formulation and exposure of the MA mixture. Release rate is dependent upon the basic matrix material, its concentration, and the amount of alkanol added. At equal concentrations, hydroxyethyl cellulose gel dissolves faster than gum tragacanth gel. For a given matrix material, the rate of dissolving increases with decreasing concentration. A 2-percent gum tragacanth gel dissolves more rapidly than a 4-percent gel. For a given quantity of matrix at a given concentration, the rate of particle release can be changed by varying the amount of alkanol added to the mixture. Rate of particle release is also dependent on the area of MA mixture exposed to the water. There are several possibilities for maintaining a relatively constant exposure area. A simple and effective method involves placing the MA mixture in a cylindrical container which is open at one end.

Evaporation reduction with MA mixtures No. 6 and No. 3 was tested in June 1964 on outdoor water tanks (274 cm in diameter by 91 cm deep). The tanks were set in the ground with the tops approximately flush with a surrounding grass lawn. Untreated evaporation rates were about 7.2 mm day^{-1}. About 50 g of MA mixture No. 6 was suspended at the water surface with a small float. This treatment reduced evaporation about 50 percent for a 2-day period. During the test, wave action disintegrated the material. To reduce disintegration by wave action, mixture No. 3 was placed in a test tube (2.2 by 17 cm). The tube was suspended from a float with the open end about 0.5 cm beneath the water surface. Over a 2-week period, alkanol particles were released at a reasonably constant rate of about 0.5 g alkanol per day. Evaporation was reduced about 40 percent with this treatment. This reduction was accomplished in spite of a heavy film of dust and algae on the water surface. Indicator oils showed that this dust and algae film could not be displaced until alkanol film pressures exceeded 30 dynes cm^{-1}.

The MA mixtures can be applied to water surfaces from floating or sunken containers and the containers can be placed from shore, boats, or aircraft. Alkanol release rates can be adjusted to suit average wind conditions. The resulting application of excess alkanol during periods of calm may be a problem on large surfaces of water but will not be a problem on small surfaces where the total cost of alkanol is low. Thus, dispersion of long-chain alkanol in a water-soluble matrix is a promising method for applying monomolecular films to reduce evaporation from small ponds and reservoirs. Additional study and development may show the method to be of value in reducing evaporation from large reservoirs.

LLOYD E. MYERS
U.S. Water Conservation Laboratory,
Route 2, Box 816-A,
Tempe, Arizona 85281

References and Notes

1. *World-Wide Survey of Experiments and Results of the Prevention of Evaporation Losses from Reservoirs*, International Commission on Irrigation and Drainage, New Delhi, India (1960); R. R. Cruse and G. E. Harbeck, Jr., *U.S. Geol. Surv. Water Supply Paper No. 1480* (1960); "Present status of evaporation reduction by chemical films," Miscellaneous Paper No. 5-475, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi (1962); V. K. La Mer, Ed., *Retardation of Evaporation by Monolayers: Transport Processes* (Academic Press, New York, 1962); "Survey of methods for evaporation control, task group report," *J. Am. Water Works Assoc.* **55**, 2 (1963); G. E. Koberg, R. R. Cruse, C. L. Shrewsbury, *U.S. Geol. Surv. Water Supply Paper No. 1692* (1963).

11 February 1965

■

Cationic Glass Electrode Response in Aqueous Solutions of Sodium Chloride and Potassium Chloride

Abstract. *The selectivity of glass electrodes suitable for potassium-ion measurements depends on the age of electrodes and the composition of the solution. An empirical equation describing the electrode potential as a function of solution composition is given for practical application in solutions containing both sodium and potassium.*

Glass membrane electrodes have been used for the determination of sodium and potassium ion activities in biological and mixed-ion solutions (*1*, *2*). Eisenman, Rudin, and Casby (*3*), in their original description of cation-selective electrodes, developed an empirical equation relating electrode potentials to cation activities in mixed-ion solutions. In its general format this equation implicitly predicted variations in bi-ionic selectivities, that is, how well an electrode "sees" one cation in preference to another. The equation is cumbersome, however, and difficult to apply to practical problems in the analysis of mixed solutions except in the limiting case of $n = 1$. It is therefore not surprising that in most experiments with such electrodes the selectivity of a given electrode for a specific cation has been assumed to be a constant.

In the application of these electrodes to biological solutions having widely different sodium and potassium concentrations, significant errors in potassium analyses may result from the foregoing assumption. An empirical equation, suitable for practical application, has therefore been derived to include variable electrode selectivity as a function of solution composition.

Capillary electrodes (*4*) (1 mm in outside diameter) of potassium selective (NAS_{27-4}) glass (in moles percent: Na_2O, 27; Al_2O_3, 4; SiO_2, 69) were used. The electrode format and associated measuring equipment have been described (*2*). All activity (a_{K^+}) measurements were made at *p*H 7 and at 25° ± 2°C. Standard solutions were made from appropriate chloride salts (reagent grade). Electrode-potential measurements in all experimental solutions were

Table 1. Data for unaged NAS_{27-4} electrode. All activities and concentrations are milliequivalents per liter.

$(a_{K^+})_{std.}$	$[Na^+]$	$[K^+]$	$\frac{[Na^+]}{[Na^+]+[K^+]}$	γ_{NaKCl}	a_{Na^+}	a_{K^+}	$\Delta E/S$	k_{KNa}
9.0	200	5	0.98	0.732	146.4	3.66	+0.393	0.127
9.0	50	5	.91	.812	40.6	4.06	+0.054	.151
9.0	5	5	.50	.902	4.51	4.51	−0.222	.196
77.0	200	50	.80	.718	143.6	35.9	−0.119	.160
77.0	50	50	.50	.774	38.7	38.7	−0.215	.213
77.0	200	200	.50	.669	133.8	133.8	+0.326	.219
77.0	50	200	.20	.702	35.1	140.4	+0.297	.342

Table 2. Data for aged NAS_{27-4} electrode. Activities and concentrations in milliequivalents per liter.

$(a_{K^+})_{std.}$	$[Na^+]$	$[K^+]$	$\frac{[Na^+]}{[Na^+]+[K^+]}$	γ_{NaKCl}	a_{Na^+}	a_{K^+}	$\Delta E/S$	k_{KNa}
77.0	100	—	1.00	0.778	77.8	—	–0.9829	0.103
77.0	200	5	0.98	0.732	146.4	3.7	–0.5985	0.107
77.0	50	5	0.91	0.812	40.6	4.1	–0.9671	0.103
77.0	200	20	0.91	0.728	145.6	14.6	–0.3984	0.111
77.0	50	20	0.71	0.796	39.8	15.9	–0.5870	0.108
77.0	20	20	0.50	0.828	16.6	16.6	–0.6218	0.105
77.0	50	30	0.62	0.787	39.4	23.6	–0.4437	0.102
77.0	200	30	0.87	0.724	144.8	21.7	–0.3162	0.107
77.0	200	50	0.80	0.718	143.6	35.9	–0.1778	0.106
77.0	50	50	0.50	0.774	38.7	38.7	–0.2596	0.094
77.0	25	50	0.33	0.789	19.7	39.4	–0.2741	0.090
77.0	200	200	0.50	0.669	133.8	133.8	+0.2917	0.104
77.0	50	200	0.20	0.702	35.1	140.4	+0.2696	0.087

bracketed by similar measurements in pure KCl solutions and were expressed as ΔE, the difference between the potential obtained in a mixed solution and that of a KCl standard (10 or 100 meq/liter). Possible errors resulting from electrode drift were thus minimized.

The value of the selectivity function, k_{KNa}, was calculated from the equation:

$$\Delta E = S \log \frac{[(a_{K^+}) + (k_{KNa})\,(a_{Na^+})]}{(a_{K^+})_{std}} \qquad (1)$$

where S is the Nernst slope factor (2.3 RT)/F. Activities of sodium and potassium were calculated from their stoichiometric concentrations, $[Na^+]$ and $[K^+]$, with estimation of the ionic activity coefficients, γ_{NaKCl}, by methods described previously (*2*). All activities, although dimensionless quantities, are referred to the same concentration scale (meq/liter), which is also used for stoichiometric concentrations.

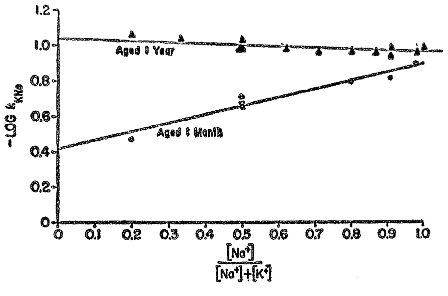

Fig. 1. Selectivity of NAS_{27-4} glass as a function of age and composition of the solution.

Data obtained with a relatively fresh (1-month old) NAS_{27-4} electrode (Table 1) show that selectivity of this electrode for potassium, in preference to sodium, varied over a wide range as a function of the relative concentrations of sodium and potassium (columns 4 and 9, Table 1). Data similarly obtained with an electrode which had been in use for approximately 1 year are given in Table 2. Significantly, the variation in selectivity with solution composition was much less pronounced than with the unaged electrode. For both aged and unaged electrodes, there was a simple straight-line relationship between log k_{KNa} and $[Na^+]/[Na^+] + [K^+]$ (Fig. 1) which could be expressed by:

$$-\log k_{KNa} = \alpha + \beta\, q \qquad (2)$$

where $q = [Na^+]/[Na^+] + [K^+]$ and α and β are numbers whose values were independent of solution composition. For the fresh electrode, values for α and β were 0.41 and 0.49, respectively, whereas for the aged electrode the respective values were 1.03 and –0.06. There were small variations in α and β as a function of pH, but these were negligible over the limited range pH 6 to 8.

A practical modification of the equation developed by Eisenman, Rudin, and Casby (*3*) for measurement of potassium activities in mixed sodium and potassium solutions may therefore be represented by:

$$E = \text{constant} + S \log [(a_{K^+}) + (a_{Na^+}) \cdot 10^{-(\alpha+\beta q)}] \qquad (3)$$

An attempt was made to fit the experimental data to the equation of Eisenman, Rudin, and Casby (*3*):

$$E = \text{constant} + S \log [(a_{K^+})^{1/n} + (k_{KNa})^{1/n}\,(a_{Na^+})^{1/n}]^n \qquad (4)$$

where k_{KNa} and n are two adjustable parameters. If k_{KNa} is assumed to be independent of solution composition, our data for the unaged electrode offers values for n ranging from 1.29 to 1.14 over the range of q from 0.2 to 0.8. For the aged electrode, calculated values for n ranged from 0.98 at $q = 0.2$ to 0.995 at $q = 0.8$. At least for the unaged electrode, Eq. 3 corresponds more closely with the experimental data.

The mechanisms of aging in such electrodes are not understood, but the data indicate that electrodes intended for activity measurements of potassium in solutions containing significant sodium concentration should be carefully evaluated for selectivity in the concentration ranges under study and should have been in use for some period of time.

EDWARD W. MOORE
JAMES W. ROSS
Department of Medicine, Lemuel Shattuck Hospital, Tufts University Medical School, Boston, Massachusetts

References and Notes

1. E. W. Moore and D. W. Wilson, *J. Clin. Invest.* **42**, 293 (1963); S. M. Friedman, S. L. Wong, J. H. Walton, *J. Appl. Physiol.* **18**, 950 (1963); H. D. Portnoy, L. M. Thomas, E. S. Gurdjian, *Arch. Neurol.* **8**, 597 (1963); R. N. Khuri, D. A. Goldstein, D. L. Maude, C. Edmonds, A. K. Solomon, *Amer. J. Physiol.* **204**, 743 (1963).
2. E. W. Moore and J. M. Dietschy, *Amer. J Physiol.* **206**, 1111 (1964).
3. G. Eisenman, D. O. Rudin, J. U. Casby, *Science* **126**, 831 (1957).
4. Orion Research Corporation, Cambridge, Mass.
5. Supported by research grant No. AM-07417-02 from the National Institute of Arthritis and Metabolic Diseases.

10 February 1965

Fission-Track Dating of Bed I, Olduvai Gorge

Abstract. *The discoveries of a series of hominid remains in the Olduvai Gorge, Tanganyika, has focused attention upon the age of the deposits of Bed I, in which both* Zinjanthropus *and* Homo habilis *were found. Because the age of 1.75 million years, as determined by the radioactive decay of potassium and argon, has been questioned several times, a fission-track age was measured for the pumice from Bed I. The result is 2.03 ± 0.28 million years, in good agreement with the result obtained by the potassium-argon decay method.*

Since a series of hominid remains were discovered in the Olduvai Gorge, Tanganyika (*1*), there has been considerable interest in the age of the de-