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Quantitative analysis of triazine herbicides in environmental samples by using high performance liquid chromatography and diode array detection combined with second-order calibration based on an alternating penalty trilinear decomposition algorithm

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ABSTRACT

A novel application of second-order calibration method based on an alternating penalty trilinear decomposition (APTLD) algorithm is presented to treat the data from high performance liquid chromatography-diode array detection (HPLC-DAD). The method makes it possible to accurately and reliably analyze atrazine (ATR), ametryn (AME) and prometryne (PRO) contents in soil, river sediment and wastewater samples. Satisfactory results are obtained although the elution and spectral profiles of the analytes are heavily overlapped with the background in environmental samples. The obtained average recoveries for ATR, AME and PRO are 99.7 ± 1.5, 98.4 ± 4.7 and 97.0 ± 4.4% in soil samples, 100.1 ± 3.2, 100.7 ± 3.4 and 96.4 ± 3.8% in river sediment samples, and 100.1 ± 3.5, 101.8 ± 4.2 and 101.4 ± 3.6% in wastewater samples, respectively. Furthermore, the accuracy and precision of the proposed method are evaluated with the elliptical joint confidence region (EJCR) test. It lights a new avenue to determine quantitatively herbicides in environmental samples with a simple pretreatment procedure and provides the scientific basis for an improved environment management through a better understanding of the wastewater–soil–river sediment system as a whole.

1. Introduction

Herbicides provide great benefits for weed control in modern agriculture domain. Triazine herbicides, such as atrazine (ATR), ametryn (AME) and prometryne (PRO), are applied in agriculture as selective pre- and post-emergence weed control for corn, rice, wheat, sugarcane, onion, etc. However, it has been estimated that only 0.1% of herbicides applied to crops reach their targets, and a large proportion remains in the environment [1]. The residues of triazine herbicides have attracted great concern worldwide and they are also in the list of chemical pollutants that need to be more heavily monitored owing to their widespread usage and their toxicity, persistence, accumulation in water, soil and river sediment. Moreover, atrazine, one of the triazine families, has also been classified as a possible human carcinogen [2]. In one word, as a result of monitoring, assessing and controlling their effects on the environment and human health, the quantitative analysis of herbicides is one of the most important fields in environmental analytical chemistry.

Until recently, a number of researches have been reported for determination of one or two triazine herbicides. Chuang et al. [3] determined atrazine (ATR) in complex sample media using immunoaffinity column chromatography. Determination of ATR in soil and water with mercury film electrode was reported by Maleki et al. [4]. The molecularly imprinted solid-phase extraction (MISPE) technique was employed for quantitative analysis of ametryn (AME) in environmental matrices [5,6]. Determination of prometryne (PRO) in water and soil by high performance liquid chromatography-ultraviolet detector (HPLC-UV) through cloud-point extraction was reported by Zhou et al. [7]. In addition, a range of analytical techniques have been investigated for their ability to detect two and more triazine herbicides [2,8–11]. While sometimes meeting with significant success, the methods, such as ion mobility spectrometry, HPLC-UV and enzyme-linked immunosorbent assay (ELISA), are time-consuming, employing different extraction procedures and generally likely to destroy the sample materials. Advantages and drawbacks of both extraction and chromatographic analysis to the triazine herbicides from environmental samples were discussed by Dean et al. [12].

High performance liquid chromatography in combination with diode array detection (HPLC-DAD) has been broadly used in determination of organic pollutants on account of its capability of

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analyzing both polar and nonpolar thermodegradable compounds. However, it is not possible to achieve perfect separation, either because of the complexity of samples or because faster chromatographic runs are preferred. Sometimes, even under the better experimental conditions, the probability of peak overlap in chromatographic separations may become quite apparent, especially for the highly complex samples. Therefore prior to quantitative analysis, a sample pretreatment procedure would be required for reducing the interference of sample matrix. However, the extraction processes are usually not selective enough, and often a number of interfering components are coextracted with the analytes of interest. As will be discussed below, a modern approach to improve the selectivity of analytical methods is the advanced second-order chemometric method, which might light to a new avenue to replace the "physical or chemical separation" with "mathematical separation" strategy through separating the signals of target analytes away from those of uncalibrated background or interferences. The benefit of the method, known as "second-order advantage", is capable to determine the content of analytes of interest even in the presence of unknown interferents [13–16]. In recent decades, a great variety of second-order calibration methods have been proposed, such as parallel factor analysis (PARAFAC) [17,18], generalized rank annihilation method (GRAM) [19], multivariate curve resolution-alternating least squares (MCR-ALS) [20], alternating trilinear decomposition (ATLD) [21] and alternating penalty trilinear decomposition (APTLD) [22]. The combination of second-order calibration method with HPLC-DAD data array has been a hot topic in current chemometric domain, and successfully applied for many practical analytical problems [21,23–27], even for removal of three-dimensional background drift in comprehensive two-dimensional (2D) liquid chromatography coupled with diode array detection (LC × LC-DAD) data [28].

In the present study, a rapid and effective strategy for simultaneous determination of ATR, AME and PRO contents in soil, river sediment and wastewater samples has been proposed, through combining HPLC-DAD with second-order calibration method based on the APTLD algorithm. The method can accurately obtain the contents of ATR, AME and PRO in complex matrices which contain co-elution of compounds and have overlapping spectra. Validation of the method, namely assessing its figures of merit, is a crucial step, not only for assessing the reliability of the results but also for consistently applying the method to future situations. Therefore, some statistical parameters and figures of merit of APTLD are evaluated. The integrated analysis of three triazine herbicides of three different environmental compartments, wastewater, soil and river sediment, allows a better understanding of the wastewater–soil–sediment system as a whole and summarizing the distribution of the herbicides pollution.

2. Experimental

2.1. Reagents and chemicals

Atrazine (ATR), ametryn (AME) and prometryne (PRO) were purchased from a Chinese Pharmacy Corporation. Stock standard solutions of ATR (45.4 μg mL^{-1}), AME (36.9 μg mL^{-1}) and PRO (35.5 μg mL^{-1}) were prepared in methanol and stored at 4 °C until used, respectively. Methanol and acetonitrile were of HPLC grade. Ultrapure water was prepared with a Milli-Q water purification system (Millipore, USA).

2.2. Instrumentation and chromatographic conditions

The HPLC system used was a LC-20AT liquid chromatographic system (Shimadzu Corporation, Japan), which consists of a degasser, four pumps, a manual injector provided with a 10 μL loop, a column oven and a diode array detector (DAD). The separation was carried out in a Hypersil-ODS analytical column (125 mm × 4.0 mm, 5.0 μm, Shimadzu, Japan). The LC solution software was used for controlling the instrument, data acquisition, and data interpretation. In the sample preparation procedure, a centrifuge (Sigma, Germany) and ultrasonic instrument (KQ-250TDB, Jiangsu, China) were used.

The mobile phase was isocratic and comprised of methanol (85%, v/v) and water (15%, v/v), pumped at a flow rate of 1.0 mL min^{-1} with sample injection volume of 10 μL. The solvents were filtered daily through a 0.45 μm cellulose membrane filter before injection into HPLC column. The column temperature was set at 30 °C. Photometric detection was performed in the range of 200–300 nm, with a spectral resolution of 1.2 nm. Data was obtained over an integration period of 640 ms per spectrum. In the MATLAB environment all home-made programs were written and further used for data analysis.

2.3. Sample collection and preparation

The soil samples and river sediment samples were collected from cropland and the bank of the Xiangjiang River in Hunan Province of China, respectively. The collected soil samples and river sediment samples were stored in plastic bags. These samples were dried at room temperature, and ground with a mortar. First, 100 g soil and river sediment samples were obtained and 100 mL of solvent (methanol:acetonitrile = 1:1 (v/v)) were added, respectively; second, the mixtures were vortexed for 30 min and left for a whole day in order to extract adequately; third, the mixtures were filtered and the solvents were evaporated to dryness, respectively; and finally the residues were reconstituted with methanol and then filtered through to 0.45 μm cellulose syringe filter before injection into HPLC column. The wastewater samples were collected from a pool in residential area in Changsha, China. The wastewater samples were filtered through filter paper to remove suspended sediments and solid materials and the wastewater samples were filtered through to 0.45 μm cellulose syringe filter before injection into HPLC column.

2.4. Analytical procedure

2.4.1. Calibration and validation samples

A calibration set of twelve samples (C1–C12) and a validation set of seven samples (T1–T7) were constructed as shown in Table 1. Calibration and validation samples were prepared by taking appropriate aliquots (0.1–1.0 mL) of methanol solutions, placing them in 10.0 mL volumetric flasks, and diluting with water to the mark. The concentrations had a proportional spacing and were randomly selected, within the linear range of concentrations and avoiding the collinearity between analytes. For the calibration set, the levels correspond to values in the range of 0–4.54 μg mL^{-1} for atrazine, 0–3.69 μg mL^{-1} for ametryn and 0–3.55 μg mL^{-1} for prometryne. In addition, the validation set was built with different concentrations of analytes within their corresponding concentration range of calibration samples, and in these samples, no interferents were added. The calibration and validation datasets were constructed to testify the performance of the APTLD algorithm in the system. Duplicate analysis was performed for each sample, and HPLC-DAD was measured in random order according to the sample number.

2.4.2. Quantitative analysis of ATR, AME and PRO in environmental samples

2.4.2.1. Soil samples. The soil samples (S1–S6) were spiked with suitable amounts of standard ATR, AME and PRO solutions, and then