DETERMINATION OF POTASSIUM ION CONCENTRATION IN SERUM USING A HIGHLY SELECTIVE LIQUID-MEMBRANE ELECTRODE

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SUMMARY

A simple method for the direct determination of the K\(^+\) concentration in undiluted blood serum is described. The reproducibility of single determinations using the readings after 60-sec contact of a valinomycin liquid-membrane electrode with the sample is 0.07 mequiv/l K\(^+\) (standard deviation). No corrections are needed for the presence of other ions in the sample solutions.

INTRODUCTION

The potassium-selective glass membranes like KAS\(_{29-5}\) and NAS\(_{27-4}\) are approx. 10 times more sensitive to K\(^+\) than to Na\(^+\). Since the concentration ratio of Na\(^+\)/K\(^+\) in blood serum is around 35–40 and since there is at best a K\(^+\) over Na\(^+\) selectivity in glass electrodes of 10, a separate measurement of the Na\(^+\) concentration is needed to correct the reading of the K\(^+\) sensor\(^4\). Because of the dependence of the selectivity constant of a potassium glass sensor on the history of the electrode, the sample composition and other factors\(^3\), the routine application of glass membrane electrodes for the K\(^+\) determination in blood serum becomes doubtful and time consuming (see ref. 3). The development of a new liquid-membrane K\(^+\) sensor using valinomycin as the ion selective component led to an electrode of fast response and K\(^+\) over Na\(^+\) selectivity of around 5000 (ref. 5). The selectivity of K\(^+\) over protons is around 18000 so that no buffering is necessary. This electrode makes possible fast and accurate determinations of the K\(^+\) concentration in blood serum.

METHODS

EMF measurements

These were carried out using a liquid-membrane sensor as described earlier\(^4\) (Philips Type IS 560-K) in combination with a calomel reference electrode (KCl std.) having aqueous 0.1 M NH\(_4\)NO\(_3\) as electrolyte between the sample and the half cell\(^5\).
All measurements were performed at room temperature using a d.c. amplifier (Diodenverstärker Type 71s, Knick, Elektronische Messgeräte, Berlin 37, Germany) with an input impedance of $>1 \cdot 10^{12} \Omega$ in combination with an integrating digital voltmeter DY-2401 C (Hewlett-Packard Co., Palo Alto, Calif., U.S.A.) and Printer (Digitaldrucker, D4, Kienzle Apparate GmbH, 7730 Villingen, Germany). The standard deviation of a single determination is $<0.1$ mV. Any pH meter of comparable accuracy would be adequate. The readings were taken 60 sec after dipping the electrodes into the sample. Using special plastic sample cups measurements with the standard electrodes described$^{5,6}$ may be performed on samples of $\leq 100 \mu l$. When changing the electrodes to another sample, they were wiped gently with soft tissue without rinsing. The electrodes were stored in an aqueous solution of 140 mequiv/l Na$^+$ and 5 mequiv/l K$^+$. For the calibration of the electrode assembly HYLAND normal clinical chemistry control serum dried (Division Travenol Laboratories, Inc., Los Angeles, Calif. 90036) was mixed similarly to manufacturers instructions with doubly distilled water and aqueous KCl solution (3 mequiv/l) to final concentrations of approx. 3.8 and 7.5 mequiv/l K$^+$, respectively. The readings of the EMF measurement on these two solutions were plotted as a function of the theoretical K$^+$ concentrations using a semi-logarithmic scale. Determinations of concentrations of unknown samples were performed by linear interpolation. The calibration was usually checked after the measurement of two sample solutions. Over periods of 2–3 h no corrections in the calibration curve were necessary.

**Measurements by flame photometry**

A flame photometer Model 143, equipped with an automatic diluter Model 144 (ratio of the dilution of 200:1) (Instrumentation Laboratory, Inc., Lexington, Mass., U.S.A.) was used. The calibration of the flame photometer was performed with twice-distilled water and a standard having a Na$^+$ concentration of 140 mequiv/l and a K$^+$ concentration of 5 mequiv/l (Instrumentation Laboratory, Inc., Lexington, Mass., U.S.A.). The stability of the instrument was checked with the standard solution after each measurement of a sample.

**Measurements by atomic absorption spectroscopy**

These were performed using a Beckman Autolam Burner, a Beckman Atomic Absorption Accessory with a hollow cathode lamp No. 910297, K-Ne, a Beckman DB-G Grating Spectrophotometer (Beckman Instruments, Division Fullerton, Calif., U.S.A.) and a H1-speed Recorder 202, Type HU No. 7-072 (W+W Electronics, Basel, Switzerland). The calibration was done with the two HYLAND serums described, at the beginning and at the end of the sample measurements. A volume of 0.1 ml of serum was diluted with 0.1 ml of a solution of 10 g LaCl$_3$ in 100 ml of doubly distilled water and 10 min later the product was centrifuged for a period of 20 min to prepare it for the measurement.

**Serum samples**

Freshly centrifuged serum was used throughout. Except for the atomic absorption studies it was examined without dilution and without any further treatment. Between measurements it was stored at 4$^\circ$.
RESULTS AND DISCUSSION

A plot of the EMF of the electrode system as a function of the logarithm of the K+ concentration is given in Fig. 1. Except for the two calibration solutions (black dots) the values given for the concentration of K+ in the serum samples were obtained by flame photometry. The standard deviation of EMF readings about the calibration straight line is 0.4 mV corresponding to 1.7% in K+ or approximately 0.09 mequiv/l K+ and is the error of a single determination of the concentration of K+ including the uncertainties of the measurement by flame photometry. It also includes the uncertainties due to the fact that the electrode responds to the activity and flame photometry to the concentration of K+. The slope of the calibration curve is 55 mV/log cK+ (c: concentration) and is close to the theoretical slope of 59.2 mV/log aK+ (a: activity) and the values obtained under more ideal conditions.

The results obtained by repeated measurement of the same sample with a single electrode as well as the data obtained on the same samples by flame photometry and atomic absorption spectrometry are given in Table I. From these results an over all reproducibility of the determinations by EMF measurements of 0.07 mequiv/l K+ (standard deviation) can be calculated, corresponding to 0.13 mequiv/l at the 95% confidence limit. For the determinations by flame photometry these values are 0.05 and 0.11 mequiv/l, respectively.

The standard deviation of the mean values obtained by flame photometry from those obtained by EMF measurement is 0.05 mequiv/l corresponding to 0.11 mequiv/l at the 95% confidence limit and is a criterion for the accuracy of the method. The reproducibility as well as the accuracy of the measurements using the liquid-membrane electrode is superior to values reported.

Fig. 2 shows the good agreement between flame photometry and EMF determinations of the concentration of K⁺ which are based on different calibration procedures in the two techniques applied. Although the standard deviation in the determinations by atomic absorption seems to be somewhat larger, the results agree with those obtained by EMF measurement.

The method of using the liquid-membrane electrode for the determination of K⁺ in blood serum as described here gives in its simple and time-saving application an accuracy and reproducibility roughly comparable to flame photometry. Since errors introduced by uncertainties in liquid junction potentials must have been

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TABLE 1
results of the determination of the concentration of K⁺ in blood serum by different methods (mequiv/l)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Liquid-membrane electrode</th>
<th>Flame photometry</th>
<th>Atomic absorption</th>
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<td></td>
<td>26.1.70 27.1.70 27.1.70 27.1.70 27.1.70 Mean</td>
<td>27.1.70 28.1.70 Mean</td>
<td>27.1.70</td>
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<td>10 a.m. 10 a.m.</td>
<td>11 a.m.</td>
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<tr>
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<td>4.70 4.63 4.69 4.62 4.62 4.652</td>
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<td>4.75</td>
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<tr>
<td>2</td>
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<td>5.15 5.10 5.125 5.05</td>
<td>5.05</td>
</tr>
<tr>
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<tr>
<td>8</td>
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<td>4.65/4.65 4.67 4.656 4.60</td>
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</tr>
<tr>
<td>10</td>
<td>4.64 4.66 4.72 4.55 4.72 4.658</td>
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<tr>
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<td>4.00 4.00 4.000 4.10</td>
<td>4.10</td>
</tr>
</tbody>
</table>

Fig. 2. Comparison of determinations of the concentration of K⁺ in blood serum by EMF measurement and flame photometry (mean values of Table II).
relatively large in the experiments carried out, a more adequate choice of reference electrode will lead to a substantial increase in accuracy. The valinomycin liquid-membrane K⁺-sensing system may as well be used in flow-through electrodes as described for the determination of Ca²⁺ (refs. 10, 11).

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REFERENCES