Enrichment-Free Rapid Detection of Phthalates in Chinese Liquor with Electrochemical Impedance Spectroscopy

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Received: 31 December 2019; Accepted: 04 February 2020; Published: 7 February 2020

Abstract: A non-invasive real-time detection technique for phthalates in Chinese liquor is proposed in this paper. This method is based on the measurement of Faradaic impedance in the presence of a redox probe, [Fe(CN)6]3−/4−, upon the absorption of phthalates to the graphene electrode surface. This absorption activity is according to the π−π stacking interactions between phthalates and the graphene working electrode which allows direct sampling and analyte preconcentration. The absorption of phthalates retards the interfacial electron-transfer kinetics and increases the charge-transfer resistance (Rct). Numerical values of Rct were extracted from a simulation of electrochemical impedance spectroscopy (EIS) spectra with the corresponding equivalent circuit. Cathodic polarization was employed prior to EIS measurements to effectively eliminate the metal ion interference. The results yielded a detection limit of 0.024 ng/L for diethyl phthalate (DEP) with a linear range from 2.22 ng to 1.11 μg. These results indicate a possibility of developing a household sensor for phthalate determination in Chinese liquor.

Keywords: in-situ preconcentration; phthalates; graphene; electrochemical impedance spectroscopy

1. Introduction

Since the outbreak of phthalates esters (PAEs) in Chinese liquor, plasticizers have been detected in beverages, infant drinks, soy sauce, vinegar, and other condiments in succession [1,2]. The potential environmental and human health impacts caused by PAEs are spreaded into our daily life [3–6]. PAEs are very widely employed as additives for polymers in plastic, particularly in polyvinyl chloride (PVC) and polyethylene terephthalate (PET), which are widely applied in rubber, cellulose, and in the production of styrene as well [7]. PAEs help to improve the flexibility, transparency, and durability of articles manufactured with polymeric matrixes due to its low production cost. Unfortunately, some illegal food producers take advantage of the above feature of PAEs, adding PAEs instead of palm oil into food products to sustain the desired texture, resulting in severe harm to consumers [8,9]. Besides intentional addition, PAEs migrate from plastic packaging to the articles of consumption. This is attributed to the fact that the plasticizer molecules are only physically attached to polymer chains rather than via primary bonding [10–12].

Currently, some of the most common and efficient approaches for detecting PAEs are gas chromatography–mass spectroscopy (GC/MS) and liquid chromatography–mass spectrometry (LC/MS) [13,14]. The aforementioned methods provide high resolution and sensitivity to determine...
multiple PAEs simultaneously. However, they are destructive techniques which require multi-step sample pretreatment and relatively high cost. Recently, some researchers have explored the application of near-infrared (NIR) spectroscopy to detect PAEs in red tea beverage. The results showed a lack of sensitivity—the detection limit was about 15.8 mg/L [15]. Zhang et al. developed an enzyme-linked immunosorbent assay (ELISA) approach which performed the analysis with elevated sensitivity and detection limit compare to NIR. However, ELISA involves complicated procedures such as antibody production, purification, and derivatizations, which hinder its application [16]. Molecularly imprinted polymers (MIP)-based electrochemical sensors have drawn prominent attention, and a di-n-butyl phthalate (DBP) electrochemical sensor was constructed applying magnetic graphene oxide and gold nanoparticles as a molecular recognition element. It showed a 222.6 ng/L detection limit with excellent repeatability (relative standard deviation (RSD), 2.5%) [17]. MIP also exhibits some notable drawbacks, such as the complicated preparation process, low binding capacity, and poor site accessibility [18]. An inter-digital sensor with multiple sensing gold electrodes fabricated on a silicon substrate using micro-electromechanical system (MEMS) device fabrication technology was reported in 2013 [19], and it provided a sensitive and rapid approach for detecting PAEs in water and juice samples with EIS. The results proved the applicability of EIS, however the reported MEMS method requires complicated working electrode fabrication. Table 1 illustrates the present state of PAEs analysis.

### Table 1. Summary of literature methods aimed at phthalates ester (PAEs) determination.

| Analytical Technique | Matrix | Compounds | LOD ng/L | Sample Pretreatment | Reference |
|----------------------|--------|-----------|----------|---------------------|-----------|
| TLC                  | Glucose| DEP       | 2.4      | Multi-step          | [20]      |
| Fluorescence         | Waste water| DEP     | 18,440   | None                | [21]      |
| GC                   | Water  | DEP       | 3.7      | Liquid phase extraction | [22] |
| (GC-MS/MS)           | Chinese liquor| DEP    | 100      | Liquid phase extraction | [23] |
| GC-MS                | Alcoholic beverages| DEP  | 700,000  | Centrifugation extraction | [7] |
| LC-DAD               | Red wine| DEP      | 2000     | Separation and elution | [7] |
| HPLC Electrochemical Sensor | Rainwater| DEP      | 200      | In-tube SPME | [24] |
| UHPLC-MS             | Chinese liquor| DINP  | 11,300   | None                | [25] |
| HPLC-MS             | Beverage| 9 PAEs  | 173      | SPE                 | [26] |

TLC: thin layer chromatography; GC: gas chromaograph; GC-MS/MS: gas chromatography tandem triple quadruple mass spectrometry; GC-MS: gas chromaographmass spectrometry; GC-DAD: liquid chromatography-diode array detector; HPLC: high-performance liquid chromatography; UHPLC-MS: ultra high performance liquid chromatography-mass spectrometry; HPLC-MS: High performance liquid chromatography-mass spectrometry. DINP: diisononyl phthalate; DBEP: dibutyl ethyl phthalate. LOD: limit of detection. SPEM: micro-dispersive solid-phase extraction; SPE: solid-phase extraction.

Although the analytical methods described above are suitable for the administration of manufacturing and quality control departments, they are helpless to dispel the concerns caused by PAEs in people’s daily life. Therefore, there is an urgent demand for the development of a facile, highly sensitive, low-cost PAEs analysis technique.

The objective of the presented work is to demonstrate an enrichment-free detection approach for PAEs analysis in Chinese liquor with electrochemical impedance spectroscopy (EIS). A graphene
working electrode was employed to accomplish the in-situ preconcentration of PAEs according to the $\pi-\pi$ stacking interactions between graphene and benzene rings in PAEs molecules. The absorption of PAEs retards the interfacial electron-transfer kinetics and increases the charge-transfer resistance ($R_{ct}$). Numerical values of $R_{ct}$ were extracted from a simulation of EIS spectra with the corresponding equivalent circuit. Cathodic polarization was employed prior to EIS measurements to effectively eliminate the metal ion interference. Figure 1 outlines the basic strategies of the PAEs sensor based on the EIS measurements applying graphene as the working electrode. This work implicates the potential of developing a household device for PAEs determination.

Figure 1. A schematic diagram illustrating the basic strategies of in situ preconcentration and detection of PAEs in Chinese liquor with electrochemical impedance spectroscopy.

2. Materials and Methods

2.1. Chemicals and Materials

All aqueous stock solutions were prepared with deionized water purified by a membrane device. Ethanol (absolute) and acetone were obtained from (Tianjin Fuchen Chemical Reagent Factory, Tianjin, China). Diethyl phthalate (DEP) was obtained from Macklin (Shanghai, China). Copper (II) chloride dihydrate, sodium chloride, and potassium ferricyanide were all obtained from (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Graphene was obtained from (YURUI Chemical Co., Ltd., Shanghai, China). The purchased graphene was 1–5 layers, its purity was greater than 95%, its thickness distribution was from 1 to 1.77 nm, with diameters ranging from 0.5 to 5 μm. C18 solid-phase extraction cartridges were purchased from CNW Technologies (Shanghai, China).

2.2. Apparatus and Software

The apparatus consists of an electrochemical workstation (CorrTest, Wuhan, China) with a conventional three-electrode system, including a glassy carbon electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a carbon rod as the auxiliary electrode. Other equipment included a KQ5200DE CNC ultrasonic cleaning machine (Shanghai, China); a DHG-9053A electric thermostatic blast drying oven (Kunshan, China); and a XB220A electronic analytical balance (Precisa). A GC7890B-MS5977B instrument from Agilent (Santa Clara CA, USA) was used for chemical analysis. For analog equivalent circuit software, CorrTest and CSStudio were used.
2.3. Preparation of Graphene Electrode

The graphene working electrode was manufactured by dropping a mixed solution containing tetrahydrofuran and graphene onto a clean glassy carbon electrode to form a thin conductive film [28,29]. Prior to each manufacturing process, the glassy carbon electrode was polished with aluminum powder and cleaned with an ultrasonic cleaner. The graphene was dispersed in tetrahydrofuran in an ultrasonic cleaner for 30 min, then 5 μL of the dispersed graphene solution was dropped onto a cleaned glassy carbon electrode. Each electrochemical measurement was carried out after the tetrahydrofuran was completely volatilized in the air.

2.4. Electrochemical Measurements

The EIS measurements were taken with a three-electrode system. The working electrode was the graphene electrode, the Ag/AgCl electrode was used as the reference electrode, and the graphite carbon rod was the auxiliary electrode. A 10 mV AC amplitude was employed with a frequency range 1 Hz–0.1 M Hz. All the testing solutions contained 0.01 M potassium ferricyanide and 0.5 M sodium chloride as supporting electrolytes.

2.5. Standard Solutions Preparation

The stock solution was made by dissolving DEP in 50% ethanol. A serial dilution was followed up to obtain 0.01 nM, 0.1 nM, 1 nM, and 5 nM DEP solutions in total volumes of 10 mL containing 10 mM potassium ferrocyanide and 0.5 M potassium chloride as electrolyte.

2.6. Interference Elimination

Cathodic polarization was employed to eliminate the metal ions interference in the liquor samples. Graphite carbon rods were used as working and auxiliary electrodes, the Ag/AgCl electrode was used as the electrical reference electrode, the polarized potential was −0.1 V vs. Ag/AgCl. An artificial liquor sample was made from 60% ethanol solution with 0.5 μM DEP and 0.5 mM CuCl₂ addition. This artificial liquor solution underwent cathodic polarization with an appointed duration prior to EIS measurement. The efficiency of copper metal ion elimination was determined by the ratio of the measured DEP concentration according to the standard curve to the original DEP concentration (0.5 μM).

2.7. Standard Addition

Concentrated DEP solution was spiked into 8 mL real liquor samples dropwise to perform the standard addition quantification. The final serial concentrations of DEP in liquor were 0, 5, and 10 μM with total volume of 9 mL. The above liquor solution underwent electrochemical polarization at −0.1 mV (vs. Ag/AgCl) to eliminate metal ion interference. After cathodic polarization, 1 mL 0.1 M potassium ferrocyanide in 0.5 M NaCl as supporting electrolyte was added for EIS measurement.

2.8. Method Validation with GC/MS

First, 10 mL of the Chinese liquor sample underwent solid-phase extraction with a C18 cartridge, which was rinsed with 12 mL 50% methanol. The sorbent was washed off by 20 mL water, the absorbed compounds were de-absorbed with 20 mL hexane, and then dried by nitrogen purge. The volume of extracts was adjusted to 10 mL for GC analysis. All samples were prepared in triplicate for repeatability tests. GC/MS experimental conditions were according to [19] in brief. External standard and standard addition were applied for the calibration curve preparation and PAEs determination in the real sample. A linear regression was employed for the calibration curve and was plotted by Excel software.
2.9. Quality Control and Quality Assurance

Quality assurance and quality control measurements were applied for all sample pretreatment and analytical procedures. Laboratory blanks (i.e., solvent and matrix) were treated equally as samples. Background variation was considered to be negligible during storage and analysis, when there was no significant difference was found (t-test, \( p < 0.05 \)) between analyte concentrations in the analytical blanks. Limits of detection (LODs) were calculated based on the signals three times greater than the standard deviations of the average background signals of the blanks.

3. Results

3.1. Advantages of Graphene Electrode

Graphene-based materials have been extensively applied because their characteristic structure endows them with a large surface area, and because of the potential for establishing \( \pi-\pi \) stacking interactions due to graphene’s delocalized electrons, allowing them to be utilized as excellent sorbents [30–32]. Herein, a graphene working electrode was employed to accomplish the PAEs’ in-situ preconcentration according to the \( \pi-\pi \) stacking interactions between graphene and PAEs which consist mainly of one benzene ring and two aliphatic ester groups attached to the benzene ring in an ortho configuration. EIS was employed to characterize PAEs’ absorption on the working electrode. The complex impedance is displayed as the sum of the real (\( Z' \)) and imaginary (\( Z'' \)) components. A typical shape of a Faradaic impedance spectrum presented in a Nyquist plot includes a semicircular region lying on the \( Z' \) axis followed by a straight line. The semicircle portion, observed at high frequencies, corresponds to the electron-transfer-limited process, whereas the linear part is characteristic of the lower frequency range and represents the diffusion-limited electron transfer process. Figure 2a, 2b shows the Nyquist plots of graphene and glassy carbon electrode with and without PAEs addition, respectively. Figure 2b appeared superimposed at high frequency with a slight deviation at low frequency, indicating the poor PAEs absorption on the surface of the glassy carbon electrode and thus a nonsignificant charge-transfer-resistance alteration. A different feature appeared on the Nyquist curves of graphene with and without PAEs addition. Figure 2a shows a pair of semicircles with different diameters, which suggests that the effective absorption of PAEs on the graphene electrode led to an increased charge transfer resistance. To achieve better resolution, a deconvolution treatment was applied to Figure 2a,b, which resulted in Figure 2c,d. In Figure 2c, two clearly separated peaks start to deviate at 223 Hz, reaching a summit at 13.6 Hz. This can be compared to Figure 2d, where two peaks are superimposed together without significant resolution.
3.2. Standard Curve

EIS measurements were carried out with a concentration series of DEP solutions from 0.01 to 5 nM on the graphene working electrode. From Figure 3a, at high frequency the diameters of the semicircle portion which represents interfacial electron-transfer resistance increased with increasing concentrations of DEP, implying that the DEP absorption on the surface of the graphene electrode was proportional to its concentration. Data pre-processing is critical at this point. A Nyquist plot simulation was carried out based on the equivalent circuit with CorrTest and CSSStudio. Simulated curves were precisely fitted with experimental Nyquist plots at high frequency in which the vital features of EIS measurement dominated. The retarded electron transfer phenomena due to the DEP absorption was expressed at high frequency. At low frequency, a tiny deviation appeared, in which the mass transfer dominated. This part of the EIS information is irrelevant for the PAEs’ determination. Simulated curves remained the major electrochemical properties of PAEs on graphene electrode. Thus, the characteristic of Nyquist plots was translated into a set of circuit elements numerical values after curve fitting. Based on the equivalent circuits, the numerical values of $R_t$ were extracted to build a linear relationship between the electron-transfer resistance and logarithmic value of DEP. Concentrations of DEP were found ranging from 0.1 to 5 nM with a slope of 1.31 and a correlation coefficient of 0.9613 (Figure 3b) and a detection limit of 0.024 ng/L [33].
Figure 3. (a) Impedance spectrum of PAEs concentration gradient. The concentration of DEP was 0, 2.22, 22.22, 222.24, and 1111.2 ng/L, respectively. The measured solution contained 0.5 M NaCl and 0.01 M K₃[Fe(CN)₆]. EIS was measured under an open circuit voltage with an AC amplitude of 10 mV and a frequency range of 1 Hz–0.1 MHz. Each concentration was measured three times, and its mean value was plotted; (b) The $R_{ct}$ values with respect to corresponding DEP concentrations. The inset shows a representative simulated Nyquist curve superposed with the experimental measurements according to corresponding equivalent circuits.

3.3. Elimination of Metal Ions Interference in the Chinese Liquor Sample

Chinese liquor is a distilled spirit made from mixed grains fermentation, which is usually stored in pottery containers after distillation for a certain period of time to obtain desired flavors. Therefore, notable metal ions migrate from the pottery jars to the liquor during the storage process [34–36]. The amount of metal ions in the liquor become problematic due to the similar hydrophobic features of the graphene working electrode and the metal ions. Metal ions adsorbed on the working electrode surface which give faulty signals during the EIS data collection for PAEs determination. Prior to EIS measurements, cathodic polarization with a graphite rod as working electrode at −0.1 V vs. Ag/AgCl was carried out to absorb or/and reduce metal ions on the surface of the graphite working electrode. Figure 4 presents the metal ion elimination efficiency vs. cathodic polarization duration. Without cathodic polarization pretreatment, only 30% of PAEs added into the artificial liquor were detected. The efficiency climbed up to 90% rapidly with increasing polarization time, and this reached a plateau after 30 min. This phenomenon was due to the low concentration of residual metal ions in the solution. The efficiency slightly increased to 98% until 40 min; the efficiency may infinitely approach 100% percent by continuing proceeding cathodic polarization long enough.
Figure 4. Metal ions elimination efficiency vs. cathodic polarization time. Graphite carbon rods were used as working and auxiliary electrode, Ag/AgCl electrode as the electrical reference electrode, polarized potential was −0.1 V vs. Ag/AgCl.

3.4. PAEs Quantification in Chinese Liquor

Standard addition was applied to determine DEP in real liquor samples in order to avoid the matrix effect. A 40 min cathodic polarization was carried out to eliminate the metal ion interference prior to EIS measurement. Detected DEP concentrations including standard deviations in real liquor are listed in Table 2. To validate the EIS measurements, GC/MS was employed to determine DEP in three liquor samples. Errors between these two sets of results were from +0.034 mg/L to −0.021 mg/L. The reason for these errors is that graphene electrode absorbs all kinds of PAEs besides DEP. As a major PAE, DEP coexists with other PAEs in liquor, and the EIS approach for PAEs analysis lacks specificity. This indicates that the presented method is suitable for total PAEs detection in liquor samples rather than for the detection of specific PAEs.

Table 2. The comparison of DEP analysis in real liquor samples with GC/MS and EIS methods.

| Sample         | EIS DEP (mg/L) | Standard Deviation (N = 3) | GC/MS DEP (mg/L) | Standard Deviation (N = 3) | Error (mg/L) |
|----------------|----------------|----------------------------|------------------|----------------------------|--------------|
| Xiaoqu liquor  | 0.149          | 0.021                      | 0.135            | 0.012                      | +0.014       |
| Daqu liquor    | 0.170          | 0.018                      | 0.191            | 0.025                      | −0.021       |
| Medicinal liquor | 1.234          | 0.020                      | 1.200            | 0.024                      | +0.034       |

4. Conclusions

A method for the in-situ preconcentration and detection of PAEs in Chinese liquor with EIS is demonstrated. The elimination of metal ions interference prior to EIS measurement minimized the possibility of false positives. Compared to the GC/MS approach for PAEs detection, the
demonstrated method offered a lower detection limit of 0.024 ng/L without a preconcentration step, and the entire PAEs analysis process was accomplished in few minutes. In terms of simplicity, speed, and low detection limits, the proposed method outperformed the techniques in the literature. We believe that these features may be incorporated into an inexpensive, rapid, and selective usable household device.

**Author Contributions:** Conceptualization, Y.X. and D.W.; methodology, Y.X.; validation, X.J.; formal analysis, X.J. and Y.X.; resources, D.W. and F.Z.; data curation, X.J.; writing—original draft preparation, Y.X., J.W. and X.J.; writing—review and editing, Y.X., X.J. and J.W.; visualization, J.W.; supervision, D.W.; project administration, D.W. and F.Z.

**Funding:** The work was financially supported by National Nature Science Foundation of China Project No. 31601560 and the National Key Research and Development Program of China (No. 2016YFC0502208 and 2018YFD0900604).

**Conflict of Interest:** The authors declare no conflict of interests.

**References**

1. Gong, Y. Application and Hazard of Phthalic Acid Ester Plasticizer. *Shandong Chem. Ind.* 2011, 40, 93–95.
2. Liu, F. Application of Plasticizer and Its Harm. *Guangdong Chem. Ind.* 2011, 38, 77–77.
3. Liu, M. Analysis of Damage and Prevention of Plasticizer. *J. Green Sci. Technol.* 2013, 4, 210–212.
4. Wang, M.S. Toxicity of Phthalate (PEAs) and Its Harm to Human Health. *Jiangsu Prev. Med.* 2011, 22, 68–70.
5. Zhan, W.C. Food Safety Metaphor for Plasticizer Storm. *Assets Financ. Adm. Inst.* 2011, 11, 11–12.
6. Zhang, T.K. From Clouding Agents to Plasticizers. *Sci Technol Vis.* 2011, 7, 66–67.
7. Salazar-Beltrán, D.; Hinojosa-Reyes, L.; Ruiz-Ruiz, E. Phthalates in Beverages and Plastic Bottles: Sample Preparation and Determination. *Food Anal. Methods* 2018, 3, 1–14.
8. Khosravi, K.; Price, G.W. Determination of phthalates in soils and biosolids using accelerated solvent extraction coupled with SPE cleanup and GC-MS quantification. *Microchem. J.* 2015, 121, 205–212.
9. Duty, S.M.; Calafat, A.M.; Silva, M.J. The relationship between environmental exposure to phthalates and computer-aided sperm analysis motion parameters. *J. Androl.* 2004, 25, 293–302.
10. Rahman, M.; Brazel, C.S. The plasticizer market: An assessment of traditional plasticizers and research trends to meet new challenges. *Prog. Polym. Sci.* 2004, 29, 1223–1248.
11. Sioen, I.; Fierens, T.; Van, H.M. Phthalates dietary exposure and food sources for Belgian preschool children and adults. *Environ. Int.* 2012, 48, 102–108.
12. Sun, X.; Zong, W.; Liu, C. Investigation on the toxic interaction of typical plasticizers with calf thymus DNA. *J. Lumin.* 2015, 161, 71–75.
13. Castle, L. Gas chromatographic-mass spectrometric determination of adipate-based polymeric plasticizers in foods. *J. Assoc. Off. Anal. Chem.* 1988, 71, 394.
14. Fung, Y.S.; Tang, A.S.K. Liquid chromatographic determination of the plasticizer di (2-ethylhexyl) phthalate (DEHP) in PVC plastics. * Fresen. J. Anal. Chem.* 1994, 350, 721–723.
15. Wang, Y.; Shi, X.; Wu, Z. Rapid Detection of Phthalate by NIR Spectroscopy. *Chin. J. Exp. Trad. Med. Formulae* 2013, 19, 86–90.
16. Zhang, M.; Wang, Y.; Yu, X. Rapid monitoring of dicyclohexyl phthalate in foods using the direct competitive ELISA. *Food Agr. Immunol.* 2014, 25, 229–242.
17. Zhuang, H.; Liu, S.; Zhang, M. Determination of Dimethyl Phthalate in Environment Water Samples by a Highly Sensitive Indirect Competitive ELISA. *Appl. Biochem. Biotechnol.* 2012, 166, 436–445.
18. Li, X.; Wang, X.; Li, L. Electrochemical sensor based on magnetic graphene oxide@gold nanoparticles-molecular imprinted polymers for determination of dibutyl phthalate. *Talanta* 2015, 131, 354–360.
19. Turco, V.L.; Di Bella, G.; Potorti, A.G.; Fede, M.R.; Dugo, G. Determination of plasticizer residues in tea by solid phase extraction-gas chromatography-mass spectrometry. *Eur. Food Res. Technol.* 2015, 240, 451–458.
20. Zhao, J.; Zhang, S. Study on the change rule of metal element content in liquor storage. *J. Sichuan Univ. Sci. Eng.* 2008, 21, 65–67.
21. Wang, Y.; Fang, Y. Analysis of Plasticizers in glucose by Thin Layer Chromatography. *J. Mod. Sci. Instrum.* 2006, 1, 102–104.
22. Li, M.; Wu, J.; Zeng, W. Determination of phthalates in water by liquid phase microextraction and gas chromatography. *Chin. J. Analy. Chem.* 2006, 34, 127–129.
23. Wang, S.; Lei, W.; Du, X. Determination of phthalate Ester Residues in Liquor by Gas Chromatography Tandem Triple Quadruple Mass Spectrometry (GC-MS/MS) with Iotopic Internal Standards. *Chem. Reag.* 2015, 37, 443–446.
24. Fernández-Amado, M.; Prieto-Blanco, M.C.; López-Mahía, P. A comparative study of extractant and chromatographic phases for the rapid and sensitive determination of six phthalates in rainwater samples. *Chemosphere* 2017, 175, 52–65.
25. Zhao, X.; Ju, X.; Qiu, S. Fast and Sensitive Detection of Diisononyl Phthalate in Liquor Sample by Molecularly Imprinted Polymer Based Electrochemical Sensor. *Russ. J. Electrochem.* 2018, 54, 636–643.
26. Santana-Mayor, A.; Socas-Rodriguez, B.; Mdm, A. Reduced graphene oxide-coated magnetic-nanoparticles as sorbent for the determination of phthalates in environmental samples by micro-dispersive solid-phase extraction followed by ultra-high-performance liquid chromatography tandem mass spectrometry. *J. Chromatogr. A* 2018, 1565, 36.
27. González-Sálamo, J.; Hernández-Borges, J.; Mdm, A. Determination of phthalates in beverages using multiwalled carbon nanotubes dispersive solid-phase extraction before HPLC-MS. *J. Sep. Sci.* 2018, 41, 2613–2622.
28. Hou, Z.; Zhou, Y.; Li, G. Preparation and Properties of Graphene Thin Films. *J. Shenyang Univ.* 2015, 27, 16.
29. Khan, U.; May, P.; O’Neill, A. Development of stiff, strong, yet tough composites by the addition of solvent exfoliated graphene to polyurethane. *Carbon* 2010, 48, 4035–4041.
30. Sinnokrot, M.O.; Sherrill, D.C. High-accuracy quantum mechanical studies of pi-pi interactions in benzene dimers. *J. Phys. Chem. A* 2006, 110, 10656–10668.
31. Tsuzuki, S.; Honda, K.; Uchimaru, T. Origin of attraction and directionality of the pi/pi interaction: Model chemistry calculations of benzene dimer interaction. *J. Am. Chem. Soc.* 2002, 124, 104–12.
32. Liu, T.; Li, Y.; Du, Q. Adsorption of methylene blue from aqueous solution by graphene. *J. Colloid. Surf. B* 2012, 90, 197–203.
33. Ramesha, G.K.; Kumara, A.V.; Muralidhara, H.B. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. *J. Colloid Interf. Sci.* 2011, 361, 270–277.
34. Wu, C.C.; Ku, B.C.; Ko, C.H. Electrochemical impedance spectroscopy analysis of A-beta (1-42) peptide using a nanostructured biochip. *Electrochim. Acta.* 2014, 134, 249–257.
35. Liu, H.; Sun, B. Effect of Fermentation Processing on the Flavor of liquor. *J. Agric. Food Chem.* 2018, 66, 5425.
36. Zhang, M.; He, L. Research progress of methanol, formaldehyde, cyanide and metal ions in Chinese liquor. *J. Food Saf. Qual.* 2015, 9, 3563–3568.

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