Measurement technologies for multi-component contaminants in food matrix and related certified reference materials

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Introduction

Chemical contaminants in food has become an issue of wide concern. To protect public health, maximum residue levels for certain contaminants such as mycotoxins, polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs), have been set in food matrix. However, accurate determination of these residues faces challenges, for example, the identification and separation of structural analogues, the stability control of calibrants, and the pretreatment and quantification of ultra-trace analytes in food matrix. The National Institute of Metrology (NIM), China has developed a series of methods and certified reference materials (CRMs) to build the metrological traceability system for these contaminants in food.

Chemical contaminants:

- **Mycotoxins**
- **Polycyclic aromatic hydrocarbons (PAHs)**
- **Phthalate esters (PAEs)**

Certified reference materials development for the chemical contaminants

Measurement challenges:

- **Identification and separation of structural analogues**
- **Pretreatment and quantitation**
- **CRM preparation**

Identification and separation of structural analogues and isomers

Through elucidating of the fragmentation mechanism of structural analogues and screening typical fragment ions, superior selectivity and reliable quantification of the PAE isomers were well achieved using LC-MS/MS.

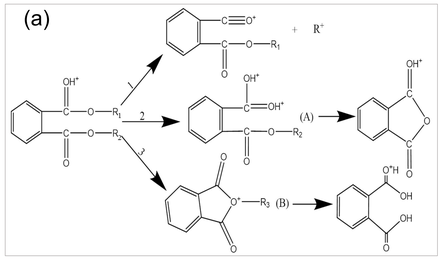


Fig. 1a The fragmentation process of 16 PAEs.

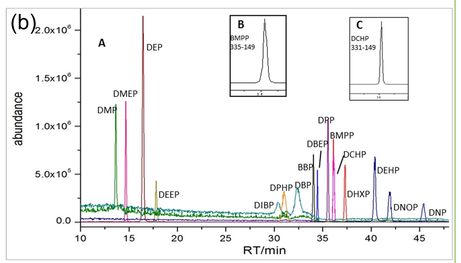


Fig. 1b TIC chromatograms of the 16 PAEs in food.

A few analogues of AFB_1 in methanol and acetonitrile were identified in the reference material candidate with UHPLC-QE Plus Orbitrap MS. Two degradation pathways have been proposed to evaluate the stability of AFB_1 solution. These findings provide useful guides for the production, storage, and transportation of solution CRMs.

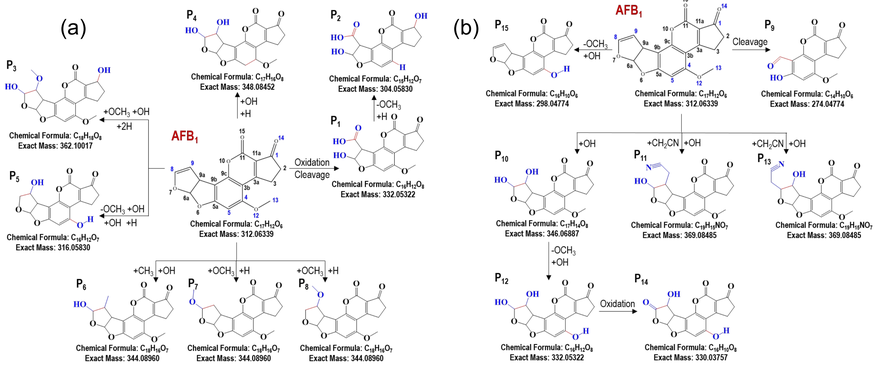


Fig. 2a Degradation pathway of the methanol solution of AFB_1 exposed to the UV light.
Fig. 2b Degradation pathway of the acetonitrile solution of AFB_1 exposed to the UV light.

Pretreatment methods were innovatively established to enhance extraction efficiency of multi-components

A facile method to extract PAEs from alcohol, milk powder, edible oil has been developed using polarity-matched integrated solvents. The extraction recovery was over 85% for 16 PAEs in those matrices.

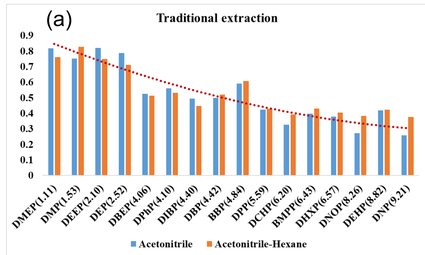


Fig. 3a Extraction efficiency of PAEs with acetonitrile and acetonitrile/hexane extraction.

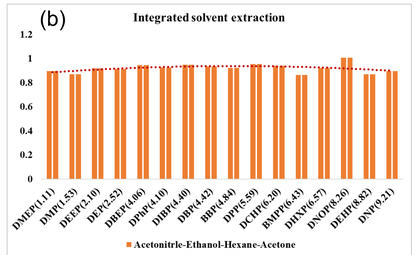
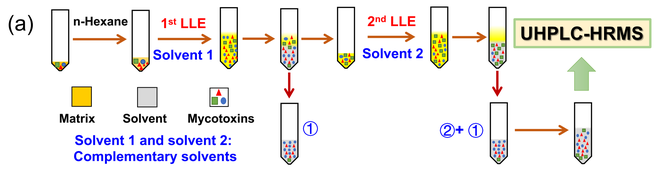


Fig. 3b Extraction efficiency of PAEs with integrated solvents extraction.

The complementary liquid-liquid extraction method was developed to enable simultaneous determination of six types of regulated mycotoxins. The extraction efficiency was up to 80.8%, and the matrix effect was reduced greatly. External calibration approach verified the good quantification property for each analyte.



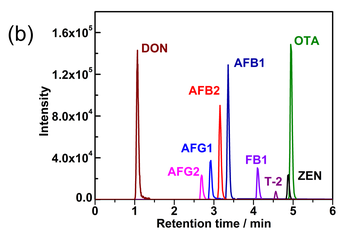


Fig. 4a Diagrammatic representation of the complementary liquid-liquid extraction (LLE) process.
Fig. 4b The typical parallel reaction monitoring (PRM) chromatograms of the nine mycotoxins under the optimal condition, including AFB_1, AFB_2, AFG_1, AFG_2, DON, OTA, ZEN, FB_1 and T-2.

Determination of ultra-low concentration analytes in food matrices

Isotope dilution mass spectrometry (IDMS) method revealed effectiveness to eliminate matrix effect and correct the procedure errors in the quantitation of ultra-low analytes. Further, it was found that the synchronous calibration method showed higher measurement accuracy compared with normal calibration method, it could effectively eliminate hydrogen-deuterium exchange errors in the IDMS method.

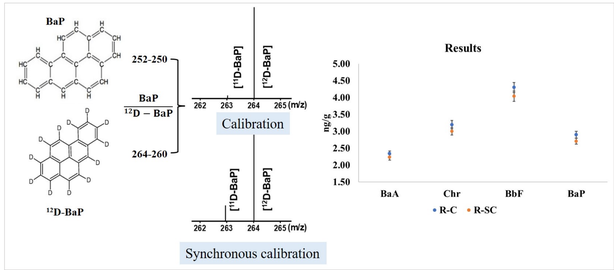


Fig. 5 Elimination of hydrogen-deuterium exchange errors in the measurement of PAHs using synchronous calibration.

Conclusion

NIM have produced a series of pure, solution and matrix CRMs of the contaminants in the food applications. More importantly, NIM have coordinated a couple of international comparisons, and the related broad scope CMCs were published on KCDB. Furthermore, NIM have launched international PTs and training programs to promote the improvement and mutual recognition of international contaminant measurement capabilities.

With the rapid development of artificial intelligence, big data technology and advanced manufacturing, the innovation of non-targeted screening, rapid identification of multiple hazards, and food omics etc., put new demands for metrology.

Metrology Traceability system for food contaminants

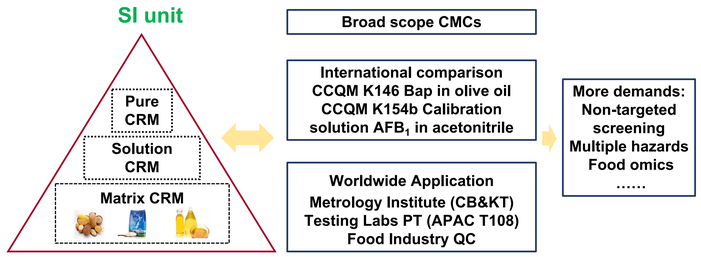


Fig. 6 The metrology traceability system for food contaminants.

Selected Publications & Patents & CRMs

[1] Xiaomin Li, Qinghe Zhang*, et al. *Anal. Methods*, 2018, 10, 3197-3206
[2] Shuangqing Li, Xiaomin Li*, et al. *ACS Omega*, 2022, 7, 40548-40557
[3] Jing Wang, Xiaomin Li*, et al. *J. Sep. Sci*, 2015, 10, 1700-1710
[4] Shuangqing Li, Xiaomin Li*, et al. *Food Chem. X*, 2023, 20, 100887
[5] Xuxin Wang, Xiaomin Li*, et al. *LWT-Food Sci. Technol.*, 2022, 171, 114170
[6] Xiaotong Zhao, Xiaomin Li*, et al. *ACS Food Sci. Technol.*, 2024, 4(2), 418-425
[7] Xiaomin Li, et al. Preparation method and application of phthalate plasticizer-containing milk powder, CN 114112597 B.2025