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Novel Approaches to Ionic Chromatography

Progress Report

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DISCLAIMER

Major progress has been made towards on-line on-demand generation of ultrapure chemicals by electrochemical means. The concentration of the generated material is governed electrochemically. As an example, consider the generation of NaOH. Even in its best commercial available form it is significantly contaminated with NaCl, $NaClO_3$, and most notably, Na_2CO_3. We generate ultrapure NaOH by feeding ordinary NaOH solutions on one side of a cation exchange membrane, also bearing a noble metal anode. On the other side of the membrane, pure water is made to flow; this channel also contains a stainless steel cathode. Under the influence of the electric field, Na^+ is electrodialytically transported and forms NaOH and H_2 on the cathode side:

$$Na^+ + H_2O + e \longrightarrow NaOH + H_2 \uparrow$$

The purity of the generated NaOH is solely limited by the purity of the influent water and leaching off from contact materials. Both the Donnan barrier posed by the cation exchange membrane and the direction of the electric field inhibits the passage of anions present in the feed NaOH across to the product channel. Not only is the product NaOH extremely pure (after electrical removal of Na^+ from this product, i.e., after electrodialytic neutralization of 30-200 mM NaOH, the specific conductance of the resulting water is 200-300 ns/cm, the theoretical conductance of pure water being 55 ns/cm), the concentration of the NaOH formed is controlled by the current.

We have successfully developed (a) an isocratic ion chromatographic system which uses on-line electrically generated NaOH as eluent (a membrane degasser removes H_2 prior to the eluent pump) and after separation, the Na^+ is removed electrodialytically by the reverse process (electrodialytic "suppressor") to convert eluting anions to the corresponding acids in a background of high purity water, permitting exquisitely sensitive conductometric detection; a manuscript describing this by Joung, Strong and Dasgupta is in preparation; (b) a gradient anion chromatographic system was developed in which a

PC-controlled programmable current source drives the eluent generator. Conductivity of the generated NaOH is measured on-line to indicate generated concentrations (current efficiency is > 95%), the concentration varies temporally as desired by appropriately programming the current source much like any other gradient chromatograph. The major difference, of course, is that no mechanical high- or low-pressure mixing means are used and only a single isocratic pump is required. The arrangement has provided by far the best gradient chromatograms heretofore realized. A paper on this by Strong, Dasgupta, Friedman and Stillian was presented at a recent international symposium on ion chromatography and a manuscript has been submitted.

Thirdly, by using a unique combination of different membranes, single step generation of gas-free electrodialytic products have been explored. The use of a perforated plate and two cation exchange membranes to generate gas-free ultrapure NaOH has been described in a recently submitted manuscript authored by Strong and Dasgupta. It is quite clear that ultrapure acids, bases, salts and buffers can also be generated in the electrodialytic current-controlled manner.

Continuing Work: Continuing work for the remainder of this budget year involves improving the electrodialytic suppressor to make a good reliable single stage gas-free device such that the NaOH generated therefrom can be recycled. A membrane-permeation conductance measurement based probe is being explored for determining the concentration of NaOH solutions in NaOH concentrations approaching 50% in the presence of several percent NaCl. We are carrying out experiments in several postsuppressor chemical manipulations and dual conductance detector measurements to help improve (a) detectability of certain analyte ions, (b) peak identification beyond retention time, and (c) assessment of peak purity. These experiments are jointly sponsored by the

Dionex Corporation. Dionex is also subsidizing our acquisition of a capillary electrophoresis instrument, we shall begin CZE separation and detection of small anions in early 1991.

Publications

Publications that have appeared since the last report acknowledging DOE support include a major three part review (Postcolumn Techniques: A Critical Perspective for Ion Chromatography. Part I. General Overview and Systems with Suppressors. Part II. Determination of Metals, Various Ionic and Ionizable Species. Part III. New Methods on the Horizon. P. K. Dasgupta, J. Chromatogr. Sci. 27: 422-448 (1989)) and a novel method of conductimetric pKa determination (Measurement of Acid Dissociation Constants of Weak Acids by Cation Exchange and Conductometry. P. K. Dasgupta and O. Nara, Anal. Chem. 62: 1117-1122, 1990). The method requires no pH measurement and the P.I. is aware that it has already been adopted in several laboratories including those of two DOE grantees. Copies are appended.

Unobligated Amounts: No significant funds (< 1%) are expected to remain unspent from FY 1990.

FY 1991 Budget. No changes are proposed from the original proposal.

Reprints removed.

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