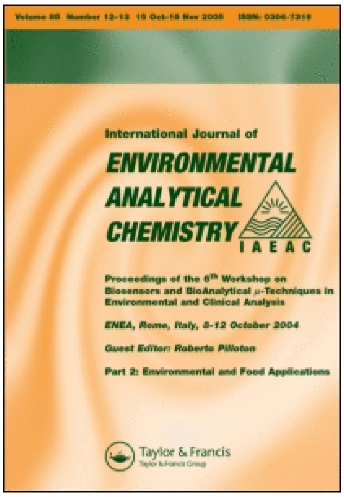

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J. C. Van Loon[a]
[a] Environmental Sciences and Engineering Group and Departments of Geology and Chemistry, University of Toronto, Toronto, Ontario, Canada

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Preparation of Selective Ion Electrodes using a Cold Polymerization Technique with Dental Acrylic†

J. C. VAN LOON

Environmental Sciences and Engineering Group and Departments of Geology and Chemistry, University of Toronto, Toronto 181, Ontario, Canada

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KEY WORDS: Calcium; chloride; selective ion electrodes.

An inexpensive method is described for the production of ion-selective electrodes using readily available dental acrylics. The method is applicable to both inorganic and organic active substances. The electrodes are finding very useful application to water analysis projects. Detailed results are given for a chloride and calcium electrode.

Developments in methods for the manufacture of ion-selective electrodes have been rapid in recent years. An expanding list of companies are offering (mainly) ionic crystal, glass, solid organic pelet and liquid ion-exchange membrane electrodes for prices ranging from $30 to $250. A variety of other electrode production methods have been recorded, including inorganic precipitates embedded in silicone rubber,[1] thermoplastic polymers,[2] and paraffin;[3] inorganic precipitate deposited on a graphite substrate;[4] powdered ceramic glasses of inorganic insoluble materials in a ceramic matrix;[5] and organic liquid ion-exchange substances polymerized into a P.V.C. film.[6,7]

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Research in this laboratory[8] has demonstrated the usefulness of thermoplastic polymer chloride electrodes in field and laboratory investigations of environmental samples. These electrodes can be easily produced in 30 min and are inexpensive (cost of materials about $2), stable and reproducible. Unfortunately, the method of manufacture requires heat and pressure, which largely negates its use for organic ion-active substances. Further, a press is required which may not be available to many workers. The following describes an electrode production method utilizing a readily available dental acrylic kit consisting of a solvent and an acrylic powder. For purposes of this report a chloride precipitate and an organophosphate calcium-type electrode are described. Working electrodes have also been produced from zirconium oxide powder, barium sulfate and various ion-exchange resins.

EXPERIMENTAL

Reagents and equipment

Hygienic acrylic, cross-linked self-curing #04004, and liquid solvent #04001 (Hygienic Dental Manufacturing Co., Akron, Ohio) were used for membrane manufacture. Glass vials (2 in. high by ½ in. diameter) were chosen so as to be of suitable size for the desired electrode body. Cutting and grinding may be done with tools generally available in any machine shop, or with home workshop tools.

Procedure for membrane manufacture

Mix acrylic and solvent (1:1, v/v) for 2 to 3 min or until acrylic seems well dissolved. Add an equal portion of active substance (precipitate, organic resin, etc.) and again mix well. More solvent may be necessary to keep the mixture fluid. In order to obtain good electrical contact in the membrane the mixture should not be too fluid. The final membrane mixture should occupy at least a depth of ½ in. in the vial. Allow the mixture to set. Break the glass vial and carefully remove any adhering glass. The membrane should be smooth and very coherent.

Procedure for liquid filling solution electrode manufacture

Depending on the thickness of the membrane, it can be cut into several pieces. Grind each piece to a thin wafer. Membranes may be fastened to a Pyrex glass or Teflon tube using an appropriate adhesive (e.g. silicone rubber cement for glass). Do not use commonly available epoxy resin glues. These do not stand up well in aqueous solutions and some exhibit appreciable ion conductivity.

Procedure for direct lead to membrane connected electrode

Prepare a mixture of acrylic solvent and precipitate in a glass vial as described above. Submerge a piece of silver foil ($\frac{3}{8}$ in. square) which has been soldered to the central wire of a shielded cable totally in the mixture. Allow membrane to harden and break glass vial. Grind excess membrane away so that the silver foil and outer surface of the membrane are separated by 1.0–1.5 mm of membrane.

Procedural discussion

Grain size of precipitate Problems resulting from leaks in the membranes may occur if precipitate particles are too large in size. In general, grinding with a mortar and pestle (no sieving) was sufficient for silver halide precipitates. Sieving was essential for precipitates. such as LaF_3, $BaSO_4$, and $BiPO_4$ to reduce the grain size to less than 400 mesh.

Membrane thickness No rule applies to all membranes. Obviously it is desirable to use as thick a membrane as possible, to maximize strength and general ruggedness. However, no response, sluggish response, or high capacitive effects result with many membranes above a thickness of 1 mm. In general, membranes of up to 1.5 mm are possible with good silver halide precipitates. However, very thin (0.1 mm) membranes are essential for many membranes made of organic active material.

Electrode details

Chloride electrodes These could be made with a liquid filling solution or with the lead directly connected to the membrane. A suitable silver chloride precipitate can be prepared by any good analytical technique. Best results were obtained with precipitates made from precipitation solutions containing slight silver excesses.

Calcium electrode The ion-active organophosphate material was crystallized by refrigeration of liquid ion-exchange solution available from commercial electrode producers. The solid was blotted dry with a piece of filter paper and mixed with the acrylic and solvent as above in a 1 : 1 mixture.

Other electrodes Electrodes made from 400-mesh powders of Chelex 100 resin (Biorad Laboratories Ltd.) and zirconium oxide ion-exchange crystals (Biorad Laboratories Ltd.) embedded in a 1 : 1 mixture with acrylic were also tested.

RESULTS AND DISCUSSION

Chloride and calcium electrodes

Silicone oil Silicone oil rubbed in a thin film over the membrane enhanced the response of both types of electrodes. This coating was applied after the electrodes had been soaked for 30 min. Electrode stability was similar to that of commercial models.

Response Electrode response times ranged from 10 to 120 sec, depending on solution concentration. In the linear response region, the mV per decade intervals were typically 31 for calcium and 54 for both the solid state and liquid filling solution chloride electrodes. Linear response occurred over the range 10^{-1} to 10^{-4}M for chloride and 10^{-1} to 5×10^{-3}M for calcium.

Electrode life time The chloride electrodes are working well more than 1 year after construction. Calcium electrodes typically last 1 to 2 months in good operating condition.

Leaking of filling solution around the membrane or along precipitate grain boundaries is the most common cause of malfunction. Leaking around the membrane is also a common symptom the author has encountered with commercial electrodes. In either case it can be easily rectified by re-cementing the membrane. Problems with leaking around grain boundaries arise from poorly formed membranes. Membranes exhibiting this malfunction should be discarded.

Interferences Interferences were tested for each type of electrode. The chloride electrodes showed interference patterns typical of silver halide membrane electrodes.[2,8] Calcium electrode interferences were in general similar to those reported for commercial electrodes and by Moody *et al.*[7]

Analysis Water samples were analyzed using the above electrodes and these results were compared with commercial electrodes or atomic absorption results where applicable. These data are given in Table I.

A year's experience using these electrodes suggests that the chloride electrode gives results which are comparable with commercial electrodes. On the other hand, the acrylic calcium electrodes (as suggested in Table I) yield positively biased results compared to atomic absorption values. No problem with either technique could be found to explain this trend. The results are, however, satisfactory for most water analysis purposes.

Applications The production of selective ion electrodes at low prices has allowed their introduction in larger scale into environmental analytical laboratory experiments. Of course every experimental set-up requires an expanded-scale millivolt meter (~ $500) and reference electrode (~ $35).

Each millivolt meter can be used with several types of electrodes either with a switching device or through a manual plug-in-plug-out routine for each electrode used. Research presently being done in conjunction with the department of Electrical Engineering at the University of Toronto will hopefully result in a millivolt meter-automated multi-electrode package with solid state memory for use in field work with electrodes.

Using the chloride and calcium electrodes and a portable Orion model 401 millivolt meter, *in situ* field monitoring student experiments have been introduced. The following are two examples, among many where interesting data were obtained.

TABLE I
Water analyses (ppm)

		Commercial electrode	Homemade liquid filling solution	Homemade solid–solid electrode
Chloride				
Tap water	$\bar{x}$[a]	36	37	38
	Sx	1.5	2.0	0.3
	n	4	5	6
Don R.	$\bar{x}$	650	640	—
	Sx	15	19	—
	n	6	6	—
Calcium				Atomic absorption
Mimico Cr.	$\bar{x}$	64	64	60
	Sx	—	0	—
	n	—	3	—
Highland Cr.	$\bar{x}$	100	110	94
	Sx	—	0	—
	n	—	3	—
Humber R.	$\bar{x}$	76	75	70
	Sx	—	2	—
	n	—	3	—
Don R.	$\bar{x}$	116	120	104
	Sx	—	0	—
	n	—	3	—

[a] $\bar{x}$, average ppm; Sx, % rel. S.D.; n, number of determinations.

Last winter the Ontario government instituted a ban against the dumping of road-salt-contaminated snow into the Toronto Harbour as a means of curbing increasing salinity in Lake Ontario. Through the continuous monitoring of the Don River during a snow storm and during the ensuing run-off period, students were able to strikingly demonstrate the futility of this ban.

Using flow-rate data provided by Water Survey of Canada—Department of the Environment—and measured chloride concentrations it was easy to show that in 2 min of peak discharge the Don River released an amount of chloride into the Toronto Harbour equal to 1000 truck loads of salt-contaminated snow (1000 truck loads is a common volume dumped after a snow storm). The Don River is only one of four major drainage basins in the Metropolitan Toronto Urban area. Added to this is the high chloride discharge directly into the lake of the Ashbridges Bay and Humber Sewage Treatment Plants.

Electrodes are potentially useful tools for 'mapping' lake waters in three dimensions while the boat is in continuous motion. Water intakes can be set at any desired depth. Water is pumped continuously through a hose into a flow-through cell containing electrodes and discharged into water.

TABLE II

Comparison of chloride values

Ship station	Chloride (ppm); continuous	Chloride (ppm); grab	Conductivity (mho 25°C)
1	30	25	379
10	48	33	448
12	58	36	465
16	43	30	—
23	26	24	333

Conductivity and temperature are two parameters which are presently monitored in this manner. Utilizing a homemade flow-through cell the Toronto Harbour area of Lake Ontario was monitored continuously for chlorode at a depth of 3 m. Table II shows results obtained during the on-stream continuous monitoring mode compared to grab samples taken and saved for later laboratory analysis.

There is a very obvious positive bias shown by results obtained with on-stream monitoring. This effect has been described by Fleet and Rechnitz[9] for the calcium electrode and by Fleet and Von Storp[10] for the cyanide electrode when used in a continuous flow mode.

Standards used for calibrating the chloride electrode were kept at the temperature of the water stream. Calibration was performed by lifting the electrodes out of the cell and immersing them in beakers with standard solution.

Despite the bias shown by the results there is no doubt that they could be used either 'as is' for some purposes, or suitably corrected using grab samples.

Other electrodes

Electrodes made from commercially available ion-exchange substances are being tested. The most extensive work in this area was done by Pungor and colleagues,[11-13] using ion-exchange resins embedded in silicone rubber. These workers concluded that substances of this type are selective to valence type and not to individual ions.

Preliminary work in our laboratory with Chelex 100 (iminodiacetic groups of a polystyrene lattice) indicates the experimental selectivities for nickel in the presence of other ions (Table III).

TABLE III
Experimentally determined selectivity shown by nickel in the presence of various common solution ions

Interfering ions	Selectivity
Na^+	1.0×10^{-2}
K^+	2.0×10^{-2}
Ca^{+2}	3.1×10^{-2}
Al^{+3}	4.2×10^{-2}

Preliminary work done with electrodes made from zirconium oxide ion-exchange crystals suggests that a good and stable, but non-selective response to most common anions is obtained. Electrodes of this type may prove useful in providing a measurement related to total anion concentrations in waters.

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