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Ultrasensitive determination with PAS is applicable to various kinds of liquid samples. However, when PAS is combined with an extraction technique, the background due to impurities, excess reagents, and instability of reagents should be low and constant as shown in this paper. When a suitable extraction method, which can highly enrich the chelate and reduce the background, is applied, various materials should be determined at sub-part-per-trillion to parts-per-trillion levels using PAS.

ACKNOWLEDGMENT

We are greatly indebted to Junko Fujita of the Laboratory of Analytical Chemistry, Kaken Co., Ltd., for skillful preparation of the reagents and samples and her useful advice regarding technical aspects of the extraction.

Registry No. 2-Nitroso-N, 132-53-6; cobalt, 7440-48-4.

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RECEIVED for review February 27, 1986. Accepted May 5, 1986.

Electrochemistry in the Gas Phase. Use of Ultramicroelectrodes for the Analysis of Electroactive Species in Gas Mixtures

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It is demonstrated that ultramicroelectrodes can be used as sensitive electrochemical detectors and sensors in the gas phase. The sensitivity of these devices depends on the electrochemical properties of the analyte and on the properties of the surface separating the ultramicroelectrode from the counter electrode. The devices are demonstrated in this work as gas-phase chromatographic detectors.

New and interesting applications of very small electrodes (ultramicroelectrodes) have been the subject several researchers in the recent literature. High rates of mass transport to, and reduced ohmic and capacitive effects at these devices allow electrochemical measurements under conditions that avoid the need for traditional electrode system environments, such as highly conducting electrolyte solutions. Electrochemical experiments in liquid- and gas-phase solvents with little or no purposely added supporting electrolyte have been reported (1-6). The electrochemical potential window is generally extended in the experiments: acetonitrile can be used in simple redox reactions to about 4 V vs. a silver reference, and under special circumstances can be used to almost 6 V. Under these conditions, it has been possible to study the voltammetry of species with very high oxidation potentials, such as short chain alkanes (7) and oxygen and the rare gases (8). Electrochemistry in low-temperature solution solid eutectic mixtures and glasses of nonaqueous solvents has also been reported (9); electrochemistry in these media permits studies of thermally stabilized reactive intermediates that may

be generated subsequent to the electron transfer. Each of the above examples makes use of the advantage of greatly reduced ohmic losses at ultramicroelectrodes.

Very small electrodes require only a small number of ion dipoles to charge the electrical double layer. The required number may easily be supplied from the free carrier population present in solutions as impurities or from the autoionization of the solvent. Likewise, some of the aforementioned examples make use of this property. We report in this work the novel use of ultramicroelectrodes in the gas phase and demonstrate their use as an electrochemical detector in gas-phase chromatography, as well as a sensitive electrochemical gas sensor. In these experiments, the charge required for the double layer is supplied from the free carrier charge at the surface of an "insulator" in contact with the ultramicroelectrode. Limiting currents measured are typically on the order of 10^{-10} to 10^{-16} A, in contrast to those measured at conventional macroelectrodes ($>10^{-9}$ A). Since the resistivity of the insulators used to mount the electrodes are on the order of $10^9 \Omega$, adequate carriers are present for double layer charging. We will show that the conductivity is also sufficiently high to allow measurement of faradaic currents in the gas phase. These experiments must be distinguished from those that have been previously described where macroelectrodes in solid electrolytes have been used. In the present case, a true flux steady state is reached in short times. Ohmic potential losses are small, and the current response can be described in a manner similar to that in conventional electroanalysis (10).

EXPERIMENTAL SECTION

A schematic diagram of a ring ultramicroelectrode gas phase detector assembly is shown in Figure 1. Gold was plated onto a 5- μ m quartz fiber by first painting a diluted solution (1:1 benzene:ethyl acetate) of Hanovia Liquid Bright Gold (Englehard Industries, Inc.) onto the fiber with subsequent firing at 625 °C

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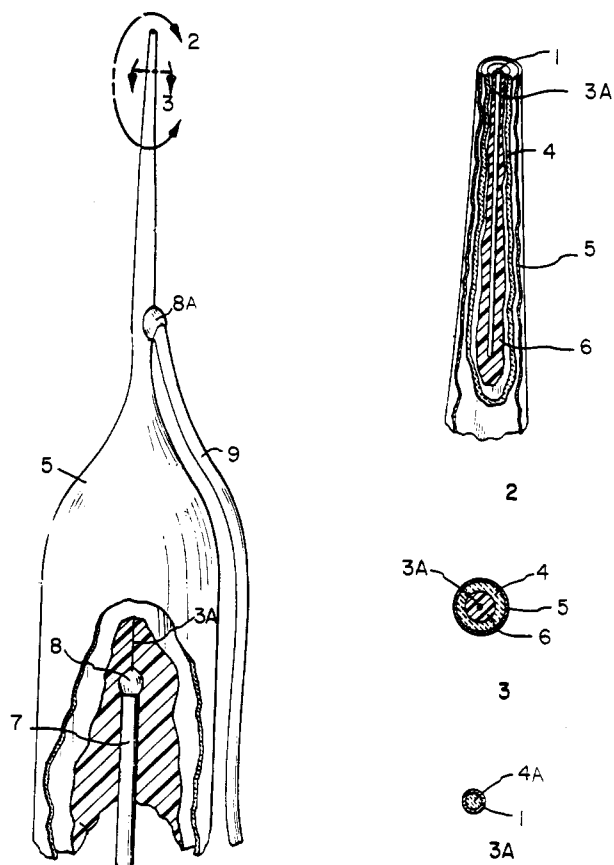


Figure 1. Ultramicroelectrode (gold ring) gas phase detector assembly. The microelectrode assembly (3A) in this case is constructed of a thin gold film (1) on a glass fiber (4A). The tip cross section (2) consists of the assembly (3A) sealed in a glass tube (4) coated with a thick metal film (5) with epoxy resin (6). The working electrode ring (1) is thus separated from the auxiliary electrode (5) by a thin ring of glass and epoxy resin. (2) details the side view of the tip. A fine copper wire (9) is soldered to the metal film for external contact to the auxiliary/reference electrode with lead solder (8A), while a similar connection is made to the microelectrode with another copper wire (7) with silver epoxy (8).

for 1 h in a tube furnace. The procedure is more easily performed by treating a bundle of the fibers simultaneously and extracting a single fiber later under a microscope for the mounting. A quartz tube (0.5–0.7 mm i.d. at the tip) is used for the outer housing and auxiliary electrode mount. Undiluted Liquid Bright Platinum or Palladium was painted onto the outside surface of the tube for a distance of about 2 cm from the tip. The tube was then fired in the tube furnace as were the fibers. A piece of insulated fine copper wire was soldered to the resulting thick film of palladium metal near the end furthest from the tip of the tube. The wire was epoxied to the glass barrel so as to prevent breakage of the connection at the solder joint.

Electrical contact was made to the gold ultramicroelectrode by attaching another fine insulated copper wire with silver loaded epoxy resin (Epoxy Technology, Inc.). The fiber was then inserted into the palladium-coated tube until it just protruded from the tip. This procedure is best performed with a mechanical manipulator under a magnifying glass or microscope. Epoxy resin was then forced into the tube from the large end with a large bore hypodermic needle and syringe so that retraction of the fiber into the tube was prevented by the outward flow of the epoxy from the tip.

When the entire assembly was dry, the tip was cut perpendicularly to the axis of the tube so that a gold ring ultramicroelectrode was exposed. The average thickness of the ring used in this work was about 1 μm .

Carbon disk ultramicroelectrodes (5 μm diameter) were constructed similarly. The carbon fiber (Hercules Corp.) was cut into 2 cm lengths. These were attached to the tip of insulated copper wire leads with conducting epoxy as described above for the rings and mounted in appropriate auxiliary electrode tube assemblies

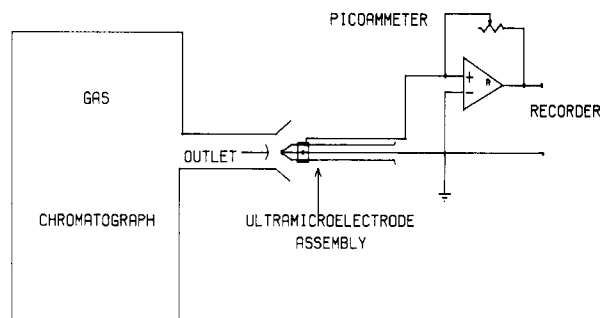


Figure 2. Schematic diagram of the GC system used.

in the same manner. All electrodes were polished on balsa wood bases with varying grades of polishing alumina before use.

The potential difference between the inner and outer electrodes was controlled with a wave form generator (Hi Tek Instruments, Model PPR1). Currents were measured with a digital picoammeter (Keithley Model 619) which was placed in series with the wave form generator and electrochemical cell. We point out that the use of relatively high impedance output devices, like the wave form generator, as current sources is justified in the light of the magnitude of the currents drawn by an ultramicroelectrode system.

The finished ultramicroelectrode assembly was mounted in a Faraday cage to reduce the capacitatively coupled noise. A gas chromatograph (Hewlett-Packard Model 700) was set up adjacent to the cage so that the gas outlet port extended inside the Faraday cage. The tip of the ultramicroelectrode was inserted inside the outlet port so that the dead volume between the column and the detector was minimized (Figure 2). When chromatograms were recorded in this manner and the peaks from the electrochemical detector and a commercial thermal conductivity detector compared after normalizing to a common peak intensity, there were no observed differences in the dispersions of the two peaks. A simultaneous record was maintained on a dual pen strip chart recorder (Houston Instruments, Inc., Omniscribe) of the response of the ultramicroelectrode and the commercially supplied thermal conductivity detector.

Experimental details of specific sets of measurements are given in the results and discussion section.

Ultramicroelectrodes can be designed that, depending on the size, will support steady-state currents in both electrolyte and resistive solutions. All very small conductive microstructures imbedded in a relatively large insulating plane will develop essentially spherical diffusion characteristics during an electrochemical reaction. Diffusion to microspheres can be shown to give rise to a steady-state flux; for instance the relaxation time for this process at a microsphere electrode is given by

$$\tau \approx r^2/4D$$

where r is the radius of the sphere and D is the diffusion coefficient of the electroactive species. This time can be made short ($<10^{-6}$ s) by the simple construction techniques described above. Currents at these structures, typically in the picoampere range, give rise to only small errors in the applied electrode potential; values in highly resistive media result in corrections typically in the millivolt region.

The electrode assembly used in this work consisted of a working ultramicroelectrode separated by a few tenths of a millimeter from the auxiliary electrode by epoxy resin and a thin glass tube. The auxiliary/pseudoreference electrode was made relatively large ($>10^6$ in area. Polarization of the reference system does not occur due to the small currents that are dissipated over the entire surface of the large reference electrode. The total resistance of the resin/glass boundary, although high in absolute terms, still is low enough for the required small currents. The typical leakage current in the system when polarized at +3 V polarization was about 600 fA when using the gold ring electrode. The electroactive analyte, dissolved in the dry nitrogen carrier gas of the chromatograph, is delivered directly to the microelectrode detector at the outlet port. (We point out here that the same assembly can be used as conveniently in a liquid chromatographic or flow injection apparatus. In these cases, supporting electrolyte is not

Table I. Response-Concentration Results for a Platinum Ring Ultramicroelectrode: Water in Ethanol

| corr coeff r | slope, nA/% H ₂ O | injected concn C_0 , % H ₂ O (v/v) | detected concn C_m , ppm | equiv current injected h_0 , μ A | equiv current detected h_m , nA |
|----------------|------------------------------|---|----------------------------------|---|---|
| 0.9998 | 4.41 | 0.1 | 0.5 | 0.8 | 2.0 |
| | | 1 | 5.3 | 8.2 | 4.3 |
| | | 2 | 11.2 | 16.4 | 8.7 |
| | | 5 | 27.7 | 41.0 | 22.0 |
| | | 8 | 44.1 | 65.6 | 36.1 |
| | | 10 | 55.5 | 82.0 | 43.8 |
| | | 13 | 72.0 | 106.6 | 57.1 |
| | | 15 | 83.1 | 123.0 | 66.2 |

required, and conventional HPLC grade solvents may be used.)

RESULTS AND DISCUSSION

Dilute water samples were prepared in dry ethyl alcohol by volumetric addition and dilution. The chromatographic column in these experiments was Carbowax 20M 3% on Chromasorb W. The dry nitrogen carrier flow rate was maintained at 60 cm³/min; the injection port temperature was 110 °C, and the column temperature was 50 °C. One-microliter injections of the water alcohol samples were made, and the response of a 1 μ m thick 100 μ m diameter platinum ring ultramicroelectrode with a platinum auxiliary electrode was measured. Harris (11) has provided a discussion of the relation between peak dispersion, injected concentration, and detected concentration, useful in the description of detection limits in systems where Gaussian peak shapes are present.

The concentration C_m detected at the peak maximum is given by

$$C_m = C_0/D_i$$

where D_i is the dispersion and C_0 is the injected concentration. For a detector that has a response h linear with concentration

$$C_m = C_0 h_m/h_0$$

where h_m and h_0 are the responses for the concentration at the maximum of the peak and at a concentration equal to C_0 , respectively. h_0 is given by

$$h_0 = (Q/V_s) \int h(t) dt$$

where $h(t)$ is the time-dependent response (the peak profile), Q is the gas flow rate (assumed to be constant here), and V_s is the volume of the sample injected. Using this method, C_m was calculated for each of the injected samples. Linearity of the ultramicroelectrode detector was checked by comparing the area of the $h(t)$ response with the injected mass of material. Results for these comparisons are given in Table I, with the correlation coefficient and slope of the response/injected concentration plot. Although a detailed analysis of the detection limits of these detectors has not yet been completed, we can offer some preliminary comments. The background dc noise level for the Pt/Pt electrode system examined has a value of +1.2 pA, and a ripple fluctuation typically of 0.9 pA peak to peak. These values varied as much as 50% depending on the care taken in producing the electrode, its handling, cleanliness of the test solutions, and quality of electrical shielding employed when using. Using these noise figures and the slope from Table I, we calculate the detection limits for water in ethanol to be $6.1 \times 10^{-4}\%$, if we define detection limits to be the concentration that gives a signal strength three times larger than the background noise level. The dynamic range is limited on the less sensitive end by the fact that at very high mass transport rates, the electrochemical reaction will be pushed into kinetic control; we then expect nonlinear behavior of concentration and current. In this case,

the appropriate modifications to the theory must be made in order to obtain quantitative results (7).

Scope of Usefulness: Comparison to Thermal Conductivity Detectors. The experiments described in this section were performed to compare the specific detectivity of the ultramicroelectrode with respect to a thermal conductivity detector (Hewlett-Packard Model 4-4188 for their Model 700 gas chromatograph). When the detector amplifier was set to maximum gain, the absolute noise level indicated on the chart recorder was about 100 μ V peak to peak.

Experiments were performed with the 5- μ m carbon disk electrode. The auxiliary pseudoreference was a 100 μ m thick palladium film. The response of the electrode system was checked initially by performing voltammetry of a 5.0 mM hexacyanoferrite solution in 0.06 M KOH and 0.70 mM diphenylanthracene in acetonitrile solution to verify the electrode dimensions and reproducibility of results. Limiting currents for each of 10 successive experiments did not vary by more than 1% in either solution.

The column of the gas chromatograph was maintained at 80 °C. The column was Carbowax 20M 3% on Chromasorb W. Injector temperature on the chromatograph was maintained at 90 °C. The carrier gas was nitrogen, and the flow rate was 30 mL/min. The effluent was first detected by the same thermal conductivity detector as mentioned above and was then detected by the ultramicroelectrode which was located about 1 mm further down the gas line from the thermal conductivity detector. In the first experiments the electrode was maintained at a potential of +3.0 V with reference to the palladium auxiliary electrode.

The response of the carbon ultramicroelectrode prepared as described in the Experimental Section could be progressively increased by appropriate conditioning. Pulsing the potential of the ultramicroelectrode from +3.0 V to -3.0 V for 5-s intervals for 30 s electrochemically reduces surface impurities and increases the sensitivity of the ultramicroelectrode markedly. This procedure was repeated once every 30 injections to maximize the response. The background noise fluctuation level of the thermal conductivity detector was about 200 μ V peak to peak. Table II illustrates relative responses (ultramicroelectrode/thermal conductivity detector) observed under these conditions. The sample injection was 1.0 μ L. Figure 3 shows a typical result for aniline at the two detectors at a relative concentration of 10000:1.

The potential of the detector was subsequently adjusted to -3.0 V. Virtually identical responses were observed for the same compounds, except the observed signals were inverted in sign. It is perfectly feasible to perform voltammetry "on the fly" during elution of the peaks, and thus detect the half-wave potential(s) for a component(s) in a chromatographic peak by virtue of the shape of the voltammetric response (12).

N-Methylamine was used to study the potential dependence of the response between 0 and +3.0 V. A polarization curve is obtained as expected, except the response is observed to fall at potentials greater than about +2.5 V. This decrease

Table II. Relative Response of Carbon Ultramicroelectrode Detector to Thermal Conductivity Detector

| compound | rel response ^a |
|---------------------------------------|---------------------------|
| <i>n</i> -hexane | 10 |
| 1-hexene | 10 |
| acetone | 20 |
| acetic acid | 10 |
| 0.1 M ammonium hydroxide | 13000 |
| isopropylamine | 10000 |
| <i>N</i> -methylacetamide | 10 |
| vinyl chloride (10 ppm in air) | 2000 |
| nitrobenzene | 500 |
| aniline | 1000000 |
| ethanol | 12000 |
| methylamine (40% in H ₂ O) | 125000 |
| formic acid | 7500 |
| triethylamine | 100000 |
| <i>N,N</i> -dimethylacetamide | 100 |
| carbon monoxide 1.03% in air | 10000 |
| ethyl acetate | 10 |
| ethylene dichloride | 24000 |
| benzonitrile | 172000 |
| ethylbenzene | 6000 |
| acetonitrile | 16000 |
| trichlorotrifluoromethane | 0 |
| toluene | 4000 |
| cyclohexanone | 10000 |
| water | 12000 |
| 3-bromothiophene | 10 |

^a Average of five runs (at +3.0 V). Ratio of calculated detection limits (ultramicroelectrode/thermal conductivity). The detection limits for each detector were obtained from extrapolated values calculated by the method described in section a. The ultramicroelectrode was maintained at +3 V with respect to the auxiliary reference.

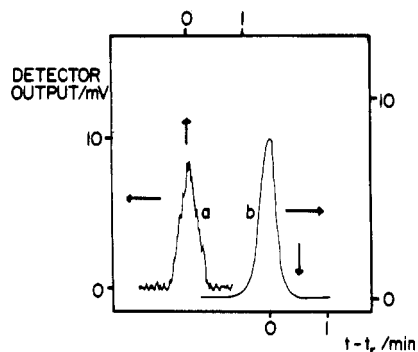


Figure 3. Response of aniline (a) at the thermal conductivity (1.0 μ L, neat aniline) detector and (b) at the ultramicroelectrode (1.0 μ L, 0.1 mM aniline in diethyl ether) detector.

is most likely due to passivation of the electrode due to polymerization of electroactive species or depletion of electrolyte in the epoxy surface by electrochemical oxidation. Degradation of the response was always accelerated by operation at higher potentials. The surface could be regenerated to the same initial response after cathodic pulse treatment as described earlier. Other compounds show similar behavior at high potentials indicating that the reaction responsible for the degradation in response is most likely due to reaction in the epoxy sealer.

Two standard gas mixtures were analyzed: carbon monoxide (1.03% in air) and pure vinyl chloride. The relative responses to those of a thermal conductivity detector were 10^4 and 2×10^3 , respectively.

If the electrode is subjected to 0.1 M NaOH solution for 30 s before use, sensitivity for most compounds is increased by a factor of 2–5. This enhancement fades after a few minutes of exposure to the gas stream. This observation is probably due to several effects. One is the evaporation of the

Table III. Relative Response of a Gold Ring Ultramicroelectrode Detector to a Thermal Conductivity Detector

| compound | rel response ^a |
|---------------------------|---------------------------|
| ethanol | 1000 |
| ethylene dichloride | 80 |
| <i>n</i> -propylamine | 50 |
| triethylamine | 50 |
| water | 3600 |
| methylamine (40%) | 6270 |
| aniline | >1000000 |
| acetonitrile | 750 |
| toluene | 220 |
| ethylbenzene | 150 |
| benzonitrile | 30000 |
| ethyl acetate | 300 |
| acetone | 120 |
| hexene | 10 |
| carbon tetrachloride | 10 |
| cyclohexanone | 3800 |
| <i>tert</i> -butylbenzene | <10 |

^a Measured as described in Table II.

water present at the surface of the epoxy surface, which will increase the resistance. A second possibility is that since electrooxidations for most compounds will proceed easier in the presence of base, there will be an increased response at any fixed high potential. In this case, a fall in the current will be expected after continued oxidation due to a depletion of base. The enhancement returns if the electrode is subsequently subjected to a 5-s submersion in water. Again the response will fade after a few runs. This procedure can be repeated a few times with less enhancement observed on each subsequent treatment. Eventually no enhancement is observed, and we assume that all of the excess KOH electrolyte trapped near the epoxy surface has either been leached out by the excess water, or reacted away, or both. Enhancement can be regenerated by treating the assembly again with the KOH solution. It is clear that permanent increases in ionic conductivity of the surface of the epoxy sealer will provide higher sensitivities, and work is in progress in this area.

Table III gives the results for a gold ring ultramicroelectrode using a platinum auxiliary pseudoreference electrode. The diameter of the ring was 50 μ m, and the average ring thickness was 1 μ m. The potential maintained between the two electrodes was +3.0 V (working vs. auxiliary).

Although there is general similarity in the responses of the carbon and gold ultramicroelectrode detectors, there are some distinct differences. Some of the differences can be explained in terms of relative activation overpotentials of the substrate on the two different surfaces, while some are not easily explained. This area is under continued investigation.

CONCLUSIONS

The results presented show that ultramicroelectrode assemblies can be used to monitor species present in the gas phase as high sensitivity. Such measurements open up a new field of electrochemistry; namely, the reaction of gas-phase species at the microelectrode; these reactions being coupled to current flow over the surface of the "insulator" used to separate the microelectrode and the counter electrode. The reactions may take place on the microelectrode or at the edge of the microelectrode; furthermore the response may be modified by incorporating catalysts at the ultramicroelectrode surface or in the "insulator", as well as by membrane coatings (12).

Therefore, topics receiving current attention include: kinetic measurements, the rates of the processes on the surface and the edge of the ultramicroelectrode, the effect of catalysts and membrane coatings.

ACKNOWLEDGMENT

The authors thank Joel Harris for his helpful comments regarding the treatment of the data. This paper is dedicated to Cheves Walling on the occasion of his 70th birthday.

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RECEIVED for review February 27, 1986. Accepted May 12, 1986. We thank the Office of Naval Research and Dow Chemical Co. for support of this work.

Neutral Carrier Based Ca^{2+} -Selective Electrode with Detection Limit in the Sub-Nanomolar Range

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In a 1:3 cation/ligand complex the ionophore *N,N,N',N'*-tetracyclohexyl-3-oxapentanediamide forms an almost ideal coordination sphere of nine oxygen atoms for the uptake of Ca^{2+} . By use of this ionophore and current membrane technology, solvent polymeric membranes with extremely high Ca^{2+} selectivities are obtained. Na^+ and K^+ are rejected by a factor of $10^{7.4}$ and 10^8 , respectively, and the detection limit of the Ca^{2+} electrode response function in an intracellular ion background is at about 100 pM Ca^{2+} .

Considerable effort is invested in the design of calcium ion selective electrodes with improved selectivity and detection limits (1-5). The most attractive sensors in this respect are based on the neutral carrier (-)-(R,R)-*N,N'*-bis[11-(ethoxycarbonyl)undecyl]-*N,N'*-4,5-tetramethyl-3,6-dioxaoctanediamide (ETH 1001) (2) introduced in 1975 (6). These sensors have been widely accepted for clinical and electrophysiological Ca^{2+} -activity measurements (7). Studies of resting and changing intracellular Ca^{2+} levels are however performed close to the sensor's detection limit, which is dictated by K^+ interference (8). Similarly, it has been claimed that the usefulness of these sensors in soil sciences is limited by cation interferences (9, 10).

The neutral carrier *N,N,N',N'*-tetracyclohexyl-3-oxapentanediamide (ETH 129) (11) was shown to form extremely lipophilic 1:3 cation/ionophore complexes with Ca^{2+} and 1:2 complexes with Mg^{2+} (12). It is therefore not surprising that the corresponding solvent polymeric membranes show a high rejection of Mg^{2+} relative to Ca^{2+} . A high selectivity for calcium over monovalent cations may be obtained through the incorporation of lipophilic anionic sites into the membrane phase of neutral carrier based liquid membranes for divalent cations (13). Thus, with adequate membrane technology, a further improvement of the selectivity of Ca^{2+} electrodes should be feasible. Here we report on a sensing system involving ETH 129 with clearly improved selectivities and detection limits, which was obtained through such interventions.

EXPERIMENTAL SECTION

Reagents. For all experiments, doubly quartz distilled water and chemicals of puriss. or p.a. grade were used.

Membranes. The solvent polymeric membranes were prepared according to ref. 14 using 1 wt % ETH 129 or ETH 1001 carrier, 66 wt % *o*-nitrophenyl octyl ether (*o*-NPOE; puriss. p.a., Fluka AG, Buchs, Switzerland), and 33 wt % poly(vinyl chloride) (PVC high molecular; purum p.a., Fluka AG). As lipophilic anionic site, potassium tetrakis(*p*-chlorophenyl)borate (KTPClPB; purum p.a., Fluka AG) was used (for concentration see below). The syntheses of the carriers ETH 1001 and ETH 129 are described in detail in ref 15 and 11, respectively.

Electrode System. Cell assemblies of the following type were used:

Hg; Hg_2Cl_2 , KCl (satd)||3 M KCl|sample solution||
membrane||0.01 M CaCl_2 , AgCl; Ag

The external half cell was a free flowing free diffusion liquid-junction calomel reference electrode (16). The solvent polymeric membranes were mounted in electrode bodies Philips IS-561 (N.V. Philips Gloeilampenfabrieken, Eindhoven, Holland).

Emf Measurements (General). The emf values were measured at $20 \pm 1^\circ\text{C}$ unless otherwise specified. The 16-channel electrode monitor used was equipped with FET operational amplifiers AD 515 KH (input impedance $10^{13} \Omega/2$ pF; bias current < 150 fA; capacity neutralization; Analog Devices, Norwood, MA). The signal was digitized by a 14-bit analog-to-digital converter DT 1744 (successive approximation, full scale ± 500 mV, Data Translation, Natick, MA). Data were acquired with a single board computer (SBC 80/20-4; SBC 116A; Intel Corp., Santa Clara, CA) programmed in assembly language, using an AMC 95/6011 arithmetic processor (Advanced Micro Computers, Santa Clara, CA). Further processing of the data was performed off-line on a HP-85 calculator (Hewlett-Packard, Palo Alto, CA), programmed in BASIC. The measured emf values were corrected for changes in the liquid-junction potential according to Henderson (17, 18). Using the Debye-Hückel theory, single-ion activities were calculated with the coefficients given in ref 19.

Selectivity Determinations. Separate Solution Method. The selectivity factors, $\log K_{\text{CaM}}^{\text{Pot}}$, were obtained in 0.1 M unbuffered solutions of the corresponding chloride salts.

Fixed Interference Method. The selectivity factors were evaluated from the electrode response functions for the primary