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Analytical Methods

Simultaneous kinetic-spectrophotometric determination of maltol and ethyl maltol in food samples by using chemometrics

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Abstract

A fast and accurate procedure has been researched and developed for the simultaneous determination of maltol and ethyl maltol, based on their reaction with iron(III) in the presence of *o*-phenanthroline in sulfuric acid medium. This reaction was the basis for an indirect kinetic spectrophotometric method, which followed the development of the pink ferroin product ($\lambda_{max} = 524$ nm). The kinetic data were collected in the 370–900 nm range over 0–30 s. The optimized method indicates that individual analytes followed Beer's law in the concentration range of 4.0–76.0 mg L^{-1} for both maltol and ethyl maltol. The LOD values of 1.6 mg L^{-1} for maltol and 1.4 mg L^{-1} for ethyl maltol agree well with those obtained by the alternative high performance liquid chromatography with ultraviolet detection (HPLC-UV). Three chemometrics methods, principal component regression (PCR), partial least squares (PLS) and principal component analysis–radial basis function–artificial neural networks (PC–RBF–ANN), were used to resolve the measured data with small kinetic differences between the two analytes as reflected by the development of the pink ferroin product. All three performed satisfactorily in the case of the synthetic verification samples, and in their application for the prediction of the analytes in several food products. The figures of merit for the analytes based on the multivariate models agreed well with those from the alternative HPLC-UV method involving the same samples.

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1. Introduction

Maltol (3-hydroxy-2-methyl-4-pyrone), a naturally occurring substance, has been marketed as a food flavor enhancing agent (Ellis, 1972). Its synthetic homologue, ethyl maltol, which is approximately six times more effective than maltol (Rennhard, 1971), has been available since 1967. These compounds are often found as flavor enhancers in many foods such as coffee, soybeans, cereals, breads, malt beverages, and chocolate milk (Heath, 1978; Hui, 1991; LeBlanc & Akers, 1989). Maltol is tasteless at the recommended application doses, rather it modifies or enhances the flavors of the foods and beverages to which it is added. However, Gralla, Stebbins, Coleman, and Delahunt (1969) has reported some concerns regarding the biological health and safety of ethyl maltol. Therefore, the determination of these two substances in foods is clearly important, and methods, which can analyze quantitatively the two compounds simultaneously, would be of particular advantage.

Some high performance liquid chromatography with ultraviolet detection (HPLC-UV) and mass spectrometry (MS) have been reported for the determination of either maltol (Ferreira, Jarauta, Lopez, & Cacho, 2003) or ethyl maltol (Liu, Wang, Yang, & Yin, 2006; Wang, Liu, Yang, Tian, & Kou, 2006) in foods. However, the above noted techniques employ expensive instruments and/or materials, and high purity solvents. HPLC-UV methods require

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suitable compounds for internal standards, which add to the cost and complexity of the analytical procedure. Moreover, reports on the simultaneous determination of the two compounds in such samples are a few (Ni, Zhang, & Kokot, 2005; Peng, Ma, & Di, 2005).

Recent publications, which described the differential kinetic spectrophotometric methods coupled with chemometrics data of interpretation, have demonstrated the success of this approach for simultaneous analysis of similar substances (Crouch, Coello, Maspoch, & Porcel, 2000; Ni, Huang, & Kokot, 2004; Ni & Wang, 2007). In particular, these spectrophotometric methods can be increasingly applied for the simultaneous determination of two homologues in food and pharmaceutical samples (Abbaspour & Mirzajani, 2006; Blanco, Coello, Iturriaga, Maspoch, & Porcel, 1999; Chamsaz, Safavi, & Fadaee, 2007; Ni, Wang, & Kokot, 2007), because it is difficult for them to be quantitatively analyzed by traditional spectrophotometry because of their overlapping UV spectra. The principles and applications of the differential kinetic methods have been reviewed (Crouch, 1993; Quencer & Crouch, 1993). Essentially, in these methods similar analyte species react with a common reagent, and differences in the reaction kinetics are used to distinguish the components without any physical separation. Chemometrics techniques are used for the processing of kinetic data. Such an approach does not require a detailed kinetic model. This is a major advantage over the conventional techniques for processing kinetic data, because such techniques rely on an accurate kinetic model of the chemical system to obtain the order of reaction and rate constants.

In this work, a differential kinetic-spectrophotometric method has been investigated for the simultaneous analysis of the two analytes, maltol and ethyl maltol. The method relies on the different kinetic responses of maltol and ethyl maltol, which react with iron(III) in the presence of *o*-phenanthroline in the sulfuric acid medium. Calibration models were built from the kinetic data derived from the analyte mixtures, and with the aid of multivariate methods of analysis such as principal component regression (PCR), partial least squares (PLS) and principal component analysis–radial basis function–artificial neural networks (PC–RBF–ANN). These models were verified, compared and applied for prediction of analytes in real samples.

2. Methodology

2.1. Kinetic models

Consider two analytes, A and B, which react with a common reagent, R, to give the absorbing products, P_A and P_B, according to the following reactions:

$$A + R \rightarrow P_A \quad (1)$$

$$B + R \rightarrow P_B \quad (2)$$

Assume that the two reactions involved, follow first or pseudo-first order kinetics with respect to the analyte. Thus, the rate equations for A and B are

$$-\frac{dc_A}{dt} = k_A c_A \quad (3)$$

$$-\frac{dc_B}{dt} = k_B c_B \quad (4)$$

where c_A and c_B are the concentrations of analytes, A and B, at time t, and k_A and k_B are the corresponding rate constants.

Integration of Eqs. (3) and (4) yields

$$c_A = c_{A,0} \exp(-k_A t) \quad (5)$$

$$c_B = c_{B,0} \exp(-k_B t) \quad (6)$$

where $c_{A,0}$ and $c_{B,0}$ are the initial concentrations of analytes, A and B, respectively.

Given the stoichiometry between the analyte and product, the concentrations of P_A and P_B at time, t, can be represented as follows:

$$c_{P_A} = c_{A,0}[1 - \exp(-k_A t)] \quad (7)$$

$$c_{P_B} = c_{B,0}[1 - \exp(-k_B t)] \quad (8)$$

where c_{P_A} and c_{P_B} represent the concentrations of P_A and P_B at time, t, during the reaction process, respectively.

When the two analytes behave independently and the spectral absorbances of their products, i.e., P_A and P_B, are additive, the absorbance of a mixture of A and B may be written as

$$\begin{aligned} A &= A_{P_A} + A_{P_B} = \varepsilon_{P_A} b c_{P_A} + \varepsilon_{P_B} b c_{P_B} \\ &= c_{A,0}\varepsilon_{P_A} b[1 - \exp(-k_A t)] + c_{B,0}\varepsilon_{P_B} b[1 - \exp(-k_B t)] \\ &= K_A c_{A,0} + K_B c_{B,0} \end{aligned} \quad (9)$$

where ε_{P_A} and ε_{P_B} are molar absorptivities of P_A and P_B, respectively; K_A and K_B are coefficients of proportionality for components, A and B, at time t, respectively, and b is the cell length.

For m standard samples, the absorbance data of kinetic systems being monitored at time, s, can be expressed in matrix form as

$$\boldsymbol{A}_{m\times s} = \boldsymbol{C}_{m\times 2}\boldsymbol{K}_{2\times s} \quad (10)$$

According to this equation, it is possible to determine the components (in this work – maltol and ethyl maltol) by a suitable chemometrics method. Thus, in this study, the kinetic data were collected from experiments and then processed by PCR, PLS and PC–RBF–ANN.

2.2. Chemometrics methods

2.2.1. Principal component regression (PCR) and partial least squares (PLS)

Principal component regression (PCR) and partial least squares (PLS) are two well-known full spectrum multivariate calibration methods (Martens & Naes, 2001). These factor analysis based methods can overcome signal over-

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