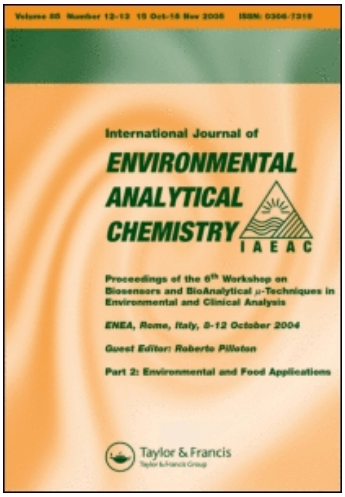

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Orion Water-Hardness Electrode: An Unexpected Response to Magnesium Ion

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To cite this Article Thompson, M. E.(1973) 'The Orion Water-Hardness Electrode: An Unexpected Response to Magnesium Ion', International Journal of Environmental Analytical Chemistry, 2: 3, 253 — 255
To link to this Article: DOI: 10.1080/03067317308076393
URL: http://dx.doi.org/10.1080/03067317308076393

Intern. J. Environ. Anal. Chem. 1973, Vol. 2, pp. 253–255

Printed in Great Britain

The Orion Water-Hardness Electrode: An Unexpected Response to Magnesium Ion†

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(*Received August 23, 1972*)

KEY WORDS: Orion, magnesium, water hardness, electrode

The Orion water-hardness electrode, while being used to measure magnesium ion activity in a series of calcium-free solutions, displayed some unanticipated changes in potential. As the overall potential change observed for one solution was 183 mV (equivalent to more than six orders of magnitude changes in magnesium-ion activity), several precautions are suggested which should be observed when using this electrode for specific purposes. In particular, it is recommended that the exchanger be pre-equilibrated with an appropriate solution if the electrode is to be used in restricted systems of known chemical composition.

The Orion water-hardness electrode, while being used to measure magnesium-ion activity in a seriesof calcium-free solutions, showed, over a period of several days, unexpected changes in potential in the same standard solution. The observed potentials gave convincing evidence that pre-equilibration of the liquid ion exchanger with the internal reference solution is highly desirable. It is equally desirable that the internal reference solution be the same as one of the standard solutions.

The electrode was assembled using 0.01M $MgCl_2$ as the internal reference solution and also as one of the standard solutions. Thus, when measuring 0.01M $MgCl_2$ solution, using a saturated KCl-calomel reference electrode, the cell would be:

$$\text{Ag,AgCl} \mid 0.01\text{M } MgCl_2 \mid \text{Liquid ion exchanger} \mid 0.01\text{M } MgCl_2 : \text{KCl(sat.)} \mid Hg_2Cl_2,\text{Hg}$$

† Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

Taking the activity of magnesium ion in 0.01M $MgCl_2$ as $10^{-2.24}$, and that of chloride ion as $10^{-1.77}$, the standard potential of theAg, AgCl half-cell as 222.2 mV, and the potential of the saturated KCl-calomel reference electrode as about 246 Mv at 25°, it can be calculated that at equilibrium the potential between the two electrodes would be 81 mV.

$$E_{Cl} = 222.2 - 59.2\,(-1.77) = 327.3 \text{ mV}$$

$$E_{Calomel} = 246 \text{ mV}$$

$$E_{cell} = 327 - 246 = 81 \text{ mV}$$

This calculation assumes that the potential across the liquid ion exchange membrane, with identical solutions on either side, is zero.

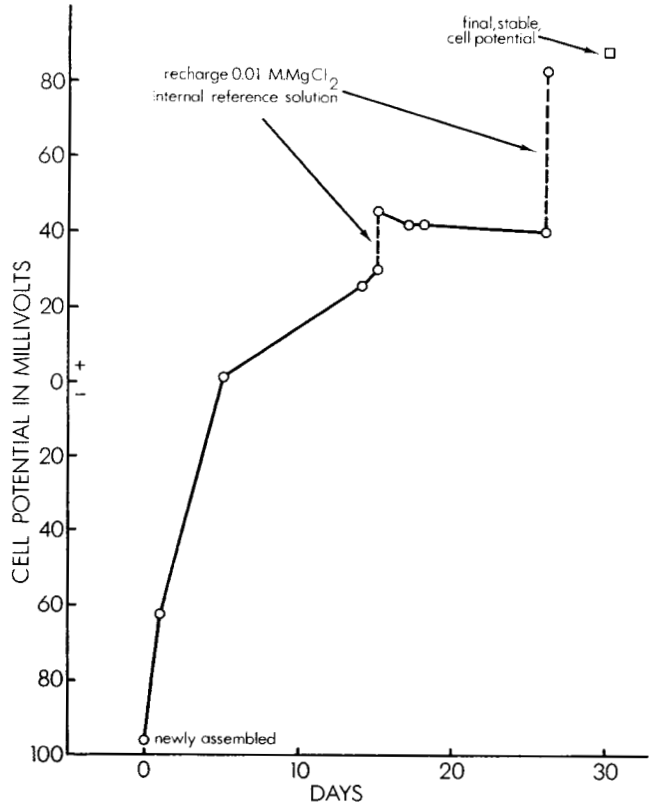

FIGURE 1 Cell potentials plotted against the number of days from the time of electrode assembly.

It was not until a few days after the electrode had been assembled that I noticed that the cell potential in the standard solution varied by a few millivolts each day and that the change was always in the same direction. Figure 1 shows the observed cell potentials plotted against the number of days from the time the electrode was first assembled. Both times that the internal reference solution was recharged with fresh 0.01M $MgCl_2$ solution the cell potential became abruptly more positive.

A stable cell potential was finally achieved by shaking the liquid ion exchanger with 0.01M $MgCl_2$ solution several times before assembling the electrode, and the stable cell potential so obtained (+87.5 mV) was close to that calculated above.

This experience convinced me that the liquid ion exchanger membranes, unlike the glass electrodes for potassium and sodium, do not equilibrate readily with new solutions unless special efforts are made to pre-equilibrate the exchanger with the particular aqueous solution. I recommend that when the electrode is to be used in restricted systems of known chemical composition, that the exchanger be pre-equilibrated with an appropriate (chloride) solution. A simple technique is to use a small separatory funnel. Only gentle shaking is needed; the water solution can be drawn off and replenished easily, if desired.