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Ultramicrodetermination of Iridium by an Automatic Reaction-Rate Method

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With 2 Figures

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Many periodate oxidations are susceptible to trace metal catalysis and these are useful for the determination of very small amounts of catalysts or promoters such as chromium\textsuperscript{1}, copper\textsuperscript{2}, iridium\textsuperscript{3}, manganese\textsuperscript{4–6}, osmium\textsuperscript{7} and ruthenium\textsuperscript{8}, as well as activators\textsuperscript{6,8,10} or inhibitors\textsuperscript{2,6}.

In a study of periodate reactions, we have found that most of the periodate reactions with various reductants such as mercury(I), antimony(III), vanadium(IV), iron(II), and bromide, chloride, ferrocyanide, sulphide, nitrite and hypophosphite\textsuperscript{6} ions were highly accelerated by trace amounts of iridium ions, in the ppb range. In the present paper, a kinetic spectrophotometric method for the ultramicrodetermination of iridium(III) is described, based on the accelerating effect of iridium(III) on the periodate photodecomposition. In this method, the time required for the photodecomposition of periodate to consume a fixed amount of periodate, and thus for the absorbance to decrease by a preselected amount, is measured automatically with a solid state "double-switching" network\textsuperscript{8,11} and related directly to the iridium concentration.

The automatic procedure is rapid, accurate, precise and simple. The sample is pipetted into the reaction cell containing the buffer, sodium periodate is injected, the start button is pressed and the data is read off a dial shortly after the start. Ultramicroamounts of iridium in the range 80–800 ng (1.0 \times 10^{-7}–1.0 \times 10^{-6} M) were determined with an accuracy and precision of about 2%.
Experimental

Instrumentation

The apparatus was the same as previously described. The "double-switching" network was adjusted to measure the time required for the recorder pen to cross preselected positions in the chart, corresponding to 0.84 and 0.75 absorbance units.

Reagents

All solutions were prepared in twice-distilled deionized water from reagent grade materials.

Sodium metaperiodate stock solution, 0.100 M. As described previously. Prepare more dilute solutions daily by dilution.

Phosphate buffer 1 M, pH 7.10. Dissolve 138 g of NaH$_2$PO$_4$·H$_2$O in water, neutralize with 5 M NaOH to a pH of 7.10 and dilute to 1 l.

Iridium standard solution. Dissolve 248.2 mg of [NH$_4$]$_3$IrCl$_6$·H$_2$O in 1 l of water; this stock solution contains 100 ppm of iridium.

All working standards, reagent solutions and samples were kept in a water bath at 24.5 ± 0.1 °C.

Procedure

Preparation of equipment. As described previously.

Preparation of iridium standards and samples. As described previously. Three standards — 20, 100 and 200 ppb of Ir, prepared by dilution from an 1-ppm Ir solution which has been boiled for 0.5 hr — are used for the construction of the calibration graph.

Measurement step. Determination of iridium. Into the thermostated reaction cell kept at 24.5 °C, pipet 1.00 ml of buffer and 4.00 ml of sample or standard iridium solution. Inject 0.100 ml of 0.015 M sodium periodate solution into the cell using a 0.1-ml Hamilton syringe, close the compartment and press at once the Start button on the U. D. I. The measurement is completed automatically and the number on the U. D. I. is recorded. Press the Reset button and empty the cell with suction. Repeat the procedure for each analysis.

Results and Discussion

Basic considerations concerning reducing and oxidizing agents, contamination, control of experimental conditions, and preparation of calibration graphs are similar to those previously reported. The