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Ultrasound-assisted low-density solvent dispersive liquid–liquid extraction for the determination of alkanolamines and alkylamines in cosmetics with ion chromatography

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ABSTRACT

A new one-step sample preparation technique termed ultrasound-assisted low-density solvent dispersive liquid–liquid extraction (UA-LDS-DLLE) coupled with ion chromatography (IC) was developed for the determination of three alkanolamines and two alkylamines in complex samples. Sample matrices were rapidly dissolved and dispersed to form cloudy solutions by using two solvents, where target analytes were transferred into acid solutions, while liposoluble substances were dissolved in cyclohexane. The obtained extracts could be used directly for injection analysis without any additional purification because the potential matrix interferences had been effectively eliminated in extraction process. The extraction efficiency could be markedly enhanced and the extraction could be quickly accomplished within 13 min under the synergistic effects of ultrasound radiation, vibration and heating. Various parameters influencing extraction efficiency were evaluated using orthogonal array experimental design. The extraction performance of the approach was demonstrated for the determination of target analytes in 15 commercial cosmetics covering very different matrices. Linearity ranges of 0.3–50 mg L^{-1} and limits of detection varying from 0.072 to 0.12 mg L^{-1} were achieved. The recoveries ranged from 86.9–108.5% with the relative standard deviations (RSDs) of 1.2–6.2%. The method was proved to be a simple and effective extraction technique that provided an attractive alternative to the analysis of trace amounts of target analytes in large numbers of cosmetics.

1. Introduction

Alkanolamines are widely used as detergents, thickeners, alkalizing agents and emulsifiers in cosmetic products. But the super-scale uses of alkanolamines in cosmetics could cause potential health risks [1]. Alkylamines maybe present as contaminants in cosmetics resulting from the decarboxylation of amino acids or the use of the impure chemical raw materials. The volatile amines such as dimethylamine (DMA) and diethylamine (DIEA) emit pungent smells that are hazardous to human health [2]. DMA can also react with nitrosation agents to form carcinogenic dimethylnitrosamine compounds [3]. According to the current European and Chinese cosmetic regulations, alkanolamines including monoethanolamine (MEA) and triethanolamine (TEA) are restricted ingredients, whose maximum allowable concentrations in rinse-off products are 0.5% (w/w) and 2.5% (w/w). The total concentrations of diethanolamine (DEA) and TEA in leave-on formulations should not exceed 5% (w/w), while dimethylamine (DMA) and diethylamine (DIEA) are prohibited for use in cosmetic formulations [4,5]. The simultaneous determination of various organic compounds still remains a major challenge because of the presence of a lot of organic substances and some inorganic salts in cosmetics that may interfere with the determination.

Sample preparation is a critical step in the overall scheme of analysis, which has direct influences on the accuracy, precision of results and detection limit of method, and also it often is the most time-consuming step of the analytical process [6]. Some conventional extraction techniques such as solvent extraction [7,8], liquid–liquid extraction (LLE) [9–11] and solid phase extraction (SPE) [12–15], have been widely used for isolating the target analytes from various matrices. The former two approaches require the use of large amounts of the high-purity organic solvents and multiple clean-up steps, which are considered to be expensive and time-consuming. The latter method also requires reletively large volumes of toxic organic solvents for purification of coated fiber and elution of target analytes, which are hazardous to the operator and unfriendly to the environment [16]. As a consequence, a variety of sample preparation techniques have

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been developed to overcome the shortcomings of these classical methods by means of reducing or even avoiding the use of organic solvents [17]. One of the most efficient procedures is the development of simplified and miniaturized SPE- and LLE-based techniques such as headspace solid phase microextraction (HS-SPME) [18], solid phase microextraction (SPME) [16,19] and dispersive liquid–liquid microextraction (DLLME) [20,21], which can considerably reduce organic solvent consumption and achieve high enrichment factors for target analytes. In addition, automation of SPME requires only slight modification of a normal gas chromatographic autosampler [22]. However, the coated fibers are generally expensive and have the limited lifetimes for some applications due to the influence of the addition of salts with supersaturation or complex matrix.

DLLME was firstly introduced by Assadi and co-workers in 2006 [23], which is an improved LLE method based on the use of microliter volumes of extraction solvent. Its applications in various matrices such as cosmetics [9], fruits and vegetables [24], food and environmental samples [25–27] have been widely reviewed. However, DLLME usually suffers from two obvious drawbacks. Firstly, it generally requires high-density solvents such as chloroform, carbon tetrachloride, tetrachloroethane or chlorobenzene, which are highly toxic and environmentally unfriendly, and may limit its applicability. For these halogenated hydrocarbons, their GC peaks partially overlap with those of some analytes. Secondly, there is a lack of compatibility between the extraction solvents and detecting instruments such as reverse-phase HPLC [25] and IC [28]. Lighter-than-water organic solvents [20,26] and ionic liquids [29] are lately introduced as extraction solvents to overcome these inherent limitations. The performance of DLLME in the extraction of organic compounds from simple matrices like aqueous samples has proved to be excellent, but it is not yet perfect in complex matrices including cosmetic samples. Therefore, it needs further improvement.

The ultrasound radiation is a powerful tool to facilitate emulsification and homogenization, which provides an efficient contact between sample matrix and extractant, accelerates the mass transfer between two immiscible phases in the extraction process, leading to enhancement of extraction efficiency with a minimum equilibrium time [30]. A detailed application of the UAE technique to the environmental and food samples has been published specifically [31]. The solvent extraction-based methods including LLE, dispersive liquid–liquid extraction (DLLE), and DLLME, etc., can easily be modified or combined with other sample preparation techniques for particular purposes. In this way, ultrasound-assisted dispersive liquid–liquid extraction (UADLLE) [29], ultrasound-assisted matrix solid-phase dispersive liquid extraction (UAMSPDLE) [32] and dispersive derivatization liquid–liquid extraction (DDLLE) [33] have been developed as good alternatives to conventional LLE. An ultrasound-assisted emulsification microextraction (UAEME) enjoying the performance advantages of both UAE and DLLME has been applied to the determination of triclosan [34], phthalate ester [35], formaldehyde [36] and nitrite [37] in cosmetics. However, large amounts of organic compounds in cosmetics can also be co-extracted along with the target analytes that will cause the serious matrix interferences. Moreover, centrifugation of large-volume samples is too difficult to carry out. Therefore, these modified DLLE and DLLME approaches are still unsuitable for the direct detection of alkanolamines and alkylamines in cosmetics, and additional clean-up procedures are generally needed. Considering the characteristic ingredients of cosmetics, the dominant organic compounds can be efficiently removed by using an appropriate organic solvent while the target analytes are still remained in the acid solutions. It can significantly simplify the operation step and obtain extracts clean enough for direct injection. Thus the development of a simple, rapid and high selectivity DLLE procedure combining extraction and cleanup in one single step is of great significance.

In this study, a novel one-step sample preparation technique called ultrasound-assisted low-density solvent dispersive liquid–liquid extraction (UA-LDS-DLLE) was developed. During the extraction process, sample matrices were rapidly dissolved and dispersed to form cloudy solution by using two solvents where target analytes were transferred into acid solutions and liposoluble substances could be completely dissolved in cyclohexane. The whole procedure was performed on the synergistic effects of ultrasound radiation, heating and vibration, which could greatly improve extraction efficiency and accelerate the extraction. The approach achieved the following two improvements for conventional DLLE. One was the simplification of extraction process through integrating extraction and cleanup into one single step, which could effectively eliminate the matrix interferences from complex matrices without any further cleanup. Another was it considerably reduced the consumption of organic solvent and operating time under the synergistic effects. A cation-exchange column was adopted for the effective separation of co-existing compounds prior to IC detection. To demonstrate the feasibility of the developed approach, UA-LDS-DLLE was applied to the assays of alkanolamines and alkylamines in commercially available cosmetics.

2. Experimental

2.1. Instrumentations

UA-LDS-DLLE experiments were carried out on a Branson 2510 ultrasonic cleaner (130 W, 42 kHz, Branson Ultrasonic Corporation, Danbury, USA), a Vortex-genie 2 vibrator (Scientific Industries INC, New York, USA) and a constant temperature water bath (Chang An Scientific Instrument Co. Ltd., Beijing, China). IC analysis was performed on an ICS-2500 ion chromatography system (Dionex, Sunnyvale, CA, USA) equipped with a GP 50 high performance quaternary gradient pump with an automated vacuum degassing system, an ED 50 electrochemical detector, a LC 30 chromatography oven and an AS 50 auto-sampler with a 25 μL sample loop.

The chromatographic separation of analytes was performed using an Ion Pac SCS 1 (250 mm × 4.0 mm i.d.) analytical column fitted with an Ion Pac SCG 1 (50 mm × 4.0 mm i.d.) guard column (Dionex, Sunnyvale, CA, USA), which was eluted with 2.5 mM MSA in 5% (v/v) acetonitrile solution at a flow rate of 0.70 mL min^{-1} under isocratic conditions. The separations and non-suppressed conductivity detections were carried out at room temperature in a chromatography oven. Quantification of target analytes was performed by the integration of the peak areas using an external standardization method.

2.2. Reagents and materials

All reagents used were of high purity analytical grade or HPLC grade and the deionized water (specific resistivity 18.1 MΩ cm^{-1}) was produced by a Millipore Milli-Q water purification system (Bedford, MA, USA). Methanesulfonic acid (MSA) and acetonitrile (ACN) were obtained from Acros Organic (Geel, Belgium). MEA (≥99%), DEA (≥99%), TEA (≥99%), DMA (≥33%) and DIEA (≥99%) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Cyclohexane and ether were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Individual stock standard solutions of each analyte at a concentration of 2000 mg L^{-1} were prepared by exact weighing of each compound and diluting with acetonitrile. These solutions were stored in a refrigerator at 4 °C. The accurate concentration of