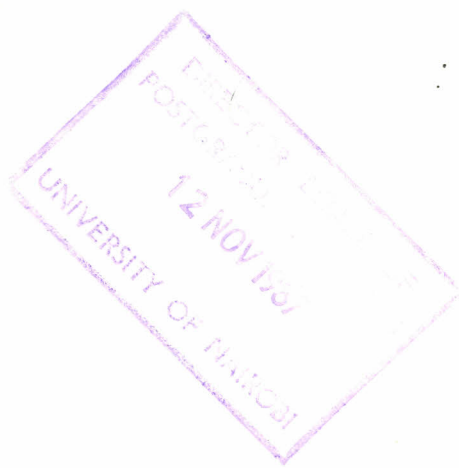


STUDIES ON INDICATOR REACTIONS FOR
CATALYTIC DETERMINATION OF TRACE
CONCENTRATIONS OF CATIONS



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A thesis submitted in partial fulfilment for
the degree of Master of Science in the
University of Nairobi.

1986

ABSTRACT

The suitability of indigo carmine - iodate and methylene blue-bromate reactions in acidic media as indicator reactions for determination of trace concentration of cations was studied spectrophotometrically.

The two substrates Indigo Carmine (λ_{\max} 610 nm $\log \epsilon$ 3.8) and methylene blue (λ_{\max} 665 nm $\log \epsilon$ 4.95) were chosen as reductants due to their sharp absorption peaks in the visible region.

1. Indigo Carmine Acidic Iodate Reaction

To elucidate the mechanism of the reaction the detailed kinetics of the reaction between indigo carmine (IC) and iodate in acidic media were studied at 25°C, monitoring the depletion of IC at 610 nm. It was found that the order of the reaction with respect to IC and iodate was unity and two with H^+ ion. The effect of neutral salts and different cations on the reaction rate was studied and Ruthenium (III) was found to have significant catalytic activity. Hence the kinetics of Ru(III) catalysed IC-iodate reaction in acidic media was studied in detail. The orders with

respect to each reactant and catalyst were determined. It was observed that the orders with respect to the catalyst, IC and iodate was unity and two with respect to H^+ ion.

Suitable mechanisms for both the uncatalysed and Ru(III) catalysed reaction were proposed based on the kinetic results. The effect of ionic strength and the presence of different cations on the Ru(III) reaction was studied. A method for determination of Ru(III) in the presence of other cations using its selective catalytic efficiency on the reaction is described.

2. Methylene blue - Acidic Bromate Reaction

In preliminary investigation it was observed that consumption rate of methylene blue (MB) increased with time indicating the presence of competitive, consecutive and autocatalytic steps. Hence the MB-acidic bromate reaction was chosen for studies to check its suitability, as an indicator reaction for determination of trace concentration of cations.

The kinetics of the uncatalysed reaction was studied monitoring the depletion of MB at 665 nm and taking pseudo excess of H^+ and

bromate ions. The log absorbance-time plot were linear for initial conditions. The orders of the reaction for the initial conditions with respect to each reaction were determined. The total order was found to be four, one each with respect to MB and bromate ion and two with respect to H^+ ion. Bromide ion was found to have considerable effect on the reaction behavior. The effect of different cations was studied and Fe(II), V(V) and Os(VIII) were found to have some catalytic effect on the catalytic reaction while other cations exerted little influence. The kinetics and mechanism of the V(V) catalysed MB-acidic bromate reaction were studied. The reaction orders with respect to MB, bromate ion and catalyst was one each and two with respect to H^+ ion. Based on the experimental results suitable mechanisms both for the catalysed and uncatalysed reactions were suggested. Calibration curves for catalytic determination of the individual cations Fe(II), V(V) and Os(VIII) were drawn and a method for determination of V(V) in presence of Fe(II) and Os(VIII) is reported.