MDPI

Editorial

Advances in Accurate Quantification Methods in Food Analysis

Xianjiang Li [1,*] and **Rui Weng** [2,*]

1   Key Laboratory of Chemical Metrology and Applications on Nutrition and Health for State Market Regulation, Division of Metrology in Chemistry, National Institute of Metrology, Beijing 100029, China

2   Key Laboratory of Agro-Food Safety and Quality of Ministry of Agriculture and Rural Affairs, Institute of Quality Standard and Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, Beijing 100081, China

*   Correspondence: lixianjiang@nim.ac.cn (X.L.); wengrui@caas.ac.cn (R.W.)

1. Introduction

Food safety is an important topic, and with the perfection of regulations and technologies, food safety is improving. However, incidents such as "toxic mineral oil" [1] and the "fipronil egg scandal" [2] occasionally trigger public tension. In addition to hazardous analytes, increasing attention has been paid to food nutrition with the aim of improving people's lives. Therefore, many researchers are working to develop and validate analytical methods to identify and quantify hazardous and nutritional analytes in foods.

In recent years, there has been especially rapid growth in the accurate quantification of food components such as pesticides [3–5], veterinary drugs [6], mycotoxins [7], amino acids [8], nucleotides [9] and organosulfur compounds [10]. Concerning food analysis, sample pretreatment aims to enrich target analytes and remove complicated matrix components (lipids, proteins, salts, acids, pigments, etc.). New extraction and purification strategies provide high specificity and efficiency for the targets. Combined strategies exhibit excellent performance in lowering matrix effects. Following this, gas/liquid chromatography–tandem mass spectrometry (GC/LC–MS/MS) is a powerful tool in guaranteeing food safety and quality. Moreover, the use of high-resolution mass spectrometry (HRMS) allows the high-throughput identification and screening of targeted/untargeted analytes.

This Special Issue welcomes any developments in novel sample pretreatment or detection techniques to realize accurate quantification in food analysis.

2. Summary of Published Articles

This Special Issue includes nine manuscripts which address the latest analytical methods for the identification and characterization of a variety of hazardous and nutritional compounds in foods.

We received four manuscripts on the topic of pesticide determination. The first manuscript is from guest editor Dr. Li, who reported an LC–MS/MS method for single-pesticide analysis in wheat flour [11]. Fosetyl-aluminum is an ionic fungicide; therefore, an extract–dilute–shoot strategy was developed with water and acetonitrile. Then, fosetyl was quantified via hydrophilic interaction liquid chromatography–tandem mass spectrometry. Finally, the developed method was used to analyze 75 wheat flour samples collected from four provinces in China. The other three manuscripts focus on multi-pesticide analysis via HRMS. Chen and coworkers coupled the QuEChERS method with time-of-flight mass spectrometry for hundreds of pesticides in cottonseed hull [12] and raw milk samples [13]. For the oily samples, acetonitrile with 1% acetic acid was selected as an extraction solvent, followed by purification with $MgSO_4$, C_{18}, or primary secondary amine sorbents. Satisfactory recovery was achieved with three spiking levels. To simplify the sample pretreatment procedure, Cao's group used the min-SPE strategy to replace QuEChERS in an analysis of 209 pesticides in tobacco [14]. The Box–Benhken design was used to optimize the parameters of water, solvent and purification volume. The commercial min-SPE device

demonstrated good performance in the removal of typical tobacco matrix interferences, including nicotine, nicotyrine and anatabine. A database library was homebuilt for qualitative and quantitative workflow, with a default matching score ≥ 75. For real sample analysis, five positive samples were quantified with matrix-matched standards.

The fifth article relates to mycotoxin detection in broiler tissues using Orbitrap [15]. An acetonitrile–water–formic acid mixture was used as an extraction solvent. A database was built with information on retention time and accurate mass for the qualitative screening and simultaneous quantification of 23 mycotoxins. Using this database, data were acquired via the full scan and data-dependent MS/MS modes. The extra-high resolution (70,000 for MS^1 and 17,500 for MS^2) was effective at avoiding false-positive results. Finally, one chicken liver was determined to be positive for zearalenone among 30 collected samples.

The sixth manuscript is a review of antibiotic determination in aquatic products from 2010 to 2020 [16]. Li and coworkers summarized the typical sample pretreatment techniques, including liquid–liquid extraction, solid-phase extraction, QuEChERS, pressurized liquid-phase extraction and microwave-assisted extraction. Since some antibiotics are bound to proteins, proper hydrolysis is required to free them and achieve accurate results. Matrix effects are common in ionization processes; thus, elimination or compensation is very important for reliable results. The authors summarized the available matrix certified reference materials from China, Australia, South Korea and Canada, which are important for the traceability of chemical measurement.

We also received one article describing the development of a method for hazardous metal ions. The work focused on arsenic (As) species, and the rice flour certified reference material NMIJ-7532a was used for method development [17]. Herein, ultrasound-assisted enzymatic hydrolysis with α-amylase was adopted to liberate As(III), As(V), monomethylarsonate, dimethylarsinic acid, arsenobetaine and arsenocholine. Then, the As species were quantified using an inductively coupled plasma mass spectrometry (ICP-MS) method. Based on the assigned values, the recovery of As(III), As(V) and dimethylarsinic acid was better than 98%.

The last two manuscripts are about nutritional analytes. Wang's group described an analysis method for three organic selenium (Se) species (selenomethionine, selenocystine and methylselenocysteine) in egg samples [18]. Since Se was widely incorporated into protein, enzymatic hydrolysis with protease XIV was optimized in sample preparation. Moreover, lipase was added to remove fat interference. Then, three targeted species were separated using ion-pairing reversed-phase chromatography systems and determined using ICP-MS. Real sample analysis demonstrated that Se-enriched eggs had more total Se and selenomethionine, while there was no significant difference in the contents of selenocystine and methylselenocysteine. Anthocyanins are complex natural compounds with limited and costly standards. Therefore, Hu and coworkers analyzed them via quantitative analysis of multi-components using single-marker QSAM with high-resolution MS [19]. Peonidin 3-O-glucoside was used as an internal reference for the nine anthocyanins. The relative correction factor was calculated using the multi-point and slope methods, and the slope method was more accurate. Additionally, there were no significant deviations in the anthocyanin content between QSAM and external standard method. Satisfactory results were obtained with the real samples.

3. Conclusions

The nine articles published in this Special Issue cover the latest advances in food analysis methods. On the one hand, a suitable pretreatment method is the key to eliminating matrix effects and lowering the detection limit, which arises due to the complexity of food components; on the other hand, HRMS exhibits excellent performance, with a trend towards multi-residue and multi-class detection. We highly encourage the creation of more Special Issues in this field to closely track current research.

Author Contributions: Conceptualization and writing, X.L.; review and editing, R.W. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Toxic Mineral Oil Found in Food Products. Available online: https://www.foodwatch.org/en/news/2021/toxic-mineral-oil-found-in-food-products/ (accessed on 18 October 2022).
2. Li, X.; Ma, W.; Li, H.; Zhang, Q.; Ma, Z. Determination of residual fipronil and its metabolites in food samples: A review. *Trends Food Sci. Tech.* **2020**, *97*, 185–195. [CrossRef]
3. Yang, B.; Ma, W.; Wang, S.; Shi, L.; Li, X.; Ma, Z.; Zhang, Q.; Li, H. Determination of eight neonicotinoid insecticides in Chinese cabbage using a modified QuEChERS method combined with ultra performance liquid chromatography-tandem mass spectrometry. *Food Chem.* **2022**, *387*, 132935. [CrossRef] [PubMed]
4. Pang, X.; Liu, X.; Peng, L.; Chen, Z.; Qiu, J.; Su, X.; Yu, C.; Zhang, J.; Weng, R. Wide-scope multi-residue analysis of pesticides in beef by ultra-high-performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry. *Food Chem.* **2021**, *351*, 129345. [CrossRef] [PubMed]
5. Weng, R.; Lou, S.; Pang, X.; Song, Y.; Su, X.; Xiao, Z.; Qiu, J. Multi-residue analysis of 126 pesticides in chicken muscle by ultra-high-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. *Food Chem.* **2020**, *309*, 125503. [CrossRef]
6. Weng, R.; Sun, L.; Jiang, L.; Li, N.; Ruan, G.; Li, J.; Du, F. Electrospun Graphene Oxide–Doped Nanofiber-Based Solid Phase Extraction Followed by High-Performance Liquid Chromatography for the Determination of Tetracycline Antibiotic Residues in Food Samples. *Food Anal. Methods* **2019**, *12*, 1594–1603. [CrossRef]
7. Li, X.; Ma, W.; Zhang, Q.; Li, H.; Liu, H. Determination of patulin in apple juice by amine-functionalized solid-phase extraction coupled with isotope dilution liquid chromatography tandem mass spectrometry. *J. Sci. Food Agric.* **2021**, *101*, 1767–1771. [CrossRef]
8. Ma, W.; Yang, B.; Li, J.; Li, X. Development of a Simple, Underivatized Method for Rapid Determination of Free Amino Acids in Honey Using Dilute-and-Shoot Strategy and Liquid Chromatography-Tandem Mass Spectrometry. *Molecules* **2022**, *27*, 1056. [CrossRef] [PubMed]
9. Zhao, Z.; Guo, Y.; Wei, J.; Chen, Q.; Chen, X. Fluorescent Copper Nanoclusters for Highly Sensitive Monitoring of Hypoxanthine in Fish. *J. Anal. Test.* **2021**, *5*, 76–83. [CrossRef]
10. Liu, P.; Weng, R.; Xu, Y.; Pan, Y.; Wang, B.; Qian, Y.; Qiu, J. Distinct Quality Changes of Garlic Bulb during Growth by Metabolomics Analysis. *J. Agric. Food Chem.* **2020**, *68*, 5752–5762. [CrossRef] [PubMed]
11. Li, X.; Wang, S.; Guo, Z.; Li, X.; Zhang, Q.; Li, H. Determination of Fosetyl-Aluminum in Wheat Flour with Extract-Dilute-Shoot Procedure and Hydrophilic Interaction Liquid Chromatography Tandem Mass Spectrometry. *Separations* **2021**, *8*, 197. [CrossRef]
12. Tong, K.; Xie, Y.; Huang, S.; Liu, Y.; Wu, X.; Fan, C.; Chen, H.; Lu, M.; Wang, W. QuEChERS Method Combined with Gas- and Liquid-Chromatography High Resolution Mass Spectrometry to Screen and Confirm 237 Pesticides and Metabolites in Cottonseed Hull. *Separations* **2022**, *9*, 91. [CrossRef]
13. Wu, X.; Tong, K.; Yu, C.; Hou, S.; Xie, Y.; Fan, C.; Chen, H.; Lu, M.; Wang, W. Development of A High-Throughput Screening Analysis for 195 Pesticides in Raw Milk by Modified QuEChERS Sample Preparation and Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry. *Separations* **2022**, *9*, 98. [CrossRef]
14. Bie, R.; Zhang, J.; Wang, Y.; Jin, D.; Yin, R.; Jiang, B.; Cao, J. Analysis of Multiclass Pesticide Residues in Tobacco by Gas Chromatography Quadrupole Time-of-Flight Mass Spectrometry Combined with Mini Solid-Phase Extraction. *Separations* **2022**, *9*, 104. [CrossRef]
15. Yang, Y.; He, Z.; Mu, L.; Xie, Y.; Wang, L. Simultaneous Determination of 23 Mycotoxins in Broiler Tissues by Solid Phase Extraction UHPLC-Q/Orbitrap High Resolution Mass Spectrometry. *Separations* **2021**, *8*, 236. [CrossRef]
16. Xiao, Y.; Liu, S.; Gao, Y.; Zhang, Y.; Zhang, Q.; Li, X. Determination of Antibiotic Residues in Aquaculture Products by Liquid Chromatography Tandem Mass Spectrometry: Recent Trends and Developments from 2010 to 2020. *Separations* **2022**, *9*, 35. [CrossRef]
17. Li, X.; Ma, Q.; Wei, C.; Cai, W.; Chen, H.; Xing, R.; Song, P. Green and Simple Extraction of Arsenic Species from Rice Flour Using a Novel Ultrasound-Assisted Enzymatic Hydrolysis Method. *Separations* **2022**, *9*, 105. [CrossRef]
18. Zhao, Y.; Wang, M.; Yang, M.; Zhou, J.; Wang, T. Determination of Selenomethionine, Selenocystine, and Methylselenocysteine in Egg Sample by High Performance Liquid Chromatography—Inductively Coupled Plasma Mass Spectrometry. *Separations* **2022**, *9*, 21. [CrossRef]
19. Li, X.; Wang, W.; Sun, S.; Wang, J.; Zhu, J.; Liang, F.; Zhang, Y.; Hu, G. Quantitative Analysis of Anthocyanins in Grapes by UPLC-Q-TOF MS Combined with QAMS. *Separations* **2022**, *9*, 140. [CrossRef]