

Application of chemometric methods to the simultaneous kinetic spectrophotometric determination of iodate and periodate based on consecutive reactions

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Abstract

A kinetic spectrophotometric method for the simultaneous determination of iodate and periodate in mixtures was proposed. The method is established on the different kinetic behaviours of the analytes which react with starch–iodide in the presence of sodium chloride in sulfuric acid medium. The kinetic data were collected from 260 to 900 nm every 10 nm, within a time range of 0–180 s at 1 s interval, and the absorbance collected at 291, 354 and 585 nm, respectively, increased linearly with the concentration between 0.1–1.2 mg L⁻¹ for both iodate and periodate. The mechanism investigation revealed that the iodate/periodate–iodide–starch system is a consecutive reaction. Subsequently, the mathematical model for the quantitative kinetic determination based on the consecutive reactions by utilizing chemometric methods was deduced, and the simultaneous determination of synthetic mixtures of iodate and periodate was then applied. Kinetic data collected at 291, 354 and 585 nm, were processed by chemometric methods, such as classical least square (CLS), principal component regression (PCR), partial least square (PLS), back-propagation artificial neural network (BP-ANN), radial basis function–artificial neural network (RBF-ANN) and principle component–radial basis function–artificial neural network (PC-RBF-ANN). The results showed that calibration model with the data collected at 354 nm had some advantages for the prediction of the analytes as compared with the ones of other two wavelengths, and the PLS and PC-RBF-ANN gave the lower prediction errors than other chemometric methods. The proposed method was applied to the simultaneous determination of iodate and periodate in several real samples; and the standard addition method yielded satisfactory recoveries in all instances.

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1. Introduction

Iodine species, such as iodate and periodate, due to their special functions as an essential micronutrient, marker of geochemically or biologically active processes, hazardous contaminant (in the form of radionuclides), and so on [1], play an important role in biological and environmental fields. Therefore, their simultaneous determinations are significant, not only for a good knowledge of biological and chemical processes, but also for health and environmental protection [2–5]. Iodate and periodate have been simultaneously determined so far by spec-

trophotometry [6–9], spectrofluorometry [9] and capillary electrophoresis methods [10]. However, some of these methods are somewhat unsatisfactory for routine analysis as serious maintenance of the experimental conditions, (e.g. a strictly control of pH [6,7], an addition of mask reagent [8] and an addition of fluorescent reagent [9]), or a time-consuming enrichment step [10] were needed.

Multicomponent kinetic method can be an alternative for simultaneous determination of two or more analytes which have similar chemical properties without any prior separation. However, it has not been fully explored owing to some practical difficulties [11]. These conventional techniques, such as the logarithmic extrapolation and the proportional equation, are really dependent of the knowledge of the reaction order and rate constants for the chemical system which are not readily available [12].

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Recently, chemometric methods, especially multivariate calibrations and artificial networks, have been introduced to improve the performance in multicomponent kinetic determinations [13]. Moreover, the results obtained from two- or multi-dimensional data, which can be handled by chemometrics, are highly robust and reliable since more valuable and complete information can be extracted from the reaction process [14–16].

Generally, multicomponent kinetic methods are based on simple first-order or pseudo-first-order reactions [17,18]. However, consecutive reactions are one of the most frequently encountered complex reactions in chemistry and can often be found in metabolic processes of many organisms [19,20]. Therefore, the intermediate species, produced in the process of the consecutive reactions, generally play a vital role in understanding the mechanism of chemical reactions, and are important for elucidating the pharmacological actions of drugs in organisms.

Hsieh and Crouch have proposed a two-rate method for simultaneous determination of L-amino acid mixtures based on a consecutive enzyme catalyzed reactions [21]. In this system, the reaction rate of one analyte is determined by two-rate constants, k_1 and k_2 , so it is possible to enlarge the differences in reaction rates between these two analytes for simultaneous kinetic methods. The two-rate method is a good data processing method for consecutive reactions, because the kinetic curve can be divided into two parts, the first part is contributed by both k_1 and k_2 , the second part is mainly contributed by smaller rate constant of k_1 and k_2 [22]. Two rates measured in the two parts of the kinetic curve thus can exhibit the differences of k_1 and k_2 between two analytes to the largest extent. Cai et al. compared the performances among the two-rate method, the classical proportional equations method and the extension proportional equations method, and concluded that the two-rate method was the best one of the three methods [23,24]. They also compared the result based on detecting the reagent in consecutive reactions with that based on detecting the final product in consecutive reactions by use of the above-mentioned three methods, and found that the method based on detecting the reagent in consecutive reactions was better because it could easily be altered to give higher sensitivity and is more favorable when the second rate constant is smaller than the first one [24,25].

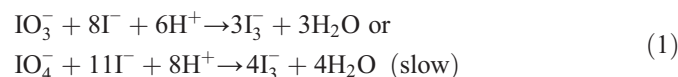
In this paper, a consecutive kinetic method for the simultaneous determination of iodate and periodate based on their reaction with starch–iodide in the presence of sodium chloride was developed. The absorbances at 291 and 354 nm, of the intermediate triiodide and the blue complex and those at 585 nm of the blue complex were collected. Furthermore, the reaction mechanism was investigated and the mathematical expressions for the quantitative kinetic determination of mixtures based on consecutive reactions with the aid of chemometric methods were also presented for the first time.

2. Theoretical background

2.1. Reaction mechanism

In the past 150 years, the reaction system of iodate/periodate–iodide–starch has been widely studied [26–32]. However, most of the reactions studied are simple one-step ones, either between iodate/periodate and iodide [27,28] or between iodine and starch

[29–32]. In this work, two simple one-step reactions will be combined and considered as a consecutive reaction. The reaction mechanism between iodate/periodate and iodide has been well established [27,28], but the mechanism for the simple reaction between iodine and starch, which gives the blue complex, is not fully understood. Considerable studies [30–32] have indicated that the blue complex results from two molecules of iodine, one molecule of iodide and one molecule of starch. And thus the following consecutive reaction paths are proposed:



For iodate and periodate have similar kinetic processes, the iodate–iodide–starch system is selected for the studies of the reaction mechanism in this paper.

When the reaction time is less than a certain time, t_1 , i.e. $t < t_1$, at which the concentrations of the produced intermediate iodine and triiodide ions are small enough, only reaction (1) will take place, and if the concentration of iodate is much smaller than the other reactants (iodide and hydrogen ion), i.e. $[\text{IO}_3^-] \ll [\text{I}^-], [\text{H}^+]$, reaction (1) can be considered as a pseudo-first-order kinetics, and thus, its rate equation can be expressed as following:

$$-d[\text{IO}_3^-]/dt = d[\text{I}_3^-]/3dt = K_1[\text{IO}_3^-] \quad (4)$$

where $[\text{IO}_3^-]$, $[\text{I}_3^-]$ and K_1 represent the concentration of the analyte iodate and the intermediate triiodide ion, and the rate constant of reaction (1), respectively.

Integration of Eq. (4) yields:

$$[\text{IO}_3^-]_t = [\text{IO}_3^-]_0 \exp(-K_1 t) \quad (5)$$

where $[\text{IO}_3^-]_0$ is the initial concentration of iodate and $[\text{IO}_3^-]_t$ is its concentration at time t .

Reaction (2) is very fast, and thus it is easy to reach equilibrium. Assume that the equilibrium constant, K_2 , is given and the iodide ion is in large excess in the reaction, the concentration of the intermediate triiodide ion, $[\text{I}_3^-]_t$, at time t can be written:

$$[\text{I}_3^-]_t = 3\Delta[\text{IO}_3^-]_t [\text{I}^-]_0 / (K_2 + [\text{I}^-]_0) \\ = 3[\text{IO}_3^-]_0 (1 - \exp(-K_1 t)) [\text{I}^-]_0 / (K_2 + [\text{I}^-]_0) \quad (6)$$

where $\Delta[\text{IO}_3^-]_t$ is the decrease of the iodate from $t=0$ to t , and $[\text{I}^-]_0$ is the initial concentration of the iodide. In addition, as mentioned above, reaction (3) will not take place in this case, and thus, the concentration of the blue complex at time t will be zero (i.e. $[\text{BC}]_t = 0$).

When the reaction time is larger than a time t_1 , i.e. $t > t_1$, the concentration of iodine is large enough to allow reaction (3) to proceed. If the concentrations of the triiodide ion and iodine are much smaller than iodide and starch, i.e. $[\text{I}_3^-], [\text{I}_2] \ll [\text{I}^-], [\text{starch}]$, reaction (3) can be also considered as a pseudo-first-order kinetics,

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