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Ion mobility-derived collision cross section database: Application to mycotoxin analysis

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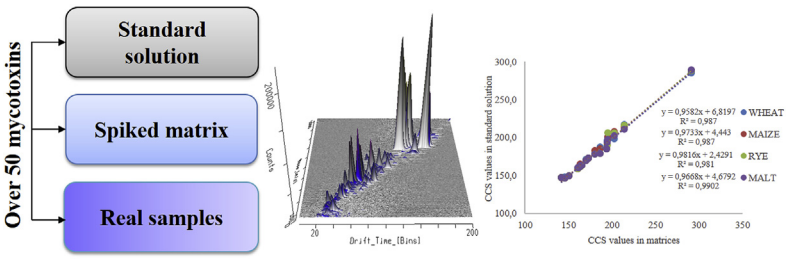
HIGHLIGHTS

- A first database for CCS values of regulated and emerging mycotoxins has been built up and validated.
- The absence of matrix effect, in spiked and naturally incurred samples, was demonstrated.
- The application of CCS values for the effective identification of toxicants in food.

GRAPHICAL ABSTRACT



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ABSTRACT

The recent hyphenation of ion mobility spectrometry (IMS) with high resolution mass spectrometry (HRMS) has risen as a powerful technique for both targeted and non-targeted screening, reducing background noise and allowing separation of isomeric and isobaric compounds. Nevertheless, such an approach remains largely unexplored in food safety applications, such as mycotoxin analysis. To implement ion mobility in routinely MS-based mycotoxin workflows, searchable databases with collusion cross section (CCS) values and accurate mass-values are required. This paper provides for the first time a traveling-wave IMS (TWIMS)-derived CCS database for mycotoxins, including more than 100 CCS values. The measurements showed high reproducibility (RSD < 2%) across different instrumental conditions as well as several complex cereal matrices, showing a mean inter-matrix precision of RSD <0.9%. As a proof of concept, the database was applied to the analysis of several spiked as well as naturally incurred cereal-based samples. In addition, the effect of adducts on the drift time was studied in a series of mycotoxins in order to understand potential deviations from expected drift time behaviors.

Overall, our study confirmed that CCS values represent a physicochemical property that can be used alongside the traditional molecular identifiers of precursor ion accurate mass, fragment ions, isotopic pattern, and retention time.

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1. Introduction

Globally, mycotoxin residue analysis in food is of great interest in terms of food safety, as well as global trade [1,2]. The large

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number of mycotoxins potentially present in a food sample (more than 400 identified so far) requires the use of efficient tools to support the identification of compounds that are not available as standards and, therefore, cannot be easily targeted within analytical methods. In this frame, high resolution mass spectrometry (HRMS) has become an important tool in the field of food contaminants since it permits the combination of target analysis with screening of non-target compounds, novel compound identification, and retrospective data analysis [3]. In addition, the recent hyphenation of ion mobility spectrometry (IMS) with high resolution mass spectrometry (HRMS) has risen as a powerful technique for both targeted and non-targeted screening, to reduce the background noise and allow the separation of isomer and isobar compounds. At first indeed, this interest was primarily oriented in separating and structurally characterizing peptides and small proteins [4,5], oligosaccharides [6] and other biomolecules. Over time, interest has spread into the identification of small molecules, to support emerging research fields such as metabolomics [7] and lipidomics [8,9].

IMS provides a third separation dimension based on the ion shape [10,11], and allows the determination of collision cross section values (CCS, Ω), which is a further unique physicochemical constant property of a molecule.

The CCS value is an orthogonal molecular descriptor that, when used in addition to retention time and mass-to-charge ratio (*m/z*), offers the opportunity to further improve and support the identification process, making it more robust and reproducible across multiple samples and timeframes [8]. Recently [12,13], the potential of CCS as an additional identification point (IP) for pesticide analysis has been discussed, in consideration of the precision and the robustness of the CCS measurement. High intra- and interday reproducibility has been reported, with relative standard deviation lower than 1% [13]. The measure of CCS values has also been demonstrated to be consistent between instruments located in three independent laboratories, and across a range of experimental conditions [9]. According to current studies, CCS values seemed to be more stable and reliable than retention-time values.

From a theoretical point of view, CCS measurement occurs in the gas phase far from the ion source, these are not affected by sample matrix. This aspect has been recently demonstrated by measuring the CCS values from a range of pesticides in a variety of different matrix extracts [12,13]. CCSs were measured within 2% of the expected value regardless of the complexity of the sample matrix, since no more than 2% difference with the values in library, measured in solvent standards was observed. In agreement, Paglia and co-workers [9] also confirmed the high reproducibility of CCS measurements of lipid classes in varying matrices. Thus, it is an argument in favor of considering CCS as valuable parameter in food safety control.

Nevertheless, such an approach remains largely unexplored in food safety applications [14,15].

The main problem in establishing the potential of this molecular property as an identification point in routine food safety analysis, is the lack of CCS database for contaminants and residues. Very recently, a few contaminant databases have been proposed (e.g. pesticides) [12,13,16] but they are far away from covering the wide range of contaminants that can be present in food samples.

So far, four major IMS separation approaches are currently commercially available coupled with MS [17,18]: drift-time IMS (DTIMS) [19,20], traveling-wave IMS (TWIMS) [21], high field asymmetric waveform IMS (FAIMS), also known as differential-mobility spectrometry (DMS) and trapped IMS (TIMS) [22]. Unlike DTIMS, TWIMS and TIMS, FAIMS does not separate ions directly based on their mobility, thus CCS recording is not possible. CCS can be directly derived from the drift time (DTIMS) or experimentally derived by using IMS calibration performed using compounds of known CCS under defined conditions (i.e., gas type and pressure) (TWIMS and TIMS instruments).

Therefore, it is evident that CCS values can be routinely measured as an integrated part of liquid chromatography (LC) HRMS experiments, and used alongside the traditional molecular identifiers like precursor ions' accurate masses, fragment ions and isotopic patterns, as well as retention times, respectively.

The purpose of this work was to generate the first database of mycotoxins based on TWIMS-derived CCS values, aiming to implement the use of ion-mobility in routine mycotoxins workflow. To establish the potential of this new molecular descriptor, CCS values were measured across a range of experimental conditions. Finally, as a proof of concept, the database was applied to the analysis of several fortified as well as naturally incurred cereal-based samples.

2. Materials and method

2.1. Chemicals

HPLC-grade methanol, acetonitrile and acetic acid were purchased from Sigma-Aldrich (Taufkirchen, Germany); bidistilled water was obtained using Milli-Q System (Millipore, Bedford, MA, USA). MS-grade formic acid from Fisher Chemical (Thermo Fisher Scientific Inc., San Jose, CA, USA) and ammonium acetate (Fluka, Chemika-Biochemika, Basil, Switzerland) were also used. Leucine-enkephalin, used as lock mass standard and poly-alanine for CCS calibration were purchased from Waters (Manchester, U.K.).

Analytical standards of mycotoxins were purchased either individually or as a mix from Sigma-Aldrich (Taufkirchen, Germany) and Biopure (Tulln, Austria). Common names and product number are included in Supporting Information file in Table S1. Zearalenone-14-glucoside (ZEN14Glc) and *cis* Zearalenone (*cis*-ZEN) were synthesized and purified in our laboratory following the previously published protocols [23,24], while zearalenone-16-glucoside (ZEN16Glc) was kindly provided by Prof. Franz Berthiller and Prof. Gerhard Adams (IFA-Tulln, University of Natural Resources and Life Science, Vienna). Deoxynivalenol (DON), alternariol (AOH), alternariol-methyl ether (AME) and ZEN glucuronides were enzymatically synthesized in our laboratory following protocols previously reported [25–28]. T2 toxin glucosides were kindly provided by Dr. Susan P. McCormick (National Center for Agricultural Utilization Research, U.S. Department of Agriculture, Peoria, United States). Standard of partially hydrolysed (pHFB) and hydrolysed (HFB) fumonisins were prepared by alkaline hydrolysis of FB standard solution, as previously reported [29]. Mixtures containing different standards were prepared in acetonitrile or methanol, depending on their chemical stability, at a concentration of 2 mg L^{-1}.

2.2. Sample preparation

Aliquots (2 g) of grounded sample were extracted by adding 8 mL of water/methanol/formic acid (25:74:1, v/v/v) solvent mixture and stirred for 60 min on a shaker. The extract was centrifuged for 10 min at 1400 rpm (Eppendorf 5417, Eppendorf) at room temperature and the clear supernatant was directly injected into LC-MS system.

To determine the matrix effect, the extract of four blank matrices (wheat, maize, rye and malt) previously checked using the above-mentioned extraction protocol, was spiked with a standard mix of 20 mycotoxins resulting in a final concentration of 2 mg L^{-1}.

Finally, 10 naturally incurred samples among them cereals (durum wheat, common wheat, debranned wheat, rye, maize), and

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