# Reports

## "Polywater": Evidence from Electron Spectroscopy for Chemical Analysis (ESCA) of a Complex Salt Mixture

Abstract. *The ESCA spectra of "polywater" show that this anomalous, high-density, viscous, nonvolatile material contains high concentrations of sodium, potassium, sulfate, chloride, nitrate, borates, silicates, and carbon-oxygen compounds with trace amounts of other impurities but very little water. On the basis of this evidence, in conjunction with reported spectroscopic and analytical experiments, it is very unlikely that a polymerized form of water has been discovered.*

"Polywater" or anomalous water has been analyzed by electron spectroscopy for chemical analysis (ESCA) techniques and found to contain the sodium and potassium salts of sulfate, chloride, nitrate, borates, silicates, and carbon-oxygen compounds as well as traces of other impurities. The complete analyses were performed on extremely small samples ($\sim 10^{-6}$ g) of "polywater." Assignment of these specific salts can account for greater than 95 percent of the total photoelectron spectrum from each sample. Electron spectroscopy for chemical analysis, the high-resolution measurement of electrons ejected from a substance during x-ray excitation, is an excellent means of analyzing small involatile samples. The observation of x-ray–produced photoelectrons from each element in characteristic regions, as well as the measurement of the chemical shift, makes possible the identification of the oxidation state of the element and therefore the chemical environment of as little as $10^{-8}$ g of a material.

Anomalous water, prepared by the condensation of water into very fine, freshly drawn capillary tubes (*1*), exhibits unusual physical (*1*) and infrared spectral properties (*2*), and it has been proposed that anomalous water is a polymer of normal water. Numerous theoretical calculations have been published supporting the nature of "polywater." However, recently Rousseau and Porto (*3*) and Kurtin *et al.* (*4*) have seriously questioned the existence of "polywater," offering evidence from electron microprobe measurements (*3*), neutron activation analysis (*3*), x-ray milliprobe measurements (*3*), spark-source mass spectra (*3*), and scanning electron micrography (*4*) in support of their claim that the samples are nothing more than hydrosols or gels of impurities with very little water present. Our ESCA studies confirm these impurity theories and permit the identification of the ions present in "polywater."

Samples of "polywater" were prepared in capillary tubes of both quartz and, in several cases, Pyrex, over pure water under conditions of both saturation and unsaturation. The capillaries containing condensate were placed in a dry atmosphere to allow the normal water to evaporate. In some cases they were sealed in a flame pending ESCA analysis prior to complete drying, whereas in other cases they were allowed to dry completely, liquefied by reexposure to a saturated atmosphere of water, and sealed pending the ESCA analysis. No systematic differences were detected between these two handling methods.

Disks of pure gold, whose ESCA background spectra were recorded, served as the target supports. One end of the capillary was cracked open, and the other end was heated gently to move the "polywater" onto the target. In some samples the presence of "polywater" was confirmed by splitting the contents of a tube—half going onto silicon, barium fluoride, or Irtran wafers for infrared analysis and the other half onto the clean gold target for ESCA. In other cases two capillaries from the same preparation were selected. One was used for infrared analysis and the other for ESCA. The infrared spectra of the "polywater" samples were similar to those already

Table 1. Ions detected by ESCA techniques in various samples of anomalous water.

| Binding energy (ev) | Sample intensity (count/sec) | | | | | |
|---|---|---|---|---|---|---|
| | Purdue sample* | | | Bell Labs sample† | | |
| | P-1 | P-2 | P-3 | B-1 | B-2 | B-3 |
| | | | *$Na^+$* | | | |
| 1072 | 1254 | 3750 | 7156 | 6546 | 1788 | 1304 |
| | | | *Oxygen* | | | |
| 534.5 | 1564 | 3740 | 6750 | 4870 | 2400 | 1621 |
| 533.5 | 1325 | 1250 | 2210 | 4560 | 2235 | Unresolved |
| 532.0 | 200 | 800 | 370 | 415 | 473 | 97 |
| | | | *$NO_3^-$* | | | |
| 407 | 150 | 440 | 397 | 505 | 48 | 62 |
| | | | *$K^+$* | | | |
| 377 | 25 | 250 | 704 | 748 | 30 | ‡ |
| | | | *Carbon* | | | |
| 287 | 3300 | 2450 | 1155 | 2875 | 3950 | 4400 |
| 285.5 | | 100 | 1100 | | 1150 | 1505 |
| 284 | 752 | 800 | 309 | 452 | 608 | 1505 |
| 282 | | | | 100 | | |
| 280 | | 50 | | | | 130 |
| | | | *$Cl^-$* | | | |
| 205 | 87 | 375 | 450 | 873 | 65 | 54 |
| | | | *Borates* | | | |
| 189.5 | 54 | 90 | | 205 | 20 | 15 |
| 188.6 | 50 | 97 | 60 | 130 | 16 | 18 |
| 187.0 | 36 | 88 | 24 | 90 | | 12 |
| | | | *$SO_4^{2-}$* | | | |
| 168 | 248 | 665 | 800 | 1243 | 398 | ‡ |
| 162 | | 108 | 72 | | | ‡ |
| | | | *$SiO_3^{2-}$* | | | |
| 100 | 350 | 305 | 58 | 28 | 33 | ‡ |

* Samples were prepared in quartz tubes, except for sample P-1, which was prepared in Pyrex. All samples were prepared over pure water. † Samples were prepared in quartz tubes, all over pure water. ‡ Not measured. Rapid scan did indicate that bands were in these regions, however.

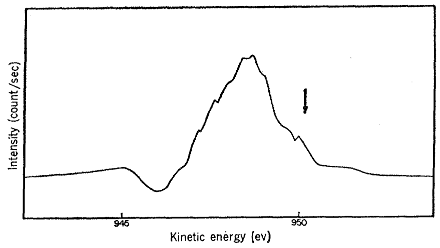

Fig. 1. The ESCA spectrum of oxygen (1*s*) in a typical sample of "polywater." The arrow represents the position of the band from oxygen in water (normal ice). Plotted is the intensity (in counts per second) as a function of the kinetic energy (KE) of the photoelectrons (in electron volts). Spectrum scanned on the Hewlett-Packard ESCA instrument.

reported (*2, 3, 5*) and varied a bit from sample to sample as also reported in the literature (*2, 3, 5*). However, they were all characterized by the presence of a strong band at about 1600 cm$^{-1}$ and weaker bands near 1400 cm$^{-1}$.

The ESCA background spectrum of the gold target was recorded with the use of AlK$\alpha$ x-rays (1486.6-ev energy) (*6*). The sample of "polywater" was then streaked onto the center of the target. Coverage of the target area was determined by noting the decrease in intensity of the gold $4f_{5/2}$ and $4f_{7/2}$ doublet at a binding energy (BE) of 87.0 and 83.3 ev, respectively. With the gold $4f_{5/2}$ band defined as equal to 87.0 ev, it was possible to measure all other binding energies relative to this standard (*7*). The data are obtained by plotting the photoelectron signal as a function of the kinetic energy (KE) of those electrons. The binding energy is obtained from

$$1486.6 \text{ ev} = h\nu(\text{x-ray}) = \text{BE} + \text{KE} + \text{correction term}$$

where the correction term results from the work function of the sample, the work function of the spectrometer, and the effects of the charging energy. This term is generally less than a few electron volts and is readily obtained by scanning the gold $4f_{5/2}$ band. Thus,

$$\text{correction term} = 1486.6 - 87.0 - \text{KE (dial reading)}$$

where KE is the measured dial reading on the spectrometer of the gold $4f_{5/2}$ band.

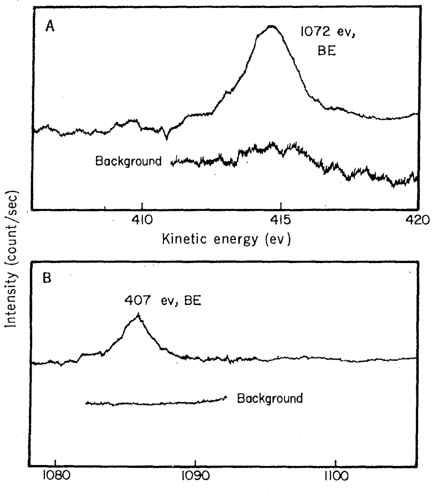

Fig. 2. The ESCA spectrum in (A) the sodium (1*s*) region and (B) the nitrogen (1*s*) (nitrate ion) region. The background of the sodium ion on gold (×10) is shown. The background in the nitrogen region is also ×10. Spectra scanned on the AEI ES 100 instrument.

Qualitative analyses of each element are readily made by measuring the binding energies of the core electrons in each atom, and the identity of the oxidation states is determined by measuring the chemical shifts (*8*). The correction term was used to relate the KE (dial reading) to the BE of some element in the sample measured within a few minutes. These shifts for many common materials have been well documented, thus making ESCA a powerful qualitative analytical tool (*9*). Since every element, except H, may be seen in the analysis in definite regions, by scanning the entire spectrum the total composition may be determined. The electrons on hydrogen are involved in the bonding molecular orbitals of the molecule, and a band in the region between 0 and 25 ev does not uniquely determine the presence of hydrogen.

Several background spectra were obtained. For each line, background spectra of the clean gold substrate, before sample deposition, were determined. Furthermore, the spectra of blank samples, made by placing a droplet of distilled water directly on the substrate, were measured. In all cases the background was very much smaller than the photoelectron signals obtained from the "polywater" sample.

Tables 1 and 2 show the ESCA results (*10*) from several samples. All samples studied showed qualitatively similar contamination in spite of independent preparations at two different laboratories (Purdue University and Bell Telephone Laboratories), and no samples were found that did not contain contaminants. In each analysis the entire spectrum was surveyed, and each line was individually analyzed in detail. No lines were neglected. The

Table 2. Ions detected in additional samples of "polywater" examined by ESCA techniques. All samples were prepared in quartz tubes over pure water; tr., trace.

| Purdue sample | | Bell Labs sample |
|---|---|---|
| P-4* | P-5 | B-4 |
| Na$^+$ | Na$^+$ | Na$^+$ |
| NO$_3^-$ | NO$_3^-$ | NO$_3^-$ |
| Cl$^-$ | Cl$^-$ (tr.) | K$^+$ |
| Borates (tr.) | SO$_4^{2-}$ | Carbon |
| SO$_4^{2-}$ | K$^+$ | Cl$^-$ |
| Silicates (tr.) | Cr$^{3+}$ (tr.) | Borates (tr.) |
| K$^+$ | Borates (tr.) | SO$_4^{2-}$ |
| Ca$^{2+}$ (tr.) | Silicates (tr.) | Silicates (tr.) |
| Al$^{3+}$ (tr.) | Carbon | Mg$^{2+}$ |
| Mg$^{2+}$ (tr.) | | Al$^{3+}$ (tr.) |
| Carbon | | |

* "Polywater" prepared from $D_2O$.

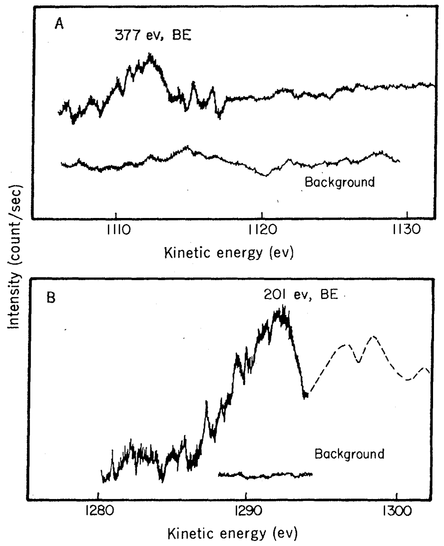

Fig. 3. (A) The ESCA spectrum of the potassium ion (2*s*) at a BE of 377 ev. (B) The chloride ion spectrum ($2p_{1/2}$, $2p_{3/2}$ doublet) centered at a BE of 201 ev. The dotted line represents the boron (1*s*) spectrum. Spectra scanned on the AEI ES 100 instrument.

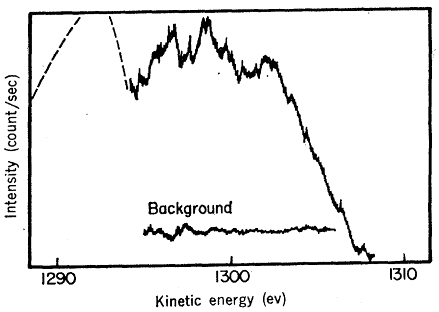

Fig. 4. The ESCA spectrum of the boron (1*s*) region. This region of the spectrum is adjacent to that of Cl (see Fig. 3). The boron (1*s*) cross section is much larger than that of chlorine (2*p*); thus, although the peaks appear to be the same height, boron is present in about 1/8 to 1/10 the concentration of chlorine. Spectra scanned on the AEI ES 100 instrument.

oxidation states of all but a few weak lines could be definitively assigned to the listed impurities without invoking the presence of a polymer of $H_2O$ units. Approximately 95 percent of the photoelectron signal could be accounted for by assignment of these well-defined contaminants. Since every element of the periodic table, except H, can be detected within the range of the ESCA instruments, a complete elemental analysis was performed.

In Figs. 1–7 we report the spectra recorded for electrons with kinetic energies up to 1450 ev and show all the peaks that were common to all the "polywater" samples studied (*11*).

In Fig. 1 the high-resolution ESCA spectrum of oxygen (1*s*) is recorded. The arrow shows the normal position of oxygen (1*s*) with a BE of 532 ev in ice and indicates the presence of a small amount of normal water. The bands to the left are characteristic of oxygen in Y-O systems in which element Y carries a high formal charge, as in sulfate or carbonate. Deconvolution of the oxygen spectra showed at least three bands in all samples and four in some samples, an indication of a variety of chemical environments of oxygen in the samples.

Figure 2A shows the $Na^+$ (1*s*) spectrum with a BE of 1072 ev, the same value as that recorded for sodium chloride. The $Na^+$ (1*s*) spectrum is very strong.

In Fig. 2B the peak is due to the nitrogen (1*s*) electron in the $NO_3^-$ ion. The BE is 407 ev, the same value as that found in pure sodium nitrate (*12*), with a chemical shift of $d = 8.0$ ev from the azide ion (*8*). The $NO_2^-$ ion at 404 ev was not detected in the samples. Ammonium salts ($d$ near 0 ev) were generally not observed; however, one sample had a small peak in that region.

In Fig. 3A the ESCA spectrum of $K^+$ (2*s*) at a BE of 377 ev is displayed, and Fig. 3B shows the ESCA spectrum of $Cl^-$ ($2p_{1/2}$, $2p_{3/2}$) centered at a BE of 201 ev. Figure 4 shows the spectrum in the boron (1*s*) region, which occurs adjacent to the spectrum of Cl. We cannot assign all those peaks but can only point out that $H_3BO_3$ and $Na_2B_4O_7 \cdot 10H_2O$ have different boron (1*s*) spectra (*13*) with different $d$ values. The chemical shifts of these borates differ by about 1 ev. It is quite likely that borates in various degrees of polymerization are present in "polywater."

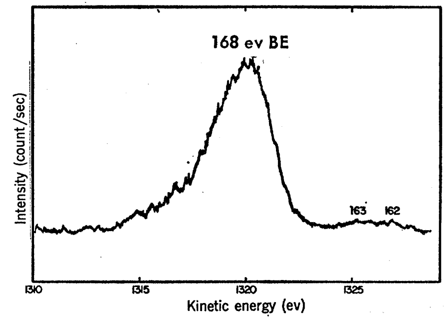

Fig. 5. The ESCA spectrum of the sulfur region. The large peak is due to sulfate. The bands at a KE of 1325 ev are real in that at ×10 scale they are above the background. They are unassigned. Spectrum scanned on the Hewlett-Packard ESCA instrument.

In Fig. 5 the sulfur ($2p_{1/2}$, $2p_{3/2}$) spectrum is shown with a mean BE of 168.0 ev. The peak for S in $Na_2SO_4$ is at 167.8 ev in the pure material, which, within experimental error, is identical with the location of the peak in "polywater." The $d$ is 5.8 ev for sulfate (*14*). The peaks near a KE of 1325 ev (BE of 163 ev) are real and above the background level, but we have not been able to assign them. The region is the place where one would expect sulfur in an oxidation state of −1 or −2 (compounds of the type RSSR or RSR) with $d$ values near zero.

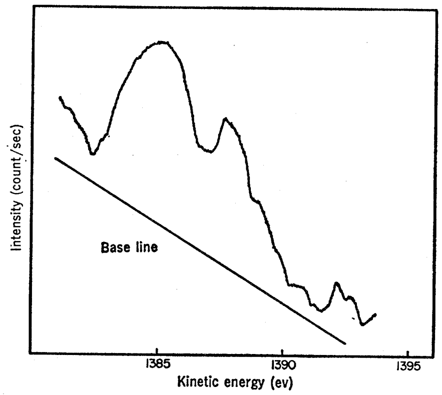

Fig. 6. The ESCA spectrum of the silicon (2*p*) region. The total counting time on this sample in this region was 4 hours. Spectra scanned on the Varian IEE instrument.

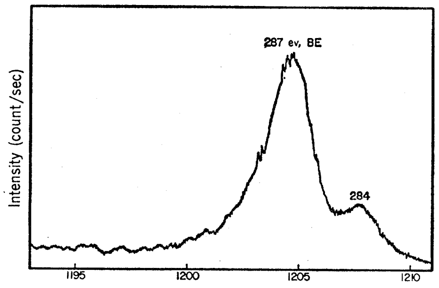

Fig. 7. The ESCA spectrum of the carbon (1*s*) region. At least three bands can be detected in this spectrum with kinetic energies of 1203, 1205, and 1208 ev. Several samples had an extra band near 1206.5 ev as well. Spectrum scanned on the AEI ES 100 instrument.

In Fig. 6 the silicon ($2p_{1/2}$, $2p_{3/2}$) region is shown. The BE's found are those of $SiO_2$ or silicates (BE of 100 ev). The rather complex band shapes demonstrate that probably numerous types of silicates are present with differing degrees of polymerization.

In Fig. 7 the carbon spectrum of one sample of "polywater" is shown. This region shows a band at a BE of 287 ev ($CO_3^{2-}$, $HCO_3^-$, or $RCOO^-$) ($d = 3.0$ ev) and a much smaller band at a BE of 284 ev ($d = 0.0$ ev) (*15*). This latter band is typical of aliphatic-type carbon ($CH_3$—, —$CH_2$—) or aromatic-type carbon. All samples had the weaker band with a BE of 284 ev (KE of 1207 ev in Fig. 7), but the intensity varied quite a bit from sample to sample. The presence of this aliphatic- or aromatic-type carbon could explain why certain "polywater" samples "burn" on exposure to lasers during Raman studies (*3*). Likewise, it could explain the fluorescence of "polywater." Since the total amount of 284-ev (aliphatic or aromatic) carbon probably represents only a few percent of the total mass of the "polywater" sample, one would not expect to see strong infrared bands in the C–H region. Some samples had small peaks with $d = -2$ ev. The bands are unassigned.

Several "polywater" samples had bands that were not common to the spectra of the rest of the samples. Calcium ion [BE = 440 ev for $Ca^{2+}$ (2*s*)] was detected in one sample; magnesium ion was detected in another; and one sample had a band at a BE of 118 ev which we assigned to $Al^{3+}$ (2*s*). Another sample had weak bands near a BE of 697, 585, and 577 ev due to $Cr^{3+}$ ($2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$).

Rich ESCA spectra have been obtained for every sample of the viscous, nonvolatile material prepared in capillaries. In each case the infrared spectra and the physical properties were similar to those claimed for "polywater."

The presence of high concentrations of ionic impurities in such a complex mixture may account for many of the strange physical properties of "polywater." Furthermore, the determination of carbon-oxygen compounds is especially significant. Salts of simple carboxylic acids quite accurately reproduce the infrared spectrum (*16, 17*). Large photoelectron signals consistent with salts of carboxylic acids have been observed in each sample in the study reported here. It is therefore very likely that this type of grouping is responsible for much of the reported infrared spectrum of "polywater" (*18*). In any event, the consistent evidence that polywater samples are highly contaminated makes it unlikely that the unique properties result from polymerized $H_2O$ units. Very probably the entire phenomenon results from a complex mixture of salts.

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2. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).

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6. D. M. Hercules, *Anal. Chem.* **42**, 20A (1970). This paper is a good summary of the state of the art in electron spectroscopy.
7. This definition, first used in the literature in this study, resulted after lengthy discussion with M. Barber of AEI, Ltd., Manchester, England. The measured value of K. Siegbahn [see (*9*)] has thus been used to correct for the spectrometer work function and any shifts due to charging of the sample.
8. Chemical shifts *d* (in electron volts) will be defined as BE in the compound minus BE in the element. The shifts range from 0 to about 20 ev [see (*9*)]. The use of *d* is suggested since this shift is related to the chemical shift, δ, used in nuclear magnetic resonance spectroscopy. Since solid nitrogen ($N_2$) is not as convenient a standard substrate, we will define the *d* scale relative to the inner nitrogen of the azide ion.
9. See, for example, K. Siegbahn *et al.*, *ESCA: Atomic, Molecular, and Solid-State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksells, Uppsala, Sweden, 1967).
10. The ESCA spectra reported were measured on three different instruments. High-resolution spectra were recorded on the Hewlett-Packard ESCA spectrometer with the use of monochromatic AlK$\alpha$ x-rays. Spectra were also recorded on the Varian IEE spectrometer in Palo Alto, California. Additional spectra were measured by R.E.D. on the AEI ES 100 spectrometer in Manchester, England.
11. All the electron spectra were studied up to a kinetic energy of 1487 ev. Electrons with binding energies lower than 1487 ev were recorded for all molecular orbitals as well as the core electrons. For example, Cl has bands at 7 ev ($3p_{3/2}$, $3p_{1/2}$) and 18 ev ($3s_{1/2}$), which are within the valence band. Bands useful for analysis are at BE = 200 to 202 ev ($2p_{3/2}$, $2p_{1/2}$) and 270 ev ($2s_{1/2}$). The BE of Cl (1*s*) is near 2823 ev, and those electrons cannot be removed with a AlK$\alpha$ x-ray with an energy of only 1487 ev. We observed bands at 201 and 270 ev for $Cl^-$.
12. R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, B. J. Lindberg, *Ark. Kemi* **28**, 257 (1967).
13. D. N. Hendrickson, J. M. Mollander, W. L. Jolly, *Inorg. Chem.* **9**, 612 (1970).
14. The binding energy of $S_8$ is 162.2 ev (sulfur 2*p*), and the *d* value is defined as 0.0 ev.
15. Graphite serves as the carbon standard.
16. E. R. Lippincott, paper presented at the 44th National Colloid Symposium (1970).
17. D. L. Rousseau, paper presented at the 44th National Colloid Symposium (1970).
18. That the infrared spectrum of "polywater" does not result from a symmetrically hydrogen-bonded polymer has been confirmed by deuteration experiments carried out independently by R. E. Davis [see *Chem. Eng. News* (29 June 1970), p. 8] and by D. L. Rousseau [this experiment is reported in (*17*)]. In each case spectra of material prepared from $D_2O$ were obtained that are essentially the same as those spectra obtained from samples prepared from $H_2O$. The bands did not undergo any isotope frequency shifts; this lack of isotope frequency shifts is not consistent with a system of $H_2O$ units. Recent spectroscopic data obtained by one of us (D.L.R.) suggests that the specific carboxylic acid salt responsible for the infrared spectrum is sodium lactate, the primary constituent of sweat (*Science*, this issue).

19. One of the authors (R.E.D.) thanks L. Wilson and M. Gross of Varian for assistance in running the Varian IEE spectrometer in Palo Alto, and M. Barber, I. Drummond, and J. Race for assistance in measuring ESCA spectra on the AEI ES 100 spectrometer in England. P. Vassen of AEI measured spark-source mass spectra on the AEI MS 702 spectrometer for the samples whose ESCA spectra are reported in Figs. 2–5 and 7. We thank J. J. Stancavish of Bell Telephone Laboratories for technical assistance in sample preparation. Studies at Purdue University were supported in part by NIH grant No. RO1 EC 00083. The spectra were deconvoluted on the Sigma 5 computer at Purdue University provided by a grant from the National Institutes of Health. Presented in part at the Polywater Symposium, 23 June 1970, at Lehigh University, Bethlehem, Pennsylvania.

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## "Polywater" and Sweat: Similarities between the Infrared Spectra

Abstract. *The infrared spectrum of "polywater" is remarkably similar to that of sodium lactate, the primary constituent of sweat. It is proposed, therefore, that this property of "polywater," and possibly others, results from accidental biological contamination. Such contamination is consistent with chemical analyses of "polywater" samples prepared both here and abroad.*

A great deal of attention has been devoted to the infrared spectrum of "polywater." Originally the spectrum was thought to be unique (*1*) and has been regarded by many investigators as the most meaningful means of monitoring the successful production of this new material. The same general spectrum has been obtained independently in several different laboratories, thus confirming its reproducibility (*1–3*). Recently, however, the "polywater" infrared spectrum has been the subject of some controversy, and similarities between it and the infrared spectra of other materials, especially salts of carboxylic acids, has been pointed out (*4*). In spite of this similarity, the infrared spectrum has still been considered to be a reliable property of "polywater," because its critics have been unable to suggest a consistent and plausible origin for the specific carboxylic acid salts needed to reproduce the spectrum.

In this report I propose that the unique material present in "polywater" samples that is responsible for the infrared spectrum may be sodium lactate, which probably originates through contamination from human sweat. Biological contamination is consistent with reported analyses of "polywater" samples prepared by many American investigators and with analyses carried out in the Soviet Union on samples prepared by B. V. Deryagin and his co-workers. Infrared spectra of sweat residues and of sodium lactate are in good agreement with "polywater" infrared spectra.

The infrared spectrum of "polywater" consists of a strong band near 1600 $cm^{-1}$, weaker bands near 1400 $cm^{-1}$, bands of variable intensity at 1100 $cm^{-1}$, and sometimes bands near 3300 $cm^{-1}$ attributable to normal $H_2O$ adsorbed on the sample. Often a single high-intensity band is observed at 1100 $cm^{-1}$, and this band has been assigned as a sulfate impurity (*2, 3*). However, in some spectra the intensity of this band is quite weak and two distinct features are discernible. For example, in the original spectrum reported by Lippincott *et al.* (*1*) there appear to be bands at about 1125 and 1050 $cm^{-1}$. There is also variation in the reported intensity and shape of the absorptions in the 1400 $cm^{-1}$ region, but the band near 1600 $cm^{-1}$ is consistently very strong and has been located at frequencies from 1595 to 1630 $cm^{-1}$. A