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Parameterisation of symmetrical peaks in capillary electrophoresis using [3/2]-type rational approximants

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Abstract

The peaks in data from electrophoresis are parameterised in terms of a resonance model. The method we describe is based on forming a rational interpolant to the data. The interpolant is converted to a resonance approximation for symmetrical peaks; the method is found to discriminate successfully against formation of a resonance approximations to asymmetrical peaks. The method would also apply to equally good quality data from GC, LC and NMR.

MSC: 41A20; 65D15; 65Z05

Keywords: Peak parameterisation; Electrophoresis; Peak matching; Rational interpolation; Resonance approximation

1. Introduction

Resonance peaks [5, Chapter 23] feature in many models of physical phenomena. In the context of our experiments with capillary electrophoresis (CE), we observe that many of the peaks are symmetrically shaped, and we find that a resonance model fits these peaks remarkably well. Consequently, 'fine' numerical data [12] can be derived for each of its parameters. We describe a fast algorithm based on the use of [3/2]-type rational interpolants for fitting such peaks. Peaks that cannot be fitted in this way are mostly asymmetrical and have a more complex structure. If these shapes are self-similar, Baker's method [1] can be used; more generally, the use of general B-splines should be considered [7]. An aim of this work

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was to determine, as far as possible, the position and width of secondary peaks appearing as shoulders on larger peaks. This is important because CE is capable of high-resolution separation in the time domain of complex mixtures of resonance peaks, whose shape and position can be used to characterise a particular chemical mixture. Thus it is important a priori that an individual peak represents a single entity. This work has therefore focused on establishing the so-called 'peak purity' of individual resonance peaks by mathematical methods. Recent work on dispersion phenomena in capillary zone electrophoresis has identified some of the technical factors that contribute to the peak dispersion observed in practice [6]. However, in the absence of a theoretical model for the shape of CE peaks, and being fully aware of the well-known numerical instability associated with over-parameterisation [10, Section 15.4], we tentatively claim that the resonance approximations help qualitatively but not quantitatively in the characterisation of secondary peaks.

One application area of this research is in the design of chemical analytical methods for the international regulatory control of "Nutraceuticals". These are food additives based on plant extracts with claimed therapeutic benefits. Commercial formulations of Echinacea species represent a particular example, where the complex mixtures of chemical compounds are separated for quality control purposes by CE. In this method, a high voltage is applied to a narrow capillary of electrolyte where the sample components are separated into discrete zones. These zones are translated into peaks in the time domain as a so-called "electropherogram" and their patterns permit comparison of a test sample with an accepted standard. One aim of this study is to match these patterns systematically and extract common features, for example relative peak positions and peak shape, among different commercial products.

The CE system employed for these experiments was a 'P/ACE MDQ System' (Beckman Instruments Inc., Fullerton, USA) with ultraviolet photodiode array detection at 320 nm. Further details are given

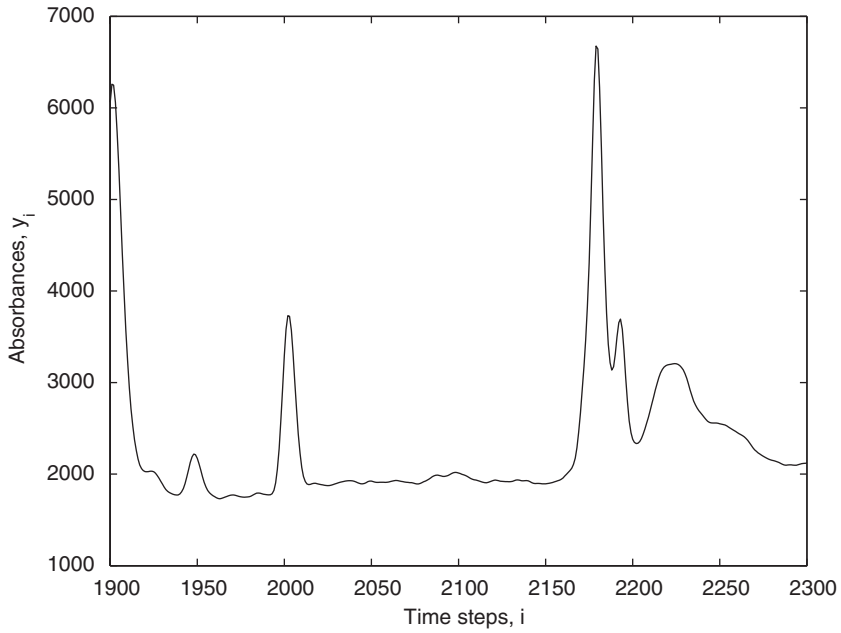

Fig. 1. An electropherogram of *Echinacea* species.