



## Carboxylated graphene oxide/polyvinyl chloride as solid-phase extraction sorbent combined with ion chromatography for the determination of sulfonamides in cosmetics



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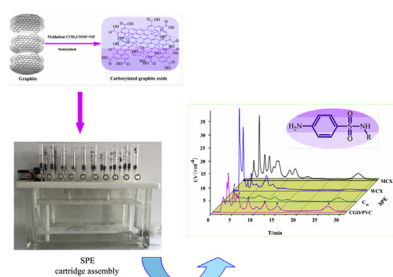
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### HIGHLIGHTS

- SPE using carboxylated graphene oxide/polyvinyl chloride as sorbent was proposed.
- Graphene oxide was synthesized and modified chemically.
- Extraction protocol was systematically optimized with multi-response optimization.
- Extraction selectivity was enhanced by introducing carboxyl group into graphene oxide.
- Extraction performance of self-assembly column was superior to commercial sorbents.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A carboxylated graphene oxide/polyvinyl chloride (CGO/PVC) material was prepared as a sorbent for the selective extraction of sulphonamides from complex sample. After being dispersed in buffer solution, sample was transferred into the prefabricated solid-phase extraction (SPE) column, which integrated extraction and cleanup into one single-step. A multi-response optimization based on the Box-Behnken design was used to optimize factors affecting extraction efficiency. Compared with the commonly commercial sorbents including MCX, WCX and C<sub>18</sub>, CGO/PVC hybrid material had higher extraction selectivity and capacity to sulphonamides. The limits of detection and quantification for seven target compounds were in the range of 3.4–7.1 µg/L and 11.4–23.7 µg/L, respectively. The self-assembly SPE cartridge was successfully used to enrich seven analytes in anti-acne cosmetics prior to ion chromatography detection with good recoveries of 87.8–102.0% and relative standard deviations of 1.2–6.4%, implying that this method was suitable for routine analysis of cosmetics.

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## 1. Introduction

Sulphonamides (SAs) are one of the most important families of antibiotics, which have been widely used for treating or preventing diseases. Antibiotics are non-allowed pharmacologically active substances in cosmetic products according to the Annexes II of Directive 76/768/EEC [1]. Certain antibiotics most probably found in cosmetic products are anti-acne medicines [2], metronidazole and chloramphenicol [3,4]. The drug abuse in cosmetics may cause potential damage to human health due to the existence of several undesirable effects [5]. Therefore, it's extremely vital to constantly monitor the presence of these non-allowed compounds in cosmetic products. The simultaneous determination of these compounds is analytically challenging owing to the presence of a lot of organic substances and inorganic salts in cosmetics.

Conventional liquid–liquid and solid phase extraction-based procedures are most commonly employed for preliminary separation and pre-concentration of non-allowed compounds in cosmetics. Sorbent is a critical factor that determines the performance of solid phase extraction (SPE), and its selectivity property can be tuned depending on how it interacts with analytes. Various types of sorbents have been investigated and used to develop analytical procedures. The early sorbents include silica-based (silica modified with groups such as C<sub>18</sub>, C<sub>8</sub>, phenyl, –CN and –NH<sub>2</sub>) [6,7] and carbon-based materials (graphitized carbon blacks and porous graphitic carbons) [8]. Nevertheless, there exist some disadvantages in two kinds of sorbents. The former is instable at extreme pH and unsuitable for extracting polar compounds due to low recovery, and the latter has strong retention for certain analytes so that it is very difficult to elute them from sorbent [9]. Subsequently, a variety of materials are synthesized or modified for specific applications. These compositive materials may be classified as molecularly-imprinted sorbents [10], immunosorbents [11], aptamers [12,13], electrospun nanofibers [14,15] and carbon nanotubes [16]. The challenges are still unresolved, in terms of extraction capacity and selectivity for trace analytes in complex matrices.

Graphene (G) is one kind of carbonaceous materials, which possesses a single-layer or few-layer thickness of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb pattern. G and graphene oxide (GO) exhibit large surface area, chemical stability, durability and corrosion resistance, and have attracted greater interest than classical materials. G and GO seem to be ideal sorbents in SPE or solid-phase microextraction (SPME), and their adsorption capacity can be attributable to the delocalized  $\pi$ -electron system allowing to  $\pi$ -stacking interaction with six-membered rings [16]. G is considered a non-polar and hydrophobic sorbent with strong affinity for ring-shaped structures, which can be used in reversed-phase SPE. GO provides diverse functional groups that are propitious to formation hydrogen bonding or electrostatic interaction with analytes, and can be employed as normal-phase SPE or SPME sorbent for the enrichment of trace organic compounds containing oxygen- and nitrogen-functional groups in environmental and biological samples [17–22]. Despite GO possesses exceptional adsorption characteristics, its practical application in classical SPE can be hampered. Even very small particles of GO in SPE cartridge will cause high overpressure in the system due to strong aggregation tendency, leading to an obvious decline in the active area and limitation the full exploitation of the potential extractability. Additionally, GO can also escape from a SPE cartridge under high pressure. These problems have promoted technological progress in GO-based SPE. Graphene's properties may be improved via chemical modifications. The carboxy groups on the surface of GO are linked to the amino groups of amino-terminated silica, leading to the creation of GO @ silica, which can be used as SPE sorbent [23]. The introduction of *p*-phenyl-SO<sub>3</sub>H group into G sheet may

improve the water-solubility of GO since the presence of a negatively-charged-SO<sub>3</sub><sup>-</sup> group occurs electrostatic repulsion that avoids aggregation of GO [24]. G is generally not an ideal sorbent for polar and ionized compounds, but when a magnetic graphene is used as a support for ionic hemimicelles and admicelles, it will exhibit much higher loading capacity than conventional materials [25,26]. These functionalized G and GO sorbents can be employed to selectively extract charged or uncharged analytes from complex samples. The matrix components or interferences and analytes can be eluted separately by controlling pH value and choosing appropriate solvent during washing and elution steps. Hence graphene-based mixed mode sorbents provide clean extracts and yield high extraction efficiency.

SAs molecules structures contain –NH<sub>2</sub> or –SO<sub>2</sub>NH– and aniline groups (the supporting information Table S1), which can interact with GO via non-covalent forces, such as electrostatic forces, hydrogen bonding,  $\pi$ – $\pi$  stacking and hydrophobic effect. Furthermore, if carboxyl is effectively introduced into GO sheet through the carboxylation of hydroxyl and epoxy groups on the surface of GO, this modification process will greatly improve the extraction selectivity of GO for SAs.

The main purpose of this work was to develop a novel SPE approach using carboxylated graphene oxide/polyvinyl chloride (CGO/PVC) as sorbent. After GO was synthesized and modified, the resulting CGO was combined with PVC to form a hybrid composite material, which was utilized for extracting antibiotics from complicated matrixes. The dispersed sample was transferred into the prefabricated SPE cartridge, which integrated extraction and cleanup into one single-step. The extraction conditions were optimized by multi-response optimization. The extraction performance of the self-assembly SPE cartridge was evaluated by comparing with commercially available sorbents. A cation-exchange column was adopted for the effective separation of co-existing compounds prior to ion chromatography (IC) detection. Finally, this method was applied to the assays of sulfonamides (SAs) in cosmetics.

## 2. Experimental

### 2.1. Reagents and materials

All reagents used were of high purity analytical grade or HPLC grade and all aqueous solutions were prepared using deionized water (specific resistivity 18.1 M $\Omega$  cm<sup>-1</sup>) produced by a Millipore Milli-Q water purification system (Bedford, MA, USA). Graphite power (99.95%, particle size  $\leq 30$   $\mu$ m) was obtained from Aladdin Industrial Corporation (Shanghai, China). Acetonitrile (ACN), methanesulfonic acid (MSA) and methanol were provided from Acros Organic (Geel, Belgium). Chloroacetic acid was bought from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Other reagents were from Guangzhou Chemical Reagents Factory (Guangzhou, China).

Analytical standards including sulfacetamide (SCT), sulfamerazine (SMR), sulfamonomethoxine (SMT), sulfadoxine (SDX), sulfadimethoxine (SDT), sulfaphenazolum (SPA), and sulfantran (SNT) were achieved from Sigma–Aldrich (St. Louis, MO, USA), and their purities were larger than 98%. Individual stock standard solutions of seven SAs of 1000 mg/L were prepared by dissolving them in ACN and stored in brown bottle at 4 °C. A series of mixed working solutions containing all the analytes were prepared daily by appropriate dilution of each stock standard solution in 15 mM MSA containing 28% (v/v) acetonitrile.

For comparative purposes, three typical types of commercial SPE cartridges involving mixed-mode polymeric sorbent, weak ion-

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