



A Spectrophotometric kinetic method for estimation of cadmium in trace level of concentrations

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Abstract

A method for the estimation of cadmium in catalytic concentrations (2×10^{-7} to 2×10^{-5} M) had been developed by measuring its catalytic effect on the auto oxidation rate of ammonium sulphite. Measurements have been done on the homogenous reaction rates by the thermal-flow method. The rate of reaction is followed by monitoring the temperature change along the flow path by sensitive thermocouples and the degree of conversion is calculated from the temperature change and the known heat of reaction. On the basis of the experimental results for the catalysed reaction, the following rate expression is derived:

$$-d[\text{O}_2]/dt = k'[\text{O}_2]^0 [\text{SO}_2]^{3/2} [\text{Cd}^{+2}]^{1/2}$$

Where k' is rate constants of intermediate steps involving free radicals. This simple dependence of rate on the Cadmium concentration leads to developing a kinetic method for estimating Cadmium concentration from its catalytic effect on this particular reaction. For a fixed initial $[\text{SO}_3^{2-}] = 0.06$ M and $[\text{O}_2] = 0.002$ M the plot of rate of oxidation versus Cadmium concentration is linear with a slope of 0.05 for Cadmium concentration varying from 2×10^{-7} M to 2×10^{-5} M. The method is sensitive up to 10^{-7} M concentration and the maximum error is approximate 3.4%.

Keywords: spectrophotometer, kinetics, oxidation, cadmium, ammonium sulphite.

Introduction

Cadmium a pollutant in natural and waste water, can be estimated in very low concentrations by atomic absorption and atomic fluorescence spectrometry^{1,2}. These are highly sensitive techniques (10^{-6} to 10^{-8} M Cd^{++}). Microgram quantities of Cadmium have been determined in water by extraction of its metal complex with ammonium pyridine dithiocarbamate in to methyl iso butyl ketone^{3,4}. Ion selective electrodes are now available for determination of Cadmium in the concentration range 10^{-5} to 10^{-6} M

In the present paper we describe a sensitive kinetic method for the estimation of Cadmium in natural or waste water. The employment of catalysed reactions for trace analysis has attracted the attention of analytical chemists during recent years. In many homogenous reactions⁵ involving catalytic species the rate of the

reaction is usually a simple function of the concentration of the catalyst or the inhibiting agent. The rates of such reactions may be extremely sensitive to the presence of the catalyst because, in general, the catalytic agent is not consumed in the reaction but participates in the reaction pathway in a cyclic manner. The development of methods for studying fast reactions makes the techniques applicable for extremely low concentrations⁶⁻⁷.

The kinetics and mechanism of auto oxidation⁸ of sodium sulphite⁹⁻¹¹ in aqueous solution have been investigated by many workers. But rate data for oxidation of ammonium sulphite¹² have been obtained. In this work the oxidation of ammonium sulphite in the absence and presence of Co^{++} ions has been investigated¹³. The auto oxidation reaction has been used for determination of Co^{++} present in this system in amounts as low as 2×10^{-7} M. the reaction was followed by the flow thermal method¹⁴⁻¹⁶, which involves the indirect measurement of the temperature along the flow path due to heat of reaction. The extent of conversion is calculated from this temperature change and the known heat of reaction¹⁷.

Materials and Methods

The essential details of the apparatus have been described elsewhere, but a brief description of the same will be pertinent. The basic features are: (1) The thermostated reactant twin storage tanks made of plastic lined stainless steel; (2) the mixing chamber and (3) the 24 gauge cadmium constantan thermocouples inserted in the mixing chambers and at appropriate positions along flow path of the reactor. The probes (2) and (3) were made entirely of plastic material in order to avoid contamination by metallic parts.

The two reactants entered the mixing chamber from opposite sides in the form of jets and the measurement of difference in temperature between the mixing chamber and the various locations along the reactor were recorded by means of a calibrated micro voltmeter. The whole equipment was assembled and standardised using previously investigated sodium hydroxide carbon dioxide system of known enthalpy of reaction. The average of second order rate constants at 30°C calculated from these trial runs agree with in 5% with the value reported.

All experiments were carried out $30^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ and an ionic strength of 0.1 M (NaClO_4). The PH was maintained at 8.5 ± 0.05 by careful addition of caustic soda. No buffers were used for fear of complicating the mechanism due to the presence of additional chemical species in the reacting system. Doubly distilled water further deionised by passing through a mixed bed ion exchange column was used for preparing all solutions.

Before each run, the oxygen solution was prepared by bubbling oxygen in to water contained in one of the feed tanks after scrubbing through solutions of caustic soda, sulphuric acid and water. The amount of dissolved oxygen in water was determined by the Winkler's method¹⁸.

Ammonium sulphite of desired concentration was charged in to the second tank. The sulphite concentration was determined by titration with alkaline iodine- iodine solution. For the catalysed runs, the Cadmium sulphate catalyst was added in equal strength to both storage tanks from a stock solution of known concentration. Sodium perchlorate was added to both the tanks to maintain an ionic strength of 0.1 M. The reactant solutions were driven by nitrogen gas pressure in to the reactor through the mixing chamber. As the reaction proceeds, temperature rises along the reactor tube and this rise was measured by the Cd-Cd thermocouples at chosen locations. The plots of potentials difference versus time of reaction were linear and the rate of reaction, expressed as rate of oxygen consumption, was calculated from the slopes of such linear plots.

Result and discussion:

Figure 1 shows the plots of temperature difference as a function of residence time in two typical runs. Such plots are linear with different slopes up to the point where oxygen was completely consumed. The rate of reaction was calculated from the heat of reaction and the slope of such linear plots. The standard enthalpy of reaction of oxidation of ammonium sulphite is $138.5 \text{ kcal mol}^{-1}$ of oxygen reacted.

The average initial concentration of each reactant was calculated by multiplying the stock solution concentration with the ratio of its flow rate to total flow rate. The temperature rise corresponding to each micro volt reading was calculated from the temperature calibration curves of the thermocouples described above.

The results of measurement of rate data for the uncatalysed and catalysed reaction are given in table 1 and 2 respectively. A plot of $\log(\text{rate})$ versus $\log[\text{SO}_4^{2-}]$ (not shown) shows a linear dependence with a slope equal to 1.5, while the reaction is independent of the dissolved oxygen concentration. An important observation in the case of catalysed reaction is that a plot of $\log(\text{rate})$ versus $\log[\text{Cd}^{++}]$ is linear with a slope equal to 0.5. These observations lead to the rate expression (1) and (2) for the uncatalysed and catalysed auto-oxidation of ammonium sulphite respectively.

Table 1: calculated data for uncatalysed kinetic runs for $(\text{NH}_4)_2\text{SO}_3\text{-O}_2$ system: effect of reactant concentrations

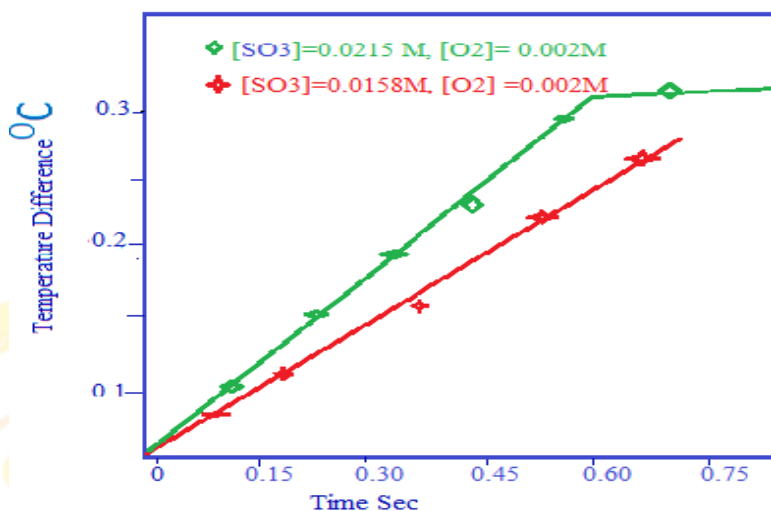


Fig.1 Plots of temperature difference versus residence time

[Reactant temp. = $30^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$, $\mu = 0.1\text{M}$]

$[\text{SO}_3^{2-}]$ M	$[\text{O}_2]$ M	Rate (mol sec^{-1})	Rate constant ($\text{lit}^{1/2} \text{mol}^{-1/2} \text{sec}^{-1}$)
0.0350	0.002	8.75×10^{-3}	1.40
0.0250	0.002	4.93×10^{-3}	1.30
0.0150	0.002	2.28×10^{-3}	1.15
0.0115	0.002	1.50×10^{-3}	1.22
0.0075	0.002	1.05×10^{-3}	1.48
0.0035	0.002	1.22×10^{-4}	1.30
0.0310	0.00315	7.32×10^{-3}	1.40
0.0310	0.00215	7.15×10^{-3}	1.40
0.0310	0.00125	7.22×10^{-3}	1.39
0.0085	0.00305	9.40×10^{-4}	1.32
0.0085	0.00078	10.15×10^{-4}	1.40
0.0085	0.00048	9.35×10^{-4}	1.32
0.0035	0.00308	2.05×10^{-4}	1.28
0.0035	0.00094	1.90×10^{-4}	1.20
0.0035	0.00032	2.05×10^{-4}	1.25

*Calculated from equation (1); average of at least three runs.

[Av. = (1.34 ± 0.09)]

Table 2 calculated data for catalysed kinetic runs for the $(\text{NH}_4)_2\text{SO}_3\text{-O}_2$ system: effect of reactant and catalyst concentrations

[Reaction Temp. = 30° ±0.50c; μ = 0.1 M]

[SO ₃ ²⁻]M	[O ₂]M	[Cd ²⁺] M	Rate (mol sec ⁻¹)	10 ⁴ rate constant (lit mole ⁻¹ sec ⁻¹)
0.0370	0.0020	1x10 ⁻⁶	7.75x 10 ⁻²	1.10
0.0188	0.0020	1x10 ⁻⁶	2.65x10 ⁻²	1.05
0.0085	0.0020	1x10 ⁻⁶	9.60x10 ⁻³	1.25
0.0060	0.0020	1x10 ⁻⁶	5.20x10 ⁻³	1.16
0.0040	0.0020	1x10 ⁻⁶	2.25x10 ⁻³	1.03
0.060	0.0030	1x10 ⁻⁶	5.12x10 ⁻³	1.16
0.060	0.0020	1x10 ⁻⁶	5.20x10 ⁻³	1.15
0.060	0.00120	1x10 ⁻⁶	5.12x10 ⁻³	1.15
0.060	0.00057	1x10 ⁻⁶	5.20x10 ⁻³	1.14
0.060	0.0020	2x10 ⁻⁷	2.30x10 ⁻³	1.15
0.060	0.0020	5x10 ⁻⁷	3.65x10 ⁻³	1.15
0.060	0.0020	1x10 ⁻⁶	5.20x10 ⁻³	1.16
0.060	0.0020	3x10 ⁻⁶	9.02x10 ⁻³	1.18
0.060	0.0020	9x10 ⁻⁶	1.55x10 ⁻²	1.18
0.060	0.0020	2x10 ⁻⁶	2.35x10 ⁻²	1.18

Average= (1.140 ± 0.055) x 10⁴

*Calculated from equation (2); average of at least three runs.

$$\text{Rate} = -d[\text{O}_2]/dt = k[\text{SO}_3^{2-}]^{3/2}[\text{O}_2]^0 \dots\dots\dots (1)$$

$$\text{Rate} = -d[\text{O}_2]/dt = k'[\text{SO}_3^{2-}]^{3/2}[\text{O}_2]^0 [\text{Co}^{2+}]^{1/2} \dots\dots\dots (2)$$

Where k and k' are observe rate constants made up of rate constant of intermediate steps probably involving free radicals. Table 1 and 2 also include the values of these rate constants calculated from equation 1 and 2. The near constancy of these values confirms that the rate expressions 1 and 2 are essentially correct.

A notably feature of this study is the significant effect of the added Cadmium ion concentration on the rate of the catalysed reaction. The addition of a very low concentration (10⁻⁶M) of Cadmium increases the rate by about ten times under identical experimental conditions (table1 and 2). Catalytic effect may be seen up to 1x 10⁻⁷ M in the low concentration limit. But when the concentration of the catalyst is increased from 2x 10⁻⁵M to 10⁻⁴M, Cadmium chows no further catalytic effect on the rate. Calculation shows that the ionic product of Cd²⁺ and OH⁻ at pH 8.5 would exceed the solubility product of Cadmium hydroxide. Limited solubility of Cadmium hydroxide may thus account for the absence of further catalytic effect on the rate at concentrations above 2x10⁻⁵M. An important observation on the lower limit of determination may be made. Although it may be possible to go below the concentration of 2x10⁻⁷M of Cadmium, it would be necessary to ensure that no catalytic species such as Cd²⁺ ions are present in the reagents or water used for making the solutions. Atomic absorption failed to detect any catalytic impurity in water used at this low level (~10⁻⁶M) and neutron activation analysis failed to detect impurities in solid ammonium sulphite of AR grade.

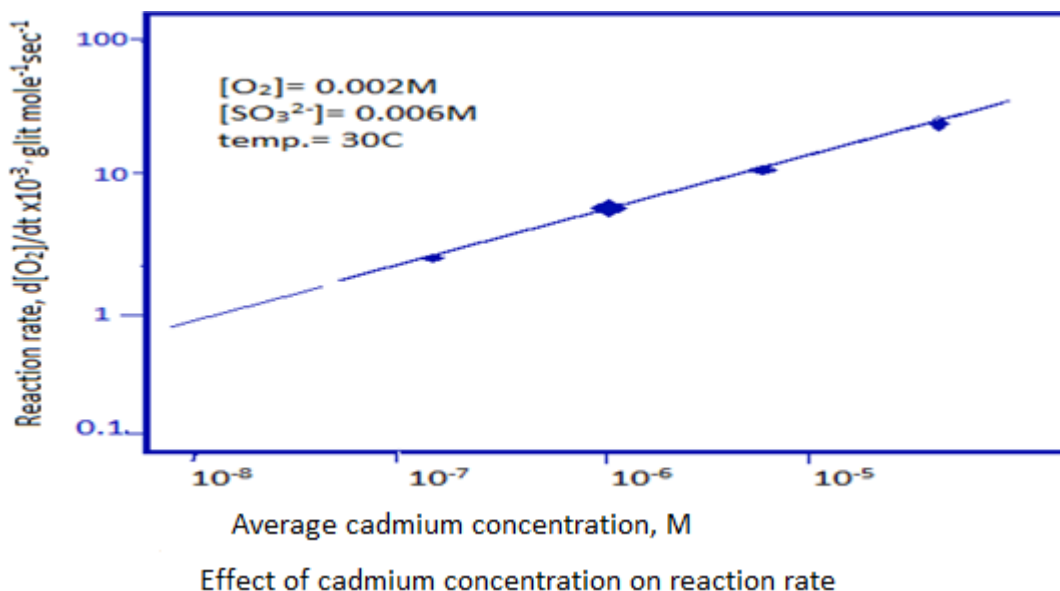


Table 3- computation of error in the proposed kinetic method for Cadmium estimation

[Cd ²⁺] (M) added	[Cd ²⁺]M found	Error(%)
2.0x 10 ⁻⁵	1.98x10 ⁻⁵	-1.0
9.0x10 ⁻⁶	8.92x10 ⁻⁶	-1.0
3.0x10 ⁻⁶	2.95x10 ⁻⁶	-2.1
1.0x 10 ⁻⁶	1.005x10 ⁻⁶	0.4
1.0x 10 ⁻⁶	1.03x10 ⁻⁶	3.0
1.0x 10 ⁻⁶	1.002x10 ⁻⁶	0.2
1.0x 10 ⁻⁶	0.994x10 ⁻⁶	-0.6
1.0x 10 ⁻⁶	1.033x10 ⁻⁶	3.3
1.0x 10 ⁻⁶	0.997x10 ⁻⁶	-0.3
1.0x 10 ⁻⁶	0.987x10 ⁻⁶	-1.3
1.0x 10 ⁻⁶	0.997x10 ⁻⁶	-0.3
5.0x 10 ⁻⁷	4.96x10 ⁻⁷	-1.25
2.0x 10 ⁻⁷	1.95x10 ⁻⁷	-2.0

*Calculated from rate data and average experimental rate constant of catalysed reaction.

The uncatalysed oxidation rates observed in the present investigation are faster than those reported by Matsura et al., who were working with extremely pure reagents. A catalytic level impurity of 10⁻⁸ M in this work is not unexpected and is, in fact, indicated by extrapolation of curve in graph to the point where the catalysed rate equals the uncatalysed rate at comparable concentration of ammonium sulphite.

Finally, the authors have demonstrated that the auto oxidation rate of ammonium sulphite in the presence of Cadmium ion may be used for determination of Cadmium ions in the concentration range of 2x 10⁻⁵ to 2x 10⁻⁷ M. the flow thermal method can be conveniently used to follow this reaction. The maximum error of the method is about 3.3% (table 3) and a sensitivity level of about 1x10⁻⁷M catalyst, which is well below most chemical methods.

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