



Fig. 2 Dark adaptation curves, that is, log threshold for test flashes plotted against time after the bleaching flash. Curves A, B, C plot measurements when the test fell near the middle of bleached areas A, B, C respectively of Fig. 1b. Curves drawn through rod branches are the exponential with half decay time of 4.5 min. Arrows A, B mark the moment when the appearance of the after image changed from Fig. 1c-d and d-e, respectively.

by a cone branch. They are normal rod curves, each being an exponential that falls to half in 4.5 min. The vertical arrows A, B indicate the moments when sector A separated itself (Fig. 1d) and segment B separated (Fig. 1e).

It is plain from Fig. 2 that the arrows, which mark the ceiling of after image intensity, correspond to a fixed ordinate in the dark adaptation curve, a fixed threshold rise above the full dark value. But it does not correspond to any flattening or ceiling of threshold rise. If Barlow and Sparrock¹ were correct in saying that the intensity of our after image was the immediate cause of the threshold rise, how could thresholds continue to rise to the left of the arrow in Fig. 2 though the after image remains unchanged in intensity?

I think many readers will be able to answer this. The week after next I shall give experimental confirmation of what they probably expect.

W. A. H. RUSHTON

Department of Zoology,
University of Cambridge

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¹ Barlow, H. B., and Sparrock J. M. B., *Science*, **144**, 1309 (1964).

Conservation of Water-damaged Written Documents by Freeze-drying

ECONOMIC considerations generally eliminate freeze-drying as a practical method for the drying of paper materials. Although we are aware of accounts in the literature about the freeze-drying of paper materials (generally filter paper) we have not seen any references to work on the freeze-drying of written documents for conservation purposes.

While a fire was being extinguished at the Greenland Regional Library in Godthåb during the winter of 1968, many valuable items (hand-written manuscripts, books, letters and so on) became wet and subsequently froze. The damaged items were transported in their frozen state to Copenhagen and held there for 2 yr while a decision was made about the drying method to be adopted. Most of the printed books were air-dried in the conventional manner, with good results considering the circumstances.

The more valuable items were hand-written letters, manuscripts and maps belonging to a mid-nineteenth century missionary to Greenland, Samuel Kleinschmidt. It was felt that the ink used in these documents would run during the melting associated with an air-drying process, thus ruining them. Our laboratory was therefore asked to undertake the freeze-dehydration of the frozen written materials.

Some preliminary experiments with modern papers and writing materials were conducted to gain some experience in handling frozen hand-written materials. These experiments

showed that temperatures up to at least 110° C can be tolerated for several hours without discoloration of the paper. The advantage of freeze-drying was made clear by a comparison experiment in which paper marked with various modern writing materials (ink, ballpoint pen, felt-tip marking pen) was immersed in water, frozen and then dried. The freeze-dried sample was perfect, whereas the writing on the air-dried sample had run.

The twenty-seven storage packets in the Kleinschmidt collection and a photograph album were transported from the Copenhagen branch of the Greenland Regional Library to the Food Technology Laboratory in insulated containers cooled with dry ice. The papers were held at -30° C until prepared for freeze-drying. The storage packets were tight fitting paper and cardboard holders of the standard type used in libraries for filing loose papers. A preliminary trial showed that, by careful manipulation of the frozen packets, these holders could easily be removed thus eliminating a large resistance to mass transfer in the packet. Both to facilitate the rate of drying and to ensure sufficient clearance between the heater shelves, some packets had to be prised apart while frozen. This was made easier by the fact that the packets consisted of groups of paper folders. Stacks of the prepared frozen papers 2 to 3 cm thick, were placed on pre-cooled, porous sample trays and conservative freeze-drying conditions were chosen so that no melting or colour change could occur. Radiant heating at a plate temperature of 45° C and a chamber pressure of 200 mtorr was used. The sample weight was monitored using the balance built into the freeze-dryer (Atlas Ray 1) and drying was continued to constant weight. The average drying time in these conditions was about 1.5 to 2 days and when the drying was complete, the chamber vacuum was slowly released.

The drying process gave perfect results for all the written paper documents. Each page separated easily and in no case did the ink run. A few of the envelopes were stuck together as some of the old wax seals had softened (probably due to the use of the elevated heating temperature). They separated on cooling though some transfer of the wax colour had occurred. It was observed that packets (usually the thicker notebooks) which had been compressed into certain shapes before freezing retained the principal features of that shape after drying; and because of the pressures which developed there was a tendency for the packets to expand like an accordion as they dried. These misshapen samples were later treated in the usual manner of pressing and rebinding.

The photograph album presented more problems, the most serious of which was the tendency of those prints which were frozen emulsion to emulsion, to stick together after drying. Whenever possible, the groups of dried prints that were stuck together were removed from the album, soaked in water and then carefully pulled apart under water. This was usually successful, although in a few cases small portions of the pictures were destroyed. An ordinary darkroom photoprint dryer was used for drying of the separated prints.

The thickness of the photoalbum (10 cm) demanded freeze-drying for 4.5 days. This time was, however, found to be slightly too short, for a group of six pictures located on the centre page was still frozen together at that time. They unfortunately melted before they could be reinserted into the freeze-dryer, ruining the ink hand-written captions. This showed that freeze-drying had indeed been necessary to successfully conserve the written documents.

JAMES FLINK*

Food Technology Laboratory,
Technical University of Denmark, Lyngby

HENRIK HØYER

Greenland Regional Library,
Copenhagen Branch, Copenhagen

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* Present address: Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.