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Application of partial least-squares spectrophotometric-multivariate calibration to the determination of 2-*sec*-butyl-4,6-dinitrophenol (dinoseb) and 2,6-dinitro-*p*-cresol in industrial and water samples containing hydrocarbons

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Abstract

The present report describes the spectrophotometric determination of 2-*sec*-butyl-4,6-dinitrophenol (dinoseb) and 2,6-dinitro-*p*-cresol, two inhibitors of the styrene polimerization, in two very different types of matrices. One of them is present in an industrial distillation tower, and contains styrene and more than 60 hydrocarbons. Partial least-squares (PLS) multivariate calibration enabled us to determine both analytes without the necessity of applying extraction processes, as well as significantly reducing the time involved in the currently applied analytical method. The limit of detection for both compounds, referred to the industrial sample, was 1.0 $\mu g\,ml^{-1}$, for concentration ranges of 0–261 $\mu g\,ml^{-1}$ (dinoseb) and 0–448 $\mu g\,ml^{-1}$ (2,6-dinitro-*p*-cresol). The method was successfully applied to real samples. In addition, dinoseb was simultaneously determined with 2,6-dinitro-*p*-cresol in hydrocarbon–water mixtures by PLS calibration. In this type of samples, the concentrations are significantly lower and thus a pre-concentration step through solid-phase extraction preceded the spectrophotometric measurements. The limits of detection for the simultaneous determination of dinoseb and 2,6-dinitro-*p*-cresol were 1.2 and 1.0 $ng\,ml^{-1}$, respectively.

Keywords: Spectrophotometry; Multivariate calibration; Partial least-squares; Solid-phase extraction; 2-*Sec*-butyl-4,6-dinitrophenol; 2,6-Dinitro-*p*-cresol

1. Introduction

Dinoseb (2-*sec*-butyl-4,6-dinitrophenol) is a phenol derivative belonging to the group of acidic herbicides [1]. Although this compound has been widely employed on numerous food and forage crops, its use as agrochemical agent was restricted by the US Environmental Protection Agency (EPA) from 1986 [2]. However, dinoseb is currently used in the chemical industry as an effective inhibitor of the styrene polymerization [3], and avoids the self-condensation of styrene in distillation towers. Another dinitrophenolic compound, 2,6-dinitro-*p*-cresol (2,6-DN-*p*-CR), is also frequently employed as inhibitor of the above-mentioned polimerization. The present work was prompted by the needs of a local industry, as will be discussed in detail below.

The concentrations of the above mentioned substances must be controlled in real time at different sampling points of the distillation process. The background matrix contains more than 60 hydrocarbons (with styrene and ethylbenzene as major constituents), and therefore the determinations of

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dinoseb or 2,6-DN-*p*-CR are difficult. Currently, they are carried out using a method adapted from the literature, which involves a tedious alkaline extraction and a subsequent spectrophotometric measurement [4,5], with contact between the analyst and very toxic compounds during rather long periods of time. We have evaluated both high-performance liquid chromatography (HPLC) and gas chromatography (GC) but, as will be discussed below, the complexity of the matrix and the low sensitivity have precluded their use.

Due to the significance to implement rapid and inexpensive analytical methods, avoiding prolonged management of hazardous chemicals, we have focussed our interest in the challenges posed by the above determination. Spectrophotometric methods are simple and rapid, but suffer from lack of specificity, especially when complex systems are treated. However, with the advent of chemometric analysis, the use of spectroscopic methods has recovered its attractiveness [6].

The first aim of the present report was to develop spectrophotometric-multivariate calibration methods for the determination of dinoseb or 2,6-DN-*p*-CR in complex hydrocarbon matrices. Specifically, partial least-squares (PLS) analysis was applied [7]. These methods were evaluated over both artificial and real samples, and their advantages were discussed.

As a second objective, our interest was focused on the analysis of water samples, which could hypothetically be in contact with these compounds. According to EPA, the maximum contaminant level (MCL) accepted for dinoseb in drinking water is 7 ng ml^{-1} [8]. When people are exposed to dinoseb at levels above the MCL for relatively short periods of time, undesirable health effects such as sweating, headache and mood changes can be observed. When the exposition is prolonged, the damage is more severe: decreased body and thyroid weight, degeneration of testes, thickening of intestinal lining. The employment of several analytical methods (HPLC, GC, capillary electrophoresis, electrochemical methods and kinetic-spectrophotometry) for the determination of dinoseb in different environmental samples has been proposed [9–19]. As in this type of samples dinoseb is present at low concentration levels, the determination is frequently preceded by either solid-phase or liquid–liquid pre-concentration extraction techniques. EPA recommends several similar methods for the analysis of dinoseb in water [20]. These methods involve hydrolysis with sodium hydroxide for 1 h, derivatization with different agents, liquid–liquid or solid-phase extractions and gas chromatography with an electron capture detector. The retention time for the dinoseb methyl derivative (59.68 min at the chromatographic conditions specified in reference [21]) illustrates the long time involved in this chromatographic analysis.

In the present paper, we describe a method for the simultaneous determination of dinoseb and 2,6-DN-*p*-CR in water samples containing hydrocarbons, combining the advantages of solid-phase extraction (sensitivity), spectrophotometry (speed and simplicity) and PLS analysis (no previous separation steps). Further, the time saving and the low-cost reagents employed make it an inexpensive method. The performances of the developed methods are discussed, including a selection of analytical figures of merit.

2. Experimental

2.1. Reagents and solutions

Dinoseb, purchased from a local supplier, was purified through a chromatographic technique using silicagel and hexane/ethyl acetate (90:10) as stationary and mobile phases, respectively. Its purity was checked by TLC chromatography and also by ^{13}C and ^{1}H NMR spectroscopies. 2,6-Dinitro-*p*-cresol (90%) and phenol were obtained from Aldrich (Milwaukee, WI, USA), methanol, toluene, hexane, ethyl acetate, ethylbenzene and styrene from Merck (Darmstadt, Germany), and xylene and benzene from Cecarelli (San Lorenzo, Argentina).

The stock solutions of dinoseb were prepared from the liquid compound, taking into account its density at 45 °C ($\delta_{45\,^{\circ}C}$ = 1.265 g cm^{-3}, [22]). For the determinations carried out in industrial matrices, stock solutions of dinoseb (ca. 6000 μg ml^{-1}) and 2,6-DN-*p*-CR, (ca. 10000 μg ml^{-1}) were prepared in toluene. From these solutions, more diluted toluene working solutions (c.a. 1000–2000 μg ml^{-1}) were obtained. For the determinations in aqueous mixtures, stock solutions of dinoseb (632.3 μg ml^{-1}) and 2,6-DN-*p*-CR (620.0 μg ml^{-1}) were prepared in methanol. The solution of alkaline methanol was prepared by mixing 30 μl of 16N NaOH solution and 50 ml of methanol.

2.2. Apparatus

Absorbance data were obtained with a Beckman DU 640 and with a Shimadzu UV 1603 spectrophotometers, using 1.00 cm quartz cells.

2.3. PLS

PLS is a multivariate calibration model which involves a two-step procedure: (1) calibration, where the relation between spectra and reference component concentrations is established from a set of standard samples, and (2) prediction, in which the calibration results are employed to estimate the component concentrations in unknown samples [7]. In the PLS-1 version, all model parameters are optimized for the determination of each analyte at a time. During the model-training step, the calibration data are decomposed by an iterative algorithm, which correlates the data with the calibration concentrations using a so-called 'inverse' model [23]. This provides a set of regression coefficients to be applied to a new sample. Before calibration, however, the optimum number of latent variables should be selected in order to avoid overfitting, by applying the cross-validation method described by Haaland [23] (see below). The PLS-1 technique