Analytical Methods

**Determination of 15 phthalic acid esters based on GC–MS/MS coupled with modified QuEChERS in edible oils**

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**ABSTRACT**

In this study, an analytical method based on the modified QuEChERS and gas chromatography tandem mass spectrometry was proposed to determine 15 phthalic acid esters in edible oils including dimethyl phthalate, diethyl phthalate, diisobutyl phthalate, dibuty l phthalate, bis(4-methyl-2-pentyl) phthalate, bis(2-ethoxyethyl) phthalate, dipentyl phthalate, dihexyl phthalate, benzyl butyl phthalate, bis(2-n-butoxylkyl) phthalate, dicyclohexyl phthalate, di-n-heptyl phthalate, diphenyl phthalate, di-octyl phthalate, and dinonyl phthalate. Calibration curves with good correlation coefficients (R > 0.990) were obtained in the range of 4–2000 μg kg\(^{-1}\). The LODs and LOQs were from 0.02 to 8.00 μg kg\(^{-1}\) and from 0.07 to 26.68 μg kg\(^{-1}\), respectively, which were significantly lower than the previous studies. Moreover, good recoveries varied from 70.11 % to 115.33 %, while repeatability ranged from 3.97 % to 11.55 %. The results showed that DBP, DIBP, and DEHP were detected in edible oils. The foregoing findings suggested that the proposed approach might be used to detect phthalic acid esters in edible oils.

**1. Introduction**

Edible vegetable oils provide essential fatty acids and various functional components for human beings (Yang et al., 2018; Du, Zhou, Li, Lyu, Liu & Ding, 2022; Giampieri, Cianciosi & Forbes-Hernández, 2020; Zhang et al., 2019). However, the presence of hazardous substances such as mycotoxins, pesticide residues and phthalates in the edible oils endangers human health (Bereketoglu & Pradhan, 2022; Dou et al., 2022; Wang et al., 2022; Yang et al., 2022; Yu et al., 2022). Among them, phthalates, commonly known as phthalic acid esters (PAEs), are synthetic endocrine disruptors (Abern et al., 2019). The risk of exposure to phthalates is increasing because of the widespread use of PEAs in mulch film for agricultural uses and packaging materials (Haji Harunarashid, Lim, & Harunani, 2017). Other sources of phthalate exposure in food, water, air, pharmaceuticals and cosmetics were also reported (Belifa, Belaid, Lo Turco, Machreki, Ben Mansour, & Di Bella, 2018; Sero, Nunez, Santos, & Moyano, 2018). Because of high liposolubility of PAEs, edible vegetable oils were susceptible to be contaminated by PAEs.

In chronic rodent studies, PAEs have been proven to be a cause of liver injury, liver cancer, teratogenicity and testicular injury (Čtvercová, Jancula, Raska, Babica, & Sovadinova, 2020). The possible endocrine-disrupting potency of PAEs has raised a great deal of public concerns (Ahmadi et al., 2017) in recent years. Moreover, phthalates have high risk of affecting animal reproductive systems (Estill, Hauser, Nassan, Moss, & Krawetz, 2019) and interfering with the development of young mammals. As a result, PAEs directly raise human health risks. Therefore, a precise and reliable detection method for PAEs is critical for food safety assurance. The limits of PAEs were set by European Food Safety Authority according to Directive 2007/19/EC based on toxicological evaluations and exposures, which specified body weight based
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phthalate (DBEP), dicyclohexyl phthalate (DCHP), di- phthalate (DHP), benzyl butyl phthalate (BBP), respectively (Laura et al., 2015). The European Union has set specified migration limits (SMLs) for PAEs of 0.3, 1.5, 9 and 30 mg kg\(^{-1}\), for DBP, BBP, diisononyl phthalate (DINP) and DEHP, respectively, based on PAEs’ occurrence in plastic materials and ease of migration into food items (Galman Graino, Sendon, Lopez Hernandez, & Rodriguez-Bernaldo de Quiros, 2018).

Consequently, trace analysis of PAEs is necessary to guarantee food safety. Especially, an accurate and reliable analytical method to simul- taneously determine PAEs in one run is highly demanded. Recently, several chromatographic methods were proposed to detect PAEs in foodstuffs based on HPLC, liquid chromatography mass spectrometry (LC-MS), liquid chromatography tandem mass spectrometry (LC-MS/MS), gas chromatography electron capture detection (GC-ECD), GC flame ionization detection (GC-FID) and GC-MS (Tian et al., 2022; Li et al., 2011). Generally, the presence of matrix effects and co-eluted isomers interferes with detection of PEAs (Fierens et al., 2012; Dil, Doustimotlagh, Javadian, Asfaram & Ghaedi, 2021). Sample preparation prior to chromatographic analysis is also vital to overcome matrix effects. For edible oils, the extraction and cleanup that decide the sensitivity of analysis method are the most challenging step before the analysis of PAEs. Soxhlet extraction (SE) and liquid–liquid extraction (LLE) are the most commonly used pretreatments to extract phthalates from high-fat samples (Sublayrolles, Montréajaud-Vignoles, Benanou, Patria, & Treilhou, 2005). A further cleanup procedure for the extracts is conducted by using size-exclusion chromatography (SEC), and florisil, alumina and silica gel SPE columns (He et al., 2022) for fat-rich foods after solvent extraction. Recently, gas chromatography tandem mass spectrometry (GC-MS/MS) was employed to quantify co-eluted isomers of phthalate diesters in vegetable oils and fat-rich diets, due to its high specificity and sensitivity (Liu, Wang, & Wang, 2013; Mota, Waktola, Novlachai, & Marriott, 2021).

As an important factor in the PAE analysis, cross contamination caused by ubiquitous presence of PAEs can result in overestimated levels and offer a great challenge to minimization and control. Glassware, dust, plastic laboratory consumables, and injector portions of GC might contain PAEs, and adsorption to glassware and solvents (Moret, Marega, Conte, & Purcaro, 2012; Marega, Grob, Moret, & Conte, 2013). Moreover, it should be noted that most of these methods lead to either incomplete or very laborious separation of PAEs from complex matrices, especially from high-fat samples, which makes PAE analysis more difficult in edible vegetable oils. To avoid cross contamination, it is urgent and significant to establish a novel, effective, and highly sensitive extraction and cleanup method for multi-residue analysis of PAEs in edible oils. The environment-friendly QuEChERS (quick, easy, cheap, effective, rugged, and safe) method might be more appropriate to detect PAEs in edible oils (Sambolino et al., 2022; Dil, Ghaedi, Asfaram, & Tayebi, 2020; Dil et al., 2020).

In this work, a novel method based on the modified QuEChERS and GC-MS/MS was proposed to determine PAEs in edible vegetable oils. This method possesses sufficient sensitivity, low LOD and overcomes cross contamination to a great degree.

2. Materials and methods

2.1. Reagents and materials

Thirty-six edible vegetable oils were purchased from local markets. Fifteen reference standards of PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(4-methyl-2-pentyl) phthalate (BMPP), bis(2-ethylhexyl) phthalate (DEHP), dibenzyl phthalate (BBP), benzyl butyl phthalate (BHPB), bis(2-n-butoxyethyl) phthalate (DBEP), dicumyl phthalate (DCMP), di-n-octyl phthalate (DnHP), diphenyl phthalate (DPHP), and dinonyl phthalate (DNP) were purchased from Supelco (PA, USA). Octadecyl-silica (C18) and PSA were provided by Agilent (USA), and graphitized carbon black (GCB) was supplied by Sigma (St. Louis, MO, USA). Methanol, Acetonitrile, and n-hexane were reagents of chro- matographic grade (Fisher Scientific, Germany). The analytical reagent grade of NaCl and anhydrous MgSO\(_4\) were supplied by Beijing Chemical Works (Beijing, China). Ultrasonic apparatus KQ-800KDE (Kunshan, China) was obtained for extraction.

In this study, all glassware was immersed in methanol overnight, then dried at 140 °C for 4 h to avoid cross-contamination with PAEs, and rinsed with methanol before use. Subsequently, blank analysis was performed to test potentially occurring PAE contamination of all reagents and glassware by GC-MS/MS.

2.2. Standard preparations

Standard stock solution was parpared with acetone containing 10 mg mL\(^{-1}\) of 15 PEAs and kept in a –20 °C refrigerator. Then, working solutions from 4 to 2000 μg kg\(^{-1}\) were diluted with acetone.

2.3. Sample preparations

0.5 g (0.001 g) edible oil were weighed at a 10 mL glass centrifuge tube. 2 mL methanol was added and mixed by vortexing for 1 min. The mixtures were ultrasonic extracted for 15 min at 30 °C. The extract was evaporated to dryness using a nitrogen flow at 40 °C. One-milliliter extract was put in a 10 mL glass centrifuge tube, and 80 mg GCB and 50 mg PSA were added. The glass centrifuge tube was centrifuged at 4000 rpm for 2 min, and subsequently vortexed for 1 min. The supernatant was gathered into a 2 mL vial for the subsequent analysis.

2.4. GC-MS/MS analysis

All the PAEs determination were preformed using Shimadzu GC 2010 equipped with a Shimadzu 8400 autosampler and 8040 GC-MS/MS system (Shimadzu, Japan). DB-5MS (30 m × 0.25 mm × 0.25 μm) was used to GC separation. At a flow rate of 1.2 mL min\(^{-1}\), the carrier gas was helium (99.999% purity). The sample extracts of 1 μL were injected with the programming temperature vaporizer (PTV) injector temperature of 250 °C and a splitless time of 0.5 min. The PTV injector temperature was designed to start at 40 °C for 1 min, then climb to 180 °C at a rate of 15 °C min\(^{-1}\) with a 4 min hold period. GC oven’s optimal temperature programming was as follows: oven temperature was set initially at 100 °C (0.2 min hold), then increased to 180 °C at a rate of 15 °C min\(^{-1}\) (2 min hold), and then increased to 280 °C at a rate of 5 °C min\(^{-1}\) (10.33 min hold).

The mass spectrometry was operated in electron ionization (EI) mode. Selected reaction monitoring (SRM) mode was used for the quantitative and qualitative analysis of 15 PAEs. All of the interface and ion source temperatures were set to 250 °C. The electron energy was 70 eV. The solvent delay time was set to 6 min. Table 1 summarizes the retention times, quantification and identification ions as well as related information for 15 PAEs.

3. Results and discussion

3.1. Optimization of extraction conditions

Because of high liposolubility of PAEs, the extraction is the most challenging step in the analysis of PAEs. The QuEChERS method involves two simple steps. First, extraction was performed with an organic solvent and salt solution, partitioning from the homogenized samples after addition of sodium chloride (Liu, Zhang, Ren, & Xie, 2020). In the present work, the extraction conditions including extraction solvent, extraction temperature and extraction time were optimized to improve the extraction efficiency of the target compounds. Among them, the
The choice of extraction solvent is crucial for the efficiency of the extraction. The organic solvents including methanol, acetonitrile, and n-hexane were taken as candidates. As shown in Fig. 1a, the highest intensities of 15 PAEs were obtained, when the methanol was used. Meanwhile, the acetonitrile could extract out the similar contents of 15 PAEs. However, the toxicity of acetonitrile is higher than that of methanol. Therefore, methanol was selected as the extraction solvent. It has been proven that the extraction equilibrium is reached earlier at an elevated temperature (Liu, Hu, Zhao, Xu, & Guan, 2005). Five temperatures (25 °C, 30 °C, 40 °C, 50 °C and 60 °C) were used to optimize the extraction temperature to get the best extraction efficiency. As shown in Fig. 1b, the intensities of 15 PAEs at the extraction temperature of 30 °C were significantly higher than others. Thus, 30 °C was selected as the extraction temperature. Additionally, the extraction time of 15 min was found to obtain the significantly higher intensities of 15 PAEs (see Fig. 1c) and was therefore chosen as extraction time with the purpose of optimizing the extraction efficiency.

### Table 1

| PAE | RT (min) | Quantification ion pair | CE | Identification ion pair (1) | CE | Identification ion pair (2) | CE |
|-----|----------|-------------------------|----|-----------------------------|----|-----------------------------|----|
| DMP | 7.13     | 163 > 77                | 24 | 163 > 92                    | 24 | 163 > 133                   | 9  |
| DEP | 8.03     | 149 > 65                | 24 | 177 > 149                   | 9  | 149 > 93                    | 12 |
| DBP | 10.19    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BMPP| 11.15    | 149 > 65                | 24 | 167 > 149                   | 9  | 149 > 93                    | 24 |
| DEEP| 12.85    | 149 > 65                | 24 | 176 > 149                   | 9  | 149 > 93                    | 24 |
| DPP | 13.37    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| DHP | 15.91    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BBP | 16.03    | 149 > 65                | 24 | 206 > 149                   | 9  | 167 > 149                   | 9  |
| DBEP| 17.67    | 149 > 65                | 24 | 193 > 149                   | 24 | 149 > 121                   | 15 |
| DCHP| 18.36    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| DnHP| 18.60    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| DPHP| 18.70    | 225 > 77                | 24 | 225 > 115                   | 33 | 225 > 141                   | 24 |
| DNOP| 21.33    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| DNP | 23.98    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BMPP| 12.41    | 167 > 149               | 24 | 167 > 149                   | 9  | 149 > 93                    | 24 |
| DEEP| 12.85    | 149 > 65                | 24 | 176 > 149                   | 9  | 149 > 93                    | 24 |
| DPP | 13.37    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| DHP | 15.91    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BBP | 16.03    | 149 > 65                | 24 | 206 > 149                   | 9  | 167 > 149                   | 9  |
| DIBP| 10.19    | 149 > 65                | 24 | 167 > 149                   | 9  | 149 > 93                    | 24 |
| DEP | 8.03     | 149 > 65                | 24 | 177 > 149                   | 9  | 149 > 93                    | 12 |
| DBP | 11.15    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BMPP| 12.41    | 167 > 149               | 24 | 167 > 149                   | 9  | 149 > 93                    | 24 |
| DEEP| 12.85    | 149 > 65                | 24 | 176 > 149                   | 9  | 149 > 93                    | 24 |
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| DIBP| 10.19    | 149 > 65                | 24 | 167 > 149                   | 9  | 149 > 93                    | 24 |
| DEP | 8.03     | 149 > 65                | 24 | 177 > 149                   | 9  | 149 > 93                    | 12 |
| DBP | 11.15    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
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| DEEP| 12.85    | 149 > 65                | 24 | 176 > 149                   | 9  | 149 > 93                    | 24 |
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| DHP | 15.91    | 149 > 65                | 24 | 149 > 93                    | 24 | 149 > 121                   | 15 |
| BBP | 16.03    | 149 > 65                | 24 | 206 > 149                   | 9  | 167 > 149                   | 9  |

![Fig. 1.](image-url) (a) Selection of extraction solvent; (b) Influence of extraction temperature on extraction efficiency; (c) Influence of extraction time on extraction efficiency; (d) Influence of the amount of PSA on extraction efficiency; (e) Influence of the amount of GCB on extraction efficiency.
achieving high extraction efficiency in a short analysis time.

3.2. Optimization of cleanup conditions

In QuEChERS, cleanup was important to overcome matrix effect and improve method sensitivity, especially for edible vegetable oils. Generally, additional cleanup of the supernatant was conducted with a dispersive solid-phase extraction (d-SPE). As a weak anion exchanger, GCB is always used to remove sugars, anthocyanins, organic acids, and other pigments, especially chlorophylls, while PSA is often used to remove sugars, anthocyanins, organic acids, and other plant phenols, and C18 can remove lipids and non-polar interference (Wang et al., 2012). In the previous study, the enrichment effect of C18 on phthalate esters was investigated (Mostafa et al., 2014). In this study, GCB and PSA were selected as adsorbents to purify crude extracts. The amounts of PSA and GCB for purifying crude extracts were optimized. As illustrated in Fig. 1d and 1e, the intensities of 15 PAEs were highest, while the LOQs were used to assess method sensitivity by injection of a series of spiked blank samples until corresponding to SNR of 10. The recoveries of LOD and LOQ were from 0.02 to 8.00 μg kg⁻¹, and from 0.07 to 26.68 μg kg⁻¹ in Table 2.

The analytes were added to the edible oil samples and left to stand at room temperature for 2 h prior to the modified QuEChERS. The samples were spiked with 3 concentrations of analytes, including 40, 200, and 400 μg kg⁻¹, respectively. The repeatability and recoveries for PEA were studied by six continuous extractions. As shown in Table 3, the recoveries of 15 analytes ranged from 70.11 to 115.33 % with RSD of 3.97–11.55 %. These results in a perfectly acceptable range, typically requiring a recovery of 70–120 % within RSD of 15 %. As shown in Table 4, the modified method was compared with the previous studies. Compared with the previous studies, the number of plastics detected in this study is higher than others except the study based on GC–MS (Bi, Pan, Yuan, & Wang, 2013). More importantly, our method could detect PAEs more sensitively. Taking DIBP as an example, LOQ of DIBP is 0.07 μg kg⁻¹, which is significantly lower than 1.7 μg kg⁻¹ in the most sensitive method (Zhang, Yang, Li, Wang, Zang & Wang, 2018). The comparison indicates that the modified QuEChERS and GC-MS/MS could overcome matrix effects and improve the sensitivity of detection method.

3.3. Method validation

Under optimal experimental circumstances, the reference standards of 15 PAEs with different calibration levels were analyzed in the linear range of 4–2000 g kg⁻¹ to build matrix matching standard calibration curves in blank extraction and validate the effectiveness of the proposed method. As shown in Fig. S1, 15 PAEs could be separated completely within 120 min with resolution of 2.0. The recoveries of 15 analytes were from 70.11 to 115.33 % with RSD of 3.97–11.55 %, which is significantly lower than 1.7 μg kg⁻¹ in the most sensitive method (Zhang, Yang, Li, Wang, Zang & Wang, 2018). The comparison indicates that the modified QuEChERS and GC-MS/MS could overcome matrix effects and improve the sensitivity of detection method.

3.4. Determination of PAEs in edible oils

The proposed method was employed to analyze edible vegetable oils including 14 soybean oils, 10 walnut oils, 6 olive oils, and 6 flaxseed oils. The results in Table S1 showed that DBP, DIBP, and DEHP were detected in these edible oils. The contents of DEHP and DIBP were 0.25–1.85 and 0.10–0.84 μg kg⁻¹, respectively, while the contents of DIBP, DBP, and DEHP in soybean oils were from 0.05 to 0.61, from 0.10 to 0.61, and from 0.25 to 1.85 μg kg⁻¹, respectively. In walnut oils, only DEHP was detected with content of 4.93 ± 0.20 μg kg⁻¹. DEHP and DBP were also identified in walnut oils and olive oils. The actual situation in foods, especially in edible oil and other high-fat products, plasticizers are very serious and need to be noted.

The findings of this approach were compared to the results of the Chinese National Food Safety Standards method. Except for DEHP in walnut oils, no PAE was detected in the four types of oils (LOD of 1500 μg kg⁻¹) under the standard method in Table S1. As results, it was found that the developed QuEChERS method combined with GC–MS/MS can detect phthalates in vegetable oils at low μg/kg level.

4. Conclusion

In this study, an analytical method was proposed based on the modified QuEChERS and GC–MS/MS to determine 15 PAEs in edible vegetable oils. In order to minimize the risk of secondary pollution and interference of complex matrix and get accurate and reliable results, the combination of 50 mg GCB and 80 mg PSA was used for purification. The modified extraction method was cheap, simple, rapid, reliable, and sufficiently sensitive. Compared with the previous studies, the method established in this study has lower LOD for 15 PAEs. The real sample detection results indicated that DBP, DIBP, and DEHP were in edible oils. This method could be also used to investigate exposure levels, accumulation, distribution and contamination traceability of PAEs in food and drugs in future.
### Table 4
Comparison of analytical method for PAEs in edible oils.

| Edible oils                        | Number of plasticizers | Sample pretreatment | Analytical technique | LOQ                  | References                                      |
|-----------------------------------|------------------------|---------------------|----------------------|----------------------|-------------------------------------------------|
| Rapeseed oil                      | 6                      | SPME                | GC-ECD              | 0.2–0.5 mg kg\(^{-1}\) | (Holodova, Prokupkova, Hajdlová, Poutská, 2007) |
| Soybean oil, sunflower seed oil, | 5                      | SPE                 | GC-FID              | 1.7–6.7 μg kg\(^{-1}\) | (Zhang, Yang, Li, Wang, Zang & Wong, 2018)       |
| corn, olive oil                   |                        |                     |                     |                      | (Shi, Zhang & Liu, 2016)                        |
| palm oil                          | 6                      | HPLC                |                     | 0.1 μg kg\(^{-1}\)    | (Ibrahim, Osman, Abdullah & Saim, 2014)         |
| Soybean oil, canola oil, corn oil, | 15                     | QuEChERS dSPE       | GC-MS               | 4.8–25.1 μg kg\(^{-1}\) | (Bi, Pan, Yuan, & Wang, 2013)                   |
| olive oil                         |                        |                     |                     |                      |                                                 |
| Soybean oil, walnut oil, olive oil| 15                     | The modified        | QuEChERS MS/MS      | 0.068–26.88 μg kg\(^{-1}\) | This study                                      |

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**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data will be made available on request.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jfochx.2022.100520.

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