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Determination of Sulphite ions Using a Whole Curve of Kinetic Run and a Fixed Time Method and Applying Partial-Least Squares

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Abstract

Chemometrics has found very important place in conservation science due to abilities to provide very sensitive and selective methods of measurements which is of great importance to achieve non-destructive techniques desirable for conservation purposes. One of the analytical tools is kinetic methods which are of increasing importance due to their sensitivity and often high selectivity.

In this paper, the application of partial least squares regression method type 1 (PLS-1, Chemometrics Toolbox) to the determination of the sulphite ions using a sensitive, selective and simple kinetic method based on the reaction of sulphite with DCIP is described.

Introduction

One of the atmospheric pollutants is sulphur dioxide (SO_2). Dissolved SO_2 can then oxidize to form sulphite ($SO_3^=$) or sulphate ($SO_4^=$) species. The oxidation process results in the production of acid, which can cause the calcium carbonate ($CaCO_3$) in the stone to dissolve [1]. Sulphite corrosion is also the cause of damages in metallic objects, though it plays a treatment roll in stabilizing corroded iron objects. In papers made of sulphite pulp, amount of sulphite ions is very important in aging of the paper and effect of atmospheric sulphur dioxide on it [2]. Therefore measurement of sulphite ions is very helpful in many aspects of conservation and restoration of cultural properties and also helps to atmospheric analysis of sulphur dioxide and its effect on cultural objects (monitoring).

In recent two decades chemometrics methods have been frequently applied for determining of mixture of chemical species in many applications. The theory and application of PLS method, in kinetic based determinations, have been discussed by several authors [3-5].

Reported herein is a kinetic-spectrophotometric method using univariate and multivariate calibration approach for determination of sulphite ions through the addition reaction of sulphite with 2,6-dichlorophenolindophenol (DCIP) at pH = 7.0 and 25^0C.

Materials & Methods

All reagents were prepared from Merck analytical reagent grade. A 662-probe type photometer (Metrohm) and a model D1 thermostatically controlled bath (HAAKE) were used. The absorbance vs. time data from photometer were collected with a laboratory-written program, in QuickBasic, and transferred to a PC for subsequent manipulation by PLS1 program. A 5.0 ml portion of buffer solution (pH = 7.0), 0.7 ml of 1.2×10^{-3} M 2,6-dichlorophenolindophenol and 2.0 ml of 3.0 M KNO_3 were mixed and diluted to the mark in a 25.0 ml standard flask with water and transferred into a jacketed cell. The photometer's probe was then immersed into the solution and fixed by using a holder. The solution was equilibrated at 25?C while it was continuously stirring by a magnetic stirrer. After that, a given amount of sulphite was injected instantly, via a syringe with the

photometer on and the absorbance vs. time data were collected by the microprocessor. The change in absorbance of each solution at 600 nm was recorded in 1 second intervals (200 data points).

Results

The decrease in absorbance of DCIP at 600nm over a fixed time is proportional to the concentration of sulphite over the range of 0.10–2.0 ?g /ml. The detection limit and RSD% are 0.06 ?g /ml and 1.1% respectively. The experimental calibration matrix for PLS calibration method was designed with 20 samples. Cross-validation method was used for selection of the optimal number of factors and a plot of cumulative PRESS against the number of factors is shown in Fig. 1. The root mean square error of prediction (RMSEP) was obtained as 0.0053.
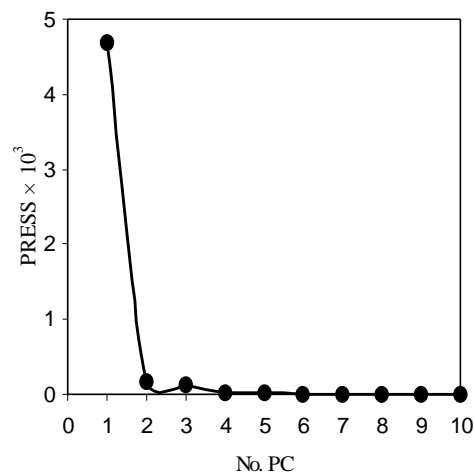

Fig. 1; Calibration of PRESS as a function of PLS-1 factors.

Conclusions

A simple multivariate calibration kinetic -spectrophotometric method for the determination of sulphite in spiked real matrix samples has been developed. Determination of sulphite based on the reaction of sulphite with DCIP with the PLS1 modelling was established, with good prediction ability in the spiked real matrix samples. As a final point, to combine PLS-1 multivariate calibration and spectrophotometric measurements constitutes a valuable tool toward the development of simple methods for monitoring sulphite in some matrixes.

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