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MICRO-REVIEW

Recent Developments in Kinetic Methods for Trace Constituents

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"Kinetic Method of Analysis" is a newly growing field in the area of analytical chemistry. During the past decade considerable efforts have been directed towards developing increasingly sensitive methods for the determination of trace constituents. Because of their high sensitivity, kinetic-catalytic methods have been recognized as offering a valuable approach to trace analysis. Many methods have been reported for kinetic determination of inorganic species like mercury, copper and nitrite, and also a few for organic species, based on their catalytic effect on ligand substitution or oxidation reactions. This micro-review covers in brief the salient features of the methodology called "Kinetic Methods of Analysis" as applied to trace determination of various species.

Key Words: Kinetic, Analytical methods, Trace constituents.

Many transition metal ions are known to be essential for life and are involved in specific biological functions. However, if present beyond a threshold concentration the same metal ions become toxic. There is another class of metal ions, which are very toxic to animal and plant life even in very minute concentration. The assessment and control of these health hazards is now considered an important social responsibility of governmental and international agencies.

The development of methods for detection, estimation and removal of pollutants has recently become an active field of analytical chemistry. This has resulted in the emergence of a new era of research called the "kinetic method of analysis". These are now ranked only next to radiochemical methods, mass spectrometry, atomic absorption and X-ray fluorescence spectrophotometry,. The kinetic method of analysis is also called as "reaction rate method" and offers some distinct advantages over the conventional analytical methods, such as simplicity, specificity, accuracy and economy.

A good deal of work has been done by Russian chemists[1–4] since the early stages of this field. Then follow the American[5–7] and Japanese workers[8, 9]. In Spain, important developments have been made by Perez-Bendito[6, 10, 11]. In India, research in this area has been carried out by the research group of Nigam[12–14] and the author of this article[15, 16]. Very recently, Chinese researchers have been doing a good deal of work in this field.[17, 18]. Few others[19, 20] made important contributions

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as judged by published work. In Fiji, research in this area has been initiated by Prasad and his research students[21, 22].

Reaction rate techniques have been used by all the workers in the development of kinetic analytical methods for inorganic and organic compounds and compounds of biological importance in a variety of complex samples[1-20]. The number of kinetic methods has increased considerably in the past few years. Under suitable and carefully controlled experimental conditions (*i.e.*, when substrate concentrate is large and other concentration terms are held constant during the course of a kinetic run), the rate can be shown to be related to the initial concentration of the catalyst by an expression of the form

$$\frac{dx}{dt} = F[C]_0 + F'$$

where the first term on right hand side represents the rate of the catalysed path (which is a simple function of the initial concentration of the catalyst $[C]_0$ and F' represents the rate of uncatalysed path. The linear plot between observed rate and catalyst concentration can serve as a calibration curve for determination of unknown concentration of a catalyst. Depending upon the magnitude of rate constant and the extent to which the reaction is followed, the time of analysis may range from fraction of seconds to several minutes. There are many possible variations of the procedure, which may be followed depending upon convenience.

The kinetic methods can also be applied for the determination of activators or inhibitors for a chosen indicator reaction. The author has established kinetic methods for estimation of catalysts, activators and inhibitors. This method can be extended to uncatalysed reactions for determination of substrates though the sensitivity is usually less than that compared to catalysed reactions.

It would be convenient to discuss some determinations from literature to illustrate the technique:

(a) **Determination of mercury:** Use is made of the catalytic effect of Hg^{2+} on the rate of reaction of potassium ferrocyanide with *p*-nitrosodiphenylamine—a very slow reaction in the absence of the catalyst. Under suitable conditions, the rate of reaction can be correlated to $[Hg^{2+}]$. A calibration curve between absorbance of the colour product of reaction after a fixed time was shown to be proportional to $[Hg^{2+}]$. As low as 8×10^{-7} M concentrations of Hg^{2+} were analysed[12].

(b) In another reaction system advantage is taken of the observation that the rate of displacement of cyanide in hexacyanoferrate(II) by N-methylpyrazinium ion is directly related to mercury concentration under carefully chosen experimental conditions. After a detailed study of mechanistic anatomy of the reaction the following relationship has been shown to hold good:

$$\frac{d[Fe(CN)_5Mpz^{2-}]}{dt} = k'[Fe(CN)_6^{4-}] + k_2'[Hg^{2+}]$$

The initial rate is determined by the fixed time procedure in which absorbance change is recorded within 15 min after time of mixing. The above equation finally yields a relationship between absorbance change after 15 min and concentration of mercury as

$$A_{15} = 5.4 \times 10^4[Hg^{2+}] + 0.0058$$

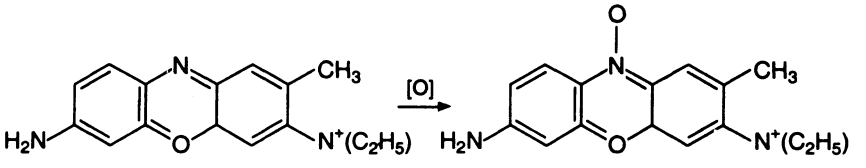
Under specified conditions the detection limit is found to be 1×10^{-8} M and average standard deviation from the least square fit plot is 1.7%. The effect of the presence of various interfering and non-interfering ions is discussed[24].

(c) **Determination of copper:** Copper has been shown to catalyse the reaction of hexacynoferrate(III) with cysteine. The catalysed reaction is much faster than uncatalysed reaction. The reaction is followed at 420 nm corresponding to the absorption band of hexacynoferrate(III). There is a direct proportionality between $[Cu^{2+}]$ concentration and the absorbance at fixed time. Cu^{2+} can be determined even at as low as 2×10^{-8} M concentration[23].

(d) **Determination of carminic acid:** The stopped-flow mixing technique has been used to develop a simple and fast kinetic method for the determination of carminic acid based on its inhibitory effect on the fluorescence intensity of the europium(III)-diphacinone-ammonia system in the presence of triton X-100.

Analytical data can be obtained within 10 s after the reactants are mixed, which minimizes manipulation and enables the ready application of the proposed method to routine analyses for carminic acid in orange soft drinks. The dynamic range of the calibration graph is 0.5–15 μg mL^{-1} and the relative standard deviation less than 4%. The analytical recoveries have been tested by applying the method directly to the analysis of samples[11].

(e) **Determination of nitrite:** A catalytic kinetic procedure for nitrite determination based on its catalytic effect on the oxidation of brilliant cresyl blue (BCB) by bromate ion in acidic media is developed[22].



BCB Colourless product

The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of BCB at its λ_{max} 595 nm. The kinetic rate equation for the oxidation of BCB can be given by the equation

$$d[BCB]/dt = k_1 + k_1'[NO_2^-]$$

where k_1 are k_1' are composite rate constant.

Calibration graph was obtained by applying the *fixed time* method under the optimum conditions. A plot of the absorbance changes after 4 min, *i.e.*, ΔA_4, *vs.* nitrite concentration in the reaction mixture is linear in the range of 1–80 ng mL^{-1} $[NO_2]$. The linear regression equation relating *initial rate*, ΔA_4 to $[NO_2^-]$ up to 80 ng mL^{-1} is given by the following equation

$$\Delta A_4 = 0.0159[NO_2^-] + 0.0145$$

which is in agreement with the proposed rate equation.

The detection limit is 5.8 ng mL^{-1} of nitrite. Nitrite in the range of 10–80 ng mL^{-1} has been determined successfully where recoveries were 97.3–103.7% with the relative standard deviation 0.1–0.8%. The typical feature of this procedure is that the determination could be carried at a normal temperature of 25°C with analysis time of 4 min.

Whereas kinetic methods of analysis have been reported for many cations present in the atmosphere, few methods for anions have been reported. There is much scope for investigations in this field and for search of newer reacting systems with the object of development of differential kinetic methods for simultaneous determination of more than one component present in a mixture. So far not much effort has been directed towards utilization of fast reacting systems for kinetic methods of analysis. It is possible to use the stopped-flow spectrophotometer and T-jump technique for monitoring rates of fast reactions. Use of T-jump will enable us to study the chemical processes of half-lives less than a fraction of microseconds.

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