Letters to the Editor

Anomalous chemiluminescence in reaction of uranium(IV) with xenon difluoride at low uranium concentrations

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Chemiluminescence in the reaction of uranium(IV) with xenon difluoride in acid aqueous solutions is characterized by a rather high excitation yield of the order of 0.1. This makes it possible to visualize the glow and to detect it at uranium concentrations of at most 10^{-9} mol L^{-1} despite a relatively low yield of chemiluminescence of uranyl ions (emitter of chemiluminescence).[1—3] But in the studies of the reaction at lower uranium concentrations (at most 10^{-10} mol L^{-1}) we observed an unusual phenomenon, namely, a decrease in the uranium(IV) concentration from one run to another led to an increase rather than a decrease in the chemiluminescence intensity (as could be expected). Moreover, in a blank run carried out without adding uranium(IV) we obtained the same kinetic curve of chemiluminescence decay as that characteristic of the reaction of uranium(IV) oxidation by xenon difluoride. The chemiluminescence intensity decreased gradually only after repeated cycles that included keeping the cell in concentrated hydrochloric acid, washing with water, and drying in an oven. Storage of the cell in 30% H_2O_2 also had almost no effect. After the cell was repeatedly (five to ten times) treated with xenon difluoride, washed, and dried, the chemiluminescence intensity was identical to the background chemiluminescence intensity due to the decomposition of xenon difluoride. This was not observed at high uranium concentrations (10^{-8} mol L^{-1} and higher).

We can assume that the anomalous behavior of chemiluminescence at low uranium concentrations is due to an increasing role of sorption processes and to other mechanisms of the reaction on the glass surface. Indeed, the concentration of xenon difluoride (oxidant) present in solution is a few mmol L^{-1}. Probably, it is important that XeF_2 reacts with silicate in the course of hydrolysis, thus deforming the glass surface and favoring "incorporation" of uranium ions into the near-surface layer in such a fashion that attempts at desorbing uranium using conventional techniques are failed.

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