

1. Primary alcohols reacted readily with carboxylic acids to afford the corresponding esters in excellent yields. The yields are much higher than 40-60% obtained by Olah under comparable condition without using the drying agent but similar to those observed in the gas phase reaction⁶. The yields were lower with secondary and tertiary alcohol presumably because of the steric effect and the competing dehydration reactions. Thus in reactions of cyclohexanol with carboxylic acids and the ester was produced only 20-46% but cyclohexene was obtained in 30-60% yields under the same condition. When tertiary alcohol was used only poor results were obtained; formation of gaseous isobutylene was visibly noticeable. This esterification procedure is, however, very efficient also for sterically hindered carboxylic acids.

The present procedure provides an efficient method for esterification of aliphatic carboxylic acids and primary alcohols. In this procedure, only a catalytic amount of the acidic resin is needed, and the heterogeneous catalyst provides for a very simple work up. Application of Nafion-H on other acid catalyzed reactions are in progress in our laboratory.

Acknowledgment. This investigation was supported by grants from the Basic Science Institute Program, Korea Ministry of Education (1989) and the Organic Chemistry Research Center sponsored by the Korea Science and Engineering Foundation.

References

1. G. A. Olah and G. K. S. Prakash, J. Sommer, "Superacids", Wiley Interscience, New York, Chapter 1, 1985.
2. K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1059 (1959).
3. J. Grodin, R. Sanger, and A. Commeyras, *Bull. Soc. Chem. Fr.*, 1779 (1976).
4. G. A. Olah, P. S. Iyer, and G. K. S. Prakash, *Synthesis*, 513 (1986) and references cited therein.
5. F. J. Waller, In, "Polymer Reagents and Catalysts", T. F. Ford, Ed., ACS Symposium Series 308; American Chemical Society, Washington, DC., Chapter 3, 1986.
6. F. J. Waller and R. W. Van Scoyoc, *Chemtech*, July, 438 (1987).
7. F. Waller, *J. Catal. Rev. Sci. Eng.* 28, 1 (1986).
8. G. A. Olah, and T. Keumi, D. Meidar, *Synthesis*, 929 (1978).

Indirect Determination of Rare Earths by Amperometric Detection for Flow Injection Analysis

In-Hyeong Yeo* Ke-Chon Choi¹, and Tae Yoon Eom[†]

Department of Chemistry, Dongguk University,
Seoul 100-715

[†]Division of Chemistry and Chemical Analysis, Korea Atomic Energy Research Institute, Daejeon 302-353

Received October 27, 1990

The rare earths are usually determined by optical emission

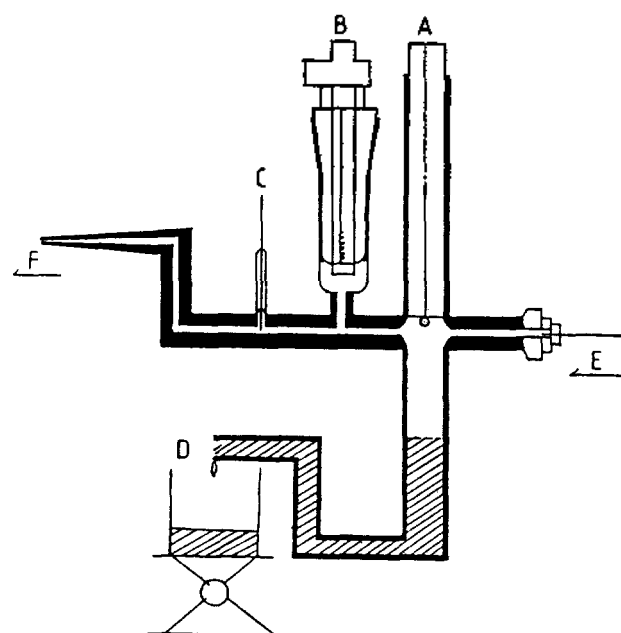


Figure 1. Electrochemical cell for flow injection analysis. A: working electrode, B: reference electrode (SCE), C: counter electrode (Pt wire), D: reservoir for mercury droplet, E: inlet F: outlet (to waste).

spectrometry^{1,2}, mass spectrometry coupled with inductively coupled plasma³, neutron activation analysis⁴ and electrochemical methods⁵⁻⁷. One of the problems with electrochemical methods is that most rare earth ions, except Sm, Eu, and Yb, are hardly reduced to their divalent state at the mercury electrode in aqueous solution⁸. The standard reduction potential of most rare earth ions is more negative than that of hydrogen ion in acidic media and so the reduction is interfered by hydrogen evolution. This is a reason why the polarographic analysis of rare earth ions is not usually employed. The detection of rare earth ions with electrochemical techniques after separation by high performance liquid chromatography (HPLC) has been reported earlier by Boissonneau *et al.*⁹. These researchers mixed ethylenediaminetetraacetic acid (EDTA) in the flow stream of rare earths at the exit of the HPLC column. The concentration of the element was then determined indirectly by measuring the concentration of free EDTA. Here, we chose diethylenetriaminepentaacetic acid (DTPA) as a ligand to determine rare earth ions by flow injection analysis. The choice of DTPA as a complexing agent has two advantages: the larger value of formation constant of DTPA with rare earth ions leads to almost all ions complexed in the flow stream, guaranteeing more quantitative determination. Oxidation potential of DTPA at a mercury electrode is less positive than that of mercury itself. Hence, anodic current for the oxidation of DTPA is not interfered with by oxidation of mercury electrode. In this work, we have demonstrated quantitative determination of the rare earth ions indirectly by amperometric techniques in flow injection analysis.

The principle of detection for flow injection analysis is as follows: A ligand such as diethylenetriaminepentaacetic acid (DTPA) is injected with a constant flow rate into a flow stream containing the rare earth ions to be determined. The

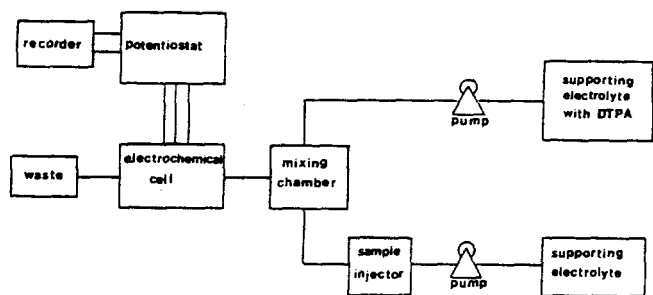


Figure 2. Diagram of experimental set-up for flow injection analysis.

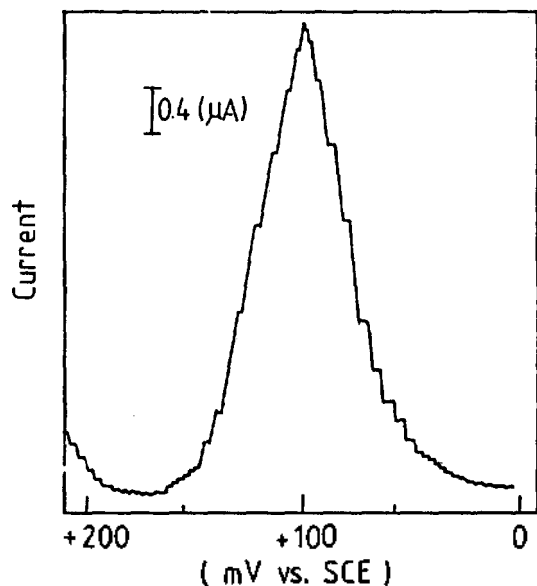


Figure 3. Differential pulse polarogram for the oxidation of 1×10^{-3} M DTPA in 1.0 M ammonium acetate buffer (pH=4.8).

reaction between the ions and the ligand occurs in the flow stream, and the reaction products and uncomplexed free DTPA reach the electrochemical cell where the free DTPA is determined. In the electrochemical cell a working electrode is polarized at a potential at which the free DTPA can be oxidized. A large background current from the oxidation of DTPA is obtained in the absence of the rare earth ion in the flow stream. The decrease in the background current due to the decrease of free DTPA by the reaction with rare earth ions is proportional to the concentration of the rare earth ions.

A three-electrode system was employed to perform electrochemical measurements. A dropping mercury electrode was served as a working electrode. A saturated calomel electrode (Model C-10, Tacussel Co.) and platinum wire were used as a reference electrode and counter electrode, respectively. The supporting electrolyte was 1.0 M ammonium acetate buffer. The electrochemical cell for flow injection analysis was made with a capillary column shown in Figure 1. The schematic diagram for flow injection analysis is shown in Figure 2. The ligand is eluted at a constant flow rate of 0.8 ml/min and mixed with the rare earth ions in a mixing chamber. The uncomplexed DTPA can be oxidized at the mercury electrode. A differential pulse polarogram for the oxidation of DTPA is shown in Figure 3 and the detection

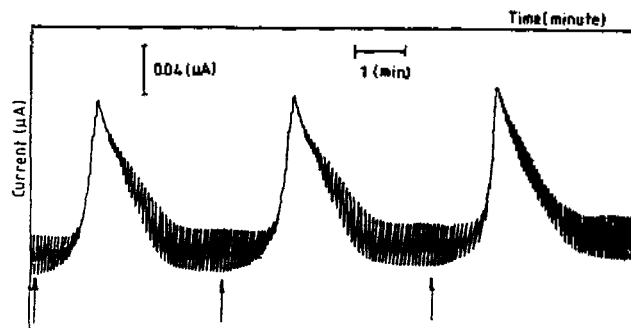


Figure 4. Chronoamperogram for the determination of Holmium. Detection potential: 100 mV vs. SCE., concentration of DTPA: 5×10^{-4} M, supporting electrolyte: 1.0 M ammonium acetate buffer (pH=4.8), concentration of Holmium: 3×10^{-5} M, flow rate: 0.8 ml/min. Arrow indicates injection point.

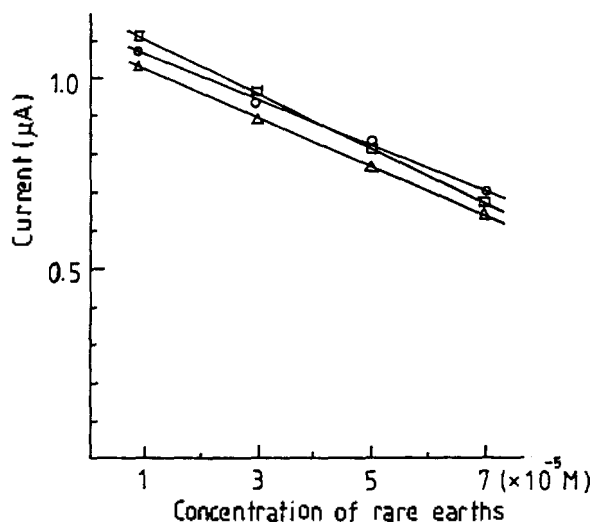


Figure 5. Plots of the peak current for the oxidation of DTPA vs. concentration of rare earth ion. (□): Tm, (○): Ho, (△): Yb.

potential at the maximum anodic current is found to be 100 mV vs. SCE. A chronoamperogram for holmium, for example, is illustrated in Figure 4.

The values of peak current for the oxidation of DTPA in the absence and presence of the rare earth ions are plotted with concentration of the rare earth ions, Tm, Ho, and Yb are shown in Figure 5. A linear relationship is shown between the peak current and the concentration of the rare earths. The detection limit is 0.5 μg for the tested ions, such as Tm, Ho, Yb, Nd, Sm, Eu, and Gd.

In summary, we have demonstrated the concept of indirect amperometric detection of rare earth ions for flow injection analysis. The detection method can be applied to any metal ions by selecting proper complexing ligand and optimum detection potential. This method also removes the unnecessary step, of the removal of dissolved oxygen, which is a required step for cathodic detection methods. Although detection limit of this report is not comparable to that of spectrometric method a more sophisticated cell design and detection scheme with solid electrode will promise to lower the detection limit.

Acknowledgement. This work was supported by Ministry of Science and Technology of Korea.

References

1. K. Iwasaki, K. Fuwa, and H. Haraguchi, *Anal. Chim. Acta*, **183**, 239 (1986).
2. V. A. Fassel, In "The Rare Earths"; F. H. Spedding, and A. H. Daane, Eds.; Krieger Publishing, Huntington, N.Y., 1971, pp. 594.
3. M. D. Palmieri, J. S. Fritz, J. J. Thompson, and R. S. Houk, *Anal. Chim. Acta*, **184**, 187 (1986).
4. S. R. Kayasth, H. B. Desai, and M. Sankardas, *Anal. Chim. Acta*, **187**, 271 (1986).
5. X. Gao, and M. Zhang, *Anal. Chem.*, **56**, 1912 (1984).
6. V. T. Athavale, R. G. Dashaeshwar, and C. S. Paqdmrabla, *J. Electroanal. Chem.*, **11**, 291 (1966).
7. N. S. Hush and J. M. Dyke, *J. Electroanal. Chem.*, **53**, 253 (1974).
8. J. W. O'Laughlin, In "Handbook on the Physics and Chemistry of Rare Earths"; K. A. Gschneidner, and L. R. Eyring, Eds.; North-Holland, Amsterdam, 1979, pp. 355.
9. J. F. Boissonneau, M. J. Repellin, and A. Eglim, *Analisis*, **8**, 230 (1980).