ORIGINAL ARTICLE

Graphene Nanoplatelets as a Solid Phase Extraction Sorbent for Analysis of Chlorophenols in Water

Krishna Chaitanya Sadanala · Bong Chul Chung

Abstract   Graphene nanoplatelets are a novel class of carbon nanostructures. They possess an ultra high surface area, and thus have great potentials for the use as sorbent materials. We herein demonstrate the use of graphene nanoplatelets as an adsorbent material for solid-phase extraction. Surface compositions of graphene nanoplatelets were examined by X-ray photoelectron spectroscopy. Scanning electron and transmission electron microscopies were performed to elucidate the morphology of graphene nanoplatelets. Three chlorophenols, 3-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenols were selected as model analytes and extracted on a graphene nanoplatelets-packed solid-phase extraction cartridge, followed by elution with alkaline methanol. The extracted chlorophenols were identified and quantified by UV-vis spectrophotometer. Under the optimized experimental conditions, good linearity ($R^2 > 0.9969$), recovery (95–103%), precision (<12%), and accuracy (<±9%) were achieved. The advantages of graphene nanoplatelets as solid phase extraction adsorbent, such as good reusability and no impact of sorbent drying, have been detailed. The present study proposes a useful method for water sample pretreatment and reveals the potential of graphene nanoplatelets as an excellent sorbent material in analytical processes.

Keywords   chlorophenols · graphene nanoplatelets · solid phase extraction · UV-vis spectrophotometry

Introduction

Solid-phase extraction (SPE) is a technique most widely used for environmental sample pretreatment due to its unique features such as high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation (Thurman and Mills, 1998). In the procedure of SPE, the type of sorbent, its structure, and its interactions with the solute play an important role in obtaining higher enrichment efficiency of analytes. Sorbent selection depends on the analyte characteristics, the sample matrix and the analytical method. Solid phase extraction procedures are used not only to extract traces of organic compounds from environmental samples but also to remove the interfering components of the complex matrices in order to obtain a cleaner extract containing the analytes of interest (Kim et al., 2005). Analytical chemistry has benefited from the advancement in other scientific areas such as nanotechnology. The discovery, synthesis, and characterization of nanoparticles and nanostructured materials with outstanding properties can be identified as one of the most relevant inputs in this context. Their use as sorbent materials in different approaches such as conventional SPE procedures, automated flow configurations, pheudophases in liquid-liquid extraction, and solid-phase microextraction fibers, has improved the sensitivity and selectivity of the underlying methods.

Graphene is an atomically thin honeycomb lattice of carbon atoms, which was first identified by Geim et al. (2009) in a simple tabletop experiment (Novoselov et al., 2004). It is considered as the basic building block of carbon nanotubes, graphite, and fullerene C60 (Chen et al., 2010). Graphene is expected to be a superior adsorbent for SPE as it possess a large specific surface area (theoretical value 2630 m²/g) (Stoller et al., 2008), suggesting a high sorption capacity. With a large delocalized π-electron system, graphene can form a strong π-stacking interaction with the benzene ring compounds (Allen et al., 2002; Dreyer et al., 2010), thus might serve as a good adsorbent for the adsorption of benzenoid-form compounds. Graphene-based materials have been adopted as sorbents for SPE (Dong et al., 2010; Liu et al., 2011; Huang et al., 2012). Because preparation of graphene is rather difficult and complex, graphene nanoplatelets (GNPs) are also

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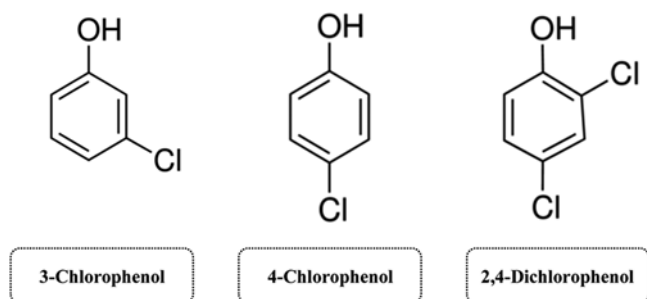E-mail: bcc0319@kist.re.kr

Fig. 1 Chemical structures of 3-Chlorophenol, 4-Chlorophenol, and 2, 4-Dichlorophenol.

intensively studied. GNPs are easier to obtain, have similar properties, and can be used in the same applications (Partoens and Peeters, 2006).

GNPs with an average thickness of 5–10 nanometers are offered in varying sizes up to 50 microns. The use of GNPs is desirable, because they are cheaper and easier to produce than single-layered graphene and carbon nanotubes (Kotov, 2006). These interesting nanoparticles are comprised of 10–30 platelet-shaped graphene sheets that are identical to those found in the walls of carbon nanotubes, but in a planar form retaining the single layer properties (Choi et al., 2010). Owing to their platelet shape, they have an exceptionally high surface area per unit mass, which is much greater than those of graphite and of carbon nanotubes (Pumera, 2009). Considering all these features, GNPs are therefore, useful in various fields of research. It can be applied as a new and efficient adsorbent material in solid phase extraction for analytical purposes.

In this work, we demonstrate a novel SPE method using GNP powder as an adsorbent. Chlorophenols (CPs) were chosen as model analytes for their high toxicity and widespread environmental occurrence (Ahlborg and Thunberg, 1980). CPs are extensively used as preservatives, fungicides, pesticides, disinfectants, and intermediates in many industries (Wegman and Hofster, 1979). They are discharged into the environment due to their huge production (Jung et al., 1997). CPs are generated from phenols during the treatment of tap water with chlorine and are considered to be one of the most obnoxious contaminants (Lezamiz and Jonsson, 2007; Mathialagan and Viraraghavan, 2008), because they deteriorate taste and produce an unfavorable smell. Moreover, they are thought to be serious health hazards due to their accumulation in moderate amounts and high toxicity (Bianchi et al., 2002; Ribeiro et al., 2002). The adsorptions of three chlorophenols, 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), and 2, 4-dichlorophenol (2, 4-DCP) on the GNPs were tested in the present study (Fig. 1). The ability of the GNPs as an adsorbent material was observed by passing the chlorophenols-containing water samples through the GNPs-packed SPE cartridges and by analyzing the extracted chlorophenols using UV-visible spectrophotometer.
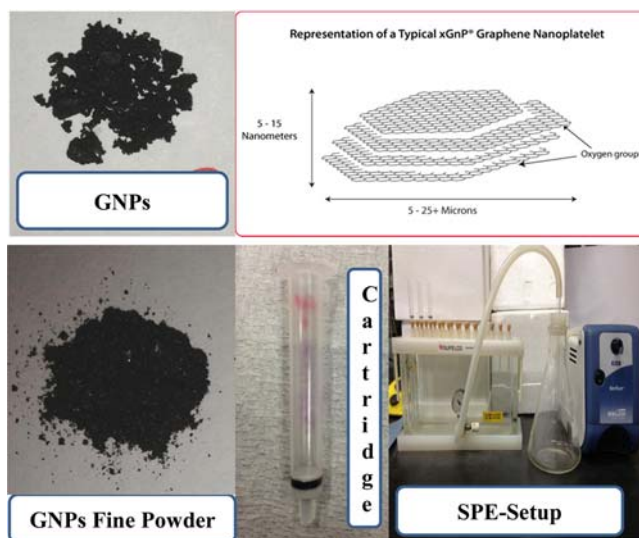

Fig. 2 GNPs-based SPE Experimental setup.

Materials and Methods

Apparatus. The SPE experiments were performed on a Supelco vacuum manifold processing station (Sigma-Aldrich, Korea), with a Dryfast vacuum pump (Welch, USA). UV-Vis absorption was recorded using Varian Carry 5000 spectrophotometer. X-ray photoelectron spectrometer (XPS, ESCSA 2000, VG Microtech, U.K.) was used to investigate the surface composition of the GNPs. The morphology of GNPs was studied using field emission scanning electron microscope (FE-SEM, S-4300SE, Hitachi, Japan), transmission electron microscope (TEM, JEM 2100F, JEOL, Japan) (Ning et al., 2013).

Reagents and materials. GNPs with thickness and length values of about 5 nm and 20 μm, respectively, were purchased from XG Sciences (USA). 3-CP, 4-CP and 2, 4-DCP, were purchased from Sigma-Aldrich (USA). Methanol (HPLC-grade) was purchased from Burdick & Jackson (USA). Sodium hydroxide was purchased from Junsei Chemical Co., Ltd (Japan). De-ionized water was purified by a Milli-Q water purification system (Millipore, USA).

The stock solutions of chlorophenols were prepared by dissolving each chlorophenol in methanol to obtain 1 mg/mL concentration. A series of working standards were prepared by mixing an appropriate amount of stock solution with de-ionized water. The alkaline methanol was prepared by adding 1.5 mL of 1 M NaOH aqueous solution to 50 mL of methanol.

Solid-phase extraction cartridges and procedures. GNPs were ground into a fine powder using mortar and pestle, and a 30-mg aliquot was weighed and loaded into a 3-mL SPE cartridge. Upper and lower frits were properly placed to avoid adsorbent loss (Fig. 2). Prior to extraction, the cartridge was preconditioned sequentially with 9 mL of methanol and 9 mL of water. The sample solution (50 mL) was passed through the cartridge at a flow rate of 1 mL/
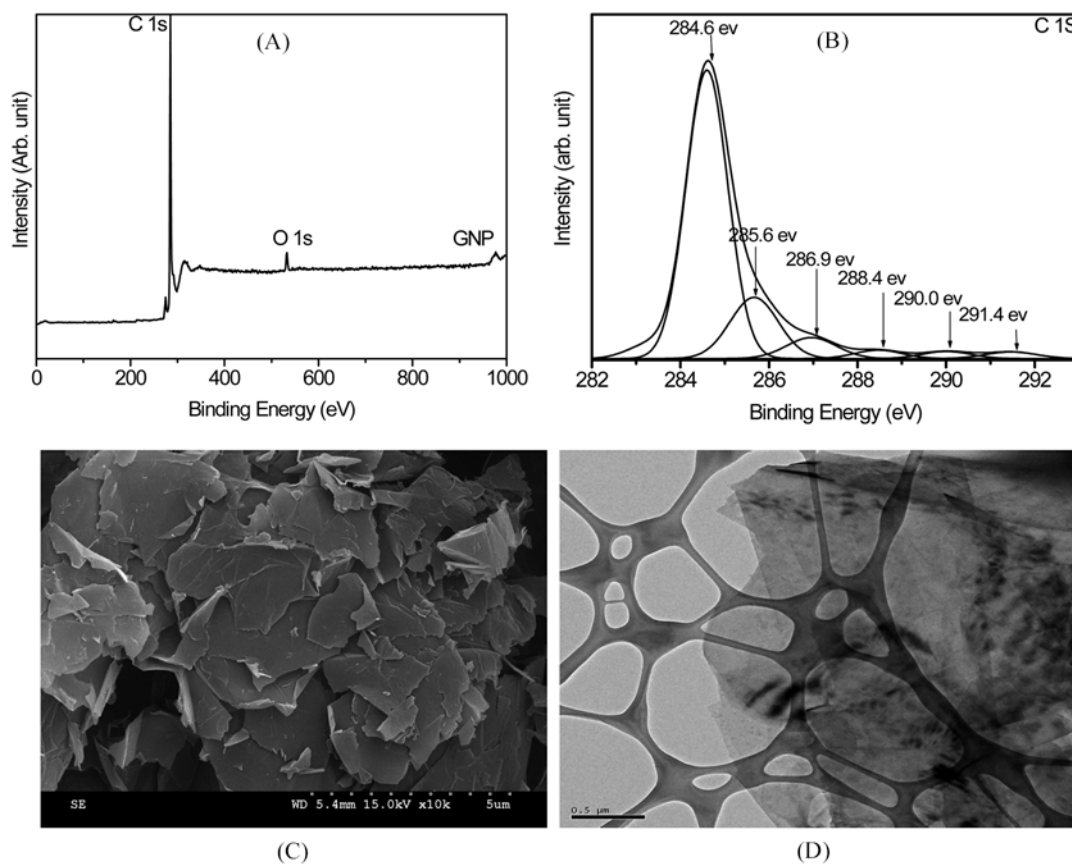
Fig. 3 Characterization of GNPs. (A) Wide scan spectra (B) High resolution scan data of GNPs (C) SEM image of GNPs (D) TEM image of GNPs

min. The cartridge was washed with 1 mL of 10% (v/v) methanol aqueous solution to remove the co-adsorbed matrix materials from the cartridge. The analytes retained on the cartridge were eluted with 2 mL of alkaline methanol. Finally the absorbance of the analytes in the eluate was detected with the UV-vis spectrophotometer system. After used for extraction, the cartridge was rewashed with 1 mL of alkaline methanol, 9 mL of methanol, and 9 mL of water. Thus the cartridge was prepared for immediate use in the next extraction (Liu et al., 2011).

Spectrophotometry. The maximum UV-Vis absorbance of 3-CP, 4-CP, and 2, 4-DCP were recorded at the wave lengths 293, 300, and 307 nm, respectively. The spectral range of 250–400 nm with a scan speed of 60 nm/min was optimized for the analysis. Baseline correction was measured using only solvent (alkaline methanol) before measuring the absorbance of the analytes in the samples.

Results and Discussion

In the present study, the adsorption efficiency of a novel SPE adsorption material, GNP, was demonstrated. The chlorophenols were extracted from water into an organic phase and were passed through the adsorbent material. The chlorophenols were further

determined under selected experimental conditions to assess linearity, recovery, accuracy, and precision.

Characterization of GNPs. Commercially available GNPs and various techniques were utilized to understand the exact surface composition and morphology of the GNPs. XPS measurements were performed to reveal the surface compositions of GNPs (Yadav et al., 2013). Wide-scan XPS of the surface of the GNPs shows two strong peaks at 285.0 eV (C 1s) and 531.6 (O 1s), which indicate the presence of oxygen functionalities on the surface of GNPs. The C 1s high resolution spectra of GNPs could be fitted with six fractional peaks, where the different asymmetric peak at 284.6 eV was ascribed to the sp^2-hybridized graphitic structure and the peak at 285.3 eV was assigned to a sp^3-hybridized orbital. The other peaks with higher binding energies located at 286.9, 288.4, and 290.0 eV correspond to C-O (alcohol, ether), -O-C=O (ketone, aldehyde) and -COO- (ester, carboxylic acid), respectively. The π-π* transition loss peak was observed at 291.4 eV (Yadav and Cho, 2013). The SEM and TEM images of the GNPs displayed the morphology of the GNPs (Yadav and Mahapatra, 2010). It is also clear that few layered-GNPs are present; the exact number of graphene layers cannot be estimated, and no large graphitic aggregates were obtained, indicating the presence of completely exfoliated states of graphene (Fig. 3).
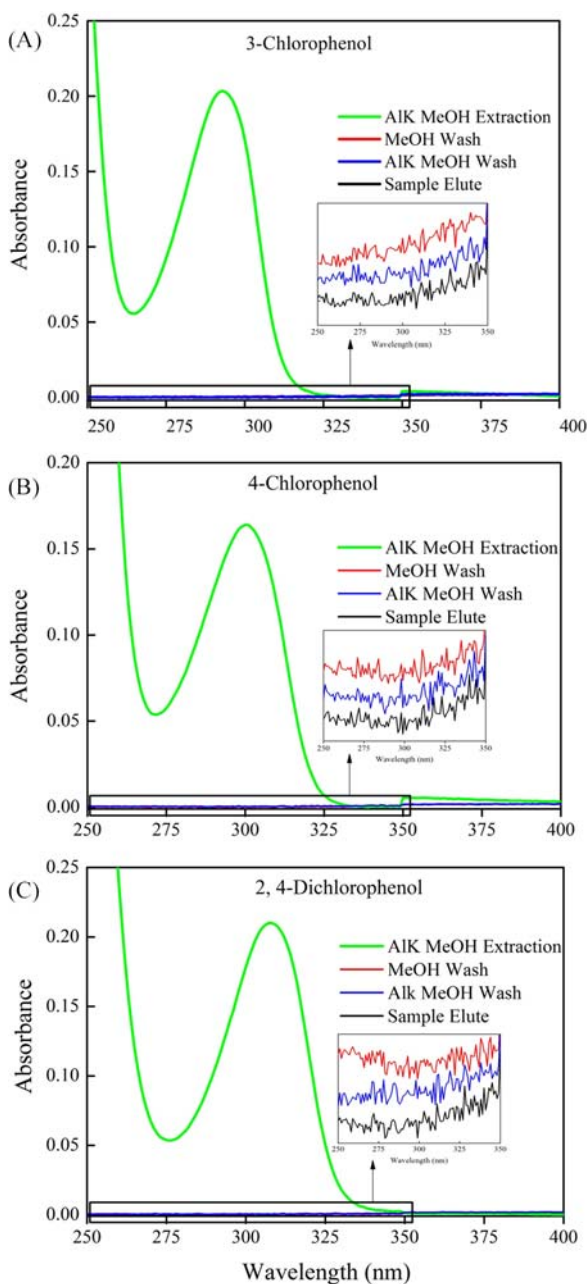
Fig. 4 UV-visible spectra of three chlorophenols (0.5 μg/mL) and the spectra of elution and washing steps in the experimental procedure, representing the adsorption of each chlorophenol on the GNPs-packed SPE cartridges.

Optimization of SPE procedures. The sorption of CPs on the GNPs-packed SPE cartridges was examined. Aqueous solutions (50 mL) of three CPs at concentrations, 0.1, 0.5, and 1 μg/mL were passed through the cartridges, and no analytes were found in the flow throughs, indicating that the GNPs-packed cartridges have a good sorption capacity for the CPs. Subsequently, the cartridge was washed with 1 mL of 10% methanol aqueous solution. Upon analysis of the collected washing solution, they were found to contain no CPs, indicating that 10% methanol solution cannot elute the analytes from the cartridge and thereby was suitable to be used as a washing solution. The volume of eluent was also optimized, and the efficient elution could only be achieved with no less than 2 mL of alkaline methanol. A sequential elution with additional 2 mL of alkaline methanol revealed the absence of CPs in the adsorbent (Fig. 4). Thus, alkaline methanol (2 mL) was confirmed as eluent. This complete elution of analytes also guarantees the reusability of the SPE cartridges. Between extractions, the cartridges were washed with alkaline methanol, pure methanol, and water to ensure that the cartridge would immediately be available for the next extraction.

Generally, for SPE, satisfactory recoveries are required in a large volume of sample solution to obtain a high enrichment factor. Therefore, 50 mL was regarded as the breakthrough volume (Jimeez-Soto et al., 2009). CPs are weakly acidic, thus the acceptor solution must be sufficiently alkaline. Hence, alkaline methanol was chosen as the solvent for elution. The alkaline condition was favorable for reducing the affinity for GNPs and facilitating the elution. The UV spectra can be utilized to identify target analytes in the UV-Vis spectrophotometer. Accordingly, each extracted chlorophenol was quantified at its own maximum adsorption wavelength (Haghi, 2011).

Analytical figures of merit. Our initial concern was checking the suitability of GNPs as the adsorbent material for the SPE procedure and its application to the target analytes. To evaluate the performance of the SPE procedure, the figures of merit were studied. The analytical response obtained via this GNPs-based SPE-UV-Vis Spectrophotometric method is summarized in Table 1. The devised method was linear over a calibration range with the correlation coefficient ($r^2 > 0.996$) for 3-CP, 4-CP and 2, 4-DCP (Fig. 5). SPE was carried out with 50 mL aqueous standards. All linear ranges were based on the maximum absorbance achieved at a defined wavelength of at least six concentrations for each CP. Good linear relationships were obtained in all three CPs studied. For optimization of the extraction conditions, the extraction

Table 1 Analytical figures of GNPs-based SPE-UV-Vis Spectrophotometric method

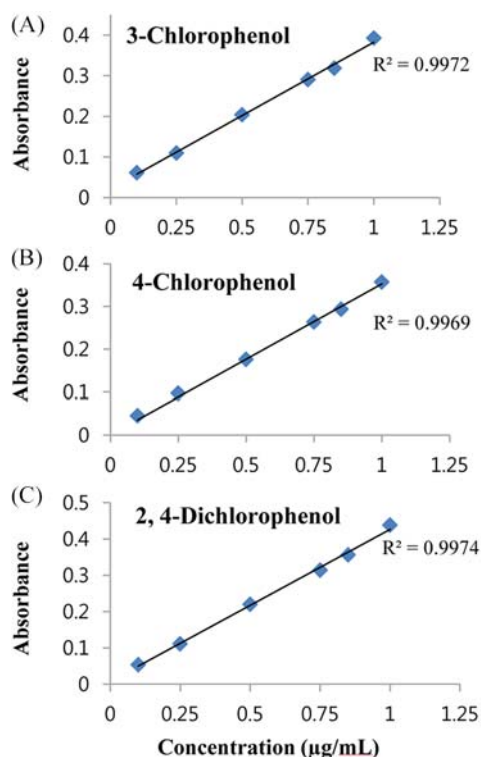| Compound	UV Wave Length (nm)	Linear Range (μg/mL)	Correlation coefficient (R^2)	Mean Recovery (%) (n=3)		
				0.1 μg/mL	0.5 μg/mL	0.75 μg/mL
3-CP	293	0.1–1	0.9972	102.1±0.9	99.4±2.0	103.7±3.4
4-CP	300	0.1–1	0.9969	101.8±1.0	95.2±3.8	102.6±4.9
2,4-DCP	307	0.1–1	0.9974	101.3±1.1	96.9±3.1	100.3±3.5

Fig. 5 Linearity profiles of three chlorophenols. (A) 3-Chlorophenol (B) 4-Chlorophenol (C) 2,4-Dichlorophenol

efficiency was evaluated based on the extraction recovery of the analytes. The extraction recovery was measured as the ratio between the amount of the analyte in the reconstituted solution and the initial amount of the analyte in the spiked aqueous sample (Wang et al., 2012). The overall recoveries of three CPs in the water samples ranged from 95.2 to 103.7%.

Precisions, expressed as coefficients of variation (% CV) and accuracies as percent relative errors (% bias), were determined from QC samples at three different concentrations, 0.1, 0.5, and 0.75 μg/mL. They are described as low-, medium-, and high-concentrations, respectively. Intraday and interday precision and accuracy were determined by analyzing consecutively three replicates of Milli-Q water spiked with CPs on day 1 for 3 days (Luo et al., 2012). The intra-day ($n=3$) precisions ranged between 4.1 and 11.5%, whereas accuracies ranged between −4.7 and 3.7%. The inter-day ($n=3$) precisions ranged between 1.0 and 6.4%, and

the accuracies ranged between −5.2 and 9.0% (Table 2). A single cartridge was used for the analysis of the calibration, intraday, and interday assay set of each analyte. In the day-to-day (interday) assays, the air-dried cartridges were stored at room temperature. Each cartridge was reused at least 12 times within 3 days, producing desired analytical results. Hence intraday assay is synonymous to cartridge-to-cartridge assay and the interday assay depicts the reusability of the cartridges. Therefore, the results demonstrate the good reproducibility and reusability of the GNPs-packed SPE cartridges. It is generally known that sorbent drying usually deteriorates the recoveries of the commonly used adsorbent materials due to a reduction in the surface area of the sorbent material. In contrast, the sorbent drying has not shown any significant impact on the analytical performance of the GNPs-packed SPE cartridges. The greater surface area of the GNPs can resist the drying affects compared to other sorbent materials.

Based on the above described results, we can realize that the advantage of GNPs mainly lies in the higher sorption capacity and is more facile to achieve complete elution with GNPs. Therefore, we ascribe the advantages of GNPs not only to its large surface area but also to its unique chemical structure. The hexagonal arrays of carbon atoms in the GNPs may have a strong π-π interaction with the target molecules (Liu et al., 2011). The molecules can readily access the surfaces of GNPs, which is favorable for both the adsorption and elution processes. These features make GNPs very attractive as an adsorbent material. Further implementation of sensitive instrumentation and increasing the range of analytes will increase the applicability of GNPs as an SPE adsorbent.

In the present study, a simple, rapid, and sensitive solid phase extraction procedure using a novel adsorbent matrix, GNPs, is described. XPS, SEM, and TEM studies have provided the characteristics of the GNPs. By using the three CPs as model analytes, the GNPs-packed SPE cartridges showed reliable and attractive analytical performance in the analysis of water samples. Other advantages of using GNPs as SPE adsorbent such as high sorption capacity, good reusability, no impact of sorbent drying, and fine reproducibility have also been demonstrated. Therefore, we suggest that GNPs are promising material for solid phase extraction procedures in analytical studies.

Table 2 Validation data of CPs spiked water samples (0.1, 0.5 and 0.75 μg/mL) using GNPs as adsorbent material

Compound	Intraday Analysis (n=3)						Interday Analysis (n=3×3)					
	Precision (RSD)			Accuracy (Bias, %)			Precision (RSD)			Accuracy (Bias, %)		
	0.1	0.5	0.75	0.1	0.5	0.75	0.1	0.5	0.75	0.1	0.5	0.75
3-CP	9.5	4.1	4.4	2.1	-0.5	3.7	6.4	2.0	2.0	1.9	-1.8	1.3
4-CP	10.6	11.2	6.4	1.8	-4.7	2.6	2.4	5.0	1.0	-4.2	1.2	1.7
2,4-DCP	11.5	6.4	4.1	1.4	-3.0	1.4	5.4	5.5	2.9	9.0	-5.2	-2.4

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