Useing net analyte signal for determination of acidity constants caffiec acid in multivariate spectrophotometric analysis systems

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Abstract

A comparative study about advantages and limitations of net analyte signal (NAS) and DATa Analysis (DATAN) program in constant acid analysis has been performed. Net analyte signal (NAS) concept, which is a part of total signal that is directly related to the concentration of the component of interest. It monitors the concentration changes of any chemical species involved in the evolutionary process without requiring any pure spectra or having previous knowledge about the presence of the interferences. NAS method has some advantages such as the use of a full spectrum realization, therefore it does not require calibration and prediction steps and only a few measurements are required for the determination. By using these methods and without any prior knowledge about the system, concentration profiles and pure spectra can be obtained from the experimental data.

Key words: net analyte signal, DATa Analysis, Acidity constant, Spectrophotometry, caffiec acid.

Introduction

Caffeic acid (CA), 3,4-dihydroxycinamic acid is the major representative of hydroxycinamic acid in wines [1]. Caffeic acid is an organic compound that is classified as hydroxycinnamic acid. This yellow solid consists of both phenolic and acrylic functional groups.Caffiec acid is present in many fruits, vegetables, seasonings, beverages (coffee, wine) and olive oil. It is found in all plants because it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass and its residues [2]. The acidity and basicity form of dyes play a very fundamental role in many analytical procedures such as acid–base titration, solvent extraction and complex formation. Different methodologies have been proposed for the experimental determination of the acid dissociation constants including1H NMR spectroscopy, capillary electrophoresis, FT-IR spectrometry, UV–Vis absorption and fluorescence spectrophotometry and potentiometry. The net analyte signal (NAS) was defined by Lorberbased on spectroscopic methods, as the part of the spectrum of a mixture that is unique for the analyte of interest, i.e., it is orthogonal to the spectra of the interferences. The NAS is the part of the signal, which is directly related to the concentration predicted by the calibration model. In mathematical terms, it is the part of a spectrum which is orthogonal to the space spanned by the spectra of all analytes except one [3]. In this work, to obtain the NAS, the two methods Lorber et al and Goicoechea and Olivieri was used, followed by the two methods were compared. One of these

methods (Goicoechea and Olivieri) is hybrid linear analysis (HLA) which can be applied provided a very accurately measured pure spectrum of the analyte is available [4, 5]. The DATAN program, proposed by Kubista and coworkers calculates spectral profiles, concentrations and equilibrium constants by utilizing equilibrium expressions that are related to the components. However, to the best of our knowledge, there is not any report in the literature so far acidity constants the determination of Caffeic acid in grey mixture using the difference of absorption spectra of the analyte at different pH values.

Results and discussion

In this study NAS were used for determination of the protolytic constants of caffeic acid by applying pH gradual change-UV-Vis spectral data (pH-spectra).The first step in NAS is choosing the analyte and calculating the rank-annihilated data matrix R-m. Here we will discuss the steps of NAS analysis for a diprotic acid, for which the R_m matrix is obtained by either annihilating the contributions of the H_2A, HA or A^{2-} species. When the contribution of one species is annihilated from the total signal, R_{-m} contains spectral information for the remaining species and the spectral contribution from other sources such as interfering species). In this article, to obtain the NAS, the two methods Lorber et al and Goicoechea and Olivieri was used, followed by the two methods were compared. Comparison between methods of NAS and DATAN represents data close to each other. The acidity constants of caffeic acid were calculated in the AN-water by applying different methods of NAS and DATAN. The obtained pK_a values from NAS and DTAN are summarized in Table 1. This comparison indicates that the NAS method is an efficient method to obtain the constants of acid.

Table 1. The calculated acidity constants of caffeic acid in various Solvent percent (AN) by various methods.

Solvent percent	Method	pK_{a1}	pK_{a2}
AN: 20%(w/w)	NAS(Lorber)	5.95	9.70
	NAS(HLA)	5.92	9.65
	DATAN	6.05	9.81

AN: 60%(w/w)	NAS(Lorber) NAS(HLA) DATAN	6.00 5.98 6.09	9.90 9.95 10.05
AN: 80%(w/w)	NAS(Lorber) NAS(HLA) DATAN	6.15 6.20 6.25	10.25 10.30 10.42

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