24.4 $\mu g/m^3$, six between 25.5 and 28.4, two between 28.5 and 32.4, and one greater than 34.

When the lead and carbon monoxide concentrations were plotted against time the curves were similar in shape. These results are shown in Fig. 1. Both pollutants show peak values at 11:00 a.m. and later at 3:00 p.m. Plots of traffic volumes typical of 1967 at 45th Street correlate excellently with the pollutant plots (Fig. 1); this would indicate fixed traffic volume for 45th Street.

We smoothed the curves by calculating moving averages for carbon monoxide, lead concentrations, and traffic volumes. We then plotted the resulting moving averages—lead concentrations against carbon monoxide concentrations and traffic volumes (eliminating time). The results produced closed curves reminiscent of Lissajous figures (Fig. 2), thereby reinforcing the idea that correlations exist between lead and carbon monoxide and lead and traffic. Two other studies (*2, 3*) also report correlation between lead and carbon monoxide. The same graph of carbon monoxide plotted against the 1967 traffic count showed that carbon monoxide was a function of traffic (Fig. 3); it can be described by the equation $x = 1.53y^{0.368}$ ($x =$ carbon monoxide in parts per million, and $y =$ traffic in vehicles per hour).

We determined lead concentrations at Central Park (12-m elevation) and 240 Second Avenue (30-m elevation) for a 10-day period during the interval 23 January 1969 through 12 March 1969. The daily average for Central Park for this period was 0.97 $\mu g/m^3$; for Second Avenue the concentration for the same period was 1.57 $\mu g/m^3$. In another recent New York City study (*4*) the investigation reported annual mean lead concentrations of 3.82 and 2.99 $\mu g/m^3$ for the Bronx and Manhattan, respectively.

Similar lead concentrations were found at other elevated monitoring sites connected with the Aerometric Network. These lower values at rooftop sites suggest the need for a vertical profile for lead. This work is now in progress, and, in addition, lead concentrations are to be monitored at other sites of high traffic volume in New York.

JOHN L. BOVÉ
STANLEY SIEBENBERG
Department of Air Resources,
51 Astor Place,
New York 10003

References and Notes

1. K. L. Johnson, L. H. Dworetsky, A. N. Heller, *Science* **160**, 67 (1968).
2. J. M. Collucci, C. R. Begeman, C. R. Kumler, K. Kumler, *J. Air Pollut. Control Ass.* **19**, 4 (1969).
3. Working Group on Lead Contamination, *U.S. Public Health Serv. Publ. 999-AP-12* (U.S. Dept. of Health, Education, and Welfare, Jan. 1965).
4. T. J. Kneip, M. Eisenbud, C. D. Strehlow, P. C. Freudnethal, 62nd annual meeting of the Air Pollution Control Administration, New York City, 22–26 June 1969.

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Potassium Ion Specific Electrode with High Selectivity for Potassium over Sodium

Abstract. *A new potassium electrode, made from valinomycin, which uses commercially available electrode configurations, responds to potassium ion concentrations from 1 mole per liter to below 10^{-6} mole per liter. It is highly selective for potassium ion over sodium ion and divalent ions and can be used for the direct determination of potassium ion in human serum. No significant complexing of potassium appears to occur in normal serum.*

Measurements of the activities of the potassium ion are fundamental to an extremely wide range of problems, from membrane transport and nerve conduction processes to the potassium budget of the ocean. Until now the only really usable electrodes for potassium have been made from glasses, such as those first suggested by Eisenman and his colleagues (*1*); these electrodes typically [$NAS_{27\text{-}4}$ glass (27 mole percent Na_2O, 4 mole percent Al_2O_3, 69 mole percent SiO_2)] have a selectivity ratio of only 5 : 1 or 10 : 1 for potassium over sodium. Unfortunately, in many of the most interesting biological and geochemical applications, measurements have to be made in the presence of large amounts of Na^+.

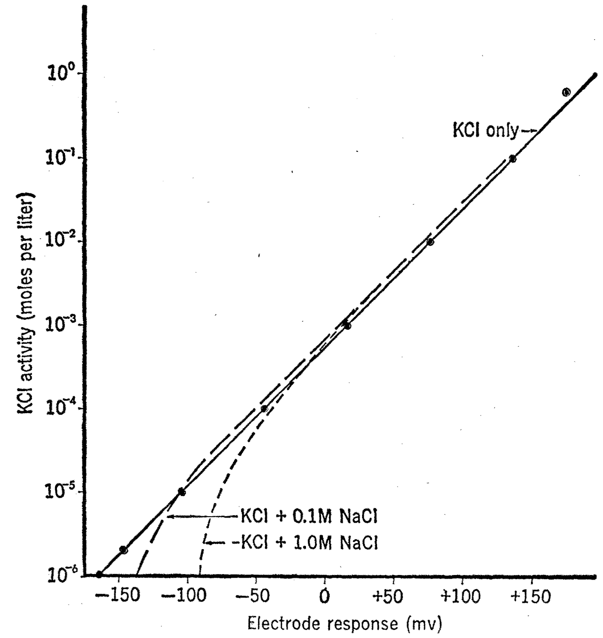
A number of antibiotics, including valinomycin, the macrotetrolide actins, and the enniatins, have the ability to strongly affect K^+ transport in mitochondria (*2*); Stefanac and Simon reported (*3*) that the actin homologs dissolved in carbon tetrachloride or benzene could be used to make electrodes which were selective to K^+ over Na^+. They reported a selectivity of 750 : 1, but this was based on a slope of only 32 mv per decade change in activity derived from a plot of electrode response as a function of K^+ activity (the theoretical Nernstian response would be 59.6 mv). Pioda and Simon (*4*) reported that a plot of the electrode response of a suspension of nonactin in Nujol-octanol gave slopes approximately equal to theoretical values for K^+ concentrations between $10^{-1}M$ and $10^{-3}M$ and had a selectivity of approximately 100 : 1. Simon (*5*) reported that valinomycin gave a selectivity of 5000 : 1 for K^+ over Na^+ and a "linear response" between $10^{-1}M$ and $10^{-5}M$.

We report here a new electrode made with commercially available materials, which has a selectivity of better than 10,000 : 1 for K^+ over Na^+ and which can be used for the direct measurement of K^+ in serum. Using commercially available valinomycin (Calbiochem, Los Angeles, California, catalog No. 676377) without further purification, and a variety of aromatic solvents (such as nitrobenzene and higher homologs, diphenylether, chlorobenzene, or bromobenzene), we have prepared 5 percent to 10 percent (by weight) valinomycin solutions; we have used the solution as the "liquid ion exchanger" in a liquid membrane electrode body (Orion 92-Series electrode bodies). A double-junction reference electrode with 5*M* lithium trichloroacetate in the outer sleeve effectively prevented contamination of the solutions by K^+.

The response of a typical electrode to pure KCl solutions is shown by the solid line in Fig. 1, which is a plot of electrode response in millivolts as

Table 1. Comparison of measurements by flame photometer and electrode of concentrations (in millimoles per liter) of K^+ in serum samples.

Sample No.	Flame	Electrode	Recheck	
			Electrode	Flame
9788	4.1	4.5	4.5	4.5
9846	4.3	4.3	4.2_5	
9803	5.1	5.0	5.0_5	
9813	4.0	4.0	3.9	
9897	4.0	4.0	4.0_5	
9886	4.2	4.2	4.1_5	
9872	4.5	4.4	4.4	
9874	4.0	4.0	4.0	
9830	4.6	4.6	4.6	
9868	4.5	4.5	4.5_5	
9866	5.7	5.7	5.7	



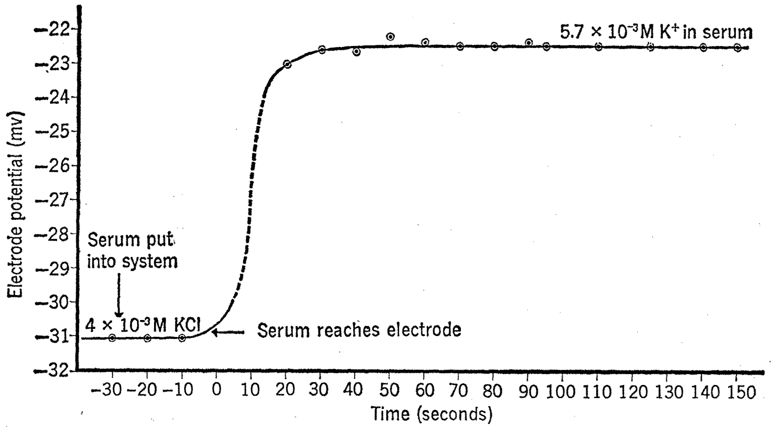


Fig. 1 (left). Response of potassium electrode to pure KCl solutions (solid line) and to KCl in the presence of 0.1*M* NaCl (long dashes) or 1.0*M* NaCl (short dashes).

Fig. 2 (above). Time for a change in electrode response for the potassium electrode between a standard solution containing $4 \times 10^{-3}M$ K^+ and 0.15*M* NaCl and the serum sample.

a function of K^+ activity. The activity values were determined by assuming that the activity coefficient of K^+ was the same as the mean ionic activity coefficient of KCl (*6*). A straight line with a slope of just under 57 mv was obtained at 20°C from $10^{-1}M$ to $10^{-6}M$. The electrode responds to potassium ion concentrations between $10^{-1}M$ and 1*M* with a slope of about 45 mv; thus it is still useful for concentration readings in this range, but the response is about 20 percent less than the theoretical Nernst slope.

The change in electrode potential between $10^{-6}M$ and $10^{-7}M$ varies between 35 and 55 mv. Work in this region requires care, and it is necessary to clean all glassware with HCl (and subsequently to rinse with water) to remove K^+ adsorbed by ion exchange onto the glass. No measurements have been obtained below $10^{-7}M$.

Selectivity of the electrode for potassium over sodium was established by redetermining the potassium activity curve in the presence of a constant background of NaCl prepared from analytical reagent-grade material. As can be seen in Fig. 1, at a concentration of 0.1*M* NaCl, the curves are identical up to a concentration of about $7.5 \times 10^{-6}M$ KCl. We interpret this to mean that at a concentration of 0.1*M* NaCl, the selectivity ratio of K^+ to Na^+ is about 13,000 : 1. At a concentration of 1*M* NaCl, the curves separate at about $3 \times 10^{-4}M$ KCl, thus indicating a lower selectivity in more concentrated NaCl solutions. This may be due to a loss of permselectivity, since the electrode response to 1*M* KCl is slightly less than Nernstian.

Similar curves not shown (for the interference range from 0.01*M* to 0.1*M*) indicate that the new K^+ electrode has a selectivity ratio of 1 : 1 for Cs^+, 50 : 1 for K^+ over NH_4^+, and 100 : 1 for K^+ over H^+, and does not appear to respond at all to Li^+. Selectivity ratios for K^+ over Ca^{2+} and Mg^{2+} are greater than 5000 : 1.

To test the usefulness of the electrode for the direct measurement of potassium in serum, a flow-through configuration was used which was identical in design to that used for serum calcium (Orion model 99-20). About 0.25 to 0.50 ml of the standard solution or serum contained in a small syringe was pumped through the electrode over a 10- to 15-minute period. The electrode response time between a standard solution (4.0 millimoles of K^+ and 150 millimoles of Na^+) and a serum sample high in K^+ is shown in Fig. 2. Electrode response is within 0.1 or 0.2 mv in 1 minute.

The K^+ concentrations of ten serum samples from a major university-affiliated Boston hospital, which had been analyzed that day for potassium (*7*), were measured on the flow-through electrode by two different operators. The results (Table 1) indicate that normal human serum does not show any significant complexing of potassium.

Much more comprehensive studies will be required to validate this electrode as a clinical tool, but these results suggest that rapid and convenient monitoring of biological fluids such as serum, kidney dialyzates, or urine, for K^+ may be a real and immediate possibility.

M. S. Frant
J. W. Ross, Jr.
Orion Research Incorporated,
Cambridge, Massachusetts 02139

References and Notes

1. G. Eisenman, D. O. Rudin, J. U. Casby, *Science* **126**, 831 (1957).
2. C. Moore and B. C. Pressman, *Biochem. Biophys. Res. Commun.* **15**, 562 (1964); B. C. Pressman, *Proc. Nat. Acad. Sci. U.S.* **53**, 1076 (1965).
3. Z. Stefanac and W. Simon, *Chimia* **20**, 436 (1966); *Microchem. J.* **12**, 125 (1967).
4. L. A. R. Pioda and W. Simon, *Chimia* **23**, 72 (1969).
5. W. Simon, paper presented at the spring meeting of the Electrochemical Society, New York, 4–9 May 1969.
6. R. M. Garrels, in *Glass Electrodes for Hydrogen and Other Cations*, G. Eisenman, Ed. (Dekker, New York, 1967), p. 346.
7. A Baird Atomic KY-1 flame photometer was used, with an internal lithium standard, at a dilution of 1 : 200.

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Placental Transfer of a Substituted Pteridine from Fetus to Mother

Abstract. In sito *near-term sheep placentas transferred triamterene (2,4,7-triamino-6-phenyl-pteridine) from the fetus much more rapidly than to the fetus. This differential transfer effect may significantly influence the distribution of exogenous and endogenous compounds between the maternal and fetal compartments.*

At present, information concerning preferential transfer of substances between mother and fetus is sparse. For most substances studied, placental trans-