I-24

RECENT DEVELOPMENTS IN THE ANALYSIS OF FLUORIDE

W. Selig

Lawrence Livermore National Laboratory, Livermore, CA (U.S.A.)

The advent of the fluoride ion-selective electrode (ISE) in 1966 considerably simplified the analysis of fluoride. Using this electrode, fluoride can be analyzed by (1) direct potentiometry (plots of emf vs log activity) and by (2) potentiometric titration vs fluoride-precipitating species. We recently reported that a graphite rod coated with poly(vinyl chloride) and dioctylphthalate can be a useful sensor for a large variety of potentiometric titrations, including that of fluoride vs La(III). However, because the organic coating will dissolve in nonaqueous media, this sensor could be used only in aqueous solution. We have investigated several types of graphite and metals as sensors in the potentiometric titration of fluoride in a partially nonaqueous medium. As expected, larger endpoint breaks than in an aqueous medium were thus obtained. The largest endpoint breaks were obtained with vitreous carbon, pyrolytic graphite, and platinum sensors, but none were as large as those obtained with the fluoride ISE. Conditioning in neutral permanganate significantly enhanced the breaks for all types of graphite, with the exception of vitreous carbon. While for most types of graphite this increase was in no case larger than twofold, it was more than sevenfold for high-density graphite. The break obtained with a platinum sensor can be enhanced by the application of a polarizing current of -2.0 μA. Pyrolytic graphite responds only in the ab plane and not at all in the c plane. A semi-quantitative study still in progress showed that any kind of conducting material seems to respond as an endpoint sensor in the titration of fluoride vs La(III). Surprisingly, every ISE used, and every metal rod used responded in the titration. This includes such sensors as a glass (pHO electrode, sodium electrode, copper rod, "lead" pencil, and some common kitchen utensils. All sensors investigated were considerably less expensive than a fluoride I SE and some may serve as suitable alternates. Obviously, none can be used in the direct potentiometric measurement of fluoride. Many, although not all, of the sensors tested showed a transient response to La(III). In retrospect, we should like to state that the potentiometric titration of fluoride would have been feasible well before the invention of the fluoride ISE in 1966, had the proper materials been examined.

This work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory Under Contract W-7405-Eng-48.