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Development of a layered double hydroxides-based air-assisted D-μSPE method in combination with HPLC for the determination of gallic acid in honey

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Abstract: Determining gallic acid in honey can provide information for assessing the nutritional value and tracing the source of honey. However, the complex matrix of honey and the low content of gallic acid may hamper the detection. Therefore, it is important to select an appropriate sample preparation method. This work established an air-assisted dispersive micro-solid phase extraction combined with a high-performance liquid chromatography method to determine gallic acid in honey. Zinc/nickel/aluminium layered double hydroxides were selected as the adsorbent to extract gallic acids in diluted honey samples. Under air-assisted extraction, the adsorbents adsorbed gallic acid in honey *via* anion exchange. Subsequently, the isolated adsorbents were dissolved in a 1% phosphoric acid solution. A high-performance liquid chromatography-UV-Vis detector was used for gallic acid detection. Under the optimised conditions, gallic acid showed good linearity over the concentration range of 0.005–10.0 mg·L^{-1} with a coefficient of determination greater than 0.999. The detection limit and quantification limit were 13.5 and 45 ng·g^{-1}, respectively. The recoveries were 89.8–93.4%, with the intra-day and inter-day relative standard deviations in the range of 0.71–1.17% and 0.76–1.27%, respectively. The method possesses the advantages of simplicity, rapidity, economy and environmental friendliness and is suitable for detecting gallic acid in honey.

Keywords: air-assisted extraction; dispersive micro-solid phase extraction; layered double hydroxide; nutritional analysis

Gallic acid is a polyphenolic substance widely present in honey, fruits, vegetables, and beverages. It has antibacterial, anti-inflammatory, antimutagenic, antioxidative, and lipid-regulating activities (Nouri et al. 2021). The contents of polyphenols in honey varied greatly with the sources, so polyphenols can be used as a marker to indicate the honey source (Becerril-Sanchez et al. 2021). Therefore, the determination of polyphenols such as gallic acid in honey provides information for evaluating the nutritional value and identifying the source of honey.

Because of the complex matrix of honey and the low content of gallic acid, it is important to choose appropriate sample preparation methods. The extraction methods

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for gallic acid in food include Soxhlet extraction (Autor et al. 2022), reflux (Lin et al. 2013), ultrasonic-assisted extraction (Ratananikom and Premprayoon 2022), microwave-assisted extraction (MAE) (Chen et al. 2007), enzyme-assisted extraction (EAE) (Hai et al. 2016), liquid-liquid microextraction (Shalash et al. 2017), and solid-phase extraction (SPE) (Michalkiewicz et al. 2008). Among these methods, Soxhlet extraction and reflux take a long time. The procedures of enzymatic hydrolysis are complicated and time-consuming. SPE is the most commonly used extraction method. However, the aggregation of solid adsorbents in SPE columns in traditional SPE methods leads to the reduction of active sites, which affects extraction efficiency and reproducibility. Dispersive micro-solid phase extraction (D-μSPE) is an improved SPE technology, which effectively improves the extraction efficiency by dispersing the adsorbents in the sample solution to increase the contact area and contact frequency between the adsorbents and the analytes (Amiri et al. 2019). Meanwhile, extraction efficiency can be enhanced by auxiliary extraction methods such as vortex, air assistance, ultrasonic treatment, and air pressure (Raterink et al. 2014; Dil et al. 2016; Adlnasab et al. 2018). Recent studies showed that compared with vortex and ultrasonic extraction, the mass transfer of analytes to adsorbent surfaces could be increased by air-assisted extraction, resulting in higher extraction efficiency (Adlnasab et al. 2018; Liu et al. 2022). In addition, air-assisted extraction requires no precise instrument, and it is cheap and convenient. However, the study of air-assisted extraction in combination with D-μSPE is limited so far, and its practicability still needs more investigation.

Layered double hydroxides (LDHs) are a kind of adsorbent composed of positively charged surface layers and interlayer spaces with anion exchange activity. The surface layers contain divalent and trivalent metal cations, and the interlayers contain water and exchangeable anions (Mittal 2021). LDHs possess strong anion exchange capacity, large specific surface area, and high adsorption capacity, and their synthesis is easy and cheap (Huo et al. 2016). In addition, LDHs are dissolvable in an acid solution with a pH lower than 4. Since most adsorbents need to be eluted with organic acids, the acid-solubility of LDHs contributed to the elimination of the elution procedure and makes the sample preparation easier; moreover, it significantly decreases the consumption of organic solvents (Tang and Lee 2013; Rajabi et al. 2017). Gallic acid has the acid dissociation constant (p*Ka*) of 4.4 (Taoufik et al. 2023). Therefore, anionic gallic acids are prevailing present forms with pH above 4.4 that LDHs may adsorb through anion exchange. The anion exchange activity of LDHs has been reported to establish SPE and magnetic SPE methods for phenolic acids in fruit juice and beer (Saraji and Ghani 2014; Ghani et al. 2018). However, the application of the LDHs-based D-μSPE method in extracting any phenolic acids like gallic acid has not been reported.

In this study, we applied air-assisted D-μSPE (AA-D-μSPE) for the first time to determine gallic acid. LDHs were used to extract gallic acid in honey *via* anion exchange and were dissolved in 6% phosphoric acid (H_3PO_4) before injection. No elution procedure was needed. The developed method shows advantages in extraction efficiency, convenience, environmental friendliness, and economic efficiency.

MATERIAL AND METHODS

Instrumentation. Chromatographic analysis was conducted on an Agilent 1260 high-performance liquid chromatography (HPLC) system (Agilent Technologies, Germany) equipped with a G7114A 1260 ultraviolet detector (Agilent Technologies, Germany). Morphological characterisation of LDHs was performed using transmission electron microscopy (TEM) (FEI Talos F200X; Thermo Fischer Scientific, USA) and scanning electron microscopy (SEM) (Thermo Scientific Apreo 2C; Thermo Fischer Scientific, USA). X-ray diffraction patterns were obtained with an X-ray powder diffractometer (XRD) (Ultima IV; Rigaku, Japan). Fourier transform infrared (FTIR) spectra were obtained with an FTIR spectrometer (Nicolet ls5; Thermo Fischer Scientific, USA). Other instruments used in this work were as follows: a high-throughput ultraviolet spectrophotometer (SPECTROstar Nano, Guangzhou Boqi Biotechnology, China), a balance (RADWAG Wagi Elektroniczne, Poland), a vortex mixer (GL-88B; Haimen Qilinbeier Instrument Manufacturing, China), a centrifuge with hermetically sealed refrigeration system (5430R; Eppendorf AG, Germany), and a ultrasonic cleaner (SB-800 DTD; Ningbo Scientz Biotechnology, China).

Reagents. Gallic acid standard (HPLC ≥ 98%) was purchased from Sichuan Weikeqi Biotechnology (China). HPLC-grade acetonitrile (ACN, greater than or equal to 99.9%), methanol (MeOH, greater than or equal to 99.9%), and phosphoric acid (H_3PO_4, 85–90%) were purchased from Macklin Biochemical (China). XFNANO Materials Tech (China) provided Mg/Al-LDHs, Zn/Al-LDHs, and Zn/Ni/Al-LDHs. Other reagents are analytically pure. Hydrochloric acid (HCl, 36–38%), sulfuric acid (H_2SO_4, 95–98%), and

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trichloroacetic acid (CCl_3COOH, 99%) were provided by Jinshan Chemical Reagent (China). A Milli-Q purification system (18.2 MΩ·cm; Merck KGaA, Germany) prepared ultrapure water.

Preparation of solutions. The 1.00 mg·mL^{-1} gallic acid stock standard solution was obtained by dissolving gallic acid in methanol, sealed and refrigerated at 4 °C. Gallic acid standard solution series with concentrations of 0.005, 0.010, 0.020, 0.050, 0.100, 0.200, 0.500, 1.00, 2.00, 5.00, and 10.00 mg·L^{-1} were prepared by the dilution of the stock solution with ultrapure water before use. The optimisation of extraction conditions was conducted with a diluted honey solution containing 1 mg·L^{-1} gallic acid, which was prepared by adding 10 µL of 1 mg·mL^{-1} gallic acid stock solution into 0.2 g blank honey sample and adding ultrapure water to a total volume of 10 mL.

Chromatographic conditions. For HPLC separation, a ZORBAX SB-C18 column (4.6 × 150 mm, 5 µm) (Agilent Technologies, USA) was used. The column temperature was 35 °C. The ultraviolet detection wavelength was set at 264 nm. The mobile phase consisted of MeOH, ACN, and 2.0 mL·L^{-1} H_3PO_4 (8:5:87, *v*/*v*). The flow rate was 0.9 mL·min^{-1}.

Samples and their preparation. Forty-eight brands of honey, including multifloral honey, acacia honey, jujube honey, vitex honey, and linden honey, were collected from local and online stores. Among these samples, 11, 16, 4, and 3 brands were labelled as produced in spring, summer, autumn, and winter, respectively.

As shown in Figure 1, ultrapure water was added to 0.2 g of honey to a fixed volume of 10 mL. Then, a micro pipettor was used to take 1 mL solution into a centrifuge tube, and 4 mg Zn/Ni/Al-LDHs were weighed and added. Gallic acid was extracted with air-assisted extraction by pumping the solution twice through a syringe. After 3 min of centrifugation at 10 000 revolutions per minute (rpm), the supernatant was discarded. Afterwards, the precipitates were dissolved with 500 µL of 1% H_3PO_4 solution by vortex for 2 min, followed by the filtration with a 0.45 µm filter membrane before being injected into the HPLC. The injection volume was 10 µL.

Method validation. The linearity calibration curve was assessed based on a plot of the peak area of gallic acid against its concentration. By measuring the standard deviation (SD) of the response value of 6 blank honey samples and the slope (m) of the calibration curve (Barfi et al. 2017), the limit of detection (LOD, 3 SD/m) and limit of quantification (LOQ, 10 SD/m) were calculated. The accuracy and precision of the method were evaluated on honey samples spiked with three concentration levels of gallic acid, i.e., adding 0.01, 0.20, and 0.40 µg gallic acid into 0.2 g honey to obtain samples spiked with 0.05, 1.00, and 2.00 µg·g^{-1} gallic acid. The intra-day precision of the method was assessed by analysing three concentrations of spiked honey samples on six replicates during the same day. The inter-day precision of the method was assessed by analysing three concentrations of spiked honey samples on three replicates for three consecutive days. Both parameters were evaluated by the relative standard deviations (RSDs).

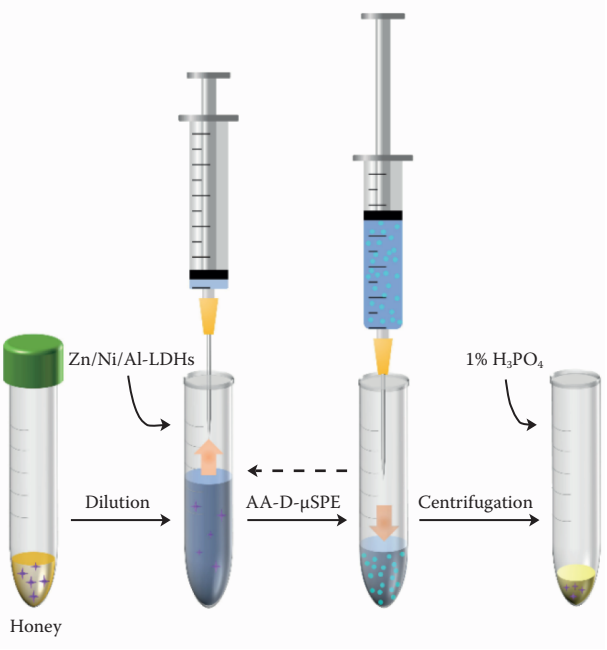

Figure 1. Schematic diagram of air-assisted dispersive micro-solid phase extraction (AA-D-µSPE)

LDHs – layered double hydroxides

Statistical analyses. The overall statistical differences among gallic acid contents corresponding to different seasons and sources were tested using the Kruskal-Wallis test (OriginPro, version 2021). Statistical significance was declared at $P < 0.05$.

RESULTS AND DISCUSSION

Characterisation of Zn/Ni/Al-LDHs. As shown in Figures 2A and 2B, SEM and TEM images of Zn/Ni/Al-LDHs indicate that the nanosheets have a typical geometric disk-like structure with a rounded edge. Their lateral dimensions are appropriately 1–2 µm. The functional groups of Zn/Ni/Al-LDHs were characterised by FTIR spectroscopy. In Figure 2C, the strong absorption peak at 3 457.78 cm^{-1} is gener-

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ated by the tensile vibration of the -OH group and the O-H bond of Zn/Ni/Al-LDHs. The absorption peaks around 1 360 cm^{-1} and 1 380 cm^{-2} are due to the bending vibrations of the C-O-H bonds. Peaks recorded below 800 cm^{-1} are attributed to M-O, M-O-M, and O-M-O metal oxide bonds of Zn, Ni, and Al metal elements. The diffraction pattern of Zn/Ni/Al-LDHs has broad peaks at 11.6, 23.5, 34.7, 39.3, 46.8, 53.1, 56.4, 60.4, and 61.8° as shown in Figure 2D, which indicates a layered structure of LDHs (Wang et al. 2022). Meanwhile, the high crystallinity of Zn/Ni/Al-LDHs is demonstrated by the strong and sharp characteristic (003) and (006) peaks.

Types and amount of LDHs. The extraction efficiencies of different types of LDHs were compared. As shown in Figure 3A, 6 mg of Zn/Al-LDHs, Mg/Al-LDHs, and Zn/Ni/Al-LDHs were weighed and added to 1 mL of diluted honey containing 1 mg·L^{-1} gallic acid. The results showed that the extraction efficiency of gallic acid by Zn/Ni/Al-LDHs was 96.7%, which was higher than that by Zn/Al-LDHs (39.2%) and Mg/Al-LDHs (69.9%). The difference in element contents of these LDHs might affect their extraction efficiency for gallic acid, as the anion exchange capacity of LDHs is affected by the layer charge density, which is determined by the ratio of bivalent metal cations to trivalent metal cations (Sajid et al. 2016). So, Zn/Ni/Al-LDHs were selected. Their amount was investigated by comparing the extraction efficiencies of 2 mg to 8 mg Zn/Ni/Al-LDHs added to 1 mL diluted honey containing 1 mg·L^{-1} gallic acid. As shown in Figure 3B, the maximum extraction efficiency of gallic acid was obtained with 4 mg of Zn/Ni/Al-LDHs. Therefore, 4 mg of Zn/Ni/Al-LDHs was sufficient for extracting 1 μg of gallic acid.

Air-assisted extraction times. The effect of air-assisted extraction times on extraction efficiency was studied. Zn/Ni/Al-LDHs (4 mg) were added to extract 1 mL of diluted honey containing 1 mg·L^{-1} gallic acid with the assistance of 2–30 numbers of syringe strokes. Figure 4 showed that the extraction efficiency of gallic acid reached 95.9% when air-assisted extraction was carried out twice.

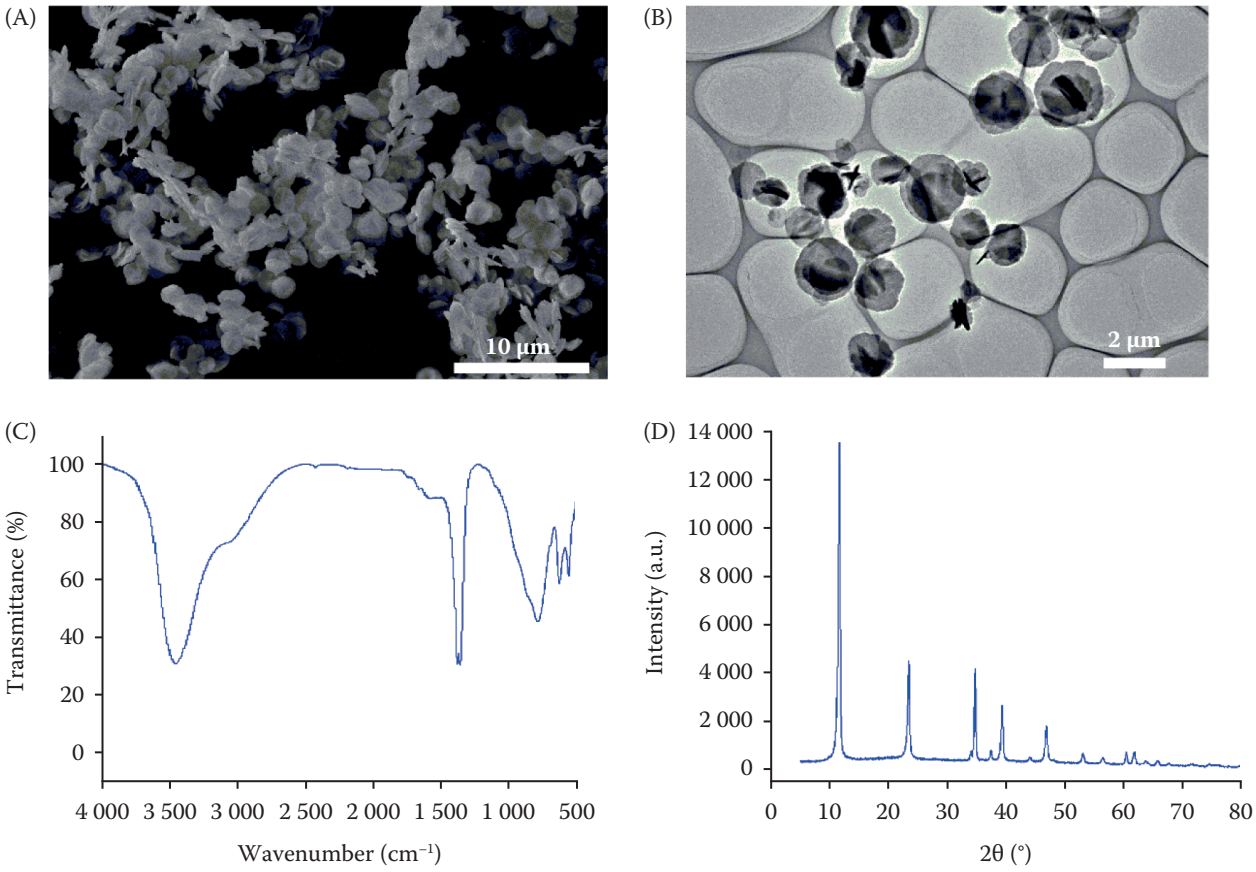

Figure 2. (A) Scanning electron microscopy and (B) transmission electron microscopy images of Zn/Ni/Al-LDHs, (C) Fourier transform infrared and (D) X-ray powder diffractometer spectra of Zn/Ni/Al-LDHs

LDHs – layered double hydroxides; a.u. – arbitrary units; 2θ – angle between transmitted beam and reflected beam

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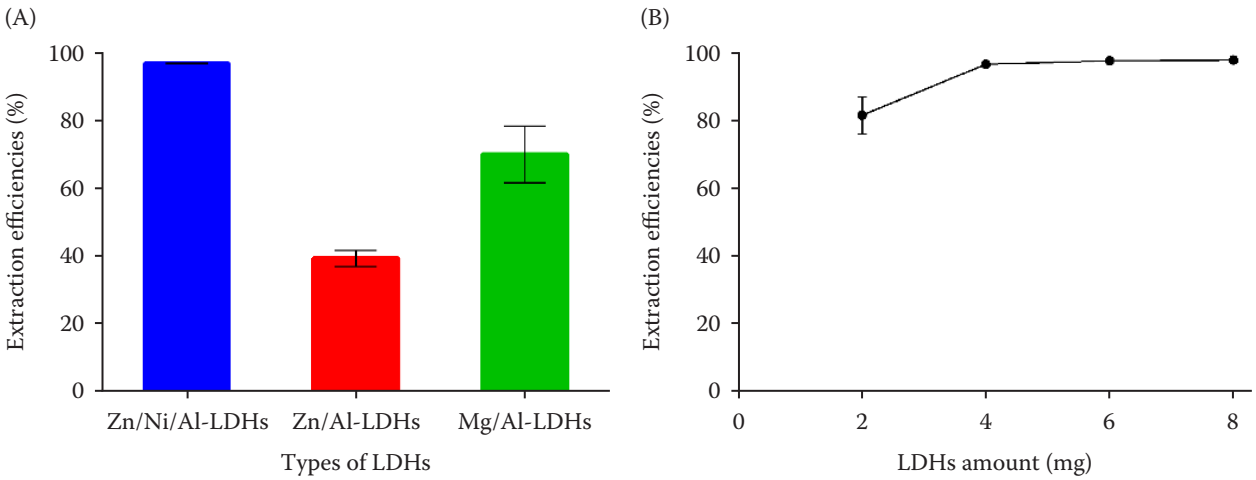

Figure 3. (A) Effect of different types of layered double hydroxides (LDHs) on the extraction efficiencies of gallic acid and (B) effect of the amount of Zn/Ni/Al-LDHs on extraction efficiencies of gallic acid

Error bars represent standard deviations for three independent experiment results

The kind, concentration, and volume of the acidic solution. Due to the acid solubility of LDHs, the elution step can be eliminated, and organic solvents can be avoided. After extracting 1 mg·L^{-1} gallic acid in diluted honey with 4 mg Zn/Ni/Al-LDHs, LDHs were dissolved in 1 mL of 6% H_3PO_4 (pH 2.8), 6% H_2SO_4 (pH 2.9), 6% HCl (pH 2.5), and 8% CCl_3COOH (pH 1.2) solutions, respectively. As shown in Figure 5A, among the three inorganic acids with similar pH, 6% H_3PO_4 obtained the highest extraction efficiency. Meanwhile, 6% H_3PO_4 achieved higher extraction efficiency in comparison with the organic acid that even possessed a lower pH, i.e. 8% CCl_3COOH. This might be affected by phosphates, which were more easily adsorbed by the interlayer of LDHs and competed with gallic acid so that the adsorbents could release the analytes. Therefore, H_3PO_4 was used as the dissolving solution. The extraction efficiency of gallic acid by dissolving LDHs in different concentrations of H_3PO_4 solutions was investigated. After extracting 1 mg·L^{-1} gallic acid with 4 mg Zn/Ni/Al-LDHs, LDHs were dissolved in 1 mL of 0.6, 1, 2, 4, and 6% H_3PO_4 solutions, respectively. As shown in Figure 5B, 1% H_3PO_4 solution exhibited the highest extraction efficiency for gallic acid. After extracting 1 mg·L^{-1} gallic acid with 4 mg Zn/Ni/Al-LDHs, the effects of the volume of 1% H_3PO_4 solution (250, 500, 750, and 1 000 µL) on the extraction efficiency of gallic acid were compared. As shown in Figure 5C, the highest extraction efficiency of gallic acid (91.2%) was obtained by dissolving LDHs with 500 µL of 1% H_3PO_4 solution. Therefore, 500 µL of 1% H_3PO_4 solution was selected as the dissolving solution for LDHs.

Adsorbent dissolution time. The dissolution time was compared to make a more complete extraction of the target. After extracting 1 mg·L^{-1} gallic acid with 4 mg Zn/Ni/Al-LDHs, 500 µL of 1% H_3PO_4 solution

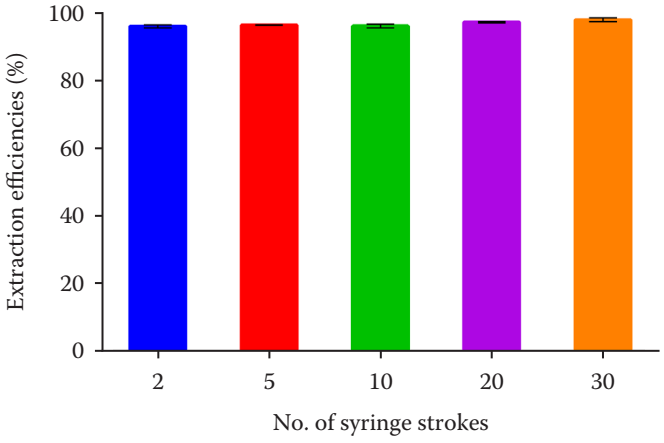

Figure 4. Effect of the number of syringe strokes of air-assisted extraction on extraction efficiencies of gallic acid

Error bars represent standard deviations for three independent experiment results

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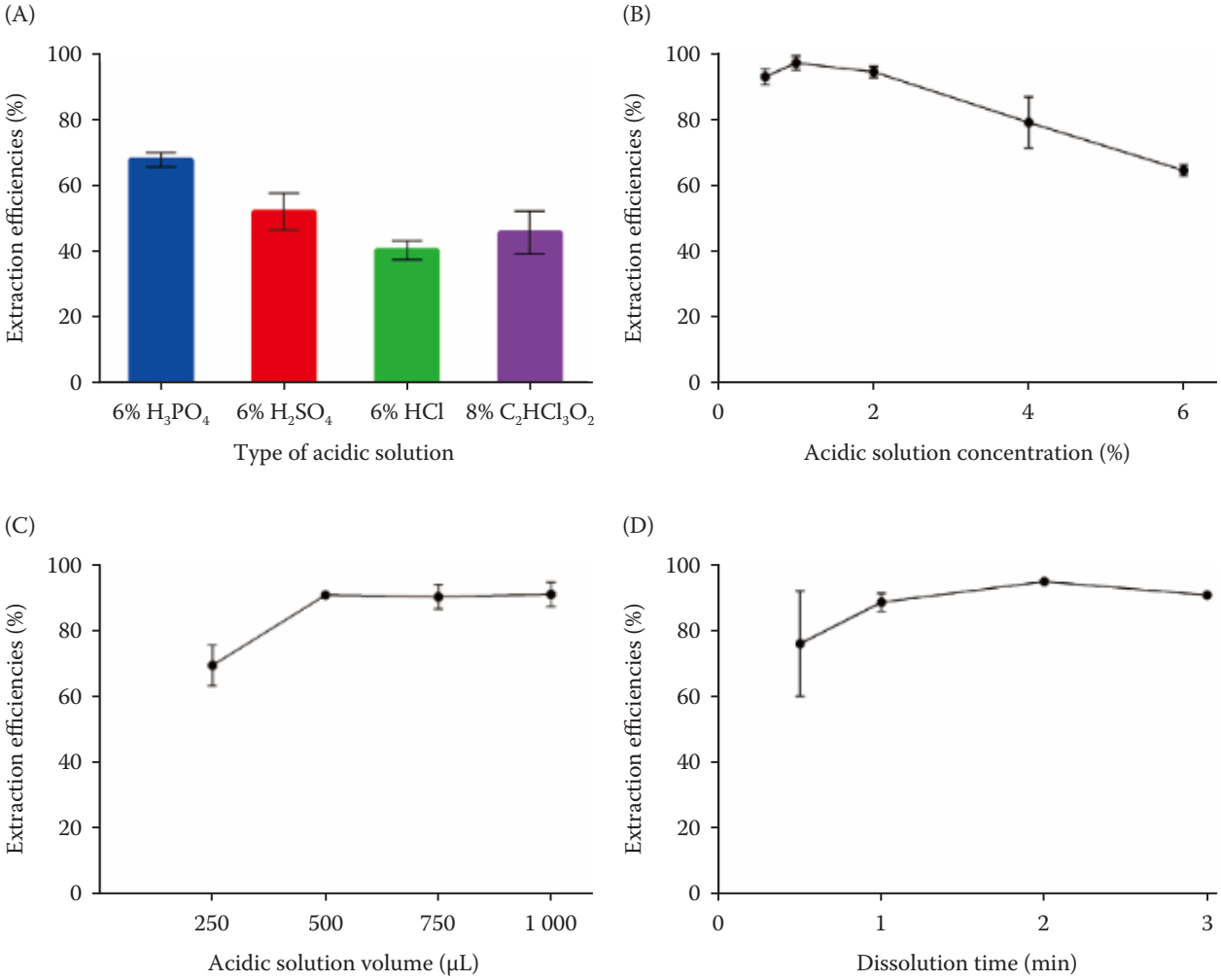

Figure 5. (A) Effect of types of the acidic solution, (B) concentrations of the acidic solution, (C) volumes of the acidic solution, and (D) dissolution time on extraction efficiencies of gallic acid

H_3PO_4 – phosphoric acid; H_2SO_4 – sulfuric acid; HCL – hydrochloric acid; $C_2HCl_3O_2$ – trichloroacetic acid; error bars represent standard deviations for three independent experiment results

was used to dissolve the adsorbents for 30 s to 3 min. As shown in Figure 5D, the extraction efficiency of gallic acid reached the maximum by vortex for 2 min.

Linear range and detection limit. Under the optimised conditions of this method, gallic acid had a good linear relationship in the concentration range of 0.005–10.0 mg·L^{-1}. The coefficient of determination was 0.9996. The linear regression equation could be expressed as $y = 31.439x - 0.7543$. The LOD and LOQ of this method were 13.5 and 45 ng·g^{-1}, respectively.

Accuracy and precision. As shown in Table 1, the recoveries of gallic acid were 89.8–93.4%. The re-

Table 1. Recoveries and precisions of the proposed method (n = 3)

Analyte	Background	Added	Found	Recoveries (%)	RSD (%)	
		(µg·g^{-1})			intra-day	inter-day
Gallic acid	0	0.05	0.047	93.4	0.71	0.76
		1.00	0.898	89.8	0.73	0.81
		2.00	1.837	91.9	1.17	1.27

RSD – relative standard deviations

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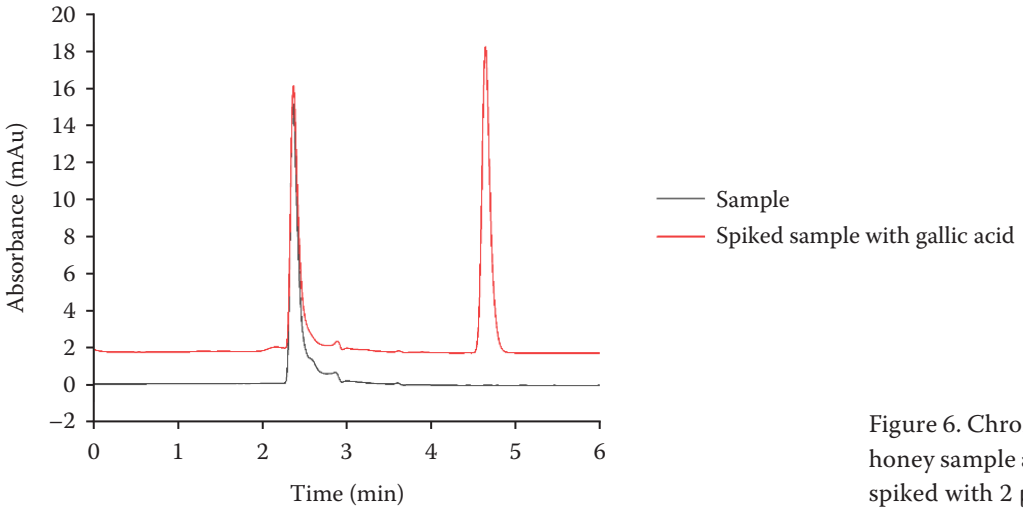

Figure 6. Chromatograms of a blank honey sample and the honey sample spiked with 2 μg·g^{-1} gallic acid

sults showed that the intra-day and inter-day RSDs were 0.71–1.17% and 0.76–1.27%, respectively. Chromatograms in Figure 6 were from blank and spiked honey samples. As shown in Table 2, the proposed method exhibited high sensitivity and accuracy compared with other reported methods for determining gallic acid.

Method application. The proposed method determined the contents of gallic acid in 48 different brands of honey from various sources. The Kruskal-Wallis tests indicated that the contents of gallic acid in honey samples from neither different seasons nor different sources showed significant differences ($P < 0.05$). As shown in Figure 7, the medians of gallic acid contents in honey samples produced in spring, summer, autumn and winter were 316, 310, 302, and 303 ng·g^{-1}, respectively. Meanwhile, the medians of contents of gallic acid from multifloral honey, jujube honey, linden honey, acacia honey, and vitex honey samples were 312, 330, 307, 307, and 317 ng·g^{-1}, respectively.

Table 2. Comparison of the proposed method with reported methods for the determination of gallic acid

Samples	Pretreatment methods	Extractants	Detection methods	Linear ranges	LODs	Recoveries (%)	References
Honey	AA-D-μSPE	Zn/Ni/Al-LDHs	HPLC	0.005–10.0 mg·L^{-1}	13.5 ng·g^{-1}	89.8–93.4	this method
Unani polyherbal formulation	sonication	70% methanol	HPLC	1.1–474 μg·mL^{-1}	0.27 μg·mL^{-1}	98.8	Kamal et al. 2021
Red wines	filtration	–	HPLC	2.5–25 mg·L^{-1}	0.09 mg·L^{-1}	97.9	Krstonosic et al. 2020
Terminalia bellirica	reflux	*Macroporous resin*	HPLC	–	–	85.0	Zou et al. 2016
Traditional Chinese medicine injections	SPE	polymeric absorbent	HPLC-MS	0.5–100 μg·mL^{-1}	0.15 μg·mL^{-1}	40.0	Sun et al. 2016
Food and plants	filtration	–	HPLC	5–50 mg·kg^{-1}	0.054 mg·kg^{-1}	114.16	Ramakrishnan et al. 2020

AA-D-μSPE – air-assisted dispersive micro-solid phase extraction; SPE – solid-phase extraction; LDHs – layered double hydroxides; HPLC – high-performance liquid chromatography; HPLC-MS – high-performance liquid chromatography-mass spectrometry; LODs – limit of detections

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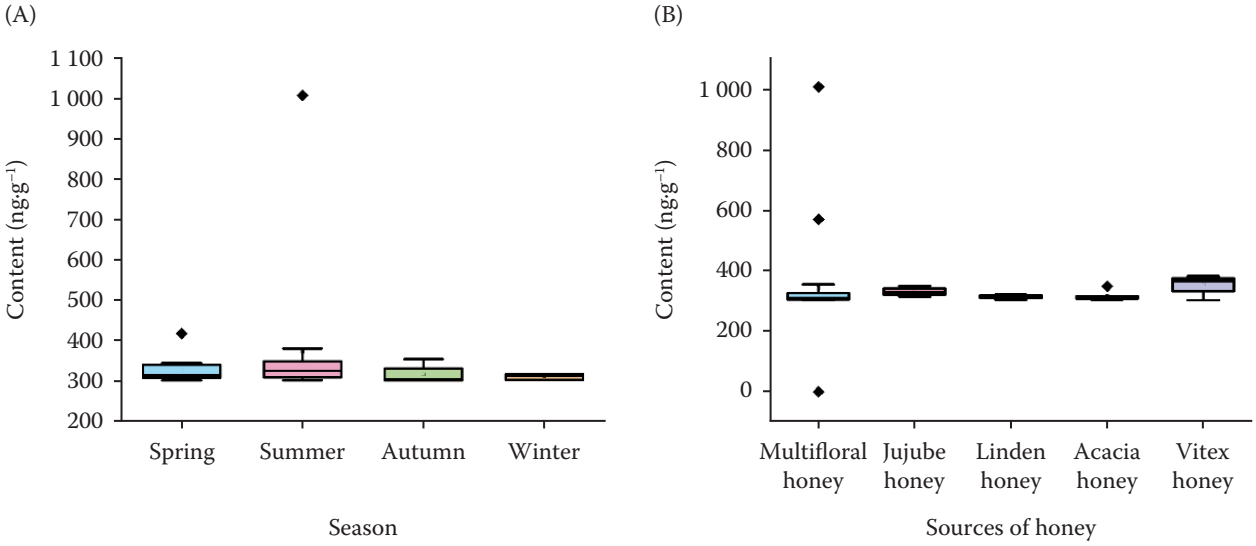

Figure 7. Contents of gallic acid in honey samples from (A) different seasons and (B) different sources

The numbers of honey samples from spring, summer, autumn and winter were 11, 16, 4, and 3, respectively; the numbers of multifloral honey, jujube honey, linden honey, acacia honey, and vitex honey were 25, 4, 5, 6, and 4, respectively

CONCLUSION

This study established a novel air-assisted dispersive micro-solid phase extraction method using Zn/Ni/Al-LDHs as suitable adsorbents to extract gallic acid in honey through anion exchange. Combining Zn/Ni/Al-LDH adsorbents with air-assisted dispersive micro-solid phase extraction for gallic acid determination avoided the elution procedure, consumed no organic solvent, and improved the extraction efficiency without needing expensive instrumentation. Therefore, the established AA-D-μSPE method was efficient, convenient, environmentally friendly, cost-effective and simple. It is suitable for the determination of gallic acid in honey.

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