TIMS ToF mass spectrometry for screening and quantitation of pesticides and pesticide metabolites in routine analysis

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Introduction

To date, high-resolution mass spectrometry (HRMS) is most commonly used for pesticide screening in food. As a relatively new analytical technique, **T**rapped **I**on **M**obility **S**pectrometry (TIMS) expands the capabilities of the HRMS by separating analytes according to their mobility characteristics thereby capturing analyte-specific “collision cross section” (CCS) values. Recently, a new TIMS time-of-flight (ToF) HRMS system has been installed at the CVUA Stuttgart for the purpose of target screening and quantitation of pesticides in plant based foodstuff. The aim is to establish the new technology as a future-oriented routine method in order to increase reliability and quality of the obtained results in pesticide identification.

Analytical key data

Ion mobility spectrometry is performed on a Bruker timsTOF Pro 2 mass spectrometer (*Pic. 1*). Besides the determination of the accurate masses, the system allowes the determination of analytes mobilitiy (1/K0) [V*s/cm^2] and corresponding specific CCS values [Å^2] within the TIMS analyzer by a gas flow and an electrical field. QuECHERs (EN 15662) extracts from routine analysis were used for screening and quantitation of pesticides and pesticide metabolites. Acquisition as well as the evaluation method (screening and quantitation) are currently still in the optimization process. The basic instrumental setup is shown in table 1.

Table 1: Basic instrumental setup

MS-System	Bruker timsTOF Pro 2
Ion source	Bruker VIP-HESI (pos and neg)
Scan range / scan rate	20-1,300 m/z
Scan mode	broadband collisional induced dissociation (bbCID)
TIMS mobility range 1/K0 [V*s/cm^2]	0.1 – 1.5
TIMS ramp time and settings	150 ms; stepping
Mass- and mobility calibration	Mixture of Na-formiate cluster and Agilent tuning mix (positive mode)
Evaluation software	Bruker TASQ 2023b
HPLC-System	Agilent 1290 Infinity II UHPLC

Observations and Interim results

Today, our screening scope includes 1,150 target analytes in total. Thereof, ion mobility data are already available for around 600 pesticides. CCS values of our analytes range from 109 to 296 Å^2.

In routine samples, CCS values are reliably determined, typically showing only a slight deviation to the target CCS values of ΔCCS <0.5%. This observation also applies to very low analyte concentrations, like for example 0.7 ppb Ametoctradin in beer (*see Fig. 1*) and complex matrices like oregano (*see Fig. 3*). Accordingly, we assess the additional mobility information obtained by TIMS as an useful option for analyte identification within screening apart from retention time and MS or MS/MS data.

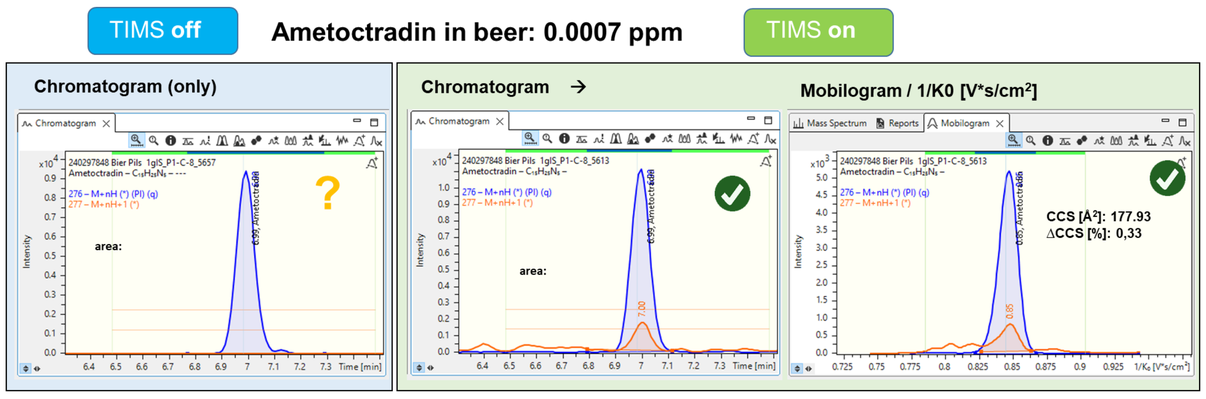

Fig. 1: Ametoctradin in beer: unclear finding with MS data only (TIMS off); confirmation by TIMS (TIMS on)

Furthermore, we observed that matrix background usually can be reduced effectively by TIMS, as extracted ion chromatograms are filterd by ion mobility data (*see Fig. 2*). In doing so, cleaner MS spectra are received and the sensitivity of the system is improved.

Pic. 1: TIMS-ToF analytical system

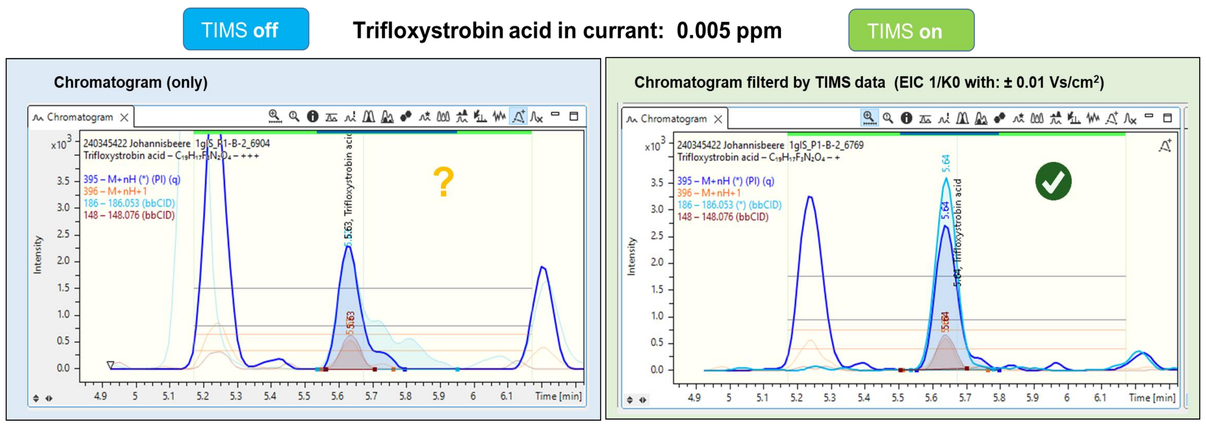

Fig. 2: Unfiltered (TIMS off) and mobility-filtered (TIMS on) chromatogram of trifloxystrobin acid in currant

Challenges

In principle, the introduction of the additional separation dimension significantly increases the complexity of system. Since mobility and mass data are mutually dependent, method parameters must be set carefully and proper assignment of both, chromatographic and mobility peaks is mandatory. We observed, that incorrect assignment of mobility peaks can cause false positive and negative findings within screening.

It also should be mentioned that some analytes *eg.* Oxadiazon, are showing two mobility peaks (Mob 1 / 2) under standard conditions, due to the formation of protomeres. In such cases the complexity increases even further, as according to our observations, the intensity ratio of the two mobility traces are subject to matrix effects, a fact which is particularly important to consider in the case of quantification.

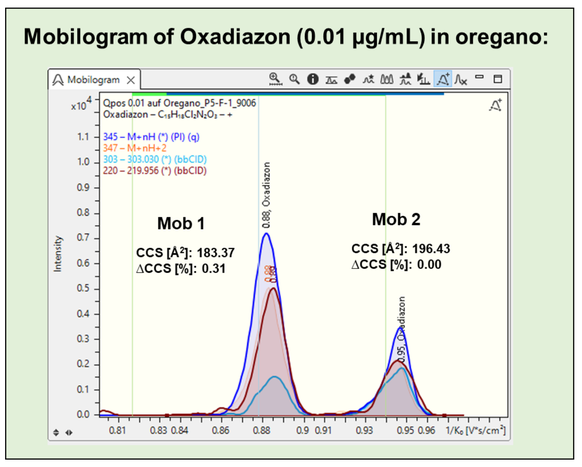

Fig. 3: Mobilogram of Oxadiazon (0.01 µg/mL) forming two mobility peaks (Mob 1/ Mob 2)

Conclusions and Prospects

According to our first experiences, TIMS technology can significantly increase reliability and quality of the results in pesticide analysis. However, due to the complexity of the data, TIMS technology can be described as challenging and further method optimization, as well as the expansion of the database with specific CCS values is needed. In future, we intend to apply the new technology also screening in the negative mode.

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