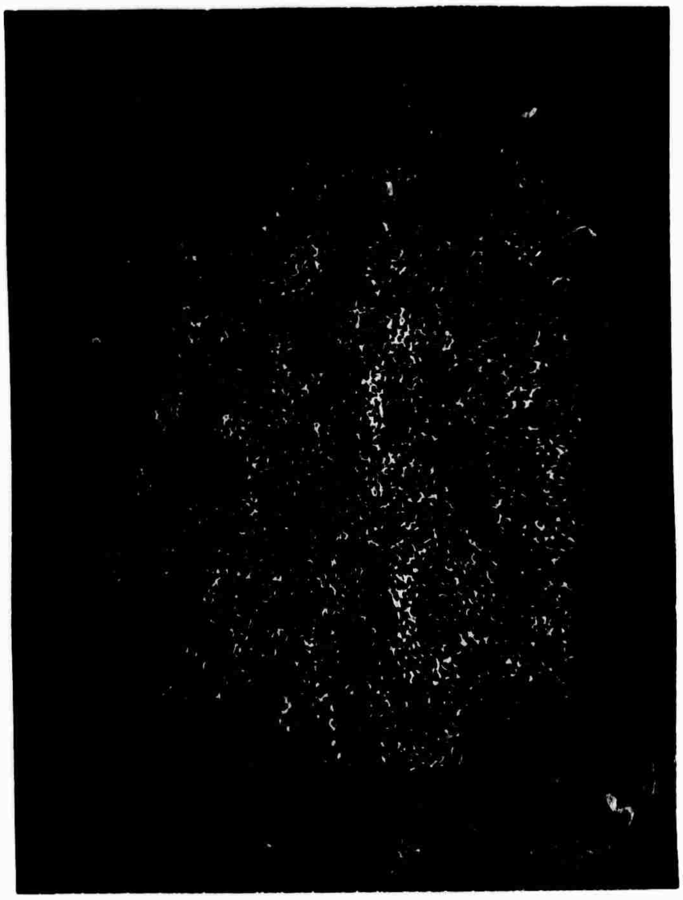
FIGURE 14. ELECTRON MICROPROBE ANALYSIS OF THE BLACK PORTION OF H_2O_2-P-1H SHOWING THE BACK SCATTERED IMAGE OF THE SAMPLE AND THE X-RAY DISTRIBUTION IMAGES FOR B, Na, AND C

H_2O_2-P-1H (BLACK)





B

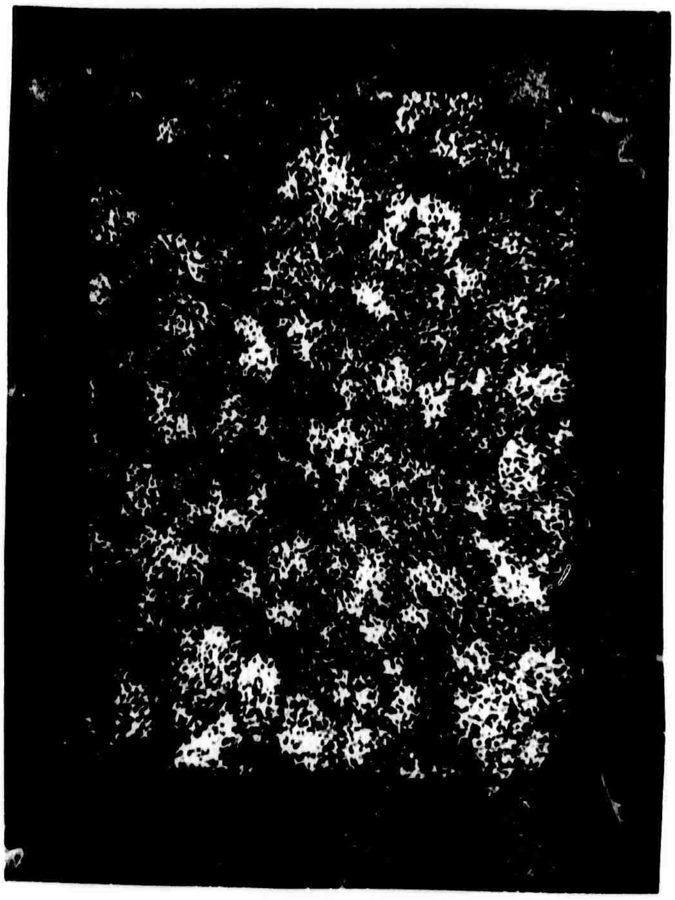


Na

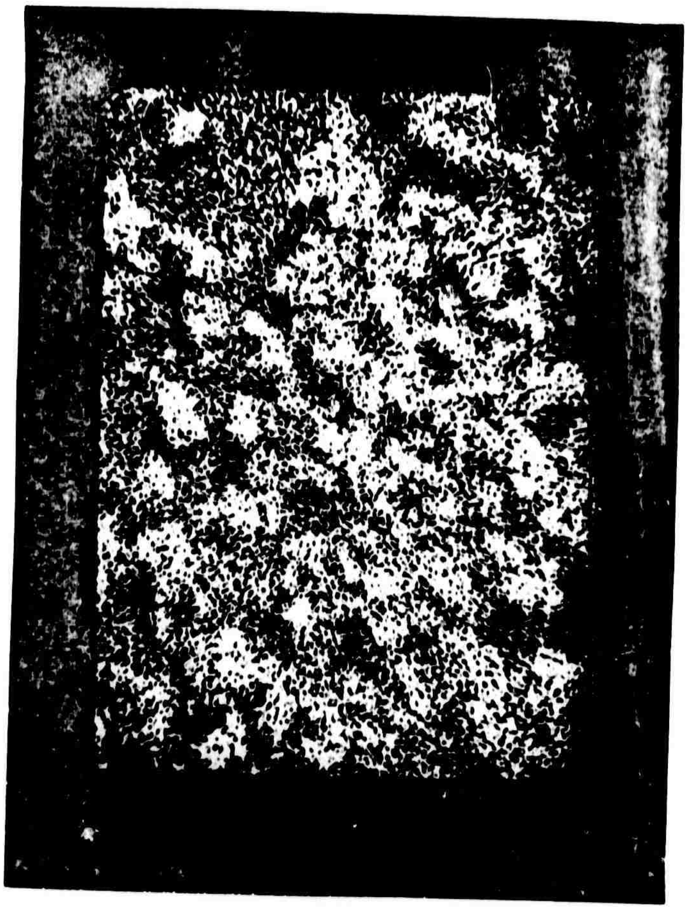
C

FIGURE 15. ELECTRON MICROPROBE ANALYSIS OF THE BLACK PORTION OF H_2O_2-P-1H SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Mg AND O, THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE, AND THE X-RAY DISTRIBUTION IMAGE FOR K

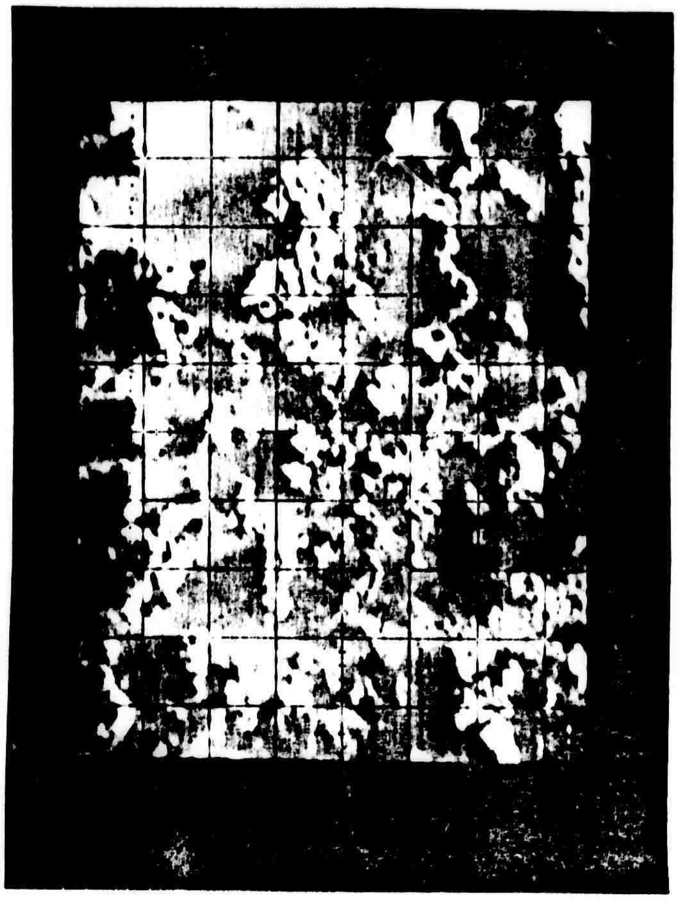
H_2O_2-P-1H (BLACK)



Mg



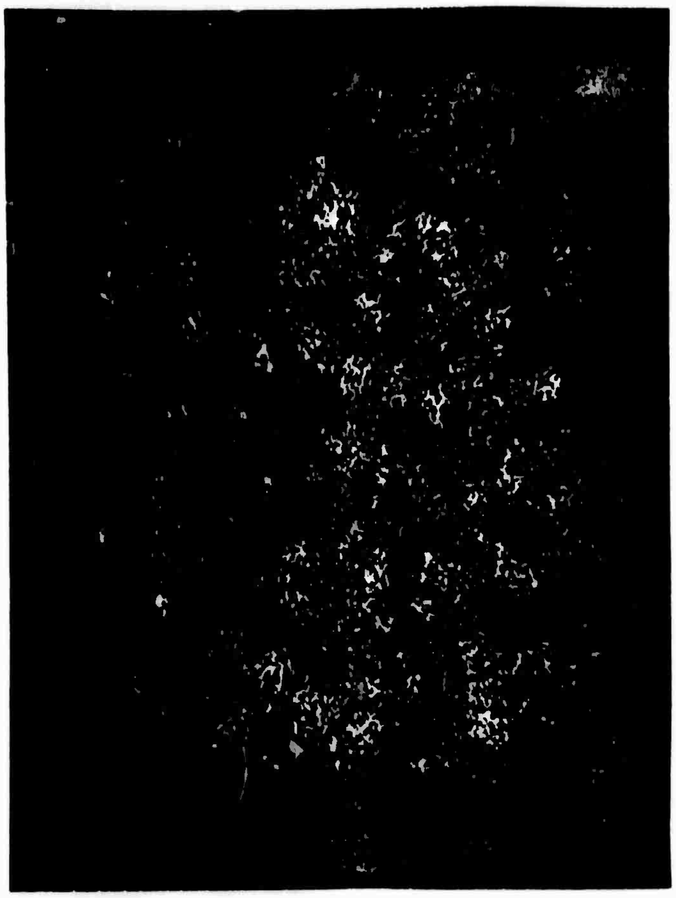
O_2



K

FIGURE 16. ELECTRON MICROPROBE ANALYSIS OF THE BLACK PORTION OF H_2O_2-P-1H SHOWING THE X-RAY IMAGES FOR Ca, Cl, S, AND Si

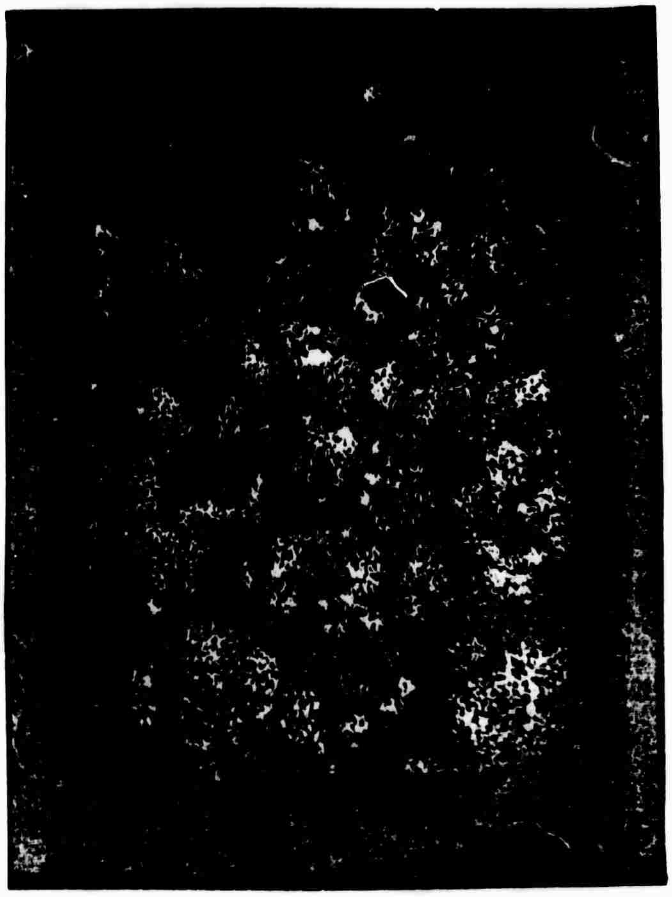
H_2O_2-P-1H (Black)



Ca

Cl

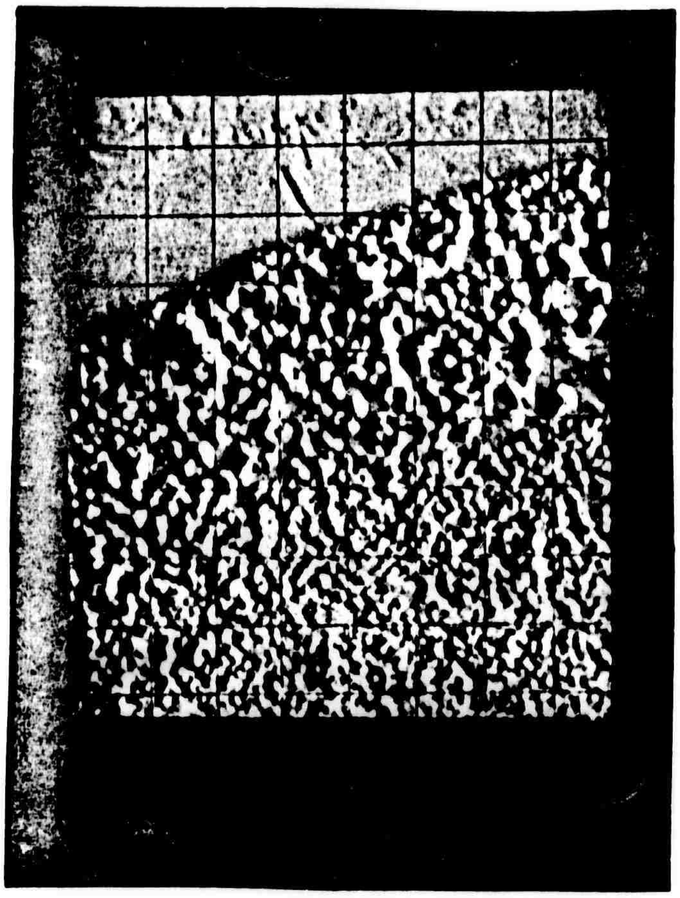
S

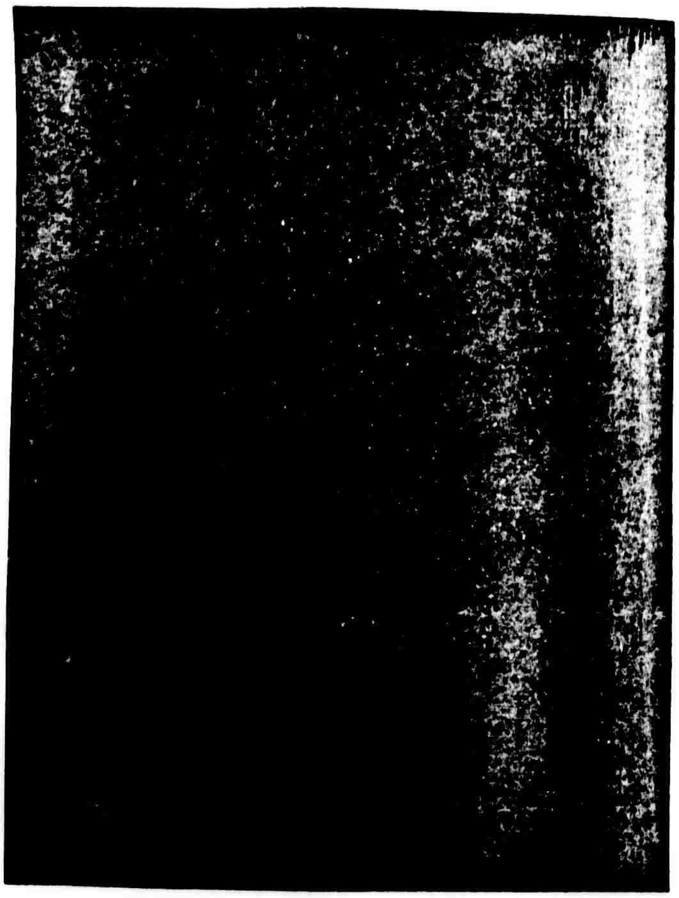


Si

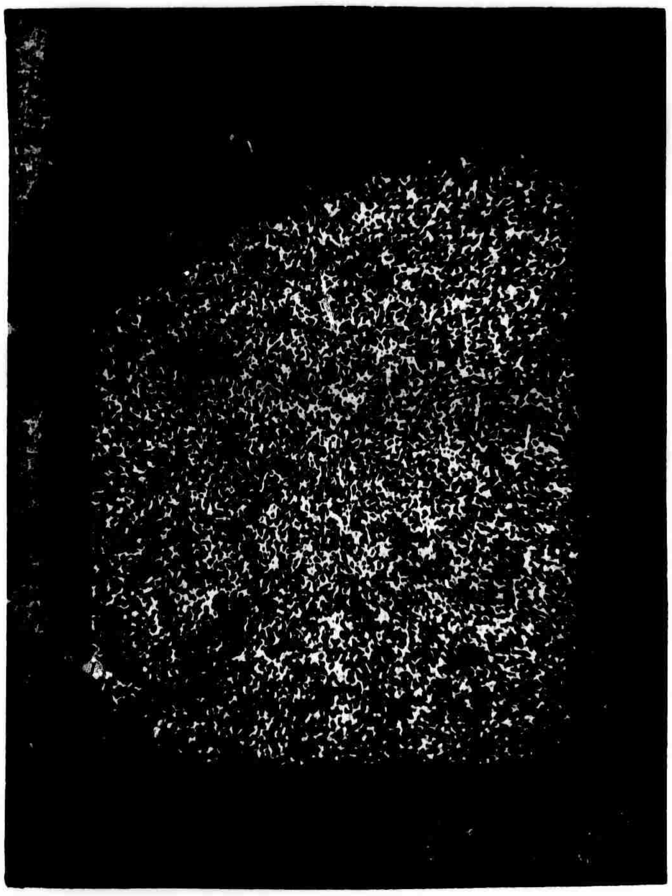
FIGURE 17. ELECTRON MICROPROBE ANALYSIS OF THE WHITE PORTION OF H_2O_2-P-1H SHOWING THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE AND THE X-RAY DISTRIBUTION IMAGES FOR B, Na, AND C

H_2O_2- P-1H (WHITE)

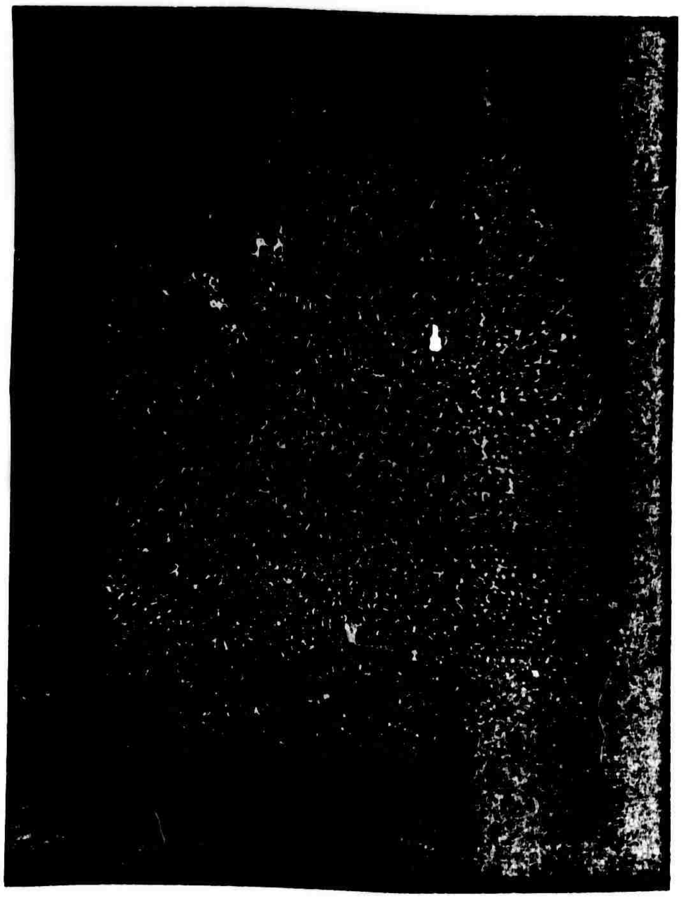




B



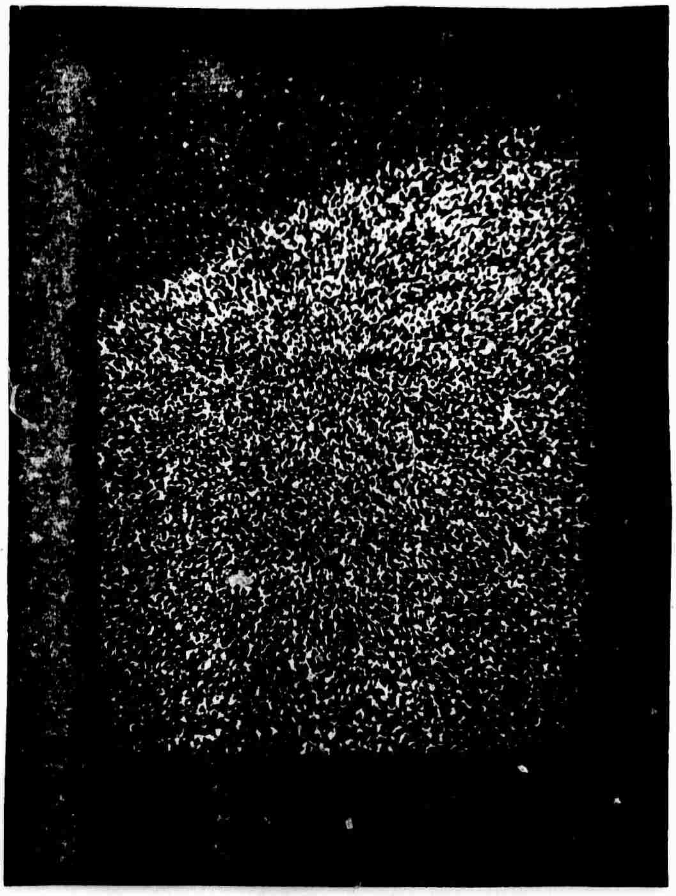
Na.



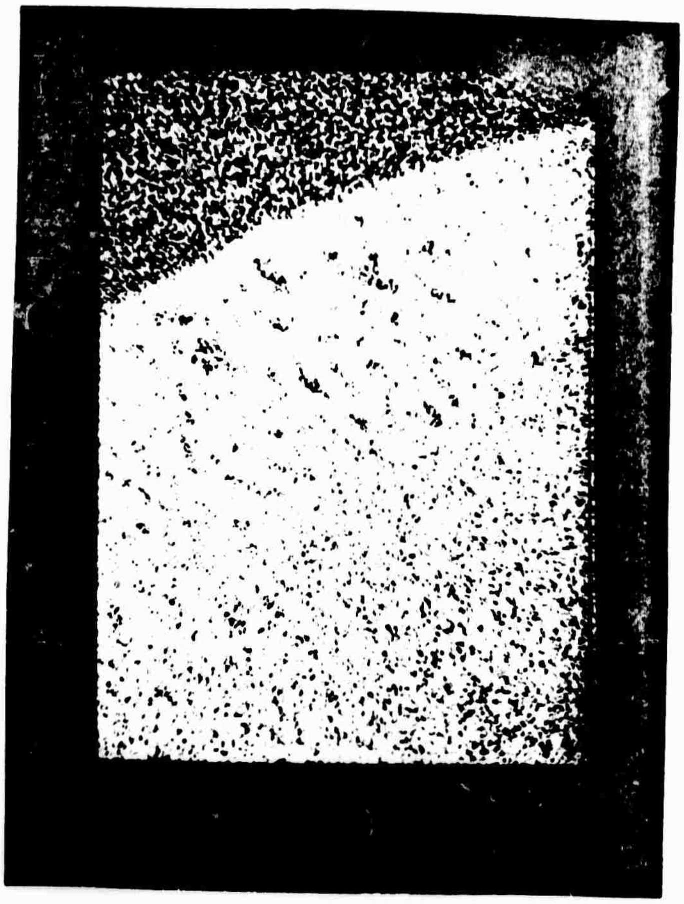
C

FIGURE 18. ELECTRON MICROPROBE ANALYSES OF THE WHITE PORTION OF H_2O_2-P-1H SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Mg AND O, THE BACK SCATTERED ELECTRON IMAGE OF THE SAMPLE, AND THE X-RAY DISTRIBUTION IMAGE FOR K

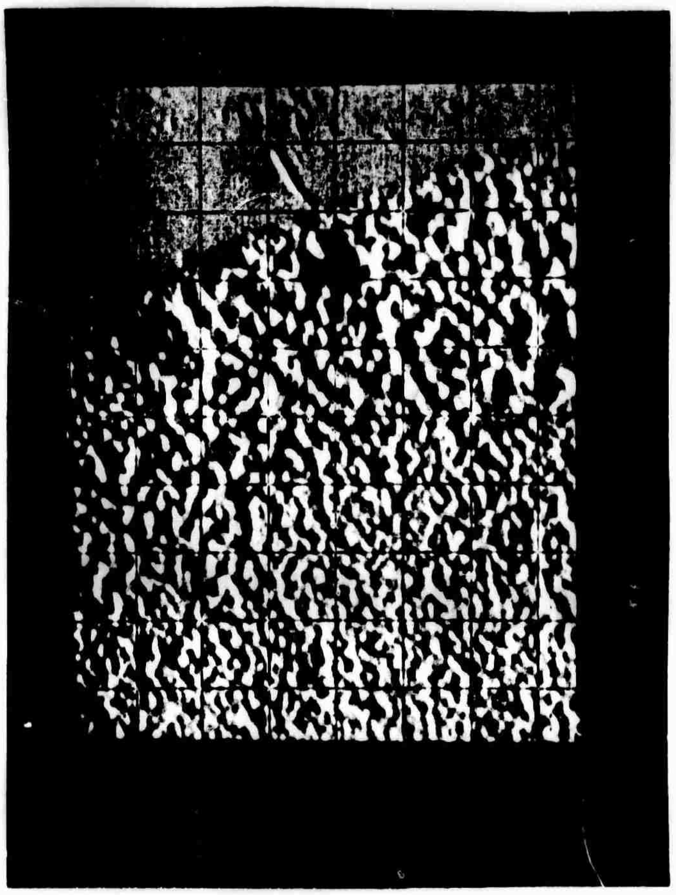
H_2O_2-P-1H (WHITE)

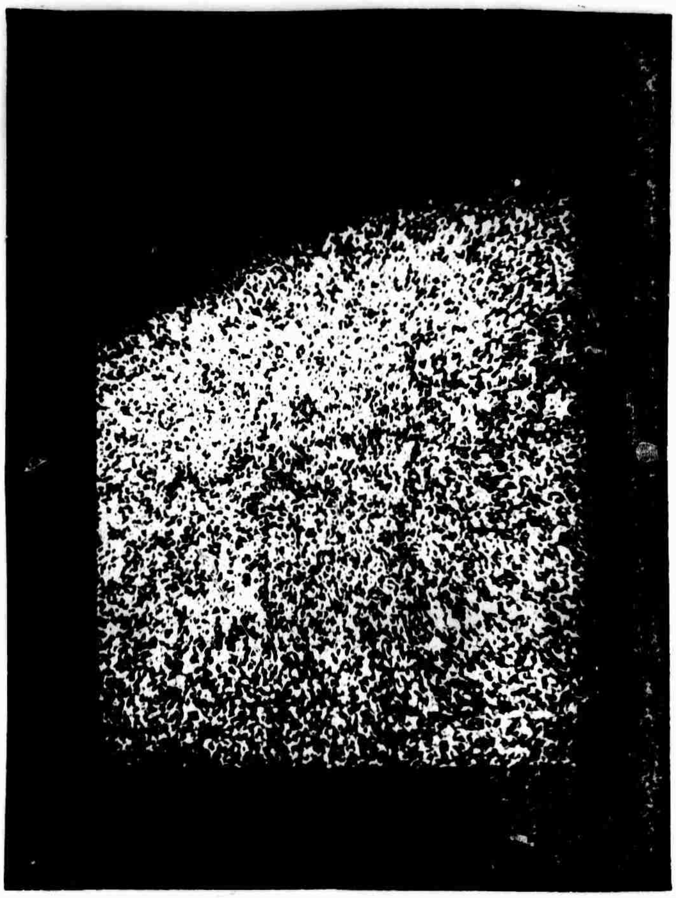


Mg



O_2

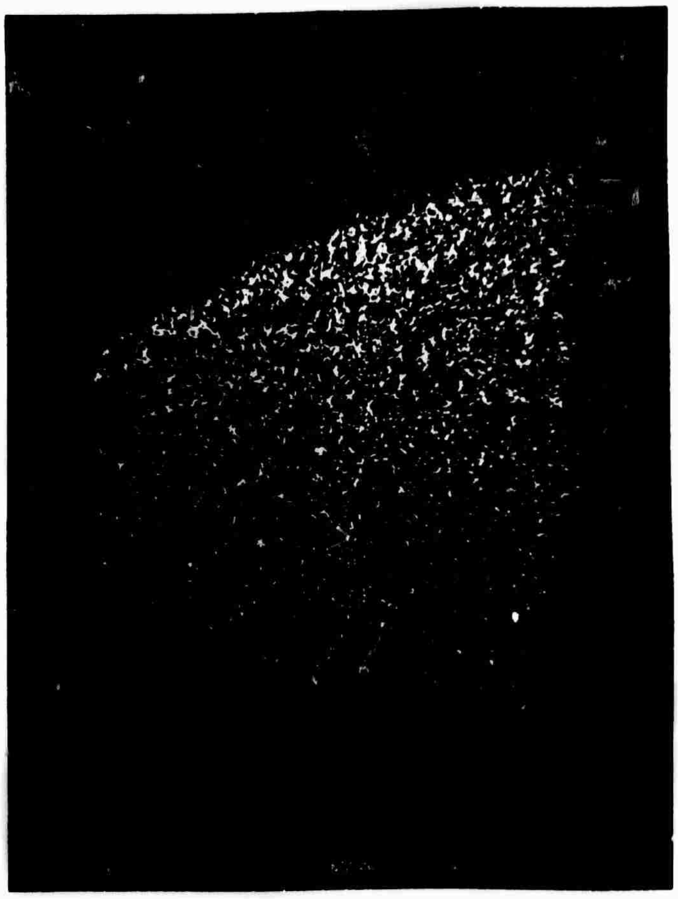




K

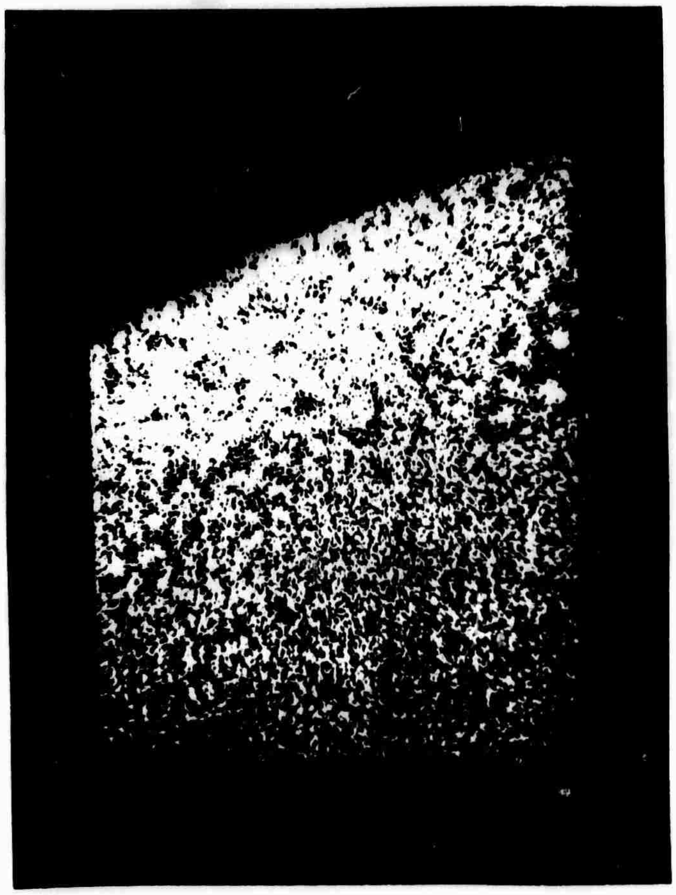
FIGURE 19. ELECTRON MICROPROBE ANALYSES OF THE WHITE PORTION OF H_2O_2-P-1 SHOWING THE X-RAY DISTRIBUTION IMAGES FOR Ca, Cl, S, AND Si

H_2O_2 - P - 1H (WHITE)

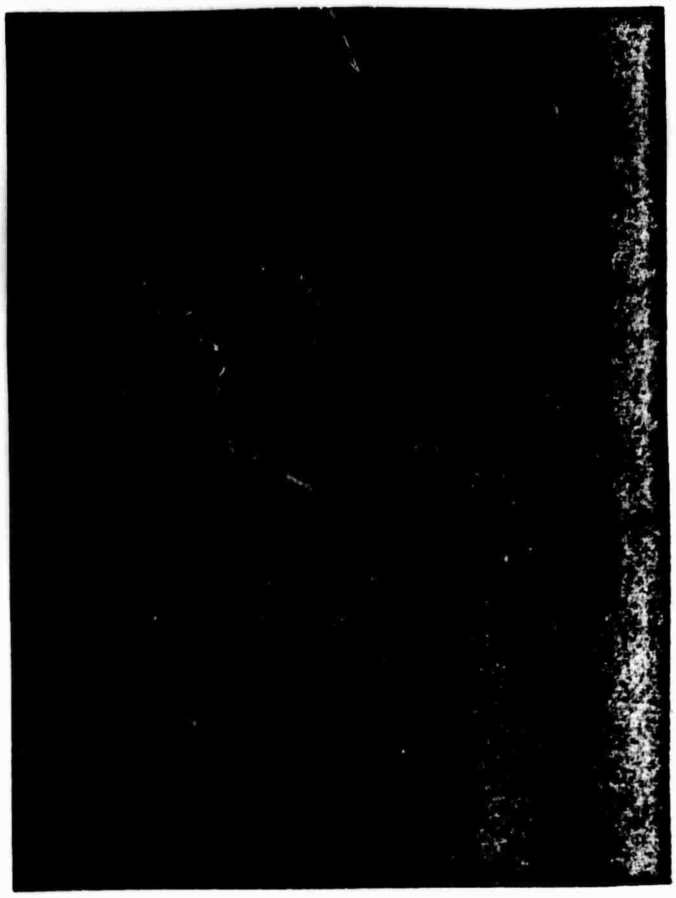


Ca

Cl



S



Si

original position. However, a heavy white film covered the area where the drop of water had been. The film was many orders of magnitude more residue than could be obtained from just a drop of water. Therefore part of the original black powder is believed to have dissolved in the water and thus spread out over the area of the drop. Figures 14, 15, and 16 are X-ray images of the black portion of this sample (H_2O-P-1H). Some of the white portion could be under the black powder particles. Figures 17, 18, and 19 are the X-ray images of the white portion of the sample. There does not appear to be any of the black material mixed in with the white material. Appendix B and Figures 11 to 19 suggest that the carbon concentration, if anything, increases upon heating from the 12.1% for H_2O_2-P-1 indicated by Table 3. The carbon is much more heavily concentrated in the black powder particles than in the white portion of the heated sample. This increase upon heating is also true of O and Cl, with O more heavily concentrated in the white portion and Cl fairly evenly distributed. The microprobe results confirm the Ca increase on heating H_2O_2-P-1. In summary, C, O, Cl and Ca all apparently increase upon heating. Since it is impossible to see how these elements could form during the heating process, it must mean that the concentration of the other elements decreased and C, O, Cl, and Ca became a bigger percentage of the total sample. The microprobe results indicate that S concentration remains about constant, but is heavier in the white portion of the sample than the black. The Si content is not affected by heating (as emission indicates), the white portion of the heated sample has almost no Si.

Vapor Water Cleaning of Capillary Tubes

Since the preparation of anomalous materials is essentially a vapor process, it was deemed advisable to repeat the liquid cleaning procedure, but using vapor water instead of liquid water. This was done by producing the vapor (as steam) in a typical pressure cooker.

The results to date have been discouraging and somewhat unproductive. The reasons for this statement can be seen in Figure 20, which shows the spectra obtained from three vapor washings of capillary tubes. The top (A) spectrum (VW-H_2O-3) is totally that of an organic molecule which is unlikely to come from the pyrex tubes. Water extraction of the rubber gasket of the pressure cooker yielded a residue which gave a spectrum identical to (A). Spectrum (B) indicates the presence of more inorganic material than (A), but still shows the presence of the gasket extract. The bottom (C) spectrum (VW-H_2O-5) is much like that of liquid water extracts of glass tubes and shows no organic gasket extract. However, even after a lengthy water extraction of the gasket, residues were sometimes obtained which gave spectra like (C); but sometimes (and randomly) the residues give spectra like either (A) or (B). Because of this gasket contamination and because repeated preparations in both cleaned and uncleaned tubes (which in a sense is a vapor cleaning) are now being carried out, the pressure cooker cleaning experiments have been discontinued.

Liquid Propanol-1 Cleaning of Capillary Tubes

Infrared Spectra

Some of the same type problems encountered in the vapor cleaning experiments gave problems in the propanol-1 washing experiments. The

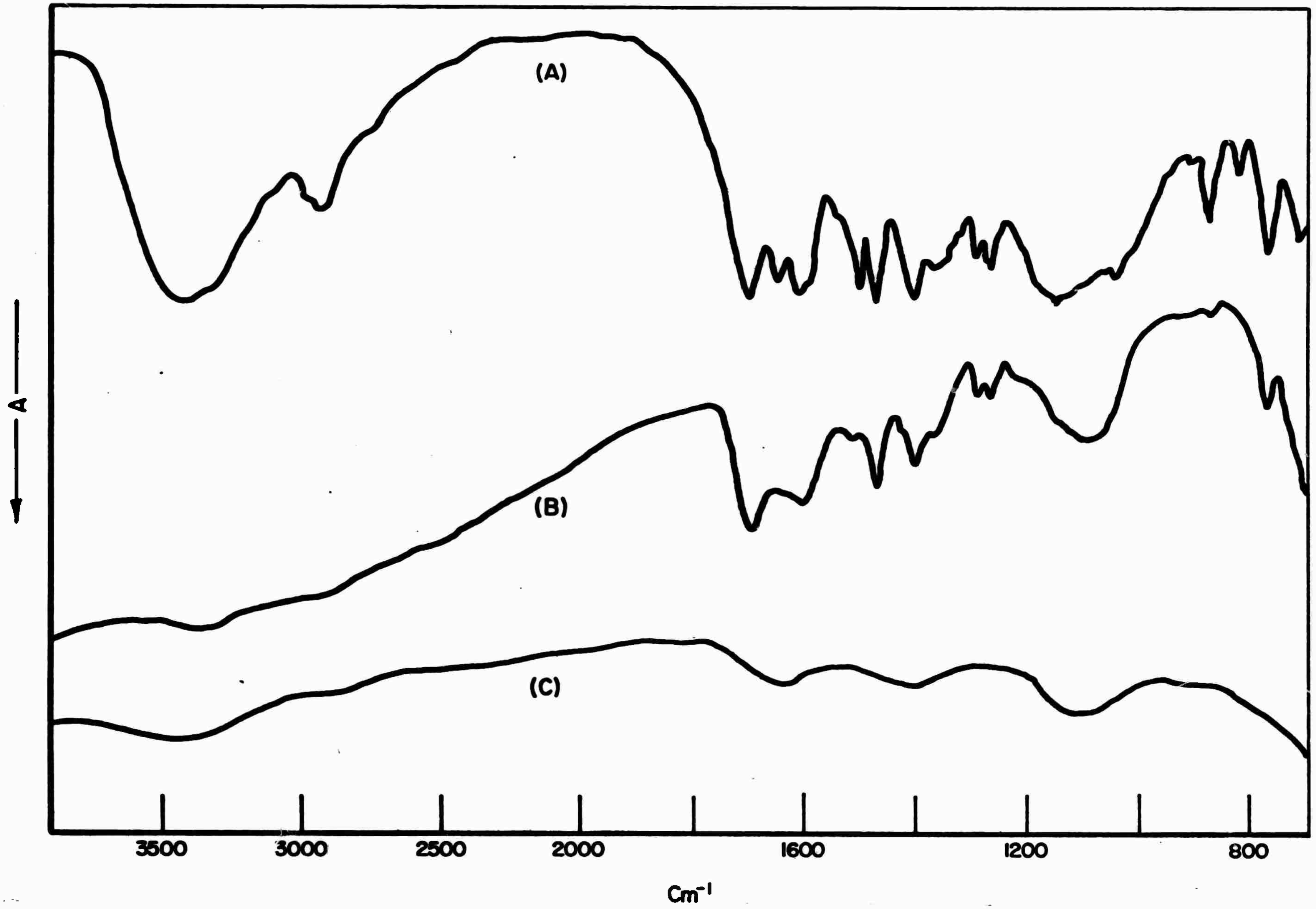


FIGURE 20. INFRARED SPECTRA OF (A) VW-H_2O-3, (B) VW-H_2O-8, AND (C) VW-H_2O-5

detection of these problems can be seen in Figure 21. The top spectrum (A) is of the residue from the first tube washing with propanol-1 (LW-Pr-1). While other materials are also present, the major component is an organic phthalate.

At first it was suspected that the phthalate might originate from the propanol-1 used for the washing. Thus the residue was obtained from evaporation of an amount of propanol-1 equal to that used for the washings. The spectrum of this material (LW-Pr-00) is shown in the middle spectrum (B) of Figure 21. While a surprisingly large residue from 99+% pure propanol-1 is indicated, only a small portion of this material is a phthlate. The spectrum of this propanol-1 residue does confirm where some of the other materials in spectrum (A) originate. However, another source of phthalate contamination is indicated. The only remaining possibility is the Saran wrap used to cover the baking dish which holds the propanol and the glass tubes. Accordingly we extracted some Saran wrap with propanol-1 and, after evaporation of the propanol-1, obtained the bottom (C) spectrum in Figure 21. This is clearly the spectrum of a phthlate and establishes the source of the additional phthalate contamination.

New washings of tubes with propanol-1 have been initiated using a glass cover for the baking dish (to eliminate the phthalate contamination) and using distilled propanol-1 (to minimize the propanol residue). These new washing experiments are still in progress.

Emission Analysis

While the propanol-1 washing samples, LW-Pr-1 and LW-Pr-2 are heavily contaminated with an organic phthalate that does not come from the

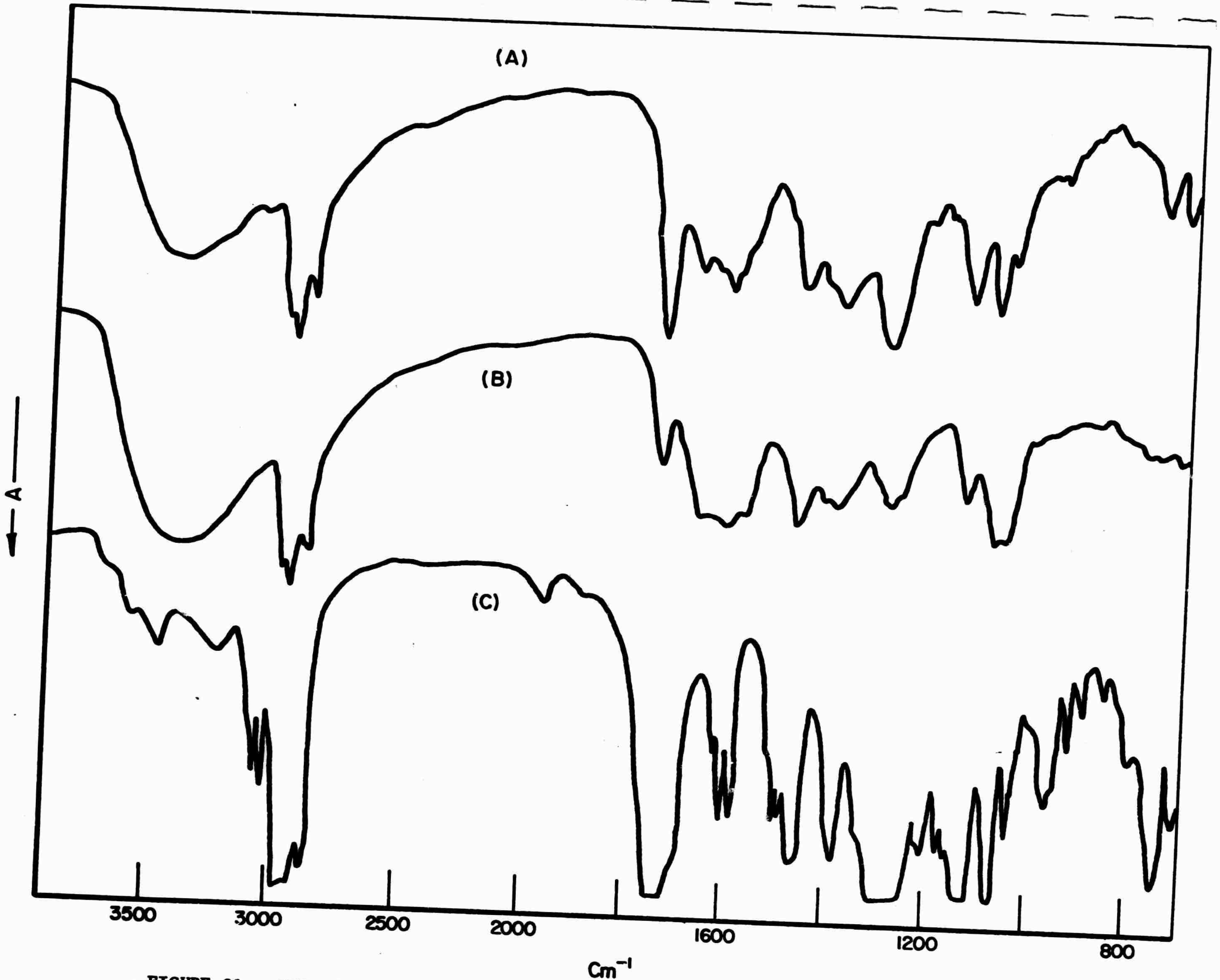


FIGURE 21. INFRARED SPECTRA OF (A) LW-Pr-1, (B) LW-Pr-00, AND (C) LW-Pr-01

washed tubes, one can still obtain much valuable information from these experiments. Partial emission values for the first two propanol-1 washes are listed in Table 6 together with those for the first two water washes.

It was anticipated that propanol-1 would be a better solvent for elements in the tubes such as carbon, but a poorer solvent than water for inorganic ions. Because of the phthalate impurity it is not possible to learn anything about elements such as carbon. However, it is obvious from Table 6 that propanol-1 is as good a solvent for inorganic ions as is water at the concentrations under consideration; maybe an even better solvent. Based on the analyses in Table 6, propanol-1 certainly seems to be a better solvent for Si, Fe, Mg, Sn, Al, and Cr, while water is a better solvent for Na, Ca, and maybe K. The second propanol-1 wash, LW-Pr-2, extracted much more material from the tubes than did the first wash, LW-Pr-1. This is especially true for B, Si, Fe, and Al. The reasons for higher solubility in the second wash are not understood. Note, however, that the second water wash extracted much more Na and K than did the first water wash.

Electron Microprobe Analysis

The electron microprobe results listed in Appendix B for LW-Pr-1 and LW-Pr-2 do not appear to be as useful as for other samples because of the phthalate impurity. However the results do confirm that water is a better solvent for K and S in pyrex than is propanol-1, but propanol-1 is as good or better solvent for Cl than is water.

TABLE 6. PARTIAL EMISSION SPECTROGRAPHIC ANALYSIS FOR LIQUID WASHINGS OF CAPILLARY TUBES

Sample	Elements (μg)									
	B	Si	Fe	Mg	Sn	Al	Na	Ca	Cr	K
LW-Pr-1	2.0	10.0	2.0	2.0	2.0	3.0	30.0	2.0	1.0	<50.0
LW-Pr-2	10.0	100.0	5.0	3.0	3.0	15.0	30.0	1.0	2.0	5.0
LW-H_2O-1	15.0	10.0	0.2	2.0	0.5	1.0	50.0	5.0	0.1	<50.0
LW-H_2O-2	3.0	3.0	0.1	0.3	0.5	0.2	>100.0	3.0	0.1	>100.0

Solvent Extractions

The observation that propanol-1 can extract inorganic ions from glass can be verified by the infrared spectra of cross-extracted portions of propanol-1 wash residues. These spectra are shown in Figure 22. The top spectrum (A) is that of the second propanol-1 residue, LW-Pr-2. Most of the spectrum is due to the phthalate contaminant. Spectrum B is that of the CCl_4 soluble portion of LW-Pr-2 and appears to be almost pure phthalate. The bottom spectrum (C) is that of the CCl_4 insoluble portion of LW-Pr-2 which closely resembles the spectra of the H_2O washes of glass tubes. Thus it appears that rather clean separations of the organic and inorganic portions of these residues can be made. For the same reasons the organics could be separated from water washing. This experimental result should prove valuable in future analyses.

Liquid Water Extractions of Crushed Glasses

Infrared Spectra

The infrared spectra of the residue of the water extraction of the seven types of crushed glass are placed in three groups as seen in Figures 23, 24, and 25. Figure 23 shows the spectra obtained from the water soluble residue of Nonex glass (A), 7052 glass (B), and cobalt glass (C). The spectra of this group of samples are characterized by a strong band in the 1350-1450 cm^{-1} range and a strong band in the 1070 to 1180 cm^{-1} region. For CG-N-1 and CG-C-1, the lower frequency band is the stronger while for CG-7052-1, the high frequency band near 1400 cm^{-1} is the stronger. In Figure 24, the spectra of water soluble residue from uranium glass (A),

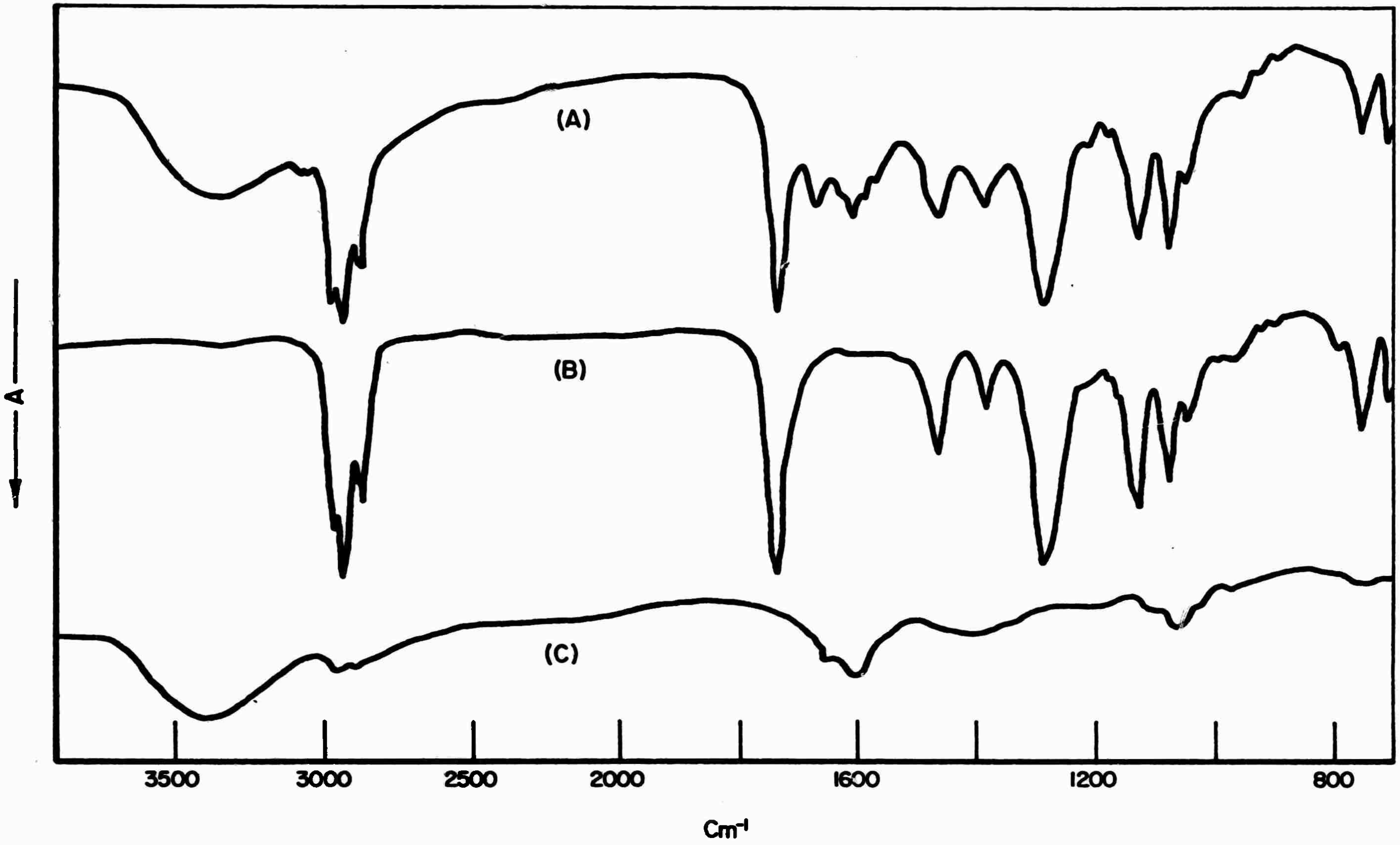


FIGURE 22. INFRARED SPECTRA OF (A) LW-Pr-2, (B) THE CCl_4 SOLUBLE PORTION OF LW-Pr-2, AND (C) THE CCl_4 INSOLUBLE PORTION OF LW-Pr-2

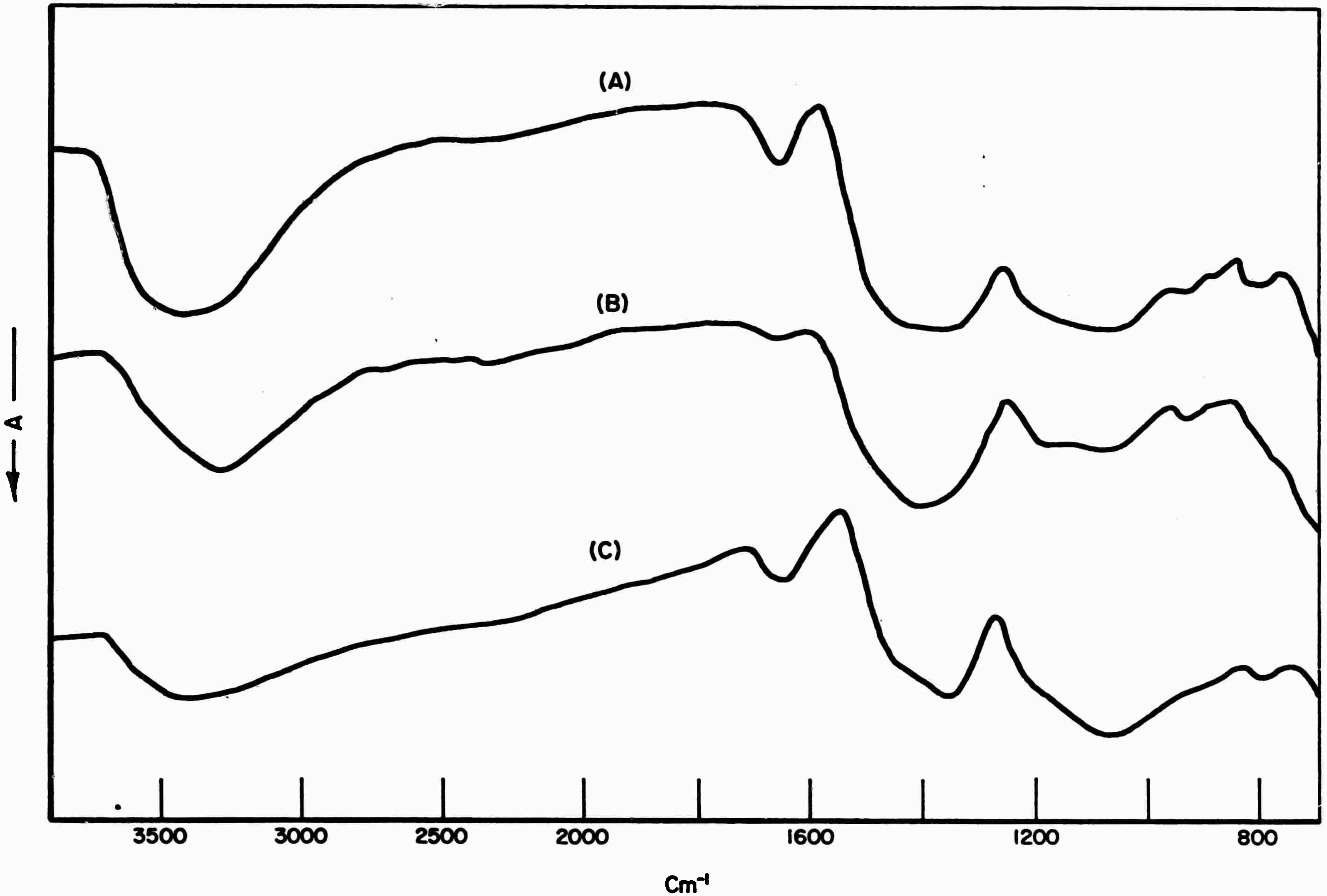


FIGURE 23. INFRARED SPECTRA OF (A) CG-N-1, (B) CG-7052-1, AND (C) CG-C-1

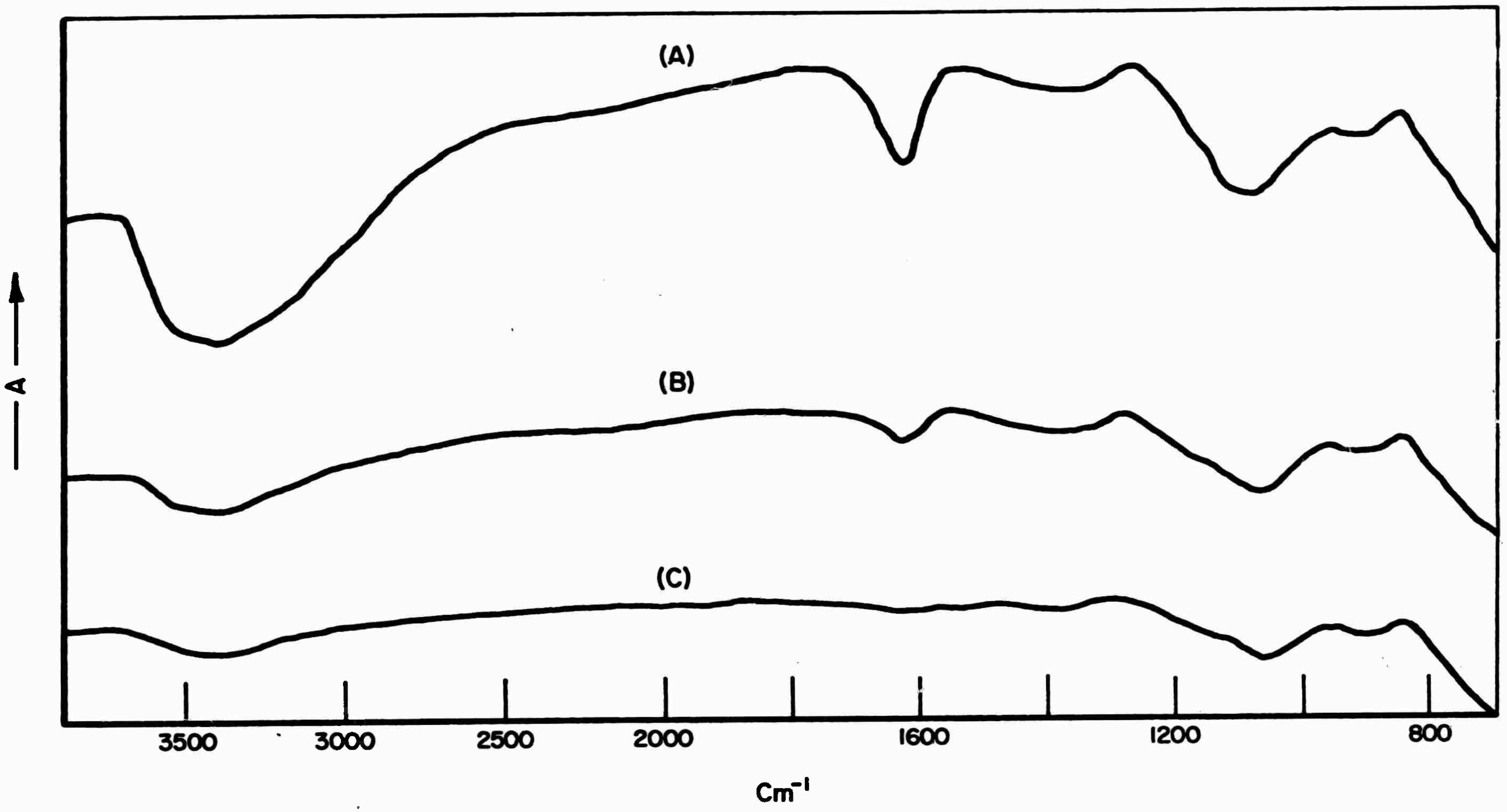


FIGURE 24. INFRARED SPECTRA OF (A) CG-U-1, (B) CG-U-1, AND (C) CG-Q-1

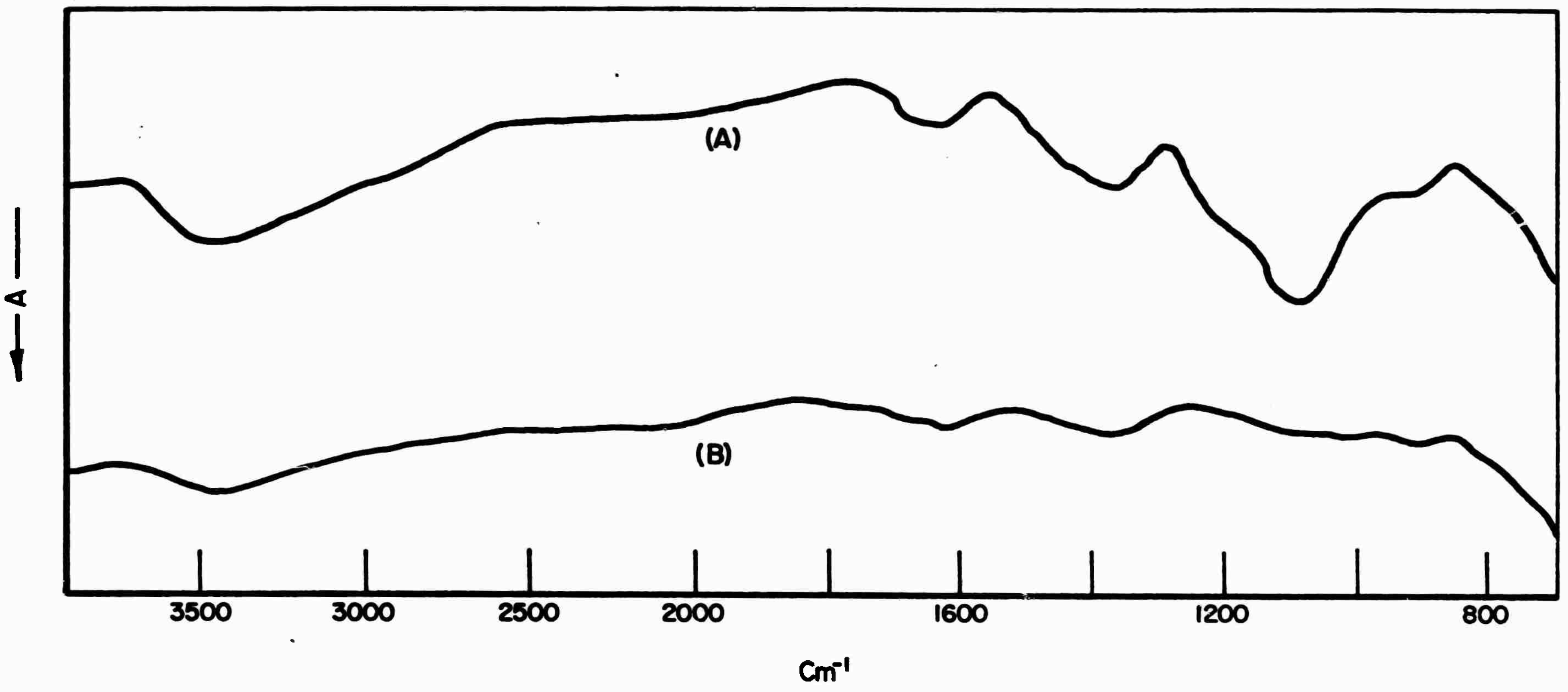


FIGURE 25. INFRARED SPECTRA OF (A) CG-P-1 AND (B) CG-H_2O-01

Vycor glass (B), and quartz glass (C) are characterized by a very weak band in the 1400 cm^{-1} region and a stronger band near 1075 cm^{-1}. The intensities of the bands in this group of samples is much weaker than the intensities of the bands in the spectra shown in Figure 24. This intensity difference between the two groups of spectra (Figure 23 versus Figure 24) reflects the difference in the amount of residue obtained by water extraction. Much more material was extracted for CG-N-1, CG-7052-1, and CG-C-1 than for CG-U-1, CG-V-1, and CG-Q-1.

The spectrum of the water extract of pyrex glass is shown in the top spectrum (A) of Figure 25. The ratio of the band near 1400 cm^{-1} to the one near 1075 cm^{-1} is intermediate between that from the group of samples in Figure 23 and the group of samples in Figure 24. The amount of material extracted from CG-P-1 also is intermediate between the amounts of material extracted from the other two groups. This difference in amount is also reflected by the fact that the intensities of all the bands of CG-P-1 are also intermediate between the intensities of the bands of the other two groups. The lower spectrum of Figure 25 is of the residue of an amount of water equal to that used for the extraction which had previously stood in a round-bottomed flask for the same length of time as the extractions. Thus it is the system blank (CG-$H_2$0-01) for the group of crushed glass experiments.

This spectrum CG-$H_2$0-01 shows that the extremely weak bands cannot account for much of the spectra of the water soluble residues from the glasses, except possibly for the 1400 cm^{-1} band of quartz.

Emission Analysis

Part of the emission analyses values for the residues from the crushed glass samples are given in Table 7. Compared to the system blank

TABLE 7. PARTIAL EMISSION SPECTROGRAPHIC ANALYSES FOR WATER EXTRACTIONS OF CRUSHED GLASSES

	Elements (μg)									
Sample	Ba	B	Si	Al	Na	Ca	K	Co	Sb	As
CG-N-1	0.3	>100.0	>100.0	3.0	>100.0	7.0	>100.0	0.1	3.0	10.0
CG-7052-1	0.3	>100.0	50.0	0.5	100.0	5.0	>100.0	0.1	0.5	1.0
CG-C-1	0.3	>100.0	>100.0	3.0	100.0	5.0	>100.0	2.0	0.5	1.0
CG-P-1	0.1	15.0	30.0	0.1	50.0	1.0	1.0	0.1	0.5	1.0
CG-V-1	0.1	15.0	20.0	0.1	5.0	1.0	1.0	0.1	0.5	1.0
CG-Q-1	0.1	3.0	15.0	0.1	1.0	1.0	1.0	0.1	0.5	1.0
CG-H_2O-01	0.1	2.0	3.0	0.1	1.0	0.5	1.0	0.1	0.5	1.0

(CG-H_2O-01), it can be seen that the elements listed in Table 7 can be extracted from some or all of the glasses in quantities substantially greater than the blank; with the possible exception of Ba. From Table 7 it is also apparent that the samples can be grouped by the amounts of various elements extracted, and these fall in the same groups as the spectra were arranged (Figures 23, 24, and 25). Thus CG-N-1, CG-7052-1, and CG-C-1 have large amounts of B, while the rest of the extracts do not.

The samples of the first group (CG-N-1, CG-7052-1, and CG-C-1) have the largest amounts of Si. CG-P-1 gives an intermediate value for Si, while the samples of the third group (CG-V-1 and CG-Q-1) give the lowest values for Si. The first group of samples shows the presence of some Al, while the rest of the samples apparently do not contain Al since the emission values are no greater than that of the system blank (CG-H_2O-1). For Na, the differences are even more distinctive. The first group of samples has 100 or more μg of Na; while the second group has 50 μg, and the third group has 5 or less μg of this element. Similar comparisons exist for most of the elements listed in Table 7. It is interesting to note that Co is detected in the residue from cobalt glass and that Sb and As are detected in the residue from Nonex glass.

The electron microprobe analysis of these samples has not yet been done. However, because of the emission results and since adequate sample is available, the microprobe studies are vitally needed. The microprobe data will provide information on possible anions such as S, O, and Cl which are present. Also, because of the extreme ranges found by emission for the cations, the corresponding anion portion for specific compounds might be deduced.

DISCUSSION

Liquid Water Cleaning of Capillary Tubes and Preparation of Anomalous Materials from Water

The interpretation of the infrared spectra of preparation of anomalous materials from water is of major importance toward achieving an understanding of the anomalous water phenomenon. Many of the current conflicting opinions concerning the formation and composition of these anomalous materials originates from differences of interpretation of the infrared spectra. Thus, attempted use of the results of the emission and electron microprobe analyses of both the tube washings and the preparations was made to aid in the interpretation of the infrared spectra.

It has been stated in the Results section that the infrared spectra of the residue from liquid water washings of tubes gave an absorption band at 1640 cm^{-1}, while the spectra of the residue from preparations of anomalous material from water gave a band at 1620 cm^{-1}. This frequency difference between the two types of sample could be most easily explained by a change in chemical composition between the washings and the preparations. However, the emission and microprobe results in Appendices B and C do not indicate any significant change in elemental composition peculiar to the residue from washings or to the residue from preparations from water. In one sense this appears to be uninformative, but from another viewpoint it does give us some information. One explanation for the band in the 1600 cm^{-1} region has been that it is due to formates, acetates, lactates, or other carboxylic acid salts (carboxylate ions). This explanation requires the presence of a metal cation which should vary with the amount or type of carboxylate. The cations listed in Appendices B and C (which include all the elements yet reported for anomalous water) do not show changes peculiar to washings or preparations, yet the spectra do show such changes. This observation is believed to be evidence against the interpretation of the 1600 cm^{-1} band as that of a carboxylate.

In the 1400 cm^{-1} region the same situation exists. The spectra of the tube washings gives a stronger band near 1360 cm^{-1}, while the spectra of the preparations indicate that the stronger band is near 1410 cm^{-1}. As for the 1600 cm^{-1} region, the emission and microprobe results do not indicate any obvious change in elemental composition that would explain the differences in the 1400 cm^{-1} region. In inorganic systems, this type of infrared spectrum could be explained by a mixture of nitrates (absorbing near

1350 cm^{-1}) and carbonates (absorbing near 1400 cm^{-1}). However, there are almost always confirming bands for nitrates and carbonates in the 800-900 cm^{-1} range. These confirming bands are not detected in the spectra of the washings and the preparations, although in some washings bands are seen between 780 and 800 cm^{-1}. Also, while N concentrations have not been determined for most of the samples, the microprobe results for C do not show the proper changes between washings and preparations. Thus there is little evidence for the presence of carbonates or nitrates to explain the changes in the 1400 cm^{-1} region.

Around 1100 cm^{-1}, the spectra of LW-H_2O-02, LW-H_2O-1, LW-H_2O-2, and possibly LW-H_2O-14 show the stronger absorption to be in the 1040 to 1090 cm^{-1} region. The remainder of the washings and the preparations have the stronger band between 1120 and 1140 cm^{-1}. From Appendices B and C it can be seen that the samples which have a stronger 1040-1090 cm^{-1} band have a higher ratio of B and Si to S than the samples having a stronger 1120-1140 cm^{-1} band. This observation supports the assignment of the bands in the 1120-1140 range as sulfate vibrations, and the bands between 1040 and 1090 cm^{-1} as B-O or Si-O frequencies, or both. The electron microprobe and emission analyses show that many elements are present in these samples, even in the preparations from cleaned tubes. While the total amount of the elements decreases for preparations in cleaned tubes, the elements detected are the same as those for preparations from uncleaned tubes or from tube washings. Thus a part of the sample from anomalous material preparations must be material extracted from the glass tubes. On the other hand, the elements thus far identified cannot account for the total material, since in the infrared spectra only the bands in the 1100 cm^{-1} region can be explained on the basis of changes in the concentrations and combinations of these elements.

Thus, since the spectral differences between washings and preparations definitely indicate a change in chemical composition, the anomalous materials prepared from water cannot be accounted for entirely on the basis of extraction of elements from the capillary tubes by liquid water.

Preparation of Anomalous Materials from H_2O_2 Solutions

Comparison of the infrared spectra and the electron microprobe results for H_2O_2-P-1 and H_2O_2-P-1H tend to support the assignment of the 1145 cm^{-1} absorption to an S-O vibration. While the infrared spectra show many changes after heating H_2O_2-P-1, the intensity of the 1145 cm^{-1} band shows only a slight change, and the electron microprobe results indicate that the S content remains fairly constant.

If C contributes strongly to the 1600 cm^{-1} absorption, it would seem likely that those samples which show a high carbon concentration would also show an increase in the intensity ratio of the 1600 cm^{-1} band to the 1400 cm^{-1} band. The electron microprobe results show that LW-H_2O-02, LW-H_2O-3, H_2O-CP-1, H_2O-UP-1, and H_2O_2-P-1H have slightly more carbon than the other samples. Yet among these five samples the 1600 cm^{-1} to 1400 cm^{-1} ratio varies greatly; going from a stronger 1600 cm^{-1} band in the H_2O-CP-1 and H_2O_2-P-1H to a stronger 1400 cm^{-1} band in LW-H_2O-02, LW-H_2O-3, and H_2O-UP-1. Thus it is not apparent that carbon contributes to the absorption near 1600 cm^{-1}.

The ratio of the intensity of the 1600 cm^{-1} to 1400 cm^{-1} bands increases on going from H_2O-UP-1 to H_2O-CP-1 to H_2O_2-P-1, while the emission results indicate the Na content decreases in the same order. A preliminary interpretation of these data would indicate that the frequency near 1400 cm^{-1} is a vibration of a Na compound, as will be discussed in the next section. The data on the crushed glass extractions support this interpretation.

The preparation from 3 percent H_2O_2 solutions (H_2O_2-P-1) shows differences in frequency in the 1600 and 1400 cm^{-1} range from the preparation from 100 percent H_2O (H_2O-CP-1 or H_2O-UP-1). Upon heating, however, the frequencies of the H_2O_2 preparation shift toward those of the H_2O preparation. And, while the frequencies of H_2O_2-P-1 in the 1600 cm^{-1} and 1400 cm^{-1} range decrease in intensity upon heating, the resultant spectrum is much like that of H_2O-CP-1.

Liquid Water Extractions of Crushed Glasses

The infrared spectra of the residues from the crushed glass extracts show a strong band in the 1400 cm^{-1} region for CG-N-1, CG-7052-1, and CG-C-1, an intermediate intensity in the 1400 cm^{-1} band for CG-P-1, and a weak band in this region for CG-U-1, CG-V-1, and CG-Q-1. This order is in direct relationship to the Na content (emission values) which are 100 or more µg for CG-N-1, CG-7052, and CG-C-1; 50 µg for CG-P-1, and 5 or less µg for CG-V-1 and CG-Q-1. This observation strongly supports the statement in the previous section that the frequency near 1400 cm^{-1} is a vibration resulting from a Na compound.

The residues from the water extractions of the crushed glass can be divided into three groups, each of which can be classified by spectral characteristics, by elemental composition, or by amount of material extracted. Unlike the comparison between tube washing and preparations, the three groups of water extracts show spectral differences which are reflected by changes in elemental composition. These results are quite encouraging toward achieving an understanding of the role impurities play in anomalous material formation. If the results of the electron microprobe analysis of the residues from the crushed glasses are found to support the spectral and emission results, then actual preparations of anomalous materials in tubes of the seven types of glass are vitally needed.

FUTURE PLANS

The results of the first six months research indicate the need to continue some phases of the research, drop other phases, and to add some new experiments. Thus the future research will include the following:

(1) The liquid water washings of capillary tubes will be discontinued insofar as evaporation of the water and analysis of the residue is concerned. Several new groups of tubes are being washed (without analysis of the residue) in order to provide more "cleaned" tubes so that the quantity of anomalous material prepared in "cleaned" tubes can be increased.

(2) The repeated, i.e., in the same tubes, preparation of anomalous material from water will be continued, using both "cleaned" and uncleaned tubes. These samples will be analyzed to determine if the elemental composition varies. Weights of the samples must be obtained to determine how the yield is changing.

(3) Efforts will continue with the propanol-1 washing experiments. If the use of a glass cover on the baking dish and distilled propanol-1 eliminate contamination, the washings will be continued until the tubes are cleaned. It is likely

that only the first few washings will be analyzed, since elimination of the evaporation and analysis greatly facilitates the washing cycle. Preparations from propanol-1 will be made from the cleaned tubes and compared to preparations from uncleaned tubes.

(4) The vapor water washings of capillary tubes will be discontinued. Comparison of the preparation in cleaned tubes to the preparation in uncleaned tubes will give us the same information, since the preparation is actually a vapor process.

(5) The anomalous material preparations from H_2O_2 solutions will be continued. Comparisons of these products to the preparations from pure water will be made.

(6) A new set of crushed glass extractions will be initiated. These experiments will consist of selecting one type of glass (such as pyrex), crushing the glass, dividing the crushed glass into several portions, and extracting each portion with a different solvent. Acidic H_2O, basic H_2O, methanol, cyclohexane, dioxane, etc. will be used. The analyses of the H_2O_2 preparations indicate that additional specific information about the effect of various solvents on glass is needed.

(7) A second water extraction of the seven different crushed glasses has already been completed. The analysis of these extracts will dictate the need to continue these extractions. In addition, tubes will be drawn from these seven glasses and preparations initiated.

(8) The pyrex capillary tubes already cleaned will be used to make preparations for analyses. The tubes that are now being washed will be used (when cleaned) to make preparations which will be combined in order to get samples large enough for distribution to other laboratories.

(9) Coordination of Battelle's Columbus Laboratories program with the program of the University of Maryland will continue and be accelerated. Preparations from cleaned and uncleaned tubes will be sent to Maryland for ESCA (electron spectroscopy for chemical analysis) analysis. ESCA will provide valuable information on the elements and types of chemical groups present. The need to identify the exact species present in the anomalous materials is becoming more apparent.

(10) Separations of the species in the anomalous materials will be attempted. This may enable us to separate or concentrate the component giving rise to the infrared absorptions in the 1600 cm^{-1} region and to identify which components give rise to the anomalous behavior of anomalous materials.

Ion exchange column separations should be ideal, but with the amount of material available, the column could potentially introduce a high percentage of contamination. The introduction of contaminants by the ion exchange column can be evaluated.

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APPENDIX A - SAMPLE NOTATION

LW-H_2O-00 - Blank, the residue obtained from just the water used for the liquid washings.

LW-H_2O-01 - First system blank for the liquid washings with water, i.e., water extract of baking dish, flask, and vial.

LW-H_2O-02 - Second system blank for the liquid washings with water.

LW-H_2O-1 - First liquid washing of pyrex capillary tubes with water.

⋮ ⋮

LW-H_2O-15 - Fifteenth liquid washing of the same pyrex capillary tubes with water.

H_2O-CP-1 - First preparation of anomalous material from water using the cleaned pyrex tubes from LW-H_2O-15.

H_2O-CP-2 - Second preparation of anomalous material from water using the same cleaned pyrex tubes as in H_2O-CP-1.

H_2O-UP-1 - First preparation of anomalous material from water using uncleaned pyrex tubes.

H_2O_2-P-1 - First preparation of anomalous material from a 3 percent H_2O_2 solution using pyrex tubes.

H_2O_2-P-1H - Sample H_2O_2-P-1 after heating in air at 400 C for 60 minutes.

LW-Pr-00 - Blank, the residue obtained from just the propanol-1 used for the liquid washings.

LW-Pr-01 - Blank, a propanol-1 extract of Saran wrap.

LW-Pr-1 - First liquid washing of pyrex capillary tubes with propanol-1.

LW-Pr-2 - Second liquid washing of pyrex capillary tubes with propanol-1.

VW-H_2O-1 - First vapor washing of pyrex capillary tubes with steam.

⋮ ⋮

VW-H_2O-12 - Twelfth vapor washing of pyrex capillary tubes with steam.

CG-N-1 - First water extraction of Nonex crushed glass.

CG-7052-1 - First water extraction of 7052 crushed glass.

CG-C-1 - First water extraction of cobalt crushed glass.

CG-P-1 - First water extraction of pyrex crushed glass.

CG-U-1 - First water extraction of uranium crushed glass.

CG-V-1 - First water extraction of Vycor crushed glass.

CG-Q-1 - First water extraction of quartz crushed glass.

CG-H_2O-01 - Blank, residue from water extraction of flask used for crushed glass extractions.

APPENDIX B

TABLE B-1. NUMERICAL VALUES FOR THE RANGE OF THE RELATIVE INTENSITY DISTRIBUTION FROM ELECTRON MICROPROBE ANALYSIS

Sample	B	Na	C	Mg	O	K	Ca	Cl	S	Si
LW-H_2O-01	0/15	125/460	50/200	25/160	800/1350	180/350	50/270	180/300,500/1400S	50/250,200/650S	200/700
LW-H_2O-02 Edge	0/5	80/225	100/350	20/50	380/850	50/125	25/120	50/1500	25/75	25/300
LW-H_2O-1 Edge	9/18	90/200	90/300	25/50	600/850	250/400	20/120	600/1000S	120/350	25/130S
LW-H_2O-1 Inside	5/15	90/200	80/160	35/50	?	400/600C	20/100,350S	1300/2500C	40/180,250S	20/120,350S
LW-H_2O-2 Edge	0/7	30/125	30/100	1/20	100/700	5000/6500CR	0/25	50/100	10/20	10/30
LW-H_2O-12 Edge	0/7	120/260	60/130	20/80	425/900	10/150	10/125	100/425	25/240	50/720
LW-H_2O-13 Edge	0/7	80/200	50/100	50/120	450/700	50/235	25/350S	55/350E,900/2200S	25/150	50/200
LW-H_2O-14 Edge	5/8	80/210S	80/130	10/35	400/1000	40/200	25/125	300/1300S	50/140	1000/1100E
LW-H_2O-14 Inside	1/5	60/180	60/110	8/20	190/350	20/40	0/5	50/350S	10/25	10/50
H_2O-CP-1 Edge	1/5	100/300	80/280	50/250	500/800	200/420	160/460	100/500,3000S	100/380	50/400,600S
H_2O-CP-1 Inside	1/5	180/300	150/350	20/65	500/700	100/300	10/30	50/150,1400/3600S	100/380	15/33,600S
H_2O-UP-1 Edge	?	40/200	125/340	50/200	200/850	100/180	100/600	120/320,500/1900S	150/430	60/200
H_2O-P-1 Edge	0/5	75/100	75/125	75/250	290/550	300/700	10/150	450/800	300/500	40/225,400/1100E
H_2O_2-P-1 Inside	0/5	75/250	50/170	50/300	350/450	550/1300	45/60	300/760	200/350	25/40
H_2O_2-P-1H Black	0/5	50/100	100/950S	100/450S	200/900S	100/700S	50/250	50/1800S	90/400	120/1800S
H_2O_2-P-1H White	0/5	80/200	10/120	50/180	400/900E	100/450	15/250	120/950	100/950	20/50
LW-Pr-1 Inside	0/7	25/320S	750/1700	5/25,225S	60/160	30/140	0/15	300/600,900/4000S	25/70	300/1250S
LW-Pr-1 Inside	0/7	60/375S	300/1500	0/25,175S	50/125,900/1200S	15/45	0/16,65S	25/200,400/2800S	10/65	600/1600S
Al Plate Blank Inside	0/2	0/5	9/15	0/15	60/90	10/12	0/5	0/9	0/5	0/5

NOTE: S = Spots or Particles
E = Edge
C = Center
CR = Large Crystals

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APPENDIX C

TABLE C-1. WEIGHTS (µg) OF ELEMENTS DETECTED BY EMISSION SPECTROGRAPHIC ANALYSIS

	Ba	B	Si	Mn	Fe	Mg	Sn	Ni	Al	Cu	Na	Ti	Ca	Cr	K	Co	Sb	As	Wt.	Wt.-K
LW-H_2O-1	2.0	15.0	10.0	<0.1	0.2	2.0	<0.5	<0.1	1.0	0.1	50.0	<0.1	5.0	<0.1	< 50.0	--	--	--	136.2	86.2
LW-H_2O-2	0.1	3.0	3.0	<0.1	0.1	0.3	<0.5	<0.1	0.2	0.1	>100.0	<0.1	3.0	<0.1	>100.0	--	--	--	>210.7	>110.7
LW-H_2O-12	<0.1	0.2	2.0	<0.1	<0.1	0.3	<0.5	<0.1	0.1	<0.1	< 1.0	<0.1	1.0	<0.1	< 50.0	--	--	--	55.8	5.8
LW-H_2O-13	<0.1	0.3	2.0	<0.1	<0.1	0.3	<0.5	<0.1	<0.1	<0.1	< 0.1	<0.1	1.0	<0.1	< 50.0	--	--	--	55.0	5.0
LW-H_2O-14	<0.1	2.0	5.0	<0.1	<0.1	0.5	<0.5	<0.1	0.2	<0.1T	10.0	<0.1	1.0	<0.1	< 50.0	--	--	--	68.9	18.9
H_2O-CP-1	<0.1	0.3	2.0	<0.1	0.1	1.0	0.5	<0.1	0.2	0.1	20.0	<0.1	2.0	<0.1	< 50.0	--	--	--	76.7	26.7
H_2O-UP-1	<0.1	5.0	10.0	<0.11T	0.5	5.0	<0.5	0.1	1.0	0.1	30.0	<0.1	5.0	<0.1	< 50.0	--	--	--	107.6	57.6
LW-H_2O-01	<0.1	2.0	5.0	<0.1	<0.1T	0.5	<0.5	<0.1	0.2	<0.1T	1.0	<0.1	1.0	<0.1	< 50.00	--	--	--	60.9	10.9
LW-H_2O-02	<0.1T	0.1	1.0	<0.1	<0.1	0.2	<0.5	<0.1	<0.1	<0.1T	< 1.0	<0.1	0.3	<0.1	< 1.0T	<0.1	<0.5	<1.0	6.5	5.5
LW-H_2O-00	<0.1	< 0.1	0.1	<0.1	<0.1	0.02	<0.5	<0.1	<0.1	<0.1	< 1.0	<0.1	<0.1T	<0.1	< 50.0	--	--	--	52.6	2.6
H_2O_2-P-1	0.1	2.0	3.0	<0.1	0.1	5.0	<0.5	<0.1	0.1	0.2	5.0	<0.1	1.0	<0.1	5.0	<0.1	<0.5	<1.0	24.0	19.0
H_2O_2-P-1H	<0.1T	1.0	3.0	<0.1	0.1	5.0	<0.5	<0.1	0.5	<0.1T	2.0	<0.1	8.0	<0.1	1.0	<0.1	<0.5	<1.0	23.3	22.3
LW-Pr-1	<0.1	2.0	10.0	0.1	2.0	2.0	2.0	2.0	3.0	1.0	30.0	0.1	2.0	1.0	< 50.0	--	--	--	107.3	57.3
LW-Pr-2	<0.1T	10.0	100.0	0.2	5.0	3.0	3.0	3.0	15.0	0.5	30.0	0.3	1.0	2.0	5.0	<0.1	<0.5	<0.1	178.8	173.8
CG-W-O	<0.1T	2.0	3.0	<0.1	<0.1	0.5	<0.5	<0.1	<0.1	<0.1T	< 1.0	<0.1	0.5	<0.1	1.0	<0.1	<0.5	<1.0	10.9	9.9
CG-7052-1	0.3	>100.0	50.0	<0.1	0.1	0.7	0.5	0.1	0.5	<0.1T	100.0	<0.1	5.0	<0.1	>100.0	<0.1	<0.5	<1.0	>359.2	>259.2
CG-C-1	0.3	>100.0	>100.0	<0.1	1.0	1.0	<0.5	0.1	3.0	<0.1T	100.0	<0.1	5.0	0.2	>100.0	2.0	<0.5	<1.0	>415.9	>315.9
CG-N-1	0.3	>100.0	>100.0	<0.1	1.0	0.5	<0.5	0.1	3.0	<0.1T	>100.0	<0.1	7.0	0.3	>100.0	<0.1	3.0	10.0	>426.1	>326.1
CG-P-1	0.1	15.0	30.0	<0.1	0.1	0.5	<0.5	<0.1	<0.1	<0.1T	50.0	<0.1	1.0	<0.1	1.0	<0.1	<0.5	<1.0	100.4	99.4
CG-Q-1	0.1	3.0	15.0	<0.1	<0.1	0.5	<0.5	<0.1	<0.1	<0.1T	< 1.0	<0.1	1.0	<0.1	1.0	<0.1	<0.5	<1.0	24.4	23.4
CG-V-1	0.1	15.0	20.0	<0.1	<0.1	0.5	<0.5	<0.1	<0.1	<0.1T	5.0	<0.1	1.0	<0.1	1.0	<0.1	<0.5	<1.0	45.4	44.4