



A novel solid-phase extraction for the concentration of sweeteners in water and analysis by ion-pair liquid chromatography–triple quadrupole mass spectrometry

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ABSTRACT

A highly sensitive method for the simultaneous trace (ng/L) quantification of seven commonly used artificial sweeteners in a variety of water samples using solid-phase extraction and ion-pair high-performance liquid chromatography (HPLC) triple quadrupole mass spectrometer with an electrospray ionization source (ESI-MS) in negative ion multiple reaction monitoring mode was developed. Ten solid phase extraction (SPE) cartridges were tested to evaluate their applicability for the pre-concentration of the analytes, and their loading and eluting parameters were optimized. Satisfactory recoveries (77–99%) of all of the studied sweeteners were obtained using a Poly-Sery PWAX cartridge with 25 mM sodium acetate solution (pH 4) as wash buffer and methanol containing 1 mM tris (hydroxymethyl) amino methane (TRIS) as eluent. The method is sound and does not require pH adjustment or buffering of water samples. The HPLC separation was performed on an Athena C18–WP column with water and acetonitrile, both containing 5 mM ammonium acetate and 1 mM TRIS as mobile phases, in gradient elution mode. The linearity, precision, and accuracy of the method were evaluated, and good reproducibility was obtained. Method quantification limits varied between 0.4 and 7.5 ng/L for different water samples. The post-extraction spike method was applied to assess matrix effects, and quantification was achieved using internal standard calibration to overcome the unavoidable matrix effects during ESI-MS analysis. The method was applied to the analysis of thirteen water samples from Tianjin, China, including wastewater, tap water, surface water, and groundwater. The method described here is time-saving, accurate and precise, and is suitable for monitoring artificial sweeteners in different water matrices.

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1. Introduction

Artificial sweeteners (ASs) are compounds containing few or no-calories and widely used all over the world as sugar substitutes in food, drinks, pharmaceuticals, and sanitary products [1–3]. Although various negative effects of ASs have been reported on animals [4–8], it is now extensively accepted that ASs are safe to humans within the legal content limits [3,9–11].

Recently, the ecotoxicology of ASs on aquatic and terrestrial organisms has drawn much attention due to the ubiquitous occurrence of ASs in the environment. Generally, the toxicity of ASs on aquatic and terrestrial organisms is low; however, several negative effects have been reported [12–14]. Sucralose (SUC) was reported to inhibit the transport of sucrose in sugarcane [12]; and the physiology and locomotion behavior of crustaceans can be affected when

exposed to SUC [13]. A recent study showed that SUC does not appear toxic to plant growth, but the authors suggested that the persistence of SUC might lead to chronic low-dose exposure with largely unknown consequences for environmental health [14]. A more recent study showed that aspartame (ASP) significantly influences the swimming behavior of zebrafish and causes their deaths at high concentrations [15]. Therefore, the possible ecotoxicological effects of ASs still need further study [16].

Though very limited, recent studies have shown that ASs are ubiquitous in the aquatic environment. Investigations in Switzerland and Germany revealed that the concentration of ASs in surface water and wastewater ranged from several hundred ng/L to 50 µg/L for acesulfame (ACE), from 0.08 µg/L to 9.1 µg/L for SUC, from 0.18 µg/L to 50 µg/L for saccharin (SAC), and from 0.13 µg/L to 190 µg/L for cyclamate (CYC) [1,2]. SUC was also found in surface waters in other European countries and in coastal and marine waters in the US at concentrations up to 1 µg/L and 0.39 µg/L, respectively [17,18]. Due to their frequent detection and persistence, ACE and SUC were even proposed as indicator compounds for the influence of sewage on receiving waters [1,2,14,19,20]. No

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reports on the occurrence of ASs in Asian countries have been published.

It is crucial to develop a highly sensitive and reliable analytical method and a simple, highly effective sample preparation technique for the simultaneous determination and extraction of common ASs at trace levels in different matrices before large-scale investigations can be conducted. Currently, several analytical methods have been reported [21–24]; however, most of them have some drawbacks, such as lacking selectivity and sensitivity and being unsuitable for compounds without chromophore groups. Mead et al. [18] developed a sensitive method for the determination of SUC using GC/MS; however, the derivatization step before GC/MS analysis is time-consuming. Liquid chromatography mass spectrometry (LC/MS) has been applied for the determination of ASs in foodstuffs and beverages [3,25,26]. The developed method is considered appropriate for testing ASs in food. However, the sensitivities of these methods may not be competent for environmental screening due to trace level of ASs in environmental samples. As for the analysis of ASs in the environment, there is a growing trend of applying liquid chromatography–triple quadrupole mass spectrometry (LC–MS/MS) due to its unique accuracy and sensitivity. To our knowledge, only the analysis method developed by Scheurer et al. [1] can be used for the simultaneous analysis of seven ASs at environmentally relevant concentrations. Their study was the first attempt at using LC–MS/MS in the analysis of ASs around the world. Currently, solid phase extraction (SPE) is the most frequently used technique for sample pretreatment due to its unique advantages. Scheurer et al. [1] and Zygler et al. [27] developed successful pretreatment methods for the simultaneous extraction of seven or more ASs using SPE. However, pH adjustment or sample buffering must be performed to achieve satisfactory recoveries using the current available methods. These steps are time-consuming for large-scale environmental investigations.

In this work, a single step SPE procedure using a PWAX SPE cartridge for the simultaneous extraction of the seven common ASs was developed. To our knowledge, this is the first report on simultaneous extraction of the seven ASs from various natural water and wastewater samples without any pH adjustment or buffering of the water samples, which could speed up sample preparation. A quantification method using ion pair HPLC–MS/MS was set up. Higher sensitivity and relative better separation were achieved using the ion pairing agent tris (hydroxymethyl) amino methane (TRIS) in the mobile phase. Accurate quantification was accomplished by internal standard calibration, with the application of three deuterium-labeled internal standard. For matrix effect assessment, the post-extraction spike method was applied. Precision, recovery, and other validation parameters were evaluated. The developed method was successfully applied for the analysis of thirteen water samples including river water, sea water, tap water, groundwater, and wastewater. To this end, the proposed method is sensitive, simple, time-saving and suitable for monitoring ASs in different water samples.

2. Experimental

2.1. Chemicals

The standards of ACE, SAC, CYC, SUC, and neohesperidin dihydrochalcone (NHDC) were purchased from Sigma–Aldrich (St. Louis, MO, USA); neotame (NEO) was purchased from USP Reference Standards (Rockville, MD, USA); ASP was purchased from Supelco (Bellefonte, PA, USA); and sucralose-d6 (SUC-d6), aspartame-d5 (ASP-d5), and acesulfame-d4 (ACE-d4), used as internal standards (ISs), were obtained from TRC (North York,

Canada). The structures of the ASs are listed in Table S1 in the Supplementary Information (SI).

HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). The ion pair reagent TRIS was obtained from Sigma–Aldrich (St. Louis, MO, USA). Milli-Q water was used throughout the study. All other solvents and reagents were of HPLC or analytical grade.

2.2. Standard solutions

For all analytes, two sets of stock solutions were prepared by dissolving 10.0 mg of each analyte in 10 mL of Milli-Q water and 10 mL of methanol, respectively. The standard solutions prepared in Milli-Q water were used for breakthrough experiments only, and the standard solutions prepared in methanol were used as spiking solutions for sample fortification and for calibration curves. The stock solutions of the three ISs were prepared in methanol (1 mg/mL), respectively. A mixed IS solution containing 10 µg/mL of the three ISs was prepared in methanol. A set of mixed working standard (50 ng/mL) was prepared in Milli-Q water before use, and used for SPE experiments.

A series of calibration solutions were prepared by diluting the mixed standard solution with methanol resulting in a concentration range of 0.1–1000 ng/mL for ACE, CYC, SAC, ASP, NHDC, and NEO and of 0.5–1000 ng/mL for SUC. In the calibration solutions, the concentration of the three ISs was 20 ng/mL.

2.3. SPE cartridges and buffers

Ten disposable SPE cartridges were tested: CNWBOND SAX 3 mL/500 mg, CNW Poly-Sery MAX 3 mL/60 mg, CNWBOND LC-18 3 mL/500 mg, CNWBOND HC-18 6 mL/500 mg, CNWBOND PHE 3 mL/500 mg, CNW Poly-Sery PWAX 3 mL/60 mg, CNW Poly-Sery HLB 3 mL/60 mg, CNW Poly-Sery PSD 6 mL/500 mg (CNW Technologies GmbH, Germany), and Waters Oasis WAX 3 mL/60 mg and HLB 3 mL/60 mg cartridges (Milford, MA, USA).

Five different wash buffer solutions and three different elution solvents were tested to optimize SPE. Acetic acid–sodium acetate buffer solutions at pH 3.6, 4.0, 4.5, and 6.0 were prepared by titration of a solution of 25 mM sodium acetate with acetic acid until the desired pH was reached. Another wash buffer solution was prepared by dissolving 0.0606 g TRIS in 500 mL of Milli-Q water (1 mmol/L). Methanol, methanol containing 2% ammonia hydroxide (v/v), and methanol containing 1 mM TRIS were evaluated as elution solvents.

2.4. Sampling and sample pretreatment

Water samples, including wastewater, tap water, surface water (including river water and sea water), and groundwater, were collected from different locations in Tianjin, China. The wastewater sources were the influent and effluent of a wastewater treatment plant (WWTP) in Tianjin, and the tap water samples were collected at public places. Surface water samples were collected from the Haihe River and Bohai Bay, and groundwater samples were collected from wells in the suburb of Tianjin. Raw samples were contained in 500 mL PP plastic bottles and stored in the dark at 4 °C until analysis. The samples were filtered at room temperature using 0.45 µm cellulose nitrate membrane filters (0.45 µm, 47 mm, Whatman, UK). No preservation agent was added.

2.5. Solid phase extraction (SPE)

Solid phase extraction experiments were performed to evaluate extraction efficiencies. The SPE cartridges were preconditioned with 6 mL of methanol, followed by 6 mL of any of the wash buffers

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