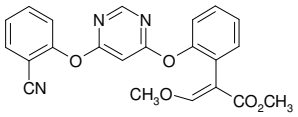
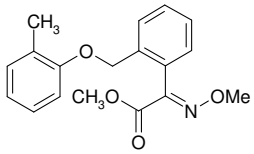
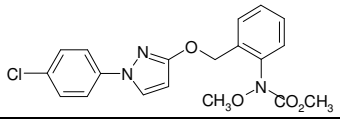
Rapid screening of stobilurins in crude solid materials (wheat grains) using DART-TOFMS

Direct control of solid materials for pesticide residues is a challenging task enabling fast contamination screening. In our study, we investigated direct analysis of strobilurin fungicides in milled wheat grains. Strobilurins, systemic pesticides originated from natural fungicidal derivatives, play an important role in control of various plant pathogens.[1,2,3] Because of their unique protective properties, significant yield enhancements and longer retention of green leaf tissue, strobilurins have been widely used in agriculture since their introduction on the market in 1992.[3] As other pesticides, these compounds are involved in control and monitoring surveys undertaken by regulation authorities.[4] Some characteristics of strobilurins are shown in Table 1.

Table 1 Strobilurins: physico-chemical characteristics.

Compound	Structure	log Kow	water solubility (mg l-1)	molecular weight
Azoxystrobin		2.5	6.0	403.4
Kresoxim methyl		3.4	2.0	313.4
Pyraclostrobin		4.0	4.6	387.8

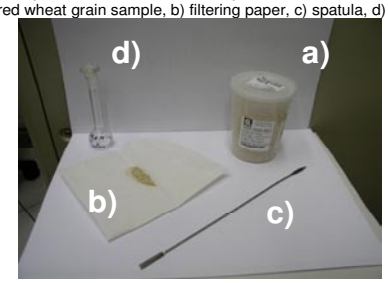
AccuTOF-DART system was used for examination of milled wheat grains containing incurred residues of azoxystrobin, kresoxim methyl and pyraclostrobin.

The DART ion source was operated in positive ion mode with helium as the ionizing medium at flow a rate of 2.7 L/min. The gas beam was heated to 130°C and the distance between the exit of the DART gun and inlet of the mass spectrometer was 12 mm. The discharge needle voltage of the DART source was set to positive

potential of 2400 V, perforated and grid electrode voltages were +150 V and +250 V, respectively. Accurate mass spectra were acquired in a range of *m/z* 100–500, spectra recording interval was 0.2 s; the peaks voltage value was set to 850 V. A mixture solution of poly(ethylene glycol) PEG 600 and 200 was used for calibration. The same calibrant was also introduced at the end of each sample analysis to perform mass drift compensation. The mass resolution of the mass spectrometer was typically 6000 ± 500 (FWHM).

Samples were introduced manually with the use of in-hand made filtering paper envelopes containing approximately 1 g of homogenous sample. The sample was spread across the edge of the envelope (see Figure 1) and placed into the DART gas stream to ionize target analytes and detect the respective peaks.

Figure 1 The only items needed for fast analysis of strobilurins in milled wheat grain are: a) incurred wheat grain sample, b) filtering paper, c) spatula, d) PEG solution.



In Figures 2, 3 and 4 a positive-ion DART mass spectrum of directly analyzed wheat grains samples showing the tested strobilurins as $[M+H]^+$. The ion identity was confirmed by elemental composition calculations as documented in Table 2 and also shown in respective Figures.

Figure 2 a) Mass spectrum of wheat grains containing incurred residues of *azoxystrobin*. b) Estimation of an element composition from exact mass measurement. The highlighted column stands for target analyte.

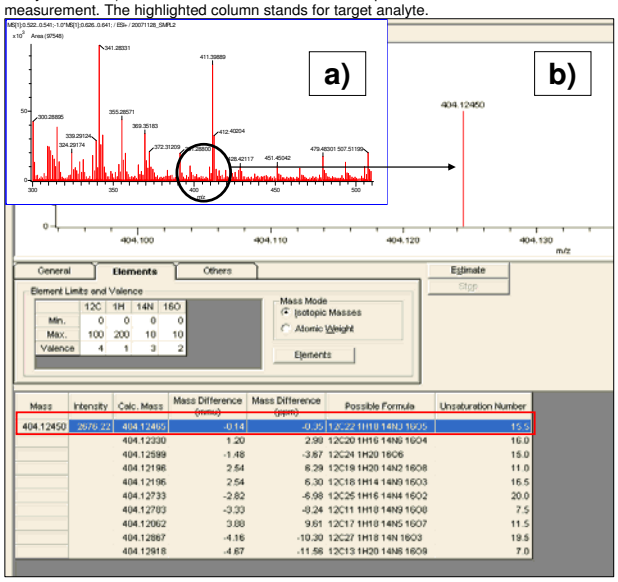


Figure 3 a) Mass spectrum of wheat grains containing incurred residues of *pyraclostrobin*. b) Estimated element composition from exact mass measurement. The highlighted column stands for target analyte.

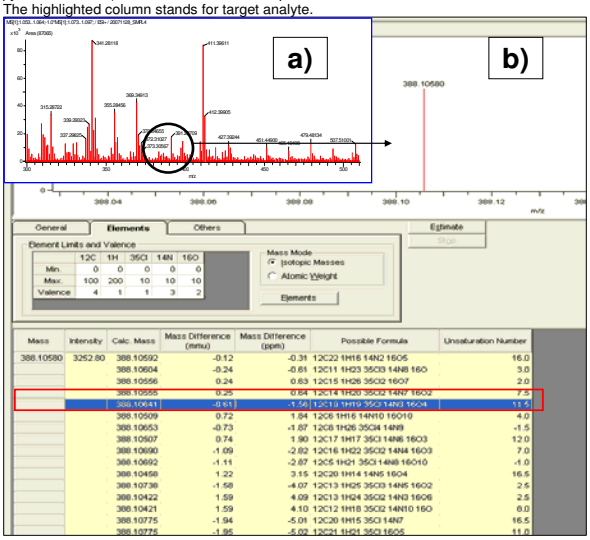


Figure 4 a) Mass spectrum of wheat grains containing incurred residues of *kresoxim-methyl*. b) Estimated element composition from exact mass measurement. The highlighted column stands for target analyte.

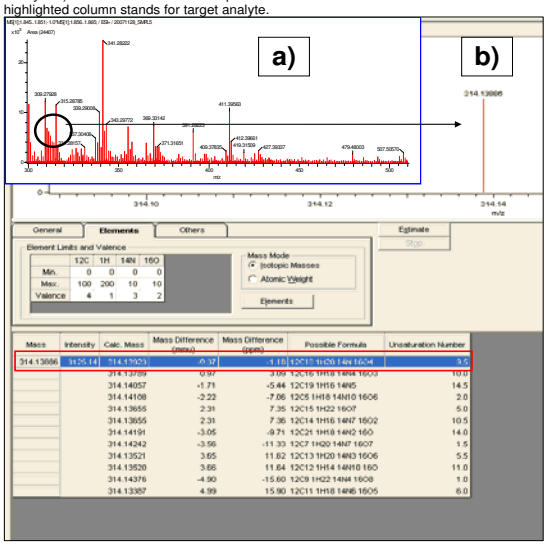


Table 2 Strobilurins identified by exact mass after direct analysis of wheat grains containing incurred residues at different concentration levels.

Compound	Exact mass (mu) $[M+H]^+$	Measured mass (mu) $[M+H]^+$	Difference (mmu)	Elemental composition	Concentration (ppb)*
Azoxystrobin	404.12465	404.12450	***-0.14***	$C_{22}H_{18}N_3O$	445
Kresoxim methyl	314.13923	314.13886	***-0.37***	$C_{18}H_{20}NO_4$	45
Pyraclostrobin	388.19641	388.10580	***-0.61***	$C_{19}H_{19}ClN_3O_4$	202

* The quantification was performed using DART-TOF MS analysis of ethyl acetate extracts of wheat grains (prochloraz was used as internal standard).[5]

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In this study,DART-TOFMS system has been demonstrated as a suitable tool for rapid screening of strobilurin fungicides, time and money consuming sample preparation and purification steps can be omitted. The exact mass measurements provide high degree of confirmation, enabled by elemental composition calculation of target analytes.

References

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3. Sauter, H., Steglich, W., Anke, T., 1999. Strobilurins: evolution of a newclass of active substances. Angew. Chem., Int. Ed. 111, 1416–1438.
4. http://ec.europa.eu/food/plant/protection/resources/mrl_pesticide.pdf
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