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Note

A Device for the Measurement of Thermoelectric Force in Biopolymer Samples*

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The construction and operation of a device for the measurement of the thermoelectric force (Seebeck effect) is described. The device is suitable for the work with oriented biopolymer samples (DNA salts) of high resistivity in the temperature range between -30°C and $+30^{\circ}\text{C}$.

When a temperature gradient is established across a sample of a solid conductor or semiconductor, an electric potential difference can be measured. In the steady state this potential difference, the thermoelectric force, is balanced by the temperature gradient: the ratio $\Delta V/\Delta T$ is the Seebeck coefficient or thermoelectric power. The solid state model used in the interpretation of this phenomenon assumes that the majority charge carriers diffuse away from the hot end of the sample. Accordingly, the cold end carries the sign of the majority charge carriers in the sample.

Although the theory of the Seebeck effect for extrinsic semiconductors is more involved than for intrinsic¹ ones, much information can be obtained by observing the magnitude and the sign of the Seebeck coefficient in dependence on the concentration and the type of impurities in the sample. Literature abounds with examples of cell construction for measurements on crystalline solids or on high resistivity polymers²⁻⁴.

Biopolymers are seldom available as crystalline solids, and quantitative interpretation of charge transfer parameters is difficult. However, the availability of some, like various DNA salts in the form of oriented films⁵ has prompted application of solid state techniques and methodology to measurements of charge transport mechanisms⁶. More specifically, the interaction of biopolymers with water, adsorbed on the surface has been shown to have profound influence both on the type and on the energy of activation for charge transfer⁶⁻⁸.

The description is given herein of a simple cell which has been successfully used in the measurements of the thermoelectric force on thin, oriented films of Na-DNA.

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THE CELL

A schematic representation of the cell used for the measurements of the thermoelectric force is given in Fig. 1. The cell consists of four semicylindrical

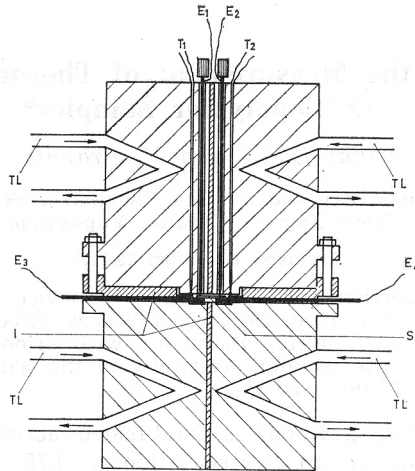


Fig. 1. The device for the measurement of the thermoelectric force (Seebeck effect). The signs indicate: S — sample; E_1 , E_2 — movable, gold plated electrodes; T_1 , T_2 — Cu-Constantan thermocouples; TL — channels for the circulation of the thermostating liquid; I — insulator between aluminum blocks («Teflon»).

aluminum parts, each with provision for circulating a thermostating liquid, TL, through channels in the body. One pair of such parts is screwed together by electrically insulated screws with PTFE («Teflon») spacers, I, between them. The upper pair has holes for two thermocouples and for two vertically adjustable gold plated electrodes E_1 and E_2 . A circular, machined plate of PTFE is serving as the spacer between the upper and lower parts of the cell. Although the PTFE insulating spacers were held thin to assure good thermal contact, the lowest resistance measured between any two insulated parts of the cell and the electrodes was in excess of 10^{13} ohms. By precise machining, the volume of the sample compartment dead space could be held very small, preventing thereby any evaporation onto, or from, the sample. The sample, S, whose dimensions in our case were $10 \times 10 \times 0.03$ mm, was held between two gold-plated plane electrodes, E_3 and E_4 . These electrodes are fixed in place and make contact with the sample along a 1 to 1.5 mm broad region. Fig. 2. shows details of the construction of the electrodes.

Note that the vertical electrodes make the measurements possible in one direction across the sample film, and the combination of one vertical and one horizontal in the other. The four separate parts enable the operator to establish temperature gradients either vertically (with the upper and lower half of the cell held at different temperatures) or horizontally (with the left hand side of the cell at one, and the right hand side at another temperature).

The cell has been used in the temperature range between -30 and $+30$ °C, although the construction materials allow use at considerably lower, as well as higher temperatures. The cell was normally held in a Faraday's cage of

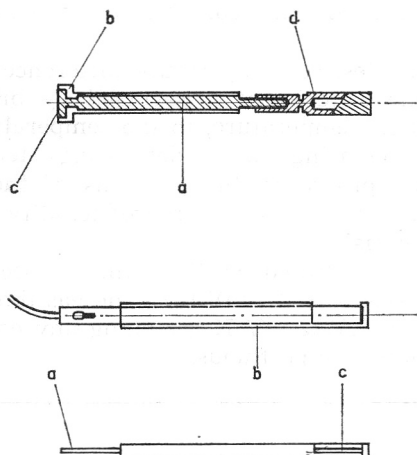


Fig. 2. Details of construction of electrodes. One of the movable electrodes shown in the upper part, one of the fixed below. The letters indicate: a — electrode body, copper; b — thin layer of insulator; c — gold plated contact surface; d — metal part used for vertical movement.

iron plates, with provision to keep the humidity low to prevent dewing on the outside surfaces and consequent electrical shorting. It has been found that best results are obtained if pure 96% ethanol was used as the circulating liquid.

MEASUREMENT PROCEDURE

The specimen is placed into the cell as shown in position S in Fig. 1. The cell is then screwed together tightly and proper electrical and hydraulic connections are made. The whole cell is first held at the same temperature in all parts by circulation of the thermostating liquid from the same circulator. Normally, polarization of electrodes to a potential difference between each pair of up to 60 mV is observed. This potential difference due to the sample resistance which was in the range from 10^{11} ohms for dry specimens, to 10^3 ohms at the highest amount of the water adsorbed, was almost constant and could be compensated for. The temperature difference between both ends could be kept constant to 0.1 °C. The readings of the potential difference between a chosen pair of electrodes were made with a high impedance electrometer (normally a Keithley Mod. 602, with specified input impedance in excess of 10^{14} ohms). Precision of measurement of the potential difference was increased by compensating the polarization potential on the low input branch of the measuring circuit by means of a precision constant voltage source (Keithley Mod. 260 Nanovolt Source).

Once the readings were taken at zero imposed temperature gradient, the second circulator was allowed to supply the thermostating liquid to a chosen pair of semicylinders (upper or lower, left or right) thus imposing a temperature gradient across or along the sample. Accordingly, one part of the sample is held at the original temperature, the other is successively brought to a lower or a higher one. The temperature difference was usually held lower than 5 °C, although experiments were done with up to 15 °C. The uncertainty of the actual temperature gradient across the sample is due to geometrical

reasons, mostly to the final, and considerable, thickness of the electrode-sample contact area.

With the maximum desired temperature difference imposed between the ends of the sample, the experiment is reversed by bringing the end which has been held at constant temperature, to the temperature of the other. Thus a set of data with »increasing« and »decreasing« temperature gradient is obtained. Reverting the procedure the positions of the cold or hot ends is exchanged, enabling a test of both the reproducibility and of the constancy of the polarisation potential.

In experiments with hydrated Na-DNA the Seebeck coefficients, α , were in the range between -0.4 to $+1.7$ mV K⁻¹, whereas those of gold are reported in the range of 0.0017 to 0.0022 mV K⁻¹, making any corrections for the electrode material contribution superfluous.

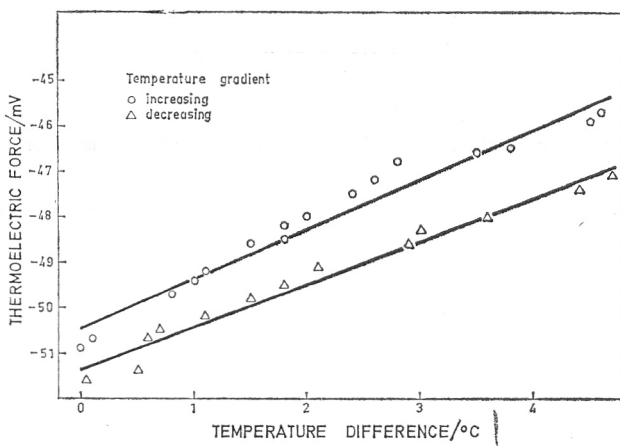


Fig. 3. Thermoelectric force — temperature difference relationship for the oriented sample of NA-DNA with 32% adsorbed water. O — Increasing temperature gradient, average temperature $t_{av} = 22.3$ °C; $\alpha = 1.1$ mV K⁻¹; Δ -decreasing temperature gradient, $t_{av} = 18.6$ °C; $\alpha = 0.94$ mV K⁻¹.

In Fig. 3. results obtained for a Na-DNA sample with 32% w/w of adsorbed water are shown. The average temperature of this experiment was 22.3 °C in the »increasing« experiment and 18.6 °C in the »decreasing«. The Seebeck coefficients were 1.1 and 0.94 mV K⁻¹, respectively. The results show that the change in the polarisation potential is significantly less than the measured effect.

Acknowledgment. The ideas of the authors on the construction of the cell were substantiated in detail by Mr. S. Puškarić.

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SAŽETAK

Uređaj za mjerenje termoelektrične sile na biopolimerima

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Opisana je konstrukcija ćelije za mjerenje termoelektrične sile (Seebeckova efekta) i rad s njom. Čelija je namijenjena radu s orijentiranim filmovima biopolimera visokih električkih otpora. Predviđeno radno područje temperatura je od -30 do $+30$ °C, iako konstrukcijski materijali dozvoljavaju rad pri višima i nižim temperaturama. Pokazani su dobiveni rezultati za orijentirani uzorak Na-soli deoksiribonukleinske kiseline s 32% adsorbirane vode, gdje je izmjereni Seebeckov koeficijent, α , iznosio $+1,1$ i $+0,94$ mV K⁻¹ za uzlazni i silazni temperaturni gradijent.

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