

boxylic 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<sub>2</sub>O 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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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,  $\delta$ , used in nuclear magnetic resonance spectroscopy. Since solid nitrogen (N<sub>2</sub>) 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<sub>3/2</sub>, 3p<sub>1/2</sub>) and 18 eV

- (3s<sub>1/2</sub>), which are within the valence band. Bands useful for analysis are at BE = 200 to 202 eV (2p<sub>3/2</sub>, 2p<sub>1/2</sub>) and 270 eV (2s<sub>1/2</sub>). The BE of Cl (1s) 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.
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14. The binding energy of S<sub>2s</sub> is 162.2 eV (sulfur 2p), 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<sub>2</sub>O were obtained that are essentially the same as those spectra obtained from samples prepared from H<sub>2</sub>O. The bands did not undergo any

isotope frequency shifts; this lack of isotope frequency shifts is not consistent with a system of H<sub>2</sub>O 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. RO1EC00083. 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. Bio-

logical 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<sup>-1</sup>, weaker bands near 1400 cm<sup>-1</sup>, bands of variable intensity at 1100 cm<sup>-1</sup>, and sometimes bands near 3300 cm<sup>-1</sup> attributable to normal H<sub>2</sub>O adsorbed on the sample. Often a single high-intensity band is observed at 1100 cm<sup>-1</sup>, 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<sup>-1</sup>. There is also variation in the reported intensity and shape of the absorptions in the 1400 cm<sup>-1</sup> region, but the band near 1600 cm<sup>-1</sup> is consistently very strong and has been located at frequencies from 1595 to 1630 cm<sup>-1</sup>. A

typical spectrum of "polywater" prepared in our laboratory at saturation conditions is shown in Fig. 1 (spectrum A). It exhibits the usual strong band at about  $1600\text{ cm}^{-1}$  and considerable structure near  $1400\text{ cm}^{-1}$  with the strongest feature in this region at about  $1420\text{ cm}^{-1}$ . As reported by Lippincott *et al.*, two bands are seen, one at  $1125\text{ cm}^{-1}$  and the other at  $1045\text{ cm}^{-1}$ . The absence of a stronger band in this range indicates that the sulfate contamination was small in this sample.

In recent investigations (5, 6) of "polywater" prepared from  $\text{D}_2\text{O}$  the material has been shown to have the same infrared spectrum as that of "polywater" prepared from  $\text{H}_2\text{O}$ . Since the deuterated material did not undergo any isotope frequency shift, it has been concluded that the "polywater" spectrum does not originate from a polymer of  $\text{H}_2\text{O}$  units. However, it has been difficult to determine an alternative origin of this spectrum, although some investigators have shown that there are materials with infrared spectra very similar to that of "polywater" (4). Of several possibilities proposed, only carboxylic acid salts have a strong band close to  $1600\text{ cm}^{-1}$ . Lippincott (7) alleged, however, that to reproduce the "polywater" spectrum *exactly* with salts of simple organic acids, formates and acetates, it is necessary that trivalent cations, not found in any reported analyses, be present.

Sensitive chemical analysis of "polywater" has consistently yielded evidence of significant contamination, and in several cases carbon has been detected. Quantitative estimates by Rousseau and Porto have indicated 5 to 35 percent carbon in "polywater" samples (3). Similarly, Page and Jakobsen found 12 percent carbon in their samples (8). Furthermore, a recent electron spectroscopy for chemical analysis (ESCA) investigation (9) of "polywater" revealed the presence of a variety of carbon compounds. In that investigation several different chemical environments could be attributed to carbon, and from the chemical shifts it was concluded that aliphatic or aromatic carbon was present and carbon bonded either as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , or  $\text{RCOO}^-$  occurred in all the "polywater" samples tested.

Deryagin and Churaev recently reported (10) that their "polywater" contained not more than 1 percent carbon but failed to give any details of their analytical techniques. However, some details of analytical experiments carried

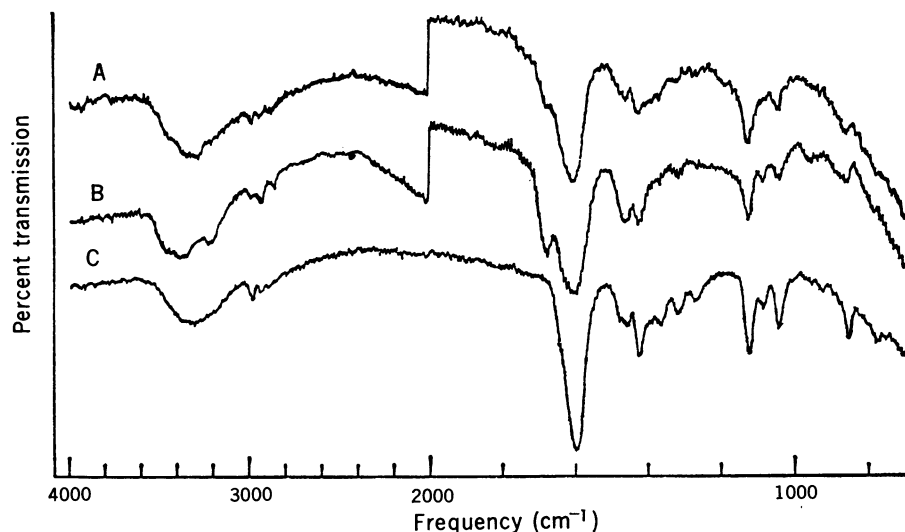


Fig. 1. The infrared spectrum of (A) "polywater," (B) sweat, and (C) sodium lactate. The discontinuities in spectrum A and spectrum B result from a change in the spectrometer grating, and the loss of intensity at low frequency is also an instrumental effect. The spectra were measured on a Beckman IR 12 infrared spectrophotometer. Silicon plates were used as the substrate material in spectrum A and spectrum B and silver chloride was used in spectrum C. Each of these materials has featureless backgrounds in this region.

out on Deryagin's samples have been presented by V. L. Tal'rose at a meeting of the Division of General and Engineering Chemistry of the Soviet Academy of Sciences held in June 1969 (11). Initially, Tal'rose did mass spectrometric analyses on 25 of Deryagin's samples and one sample from a foreign (non-Russian) laboratory. Every one of these samples was found to contain organic substances, including lipids and phospholipids in very high concentrations. Tal'rose reported that a later analysis on five additional samples prepared by Deryagin in a new apparatus showed a smaller percentage of organic contamination.

To study in greater detail the effects possible biological contamination may have on the properties of "polywater," infrared spectra from several sweat residues were obtained. The liquid sweat samples were isolated by pressing the liquid from cotton and woolen fabric that had become saturated with male upper-body sweat after extensive physical exertion. Samples of this liquid were then placed on silicon plates and allowed to evaporate to dryness for infrared analysis. Spectrum B (Fig. 1) is a representative example. This spectrum has a strong line at  $1600\text{ cm}^{-1}$ , as does "polywater," and a band at  $1420\text{ cm}^{-1}$ . Furthermore, it contains bands at  $1045$  and  $1125\text{ cm}^{-1}$ . In one sample studied a much stronger band was seen near  $1100\text{ cm}^{-1}$ , consistent with large variations of this band in

"polywater" samples. In general, the frequencies of the bands found in sweat are in good agreement with those found in "polywater," although some of the relative intensities are different. These variations no doubt result from slightly different relative concentrations of some of the compounds found in "pure" sweat as compared to those found in "polywater."

The composition of sweat has been studied (12) extensively, and, in addition to water, its primary constituents are Na, Cl, K, Ca,  $\text{SO}_4^{2-}$  plus many organic acids (13). The most concentrated organic material is lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , and the infrared spectrum of its sodium salt is shown in Fig. 1 (spectrum C). Clearly, the spectrum of sodium lactate is in good agreement with both the "polywater" spectrum and the sweat spectrum, with its strongest bands at  $1600$ ,  $1420$ ,  $1125$ , and  $1045\text{ cm}^{-1}$ . The broad band at  $3300\text{ cm}^{-1}$  results from absorbed  $\text{H}_2\text{O}$  (sodium lactate is hygroscopic) and heating the sample while it was in the spectrometer reduced the band by more than a factor of 5 (14).

Variations in individual "polywater" spectra and additional bands sometimes seen probably result from some of the many additional impurities found in "polywater" samples. These include other organic acids (15), borates, silicates, carbonates, bicarbonates, sulfates, and nitrates (9). [For example, nitrate seen in some analyses (9, 16) probably

accounts for the strong feature seen at  $1365\text{ cm}^{-1}$  in various samples.]

The high concentration of impurities in "polywater" samples that exhibit the appropriate infrared spectrum and the failure of the absorption bands to undergo isotope frequency shifts on deuteration make it very unlikely that the spectrum originates from polymerized  $\text{H}_2\text{O}$  units. The evidence presented here is consistent with this assumption and shows that sodium lactate, the primary constituent of sweat, may account for the main features of the infrared spectrum (17).

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3. D. L. Rousseau and S. P. S. Porto, *ibid.*, p. 1715.
4. A discussion of alternative explanations for the infrared spectrum is given in (5).
5. D. L. Rousseau, paper presented at the 44th National Colloid Symposium (1970) (proceedings to be published in *J. Colloid Interface Sci.*).
6. R. E. Davis, personal communication. These data have been reported in *Chem. Eng. News* (29 June 1970), p. 8.
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10. B. V. Deryagin and N. V. Churaev, paper presented at the 44th National Colloid Symposium (1970).
11. A report of this presentation by B. V. Deryagin was written by V. Zhvirblis [*Khimiya Zhizn'* (Russian) No. 12 (1969), pp. 37-44] [translation *Joint Publ. Res. Serv. No. 50006* available from Clearinghouse for Scientific Information, Springfield, Va., 1970].
12. S. Robinson and A. H. Robinson, *Physiol. Rev.* **34**, 202 (1954).
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14. The band near  $3300\text{ cm}^{-1}$  is quite strong in all three of the spectra presented here. However, it may be readily assigned to absorbed  $\text{H}_2\text{O}$  resulting from the deliquescent property of these materials. Results of  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$  exchange experiments (5) indicate that in "polywater" samples this band is very sensitive to the experimental conditions (temperature and humidity), thereby accounting for some of the differences among various spectra reported in the literature. To confirm that this band in spectrum C (Fig. 1) resulted from adsorbed  $\text{H}_2\text{O}$ , a heater was placed around the sample such that the spectrum could be measured at about  $150^\circ\text{C}$ . Heating resulted in the drastic reduction of this band relative to the other bands in the spectrum, thus verifying that it could be attributed to  $\text{H}_2\text{O}$  and was not attributable to sodium lactate.
15. One would expect that other organic acids in sweat would play the most important role in altering the spectrum of "polywater."
16. E. R. Lippincott, personal communication.
17. We may only speculate on the source of the biological contamination in samples prepared in various laboratories. In some instances it may have resulted from accidental handling of the capillaries or of the preparation vessel. Another possibility that we believe to be the more likely source of the biological contamination is the absorption by the capillaries of aerosol particles released by humans. The presence of an aerosol cloud surrounding individuals (not too dissimilar from the cloud surrounding Pippen in "Peanuts") is a well-known phenomenon encountered in several areas of scientific endeavor. In the space program this aerosol cloud has presented a cleanliness problem; in military applications it has been utilized as a means for the remote detection of people; and in studies of disease control it has been found that bacteria are transmitted in this cloud. The exact nature of the cloud depends on the environmental conditions such as humidity, ventilation, and temperature, and on the specific individual's age, health, and clothing. The condensation of components from this aerosol cloud in the freshly drawn capillaries may be the source of biological contamination in many laboratories.
18. I thank S. Meiboom and M. M. Rochkind for helpful discussions, and C. L. French and D. C. Krupka for sweat samples.
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as well as other possible excavations within the Seibold Slough, is here designated the Seibold Site (2). The area closely surrounding the excavation and slough is in cultivation, but prairie exists where the terrain is undisturbed.

Active glacial ice existed in the general area until about 13,000 years before the present (B.P.) (3, 4). With subsequent melting and thinning of the ice, englacial debris was concentrated on the surface, forming a blanket of supraglacial till a few tens of meters thick. Insulation by the till allowed stagnant masses of ice to persist for thousands of years; some ice existed at least as late as 9000 years B.P. Both the till and buried ice were distributed irregularly, and when the last ice melted irregular hills and depressions resulted, giving rise to a completely nonintegrated drainage. The Seibold Slough occupies one of these depressions.

The stratigraphic sequence exposed at the site (autumn 1969) is about 4.3 m thick and consists of seven units. All units, except perhaps the lowest, thicken and dip toward the west end of the excavation. The lowest unit (unit 1) is gray, pebbly, sandy to clayey silt. This unit is at least 97 cm thick. We found only rare shells of the snail *Gyraulus parvus* within it. The overlying unit (unit 2) is gray, laminated, sandy to clayey silt. It is up to 40 cm thick and is poorly fossiliferous, having yielded only ostracod shells and fish fragments.

Unit 3 ("fish bed") is green, gray, and brown, laminated, organic mud or "gyttja." It has a maximum thickness of 61 cm at the west end of the excavation. Megascopic laminae are a fraction of a millimeter to 3 mm thick and are distinguishable by color and texture; the lighter laminae are poorer in organic material. Examination of thin sections reveals that each megascopic lamina consists of about 10 to 20 sets of alternating organic-rich and organic-poor laminae. Measurements of 124 sets of these laminae give an average of 9.3 sets per millimeter of sediment. The sediment consists of about 50 to 60 percent organic matter (most of which is translucent and light to dark brown, greenish-brown, or green in thin section), 20 to 30 percent micrite (probably derived mostly from Charophyceae), and minor amounts of terrigenous fine sand, silt, and clay. It is highly fossiliferous and fish are the conspicuous organisms.

Overlying the fish bed is unit 4, light to medium gray, silty, calcareous

## Paleolimnology of Late Quaternary Deposits: Seibold Site, North Dakota

**Abstract.** *A unique late Quaternary lacustrine deposit has been discovered recently on the Missouri Coteau of North Dakota. A diverse, extremely well-preserved biota of more than 160 species has been recovered primarily from an organic mud deposited about 9500 years before the present. The lacustrine body shallowed gradually as the climate became drier.*

In the autumn of 1969, an extremely diverse and unusually well-preserved fossil assemblage was discovered in a late Quaternary lacustrine deposit in southeastern North Dakota (1); fish, a frog, beaver, and muskrat form part of this assemblage. We present here our preliminary findings.

Fossils were recovered from an excavation on the floor of an intermittent pond in the SW $\frac{1}{4}$  NW $\frac{1}{4}$  section 21,

township 141 north, range 67 west, about 17 km southeast of Woodworth, Stutsman County, North Dakota. This pond, herein called the Seibold Slough (2), occupies a subcircular depression, one of hundreds of thousands of similar depressions on the Missouri Coteau. This depression, approximately 100 m in diameter, is completely enclosed by low hills a few meters high. The excavation (about 52 m long by 22 $\frac{1}{2}$  m wide),