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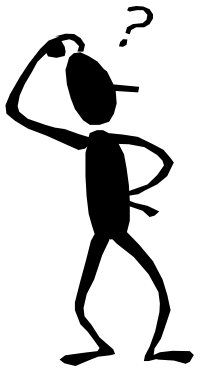
AMBIENT MASS SPECTROMETRY IN FOOD QUALITY / SAFETY

Jana Hajšlová, Tomáš Čajka, Lukáš Václavík



Prague, 26-27 April, 2010

History….events preceding this meeting

2005 - DART and DESI reviews introducing challenges of Ambient desorption mass spectrometry published

2006 - 17th International mass spectrometry congress, Prague Jeol exhibits DART - AccuTOFMS

2007 - ICT negotiates with Jeol, first tests carried out in Paris Centre

2008 - DART research initiated at ICT, first papers published

2008 - DART TOF MS incorporated into Biocop project together with DESI, Analysis of strobilurins, common ICT, RIKILT Fera paper published in Anal. Chem.

2008 - DART TOF MS involved in Conffidence project for pesticide residue analysis

2009 - AOAC, Philadelphia, US - meeting Brian Musselman common steps planned

2009 - DART research introduced on occasion of RAFA „baby“ DART coupled with Orbitrap MS

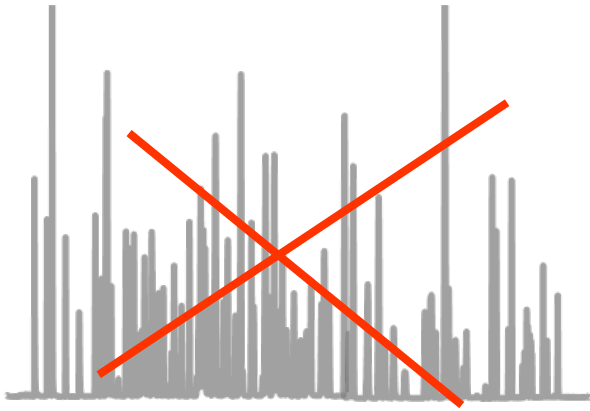
NEW

Novel analytical strategy:

AMBIENT MASS SPECTROMETRY

...opens the doors to many challenging applications in various areas of food / environmental analysis

- **Reduced / minimal sample prep**
- **No chromatographic separation**



DESI
Purdue Univ. USA

JOURNAL OF MASS SPECTROMETRY
J. Mass Spectrom. 2005; **40**: 1261–1275
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jms.922

JMS

SPECIAL FEATURE:
PERSPECTIVE

Ambient mass spectrometry using desorption electrospray ionization (DESI): instrumentation, mechanisms and applications in forensics, chemistry, and biology

Zoltán Takáts,* Justin M. Wiseman and R. Graham Cooks*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

DART
JEOL, USA

Anal. Chem. **2005**, *77*, 2297−2302

Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions

Robert B. Cody,*,† James A. Laramée,‡ and H. Dupont Durst§

JEOL USA, Inc., 11 Dearborn Road, Peabody, Massachusetts 01960, EAI Corporation, 1308 Continential Drive,

ARTICLE IN PRESS

Trends in Analytical Chemistry, Vol. XX, No. X, 2008

Review

Ambient desorption ionization mass spectrometry

Andre Venter, Marcela Nefliu, R. Graham Cooks

The ambient ionization methods retain the signature advantages of MS:

➡ speed

➡ chemical specificity

➡ low detection limits

moreover: NO SAMPLE SEPARATION IS EMPLOYED!!!

or SAMPLE PPREPARATION IS MINIMAL

Challenges offered by direct analysis in real time (DART) and related desorption ionization techniques in food quality and safety analysis

TRAC, submitted, April, 2010

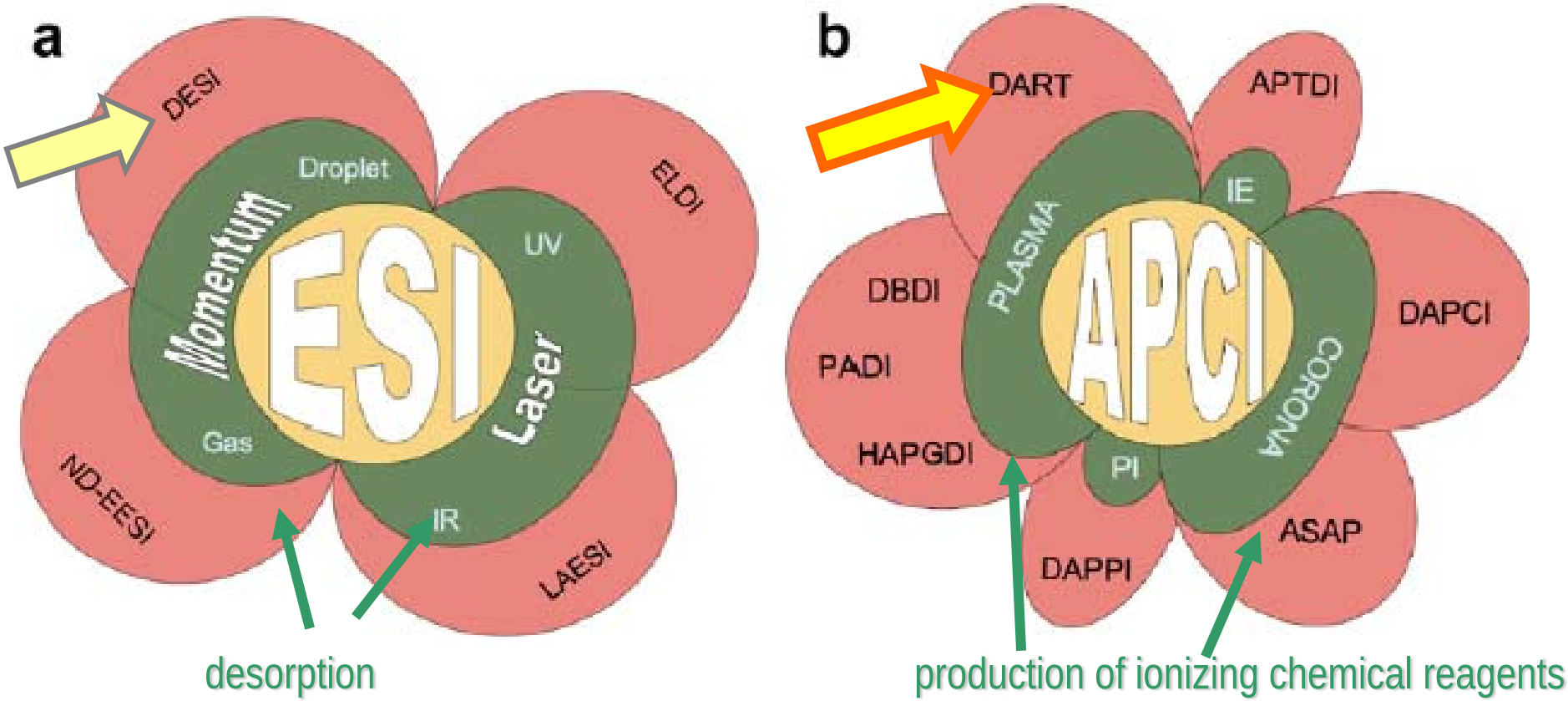
Jana Hajslova*, Tomas Cajka and Lukas Vaclavik

Institute of Chemical Technology, Prague, Faculty of Food and Biochemical Technology, Department of Food Chemistry and Analysis, Technicka 3, 16628 Prague 6, Czech Republic

A b s t r a c t

Direct analysis in real time (DART) is an ambient ionization methods undergoing rapid development. With the minimal pre-treatment, ionization of both liquid and solid samples outside the mass spectrometer (MS) in the ordinary atmosphere is feasible. This solvent-free approach relays upon fundamental principles of atmospheric pressure chemical ionization (APCI). The current review highlights and critically assesses application of DART and related desorption ionization techniques coupled to various types of MS analyzers in target/non-target analysis of complex matrices represented by foodstuffs. Based on existing studies, DART–MS is presented as a simple, memory-free, high-throughput tool for (*i*) qualitative confirmation of chemical identity, (*ii*) metabolomic fingerprinting and (*iii*) quantification of food components including trace organic contaminants. Practical aspects of DART–MS use, as well as achievable performance characteristics with regard to current food analysis regulation and legislation are discussed.

AMBIENT DESORPTION IONIZATION METHODS



a Techniques where ESI mechanisms are mainly responsible for ionization.

b Methods where chemical ionization is responsible for ionization

(photoionization - PI, ion evaporation - IE and electrical discharge)

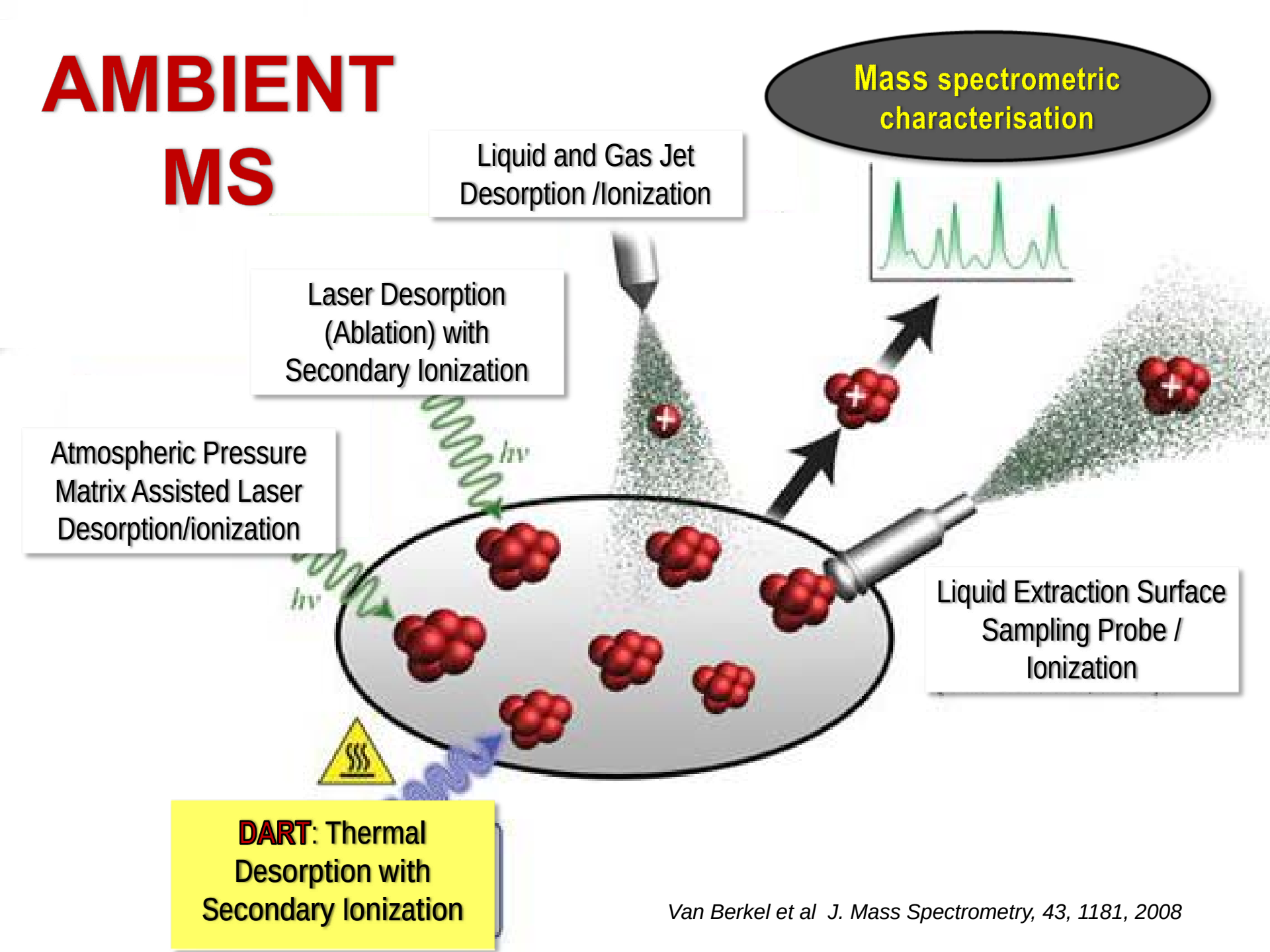
AMBIENT MS

Mass spectrometric characterisation

Liquid and Gas Jet Desorption /Ionization

Laser Desorption (Ablation) with Secondary Ionization

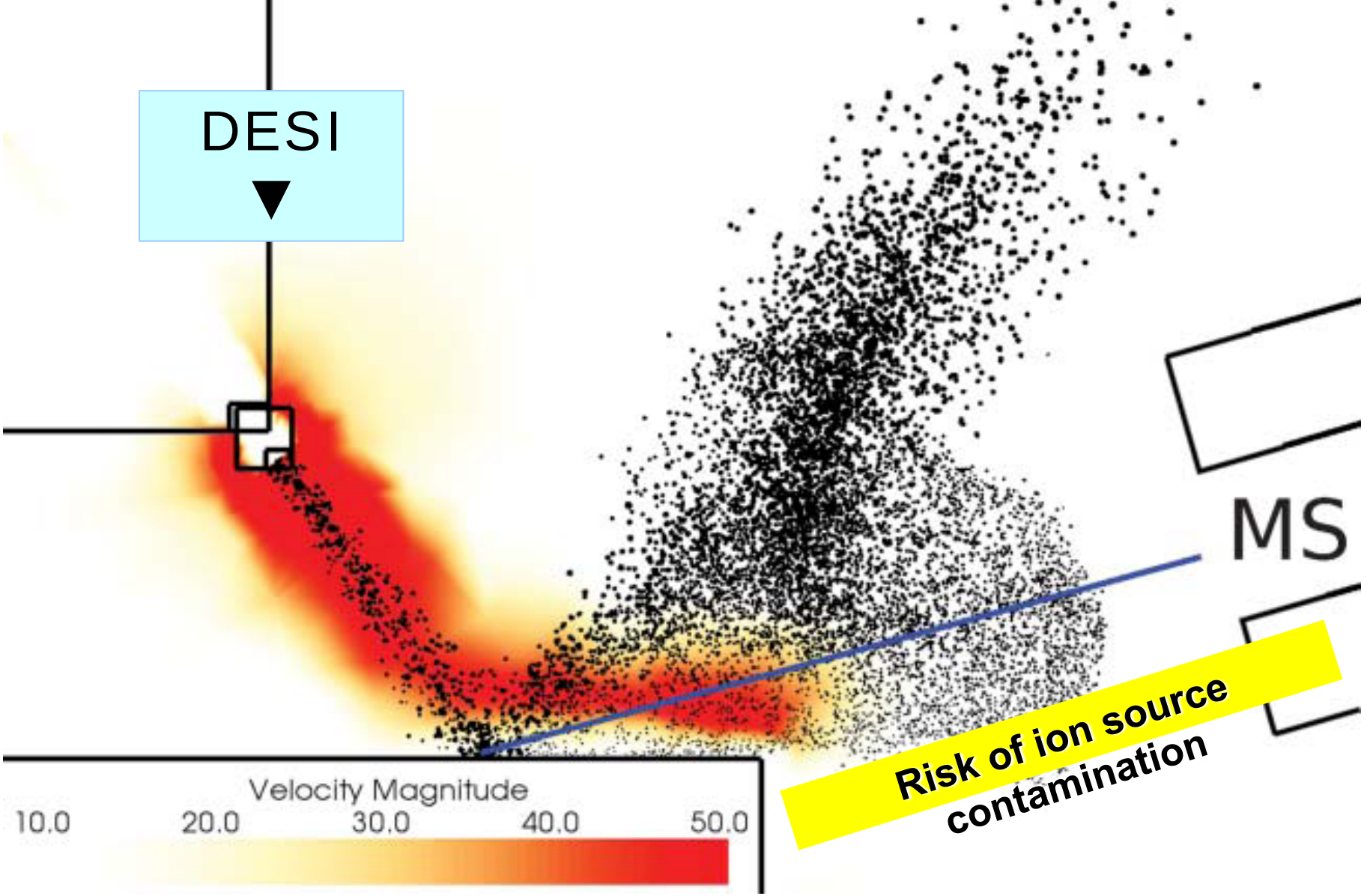
Atmospheric Pressure Matrix Assisted Laser Desorption/ionization



Liquid Extraction Surface Sampling Probe / Ionization

DART: Thermal Desorption with Secondary Ionization

Van Berkel et al J. Mass Spectrometry, 43, 1181, 2008

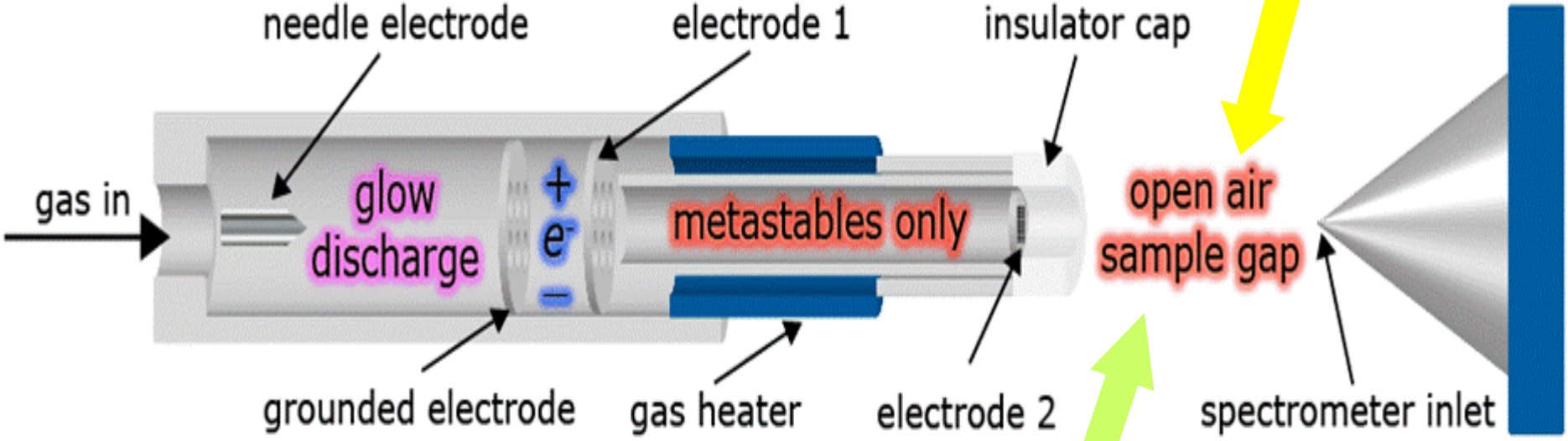


Spray and fluid velocity illustration. Droplets are black spheres eight times their actual size. Background color indicates velocity magnitude of surrounding fluid. The blue line shows the optimum collection angle from experiments (~ 10°)

The DART Ion Source

(Jeol)

The space where the sample is placed



Excited-state atoms or molecules M * interact with sample and atmosphere

Steps occurring together, or separately, under the influence of a particular agent:

- **DESORPTION** – a change in phase (e.g., solid to vapor)

- **IONIZATION** - an acquisition of charge by neutral analyte molecules

Penning Ionization

- Metastable atoms or molecules react with analytes that posses ionization potentials less than the metastable energy:

$$M^{*} + S \rightarrow S^{+\cdot} + M + \text{electron}$$

Proton Transfer

$$He(2^3S) + H_2O \rightarrow H_2O^{+\bullet} + He(1^1S) + electron$$

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + OH^\bullet$$

$$H_3O^+ + nH_2O \rightarrow [(H_2O)_nH]^+$$

$$[(H_2O)_nH]^+ + M \rightarrow MH^+ + nH_2O$$

- Metastable atoms react with atmospheric water to produce ionized water clusters
- Dominant reaction mechanism when helium carrier used: $He(2^3S)$ energy = 19.8 eV
- Huge reaction cross section: 100 A^2

DART is electric discharge-based ambient ionization technique

The ionization process in DART is a variation of APCI,
reagent-ion population originates from the gas phase reactions of the metastable He atoms produced in the discharge

Negative ions

- Direct (M-.)
  - *ionic compounds, some electrophiles*
- Proton abstraction $[M-H]^-$
  - *acidic compounds, nitroaromatics*
- Adduct formation [M+X]-
  - *Unstable nitro compounds, some halocarbons*

Positive ions

- Direct (M^+, $M^{+\cdot}$)
  - *ionic compounds, low-IP organics*
- Proton transfer $[M+H]^+$
  - *Bases, alkenes, small alcohols, ethers, ketones, aldehydes*
  - *H/D exchange*
- Other adducts [M+Z]+
  - *Polar compounds, ethers, ketones, acids, peroxides*

Overall aim of the Work package

Development of rapid screening methods for a specific class of fungicides (strobilurins) in cereals

WP6 Pesticides: target values for Strobilurin SPR bioassay

- ***Extraction time:***

  Maximum of 3 hours for 20 samples

- ***Working characteristics:***

  LODs < 0.05 mg/kg (LOQs < 0.1 mg/kg)

  Repeatability - %CV < 40

➔ Is it possible to achieve these objectives also by DART?

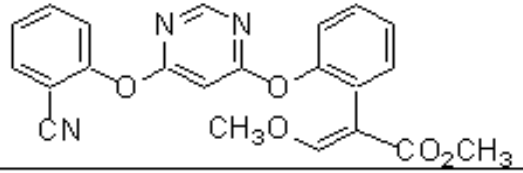
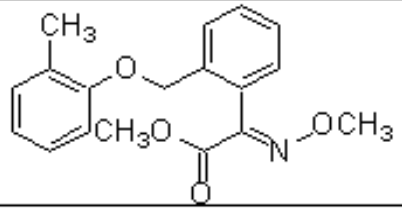
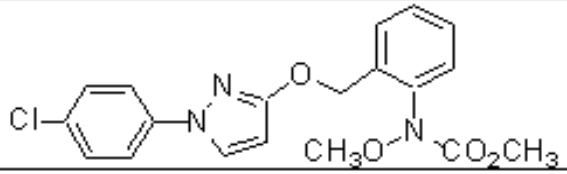
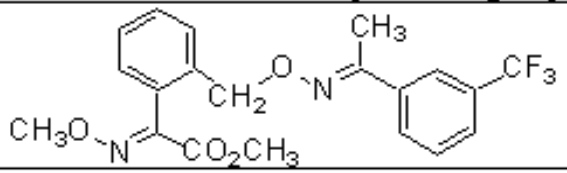
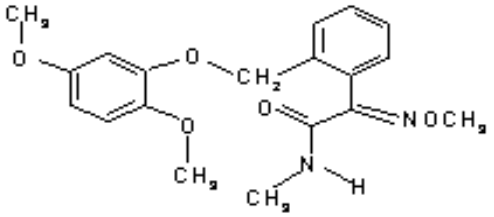
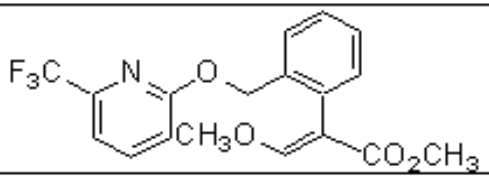
WP6 – Tasks in 2009

No.	Description	By	Status
T6.18.	[illegible]	M 53	✓
T6.19	[illegible]	M 55	✓
T6.20	[illegible] methods.	M 57	✓/In progress
T6.21	Conduct an inter-laborat[illegible] the optimised ambient mass spectrometry methods.	M 60	In progress
T6.22	To design, develop and characterise oligonucleotide-binding reagents for the target strobilurins.	M 52	×
T6.23	To produce sufficient quantities of the optimum binder for assay development.	M 54	×
T6.24	To develop a prototype assay incorporating the oligonucleotide binder.....	M 58	×
T6.25	To prepare a draft SOP for the procedure developed in T6.24.	M 60	×

Stop decision taken by TMG





Compound	Structure	MRL (mg/kg) in wheat			K_{ow} logP
		UK	Codex	EU	
Azoxystrobin		0.3	none	0.3	2,5
Kresoxim-methyl		0.05	0.05	0.05	3,4
Pyraclostrobin		0.2	none	none	3,99
Trifloxystrobin		0.02†	none	0.05*	4,5
Dimoxystrobin		0.05†	none	none	3,1
picoxystrobin		0.05†	none	0.05*	3,6

*proposed MRL

† temporary MRL

Work to be completed at ICT Prague…

(i) Inter-laboratory Comparison (samples delivered November 10, 2009)

(ii) Comparison of performance characteristics (e.g., repeatability of the measurement, limits of detection, exploiting of high mass resolving power) of DART–TOFMS and DART–Orbitrap MS

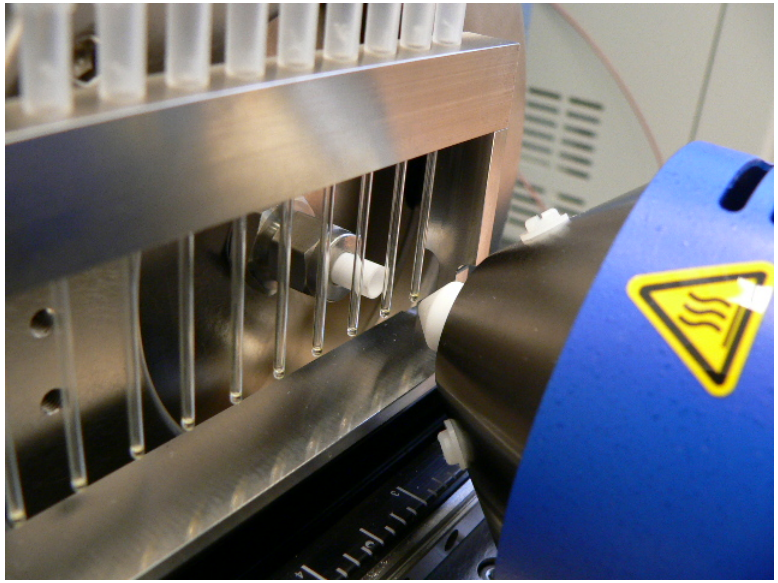
(iii) Comparison of extraction techniques: EtOAc extraction *vs.* QuEChERS



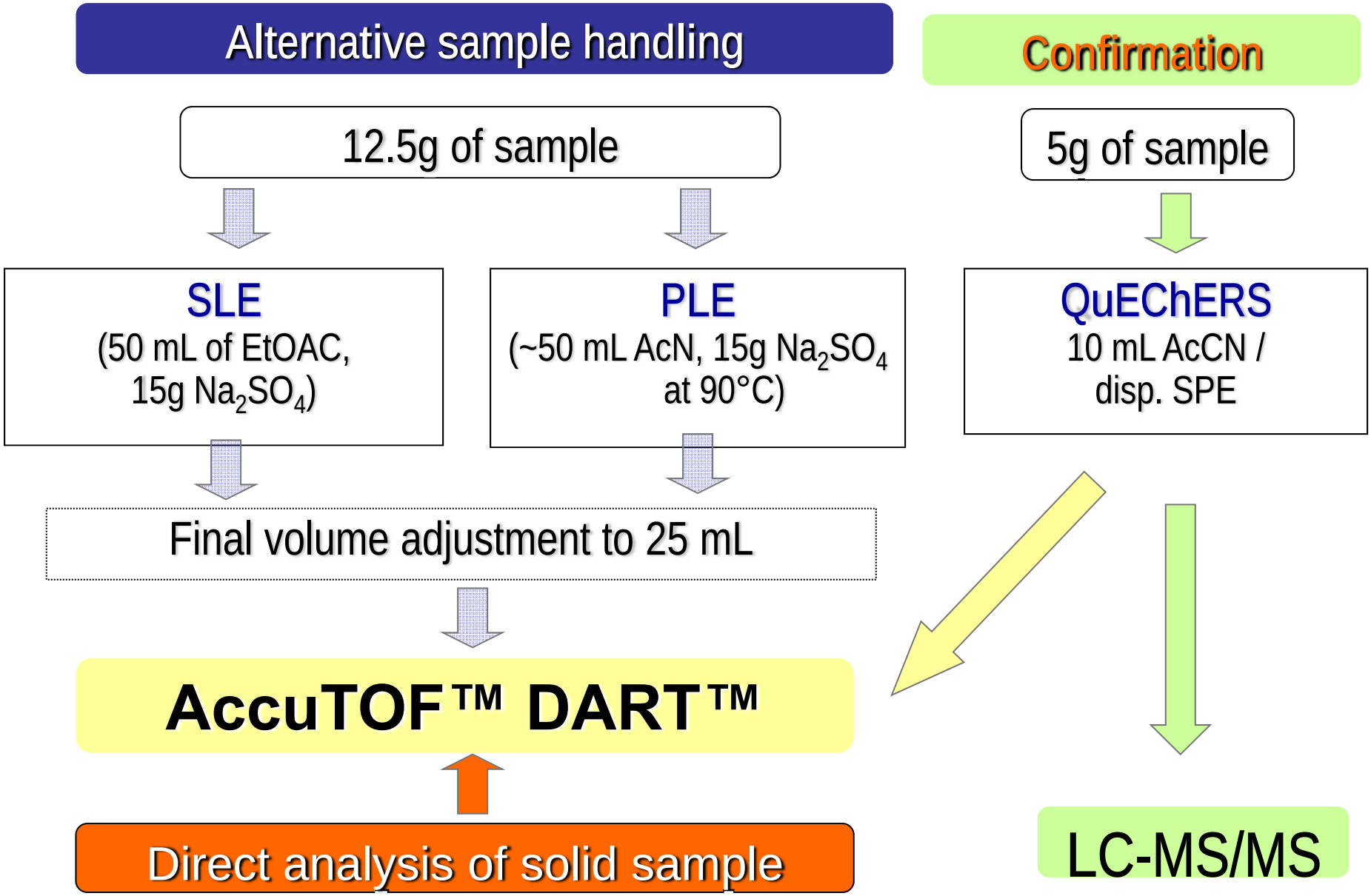


Work to be completed at ICT Prague…

(iv) Testing of a new generation of DART ion source "Baby DART" → improvement of performance characteristics expected…

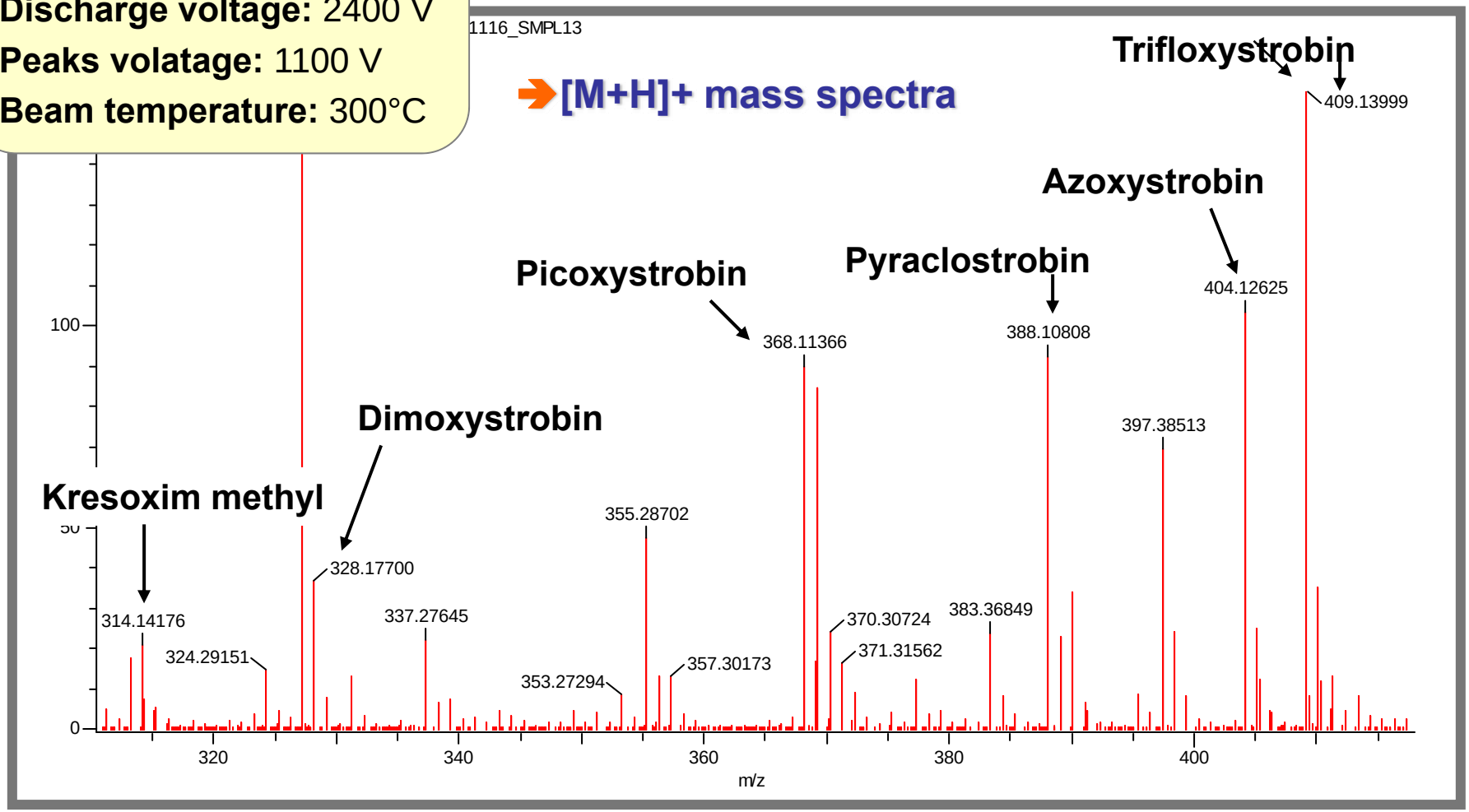


EXPERIMENTAL SET-UP



Identification of analytes in wheat extract

Polarity: positive (DART+)
Helium flow rate: 2.6 L/min
Discharge voltage: 2400 V
Peaks volatage: 1100 V
Beam temperature: 300°C

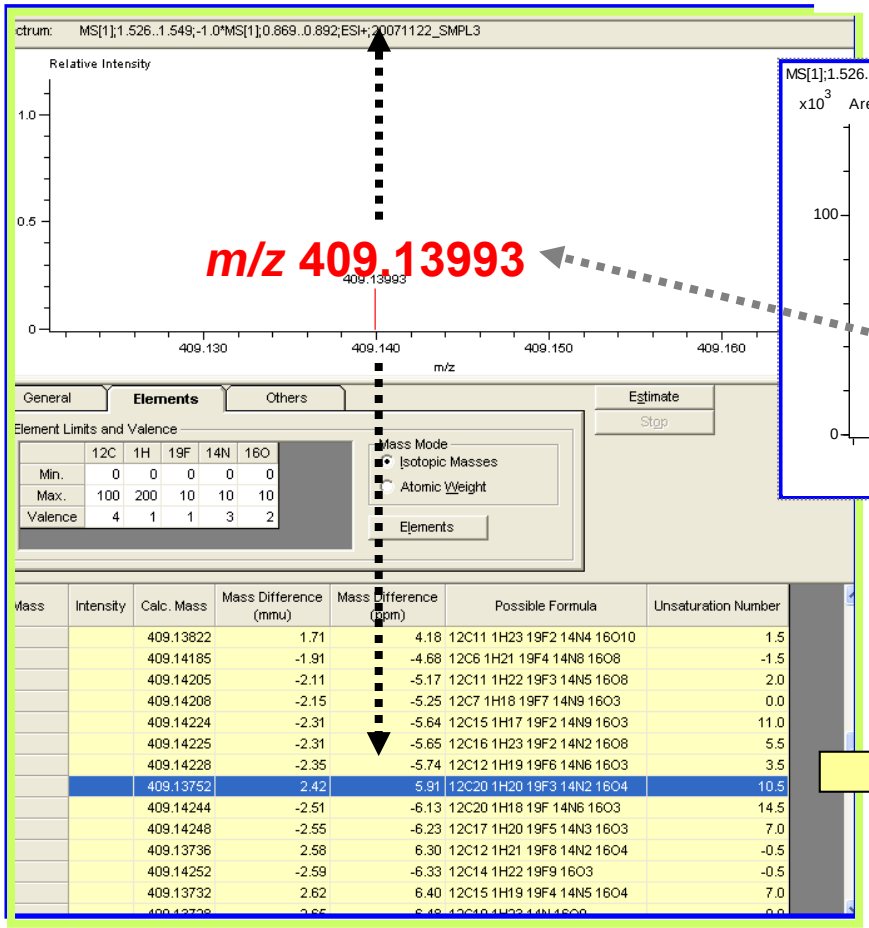


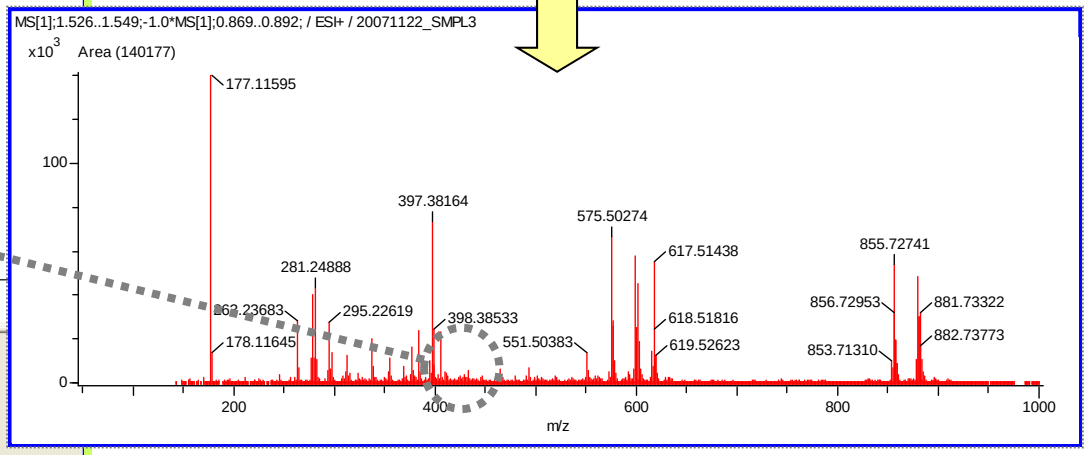
Crude ethyl acetate extract spiked with strobilurins at 120 µg/kg

Identification of analyte at “baby food” level

Estimation of element composition

[M+H]+ mass spectrum, crude ethyl acetate extract spiked with strobilurins at 12 µg/kg

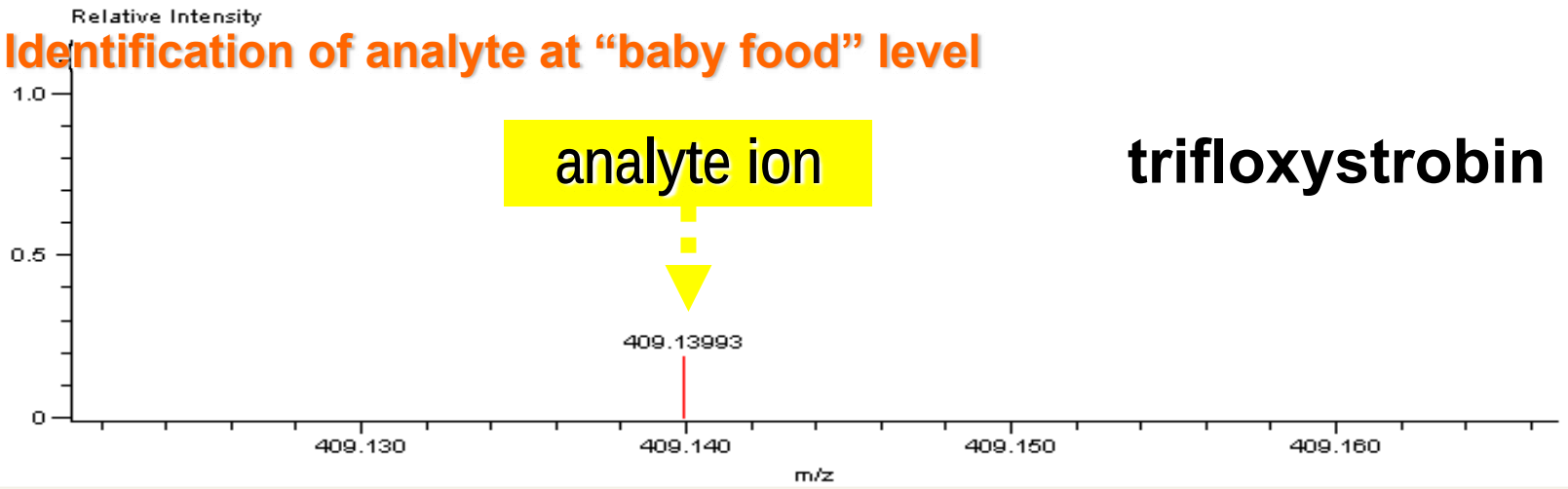




Mass difference from accurate trifloxystrobin mass – 5.91ppm (*m/z 409.13993 vs. 409.13752*)

ectrum: MS[1];1.526..1.549;-1.0*MS[1];0.869..0.892;ESI+;20071122_SMPL3

Identification of analyte at “baby food” level



analyte ion

trifloxystrobin

General | **Elements** | Others

Estimate

Stop

Element Limits and Valence

	12C	1H	19F	14N	16O
Min.	0	0	0	0	0
Max.	100	200	10	10	10
Valence	4	1	1	3	2

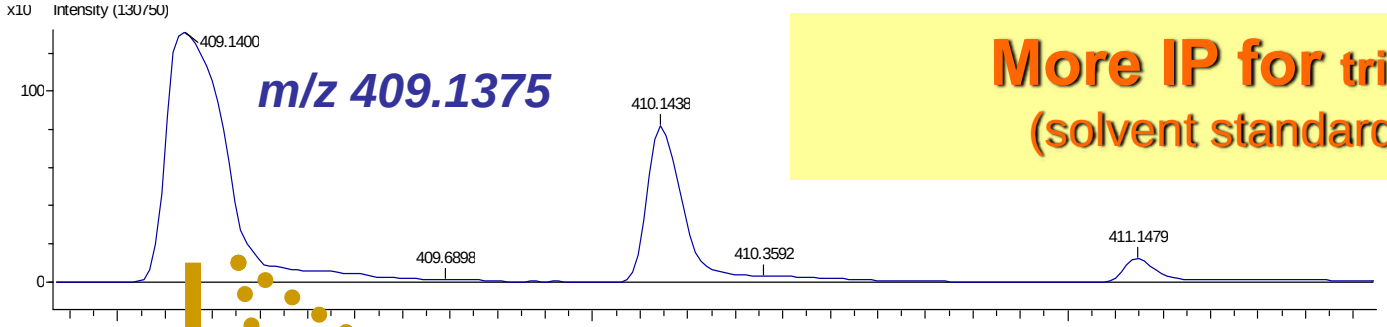
Mass Mode
- (•) Isotopic Masses
- ( ) Atomic Weight

Elements

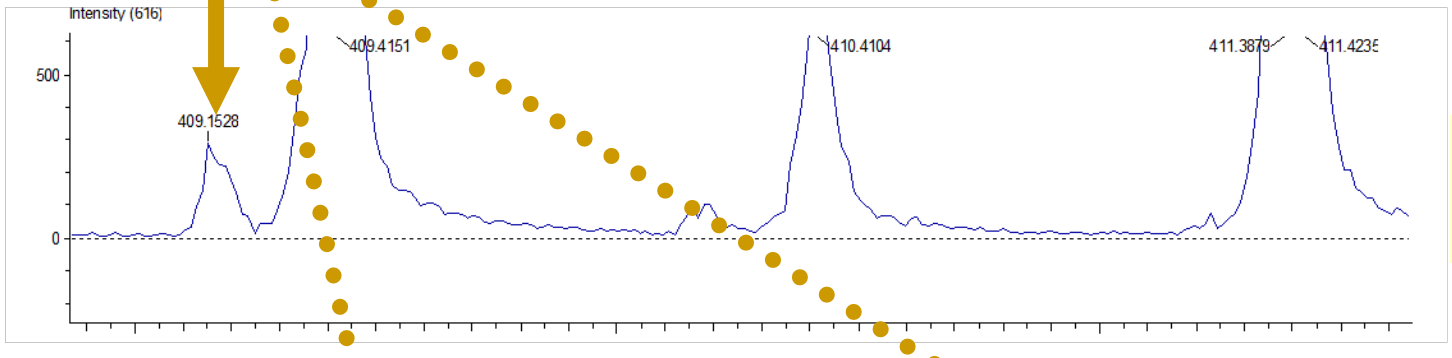
elemental composition

Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
		409.13822	1.71	4.18	12C11 1H23 19F2 14N4 16O10	1.5
		409.14185	-1.91	-4.68	12C6 1H21 19F4 14N8 16O8	-1.5
		409.14205	-2.11	-5.17	12C11 1H22 19F3 14N5 16O8	2.0
		409.14208	-2.15	-5.25	12C7 1H18 19F7 14N9 16O3	0.0
		409.14224	-2.31	-5.64	12C15 1H17 19F2 14N9 16O3	11.0
		409.14225	-2.31	-5.65	12C16 1H23 19F2 14N2 16O8	5.5
		409.14228	-2.35	-5.74	12C12 1H19 19F6 14N6 16O3	3.5
		409.13752	2.42	5.91	12C20 1H20 19F3 14N2 16O4	10.5
		409.14244	-2.51	-6.13	12C20 1H18 19F 14N6 16O3	14.5
		409.14248	-2.55	-6.23	12C17 1H20 19F5 14N3 16O3	7.0
		409.13736	2.58	6.30	12C12 1H21 19F8 14N2 16O4	-0.5
		409.14252	-2.59	-6.33	12C14 1H22 19F9 16O3	-0.5
		409.13732	2.62	6.40	12C15 1H19 19F4 14N5 16O4	7.0

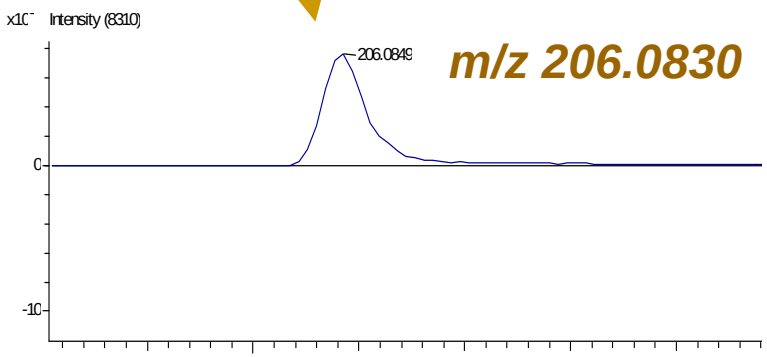
More IP for trifloxystrobin
(solvent standard, 50 µg/kg)

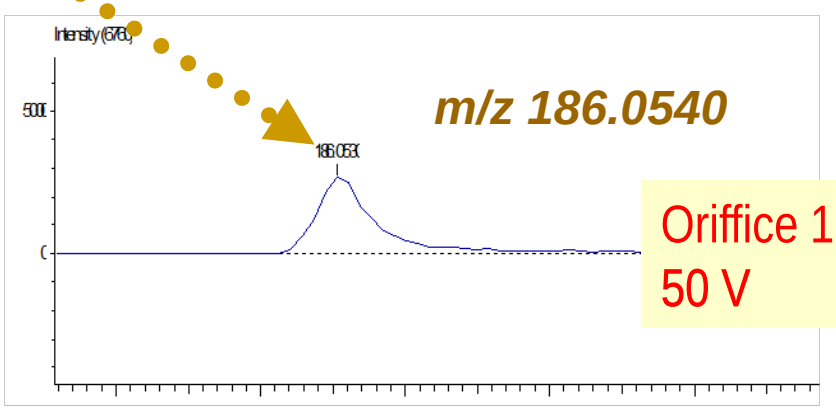


Oriffice 1 voltage
20 V (standard set-up)



Oriffice 1 voltage
50 V





Oriffice 1 voltage
50 V

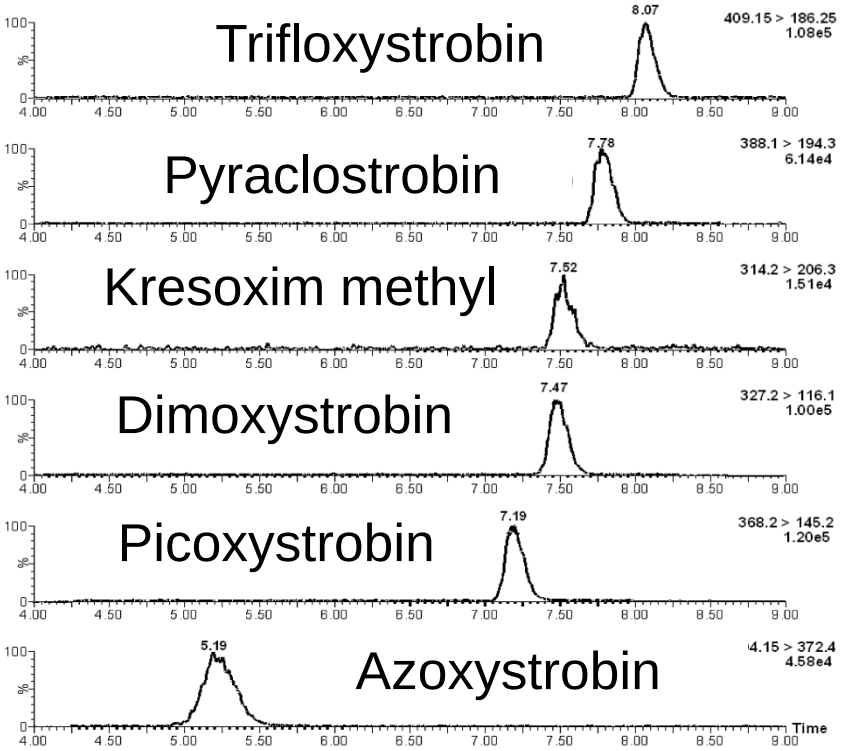
Cone induced fragmentation → Enhanced confirmation

Confirmation method: LC-MS/MS

Quattro Premier XE (Waters)

Column: Discovery C18 150 × 3 mm, 5µm (Supelco)
Mobile phase: 10mM amonium acetate - methanol
Flow rate: 0.3 ml/min
Injection volume:5 µl
Column temperatuire: 40 °C

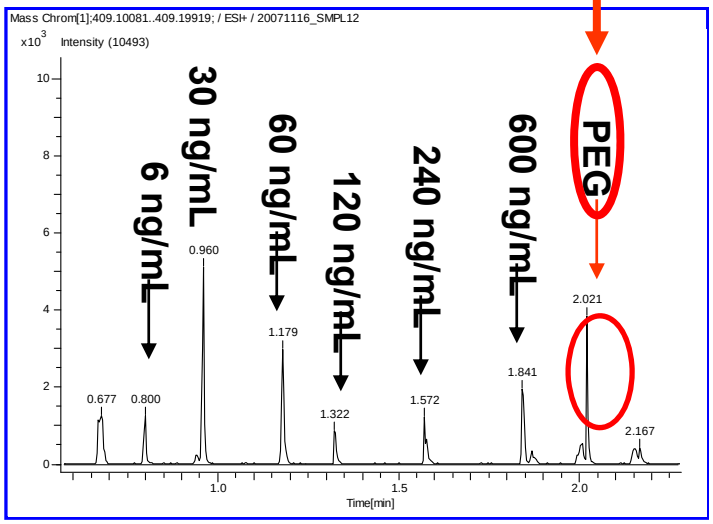
Ionization: ESI
Polarity: positive
Capillary voltage: 3200V, one: 50V
Source temperature: 120°C
Desolvatation temp.: 350°C



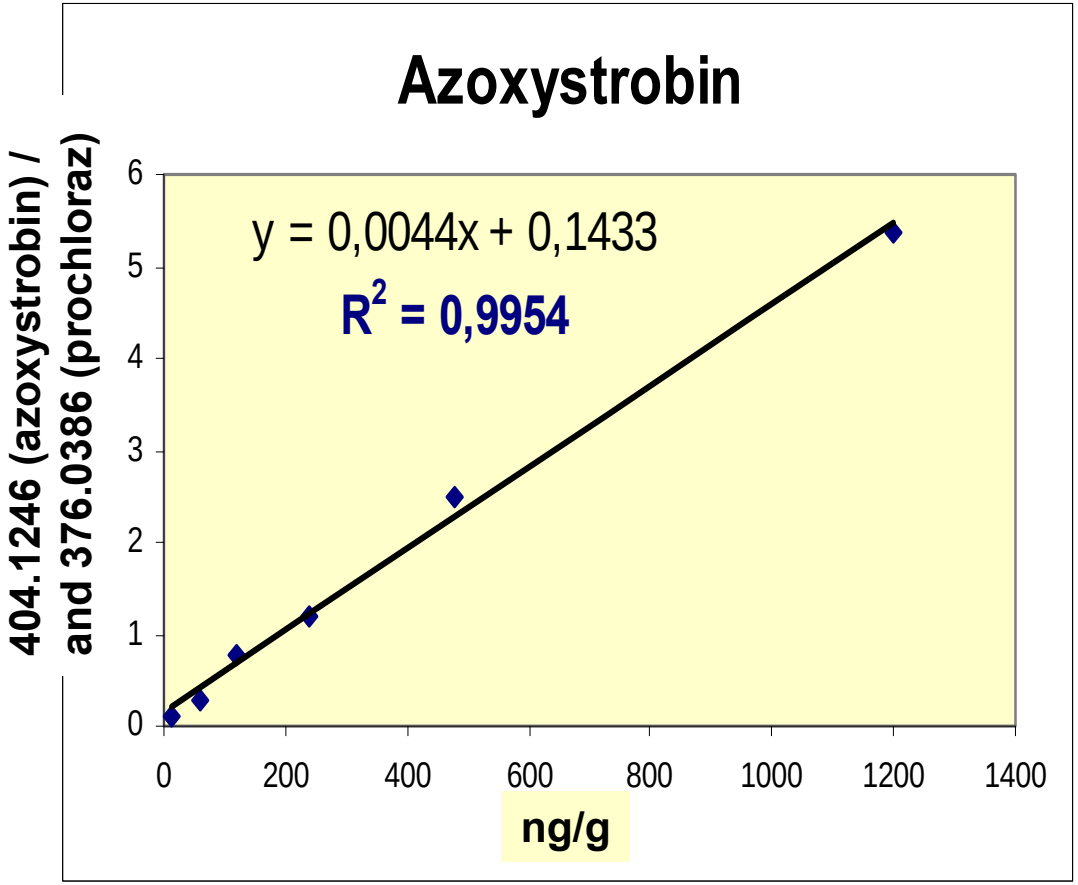
CALIBRATION – matrix matched standard

Internal standard (prochloraz) added into crude extracts, 200 µg/mL

correction of mass drift



„On-line“ injections



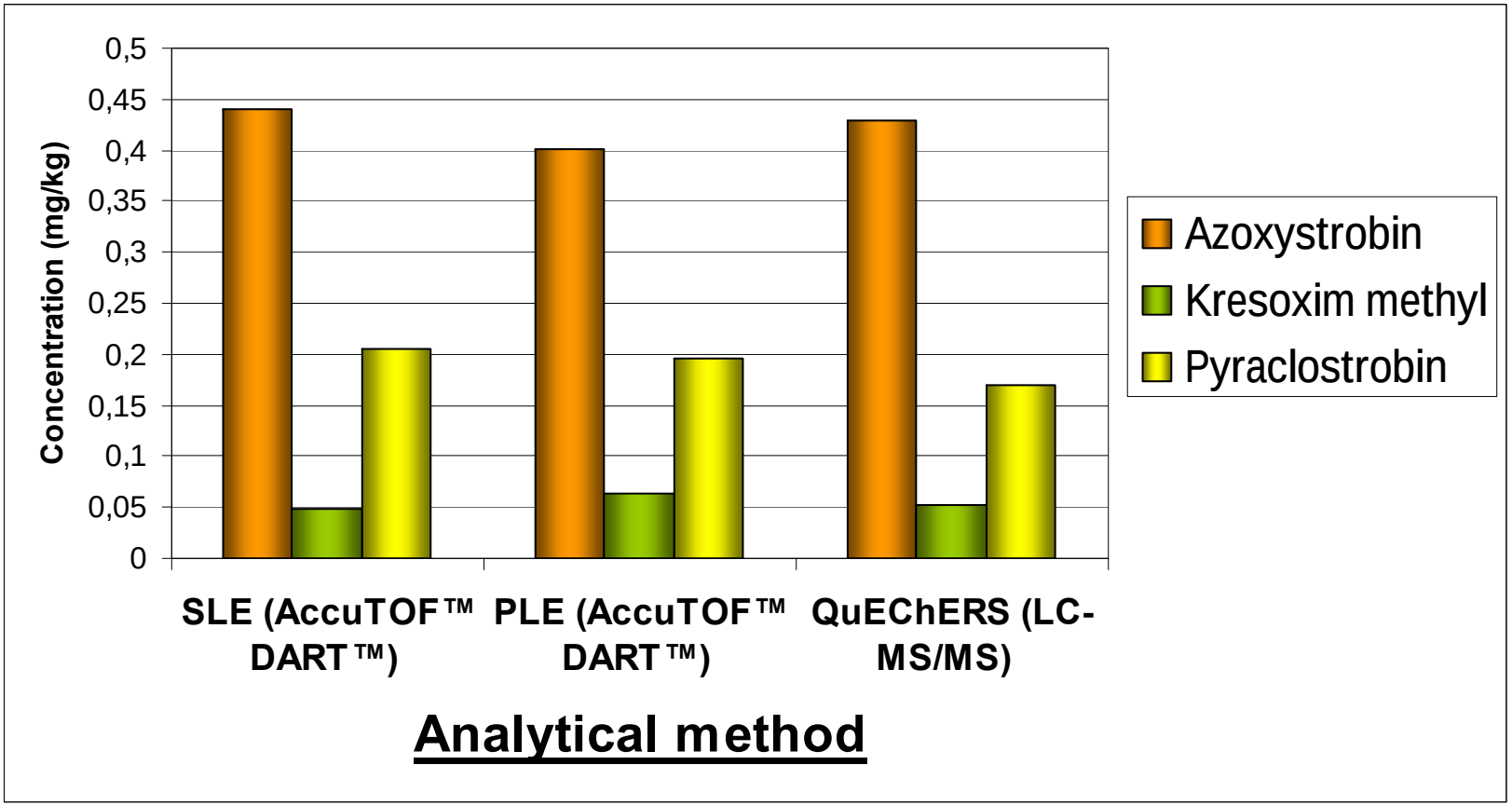
PERFORMANCE CHARACTERISTICS

wheat grains spiked by strobilurins at 60 µg/kg

METHOD	Recoveries	Repeatability (RSD, *n*=5)	LOQs (ug/kg)
SLE **AccuTOF™ DART™**	**82–91%**	**8–15%**	**12–30**
PLE **AccuTOF™ DART™**	**80–94%**	**14–19%**	**12–30**
QuEChERS **AccuTOF™ DART™**	**89–95%**	**8–11%**	**12–30**
QuEChERS LC-MS/MS	**93–97%**	**4–7%**	**1–4**

- no matrix effects related to ionization were observed in crude extracts
- possible interferences at ions of analyes (close m/z from matrix)

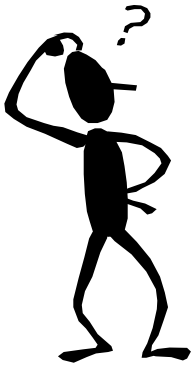
Incurred residue analysis
- wheat grains (BIOCOP test material)



Further simplification

→ DIRECT mesurement

?



Sample preparation for direct measurement

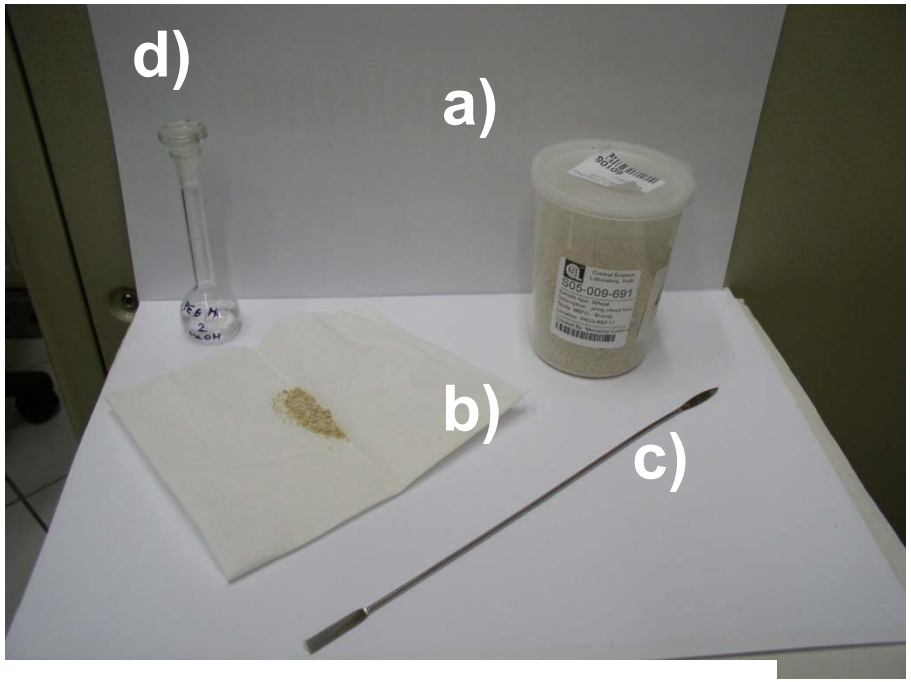
DART TOFMS

cca 1g of sample

2´

filling
a paper
“envelope”

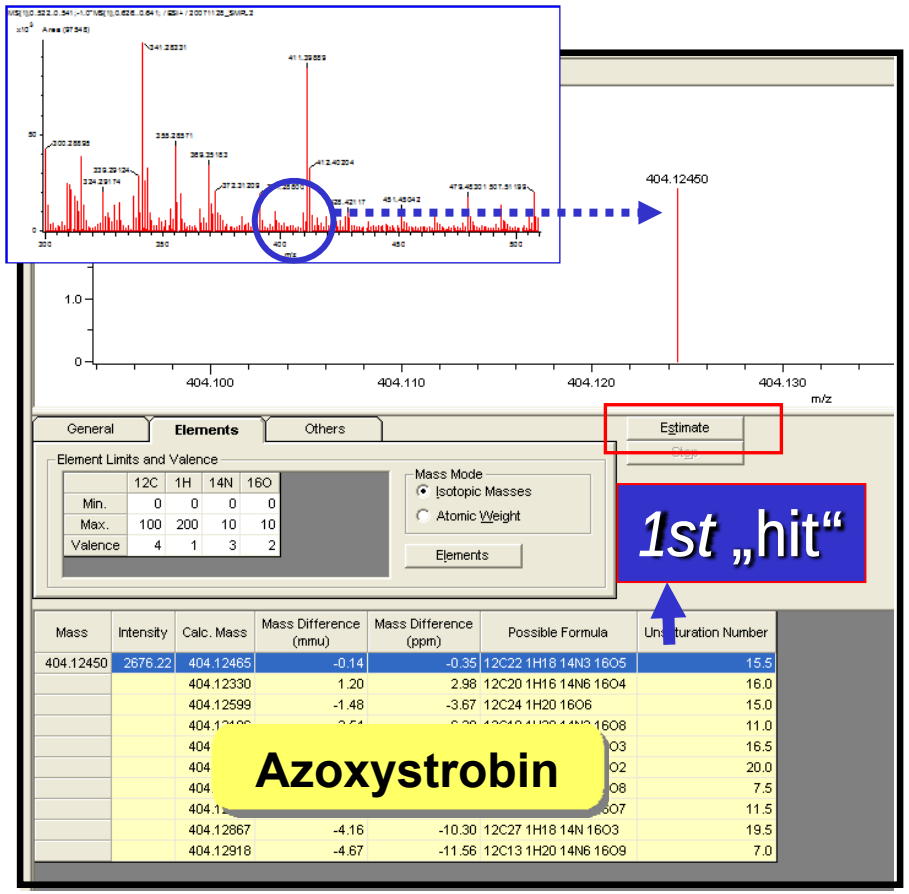
AccuTOF™ DART™

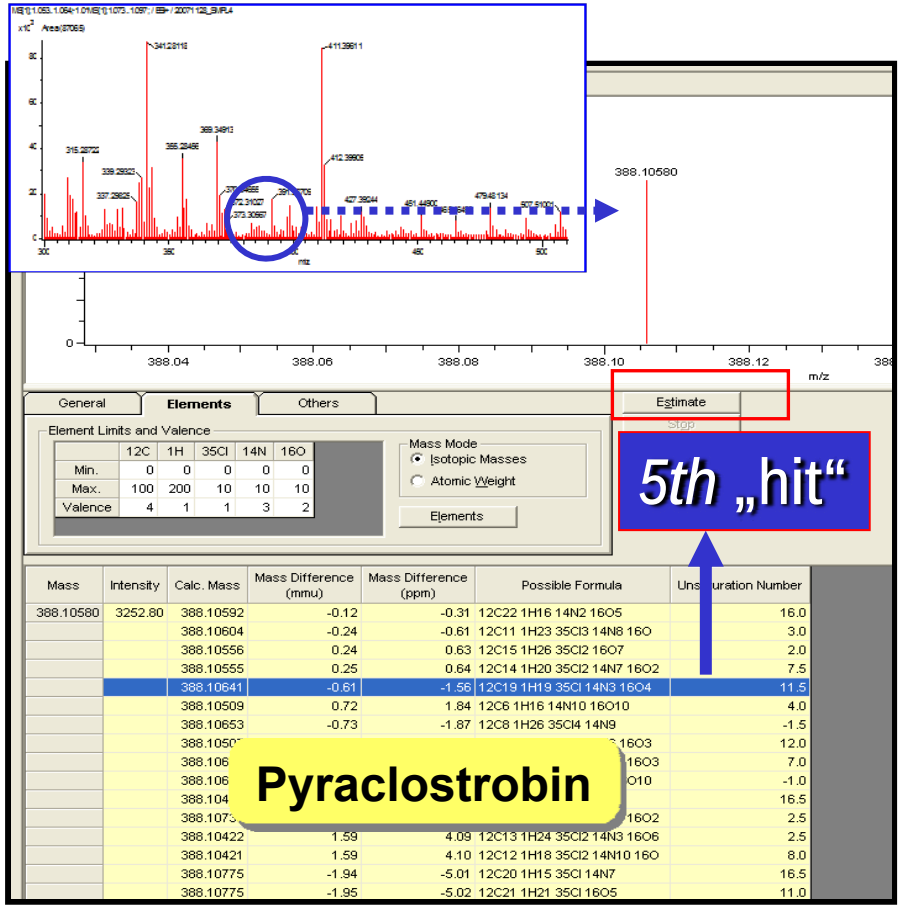


Items used for analysis:

a) incurred wheat grain sample
b) filtr paper
c) spatula
d) PEG standard solution

DIRECT SCREENING OF INCURRED RESIDUES
- wheat grains (BIOCOP test material)

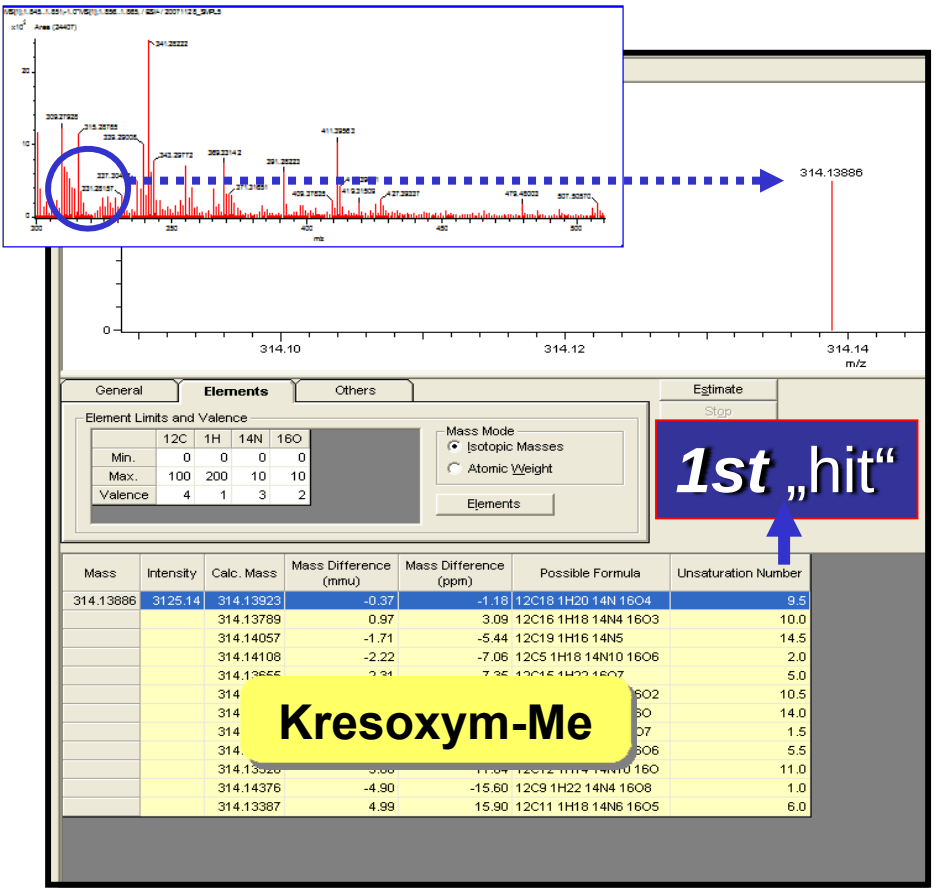




Mass difference –0.35 ppm
(429 µg/kg)

Mass difference –1.56 ppm
(170 µg/kg)

Incurred residues screening - wheat grains (BIOCOP test material)



Mass difference **–0.37 ppm**

(concentration **52 µg/kg**)

AccuTOF™ DART™ provides simple and fast confirmation of strobilurins in wheat at MRL levels.

analytical chemistry

Control of Strobilurin Fungicides in Wheat Using Direct Analysis in Real Time Accurate Time-of-Flight and Desorption Electrospray Ionization Linear Ion Trap Mass Spectrometry

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Ambient mass spectrometry has been used for the analysis of strobilurin residues in wheat. The use of this novel, challenging technique, employing a direct analysis in a real time (DART) ion-source coupled with a time-of-flight mass spectrometer (TOF MS) and a desorption electrospray ionization (DESI) source coupled with a linear ion trap tandem MS (LIT MS^n), permitted a direct screen of the occurrence of target fungicides in treated grains in less than 1 min. For quantification purpose by DART-TOF MS, an ethyl acetate extract had to be prepared. With the use of a prochloraz as an internal standard, the performance characteristics obtained by repeated analyses of extract, spiked at 50 $\mu g\ kg^{-1}$ with six strobilurins (azoxystrobin, picoxystrobin, dimoxystrobin, kresoxim-methyl, pyraclostrobin, and trifloxystrobin), were in the following range: recoveries 78−92%, repeatability (RSD) 8−15%, linearity (R^2) 0.9900−0.9978. The analysis of wheat with incurred strobilurin residues demonstrated good trueness of data generated by the DART-TOF MS method; the results were in a good agreement with those obtained by the conventional approach, i.e., by the QuEChERS sample handling procedure followed by identification/quantification em-

pathogens, such as powdery mildews (ascomycetes) and rusts (basidiomycetes). The various strobilurins differ in their systemic properties, some of them are partially systemic and others redistribute themselves around the plant in the wax layer/epidermal cells by vapor action. In addition to strobilurins' fungicidal effect, these chemicals may induce physiological alteration (e.g., increase of endogenous cytokinin levels, stimulation of ethylene biosynthesis, increase in CO_2 assimilation), thus performing as bioregulators, particularly in cereals which become ripe in a shorter period of time as compared to nontreated ones. The resulting longer retention of green leaf tissue and significant yield enhancements are the benefits of the their use in agriculture.[3] With the exception of kresoxim-methyl, strobilurins are not classified as internationally accepted Pesticide Action Network Bad Actors,[4] meaning that they are not (i) highly acutely toxic, (ii) cholinesterase inhibitors, (iii) known/probable carcinogens, (iv) known groundwater pollutants, or (v) known reproductive or developmental toxicants. With regards to strobilurins, widespread use (for instance global consumption of azoxystrobin which is registered for over 400 crop/disease systems[2] was more than 5000 t in 2007[6]), development of analytical procedures enabling a

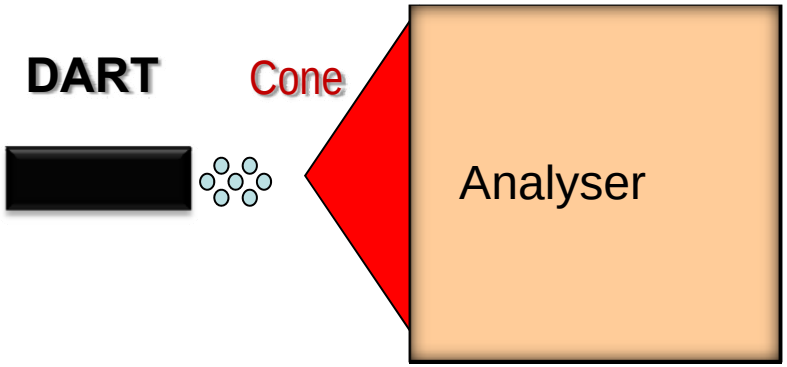
Schurek J. et al., *Anal. Chem*. 80, 9567–9575 (2008), doi: 10.1021/ac8018137





APPROACH #1

DART–TOFMS

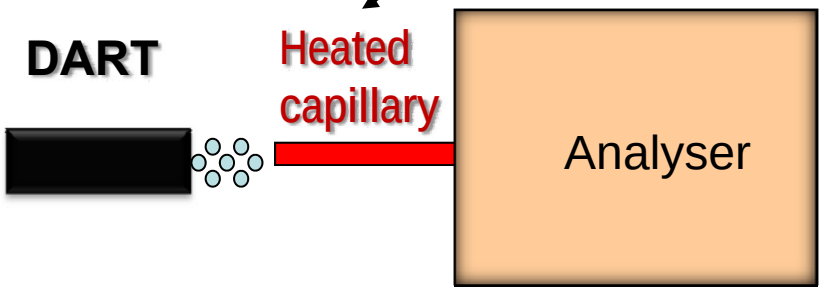


Transfer of the technique…

APPROACH #2

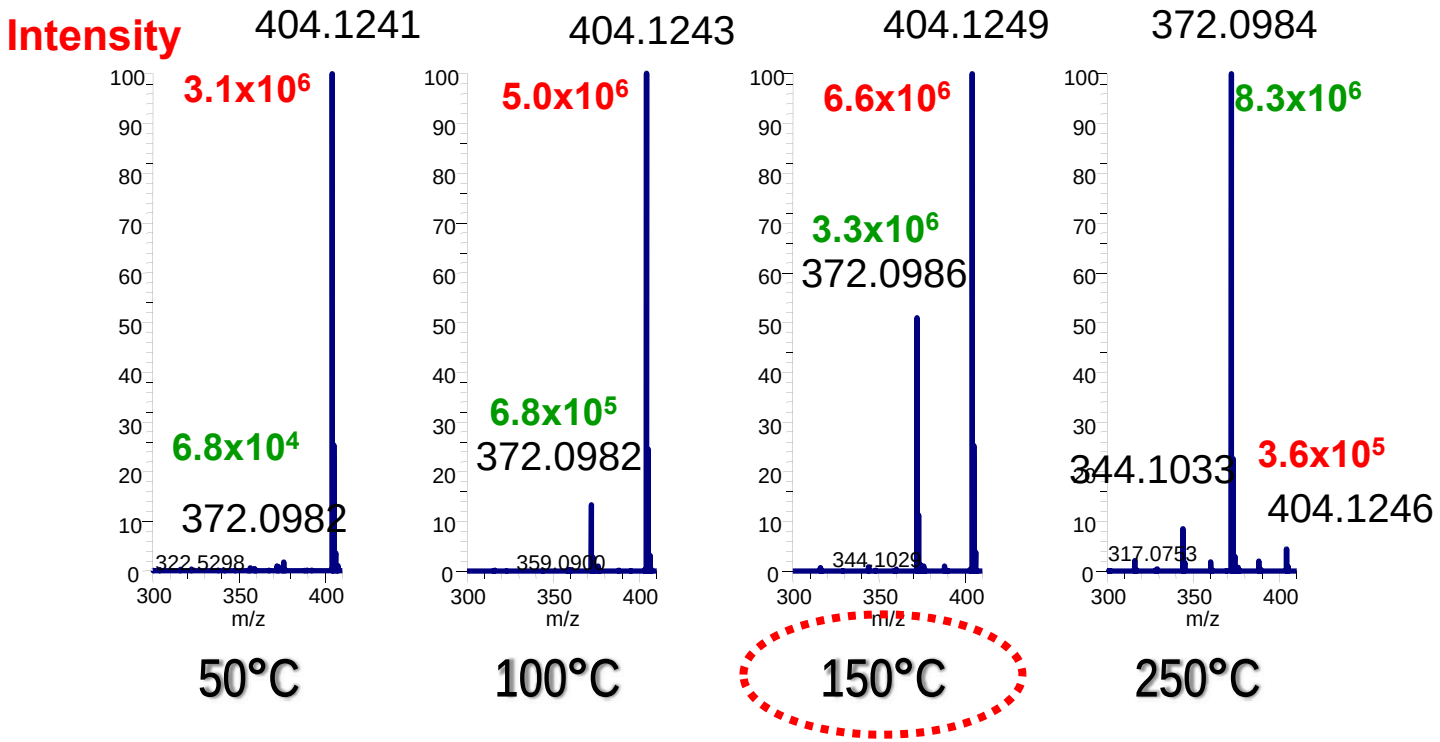
DART–Orbitrap MS

New problem emerged…



DART–Orbitrap MS:
Influence of capillary temperature on the fragmentation

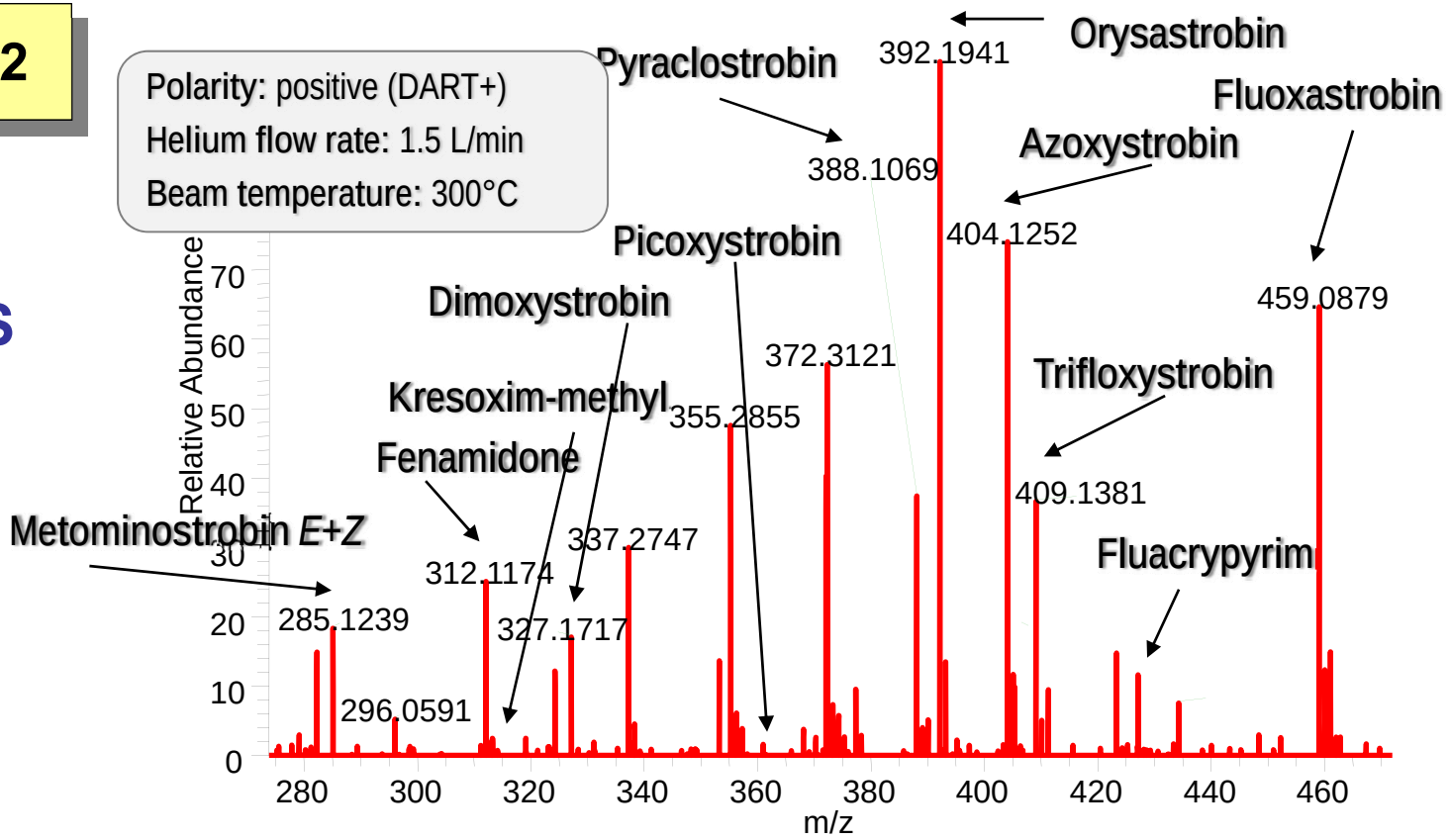
Example: Azoxystrobine, $[M+H]^+$ 404.124



APPROACH #2

DART–Orbitrap MS

Polarity: positive (DART+)
Helium flow rate: 1.5 L/min
Beam temperature: 300°C



Purified (PSA, C18) QuEChERS extract (wheat) spiked with strobilurins at 1 mg/kg

DART–Orbitrap MS: matrix effects

Azoxystrobine

$[M+H]^+$ 404.124

Standard in pure solvent

Matrix-matched standard (wheat extract)

QuEChERS

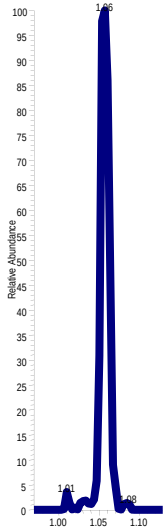
cleanup: 150 mg PSA + 50 mg C_{18} per mL

QuEChERS

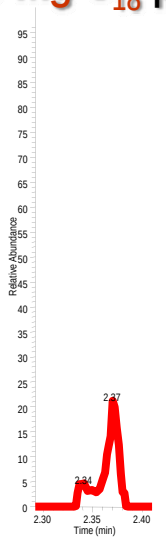
cleanup: 50 mg PSA per mL

QuEChERS

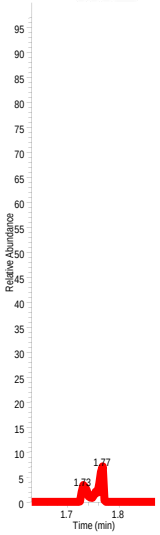
crude extract



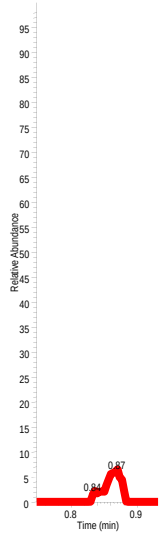
1000 ng/mL



1000 ng/mL/0.5 g



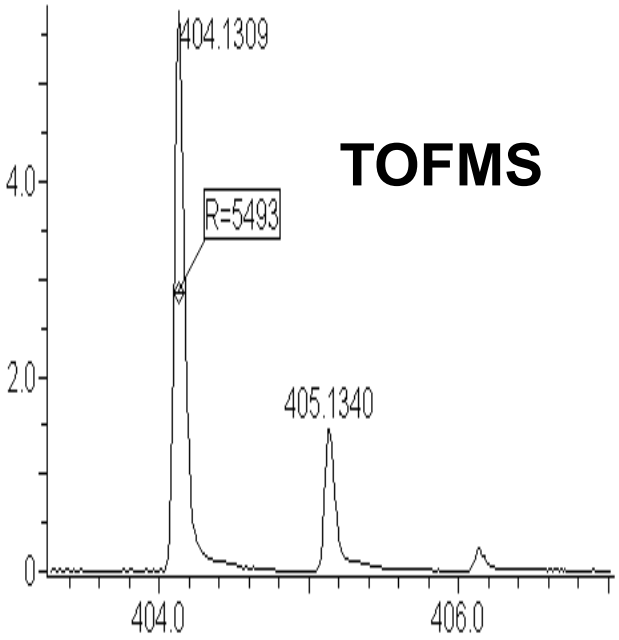
1000 ng/mL/0.5 g



1000 ng/mL/0.5 g

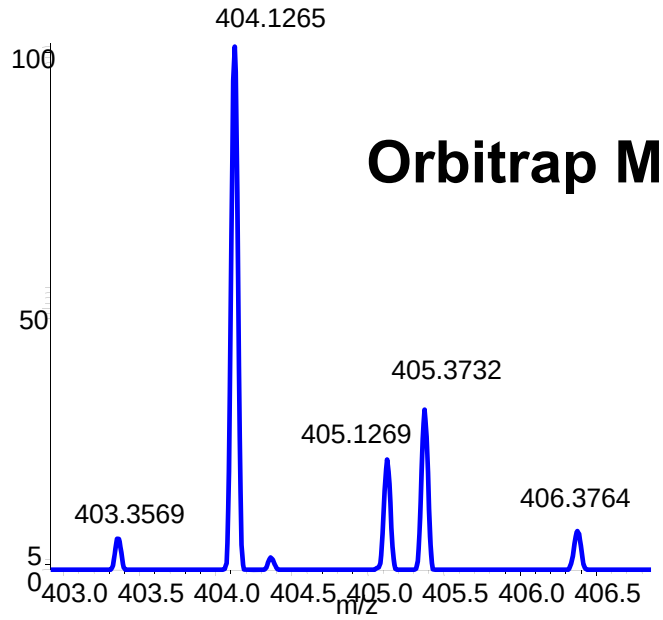
DART–TOFMS *vs.* DART–Orbitrap MS: Influence of mass resolving power

5,500 fwhm



TOFMS

10,000 fwhm



Orbitrap MS

CON*ff*IDENCE project

WP-1c

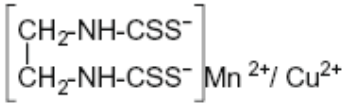
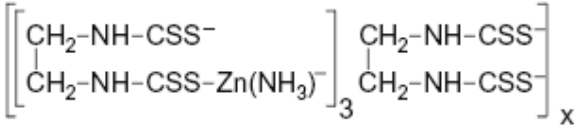
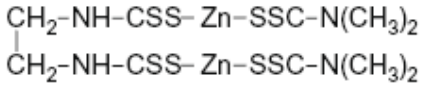
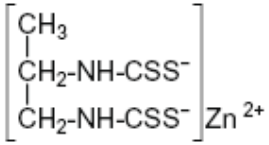
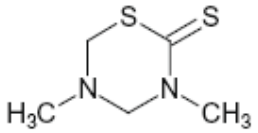
Simplified MS screening tool for the analysis of dithiocarbamates in intact vegetables/fruits

Overview of DTCs

Name	Annex I[1]	Formula	CAS No.	Solubility in water (g/L, 20°C)	Solubility in organic solvents
Ziram	+	$[(CH_3)_2N\text{-}CSS^-]_2Zn^{2+}$	137-30-4	0.06	Chloroform, carbon disulfide
Ferbam	–	$[(CH_3)_2N\text{-}CSS^-]_3Fe^{3+}$	14484-64-1	0.13	Chloroform, acetone, acetonitrile
Asomate[2]	–	$[(CH_3)_2N\text{-}CSS^-]_3As^{3+}$	3586-60-5	n.d.f.[3]	n.d.f
Thiram	+	$(CH_3)_2N\text{-}CSS\text{-}SSC\text{-}N(CH_3)_2$	137-26-8	0.018	Chloroform, dichloromethane, acetone,
Metam	+	$(CH_3)_2NH\text{-}CSS^-Na^+$	144-54-7	722	Acetone, ethanol
Nabam	–	$\left[\begin{array}{l}CH_2\text{-}NH\text{-}CSS^-\\CH_2\text{-}NH\text{-}CSS^-\end{array}\right] 2\ Na^+$	142-59-6	200	p.i.[4]
Zineb	–	$\left[\begin{array}{l}CH_2\text{-}NH\text{-}CSS^-\\CH_2\text{-}NH\text{-}CSS^-\end{array}\right] Zn^{2+}$	12122-67-7	p.i.	p.i
Maneb	+	$\left[\begin{array}{l}CH_2\text{-}NH\text{-}CSS^-\\CH_2\text{-}NH\text{-}CSS^-\end{array}\right] Mn^{2+}$	12427-38-2	p.i.	p.i.
Mancozeb	+	$\left[\begin{array}{l}CH_2\text{-}NH\text{-}CSS^-\\CH_2\text{-}NH\text{-}CSS^-\end{array}\right] Mn^{2+}/\ Zn^{2+}$	8018-01-7	p.i.	p.i.

G. Crnogorac, W. Schwack, *TrAC-Trend Anal Chem*, 28, 40–50 (2009)

Overview of DTCs

Mancopper	–		53988-93-5	p.i.	p.i.
Metiram	+		9006-42-2	p.i.	p.i.
Polycarbamate[5] (Bis-Dithane)	–		64440-88-6	n.d.f.	n.d.f.
Propineb	+		12071-83-9	p.i.	p.i.
Dazomet	–		533-74-4	3	Chloroform, acetone, cyclohexane

G. Crnogorac, W. Schwack, *TrAC-Trend Anal Chem*, 28, 40–50 (2009)

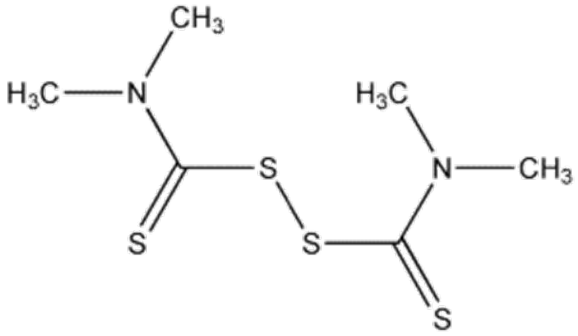
Activities and achievements

- **Optimisation of DART–TOFMS instrumental parameters for thiram and ziram**

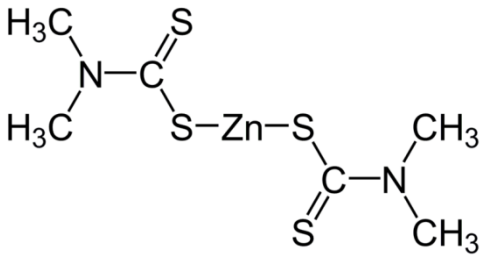
- **Sample preparation for the determination of thiram and ziram in fruits (pears) using DART–TOFMS**

- **Validation study**

Thiram

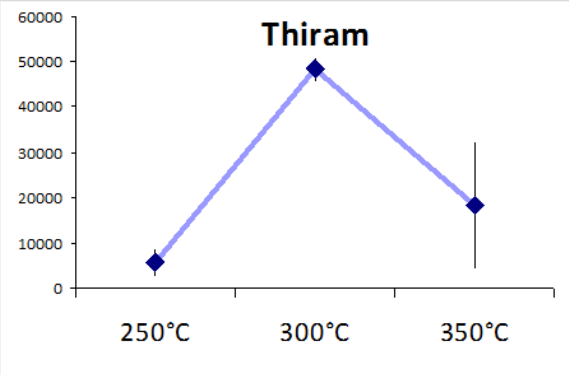


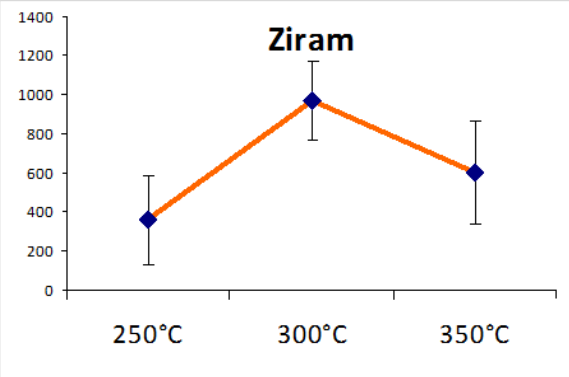
Ziram



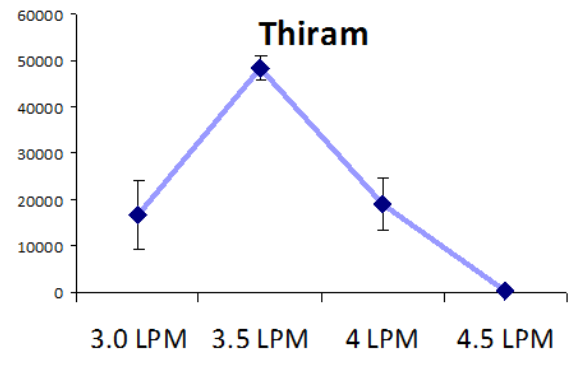
Activities and achievements

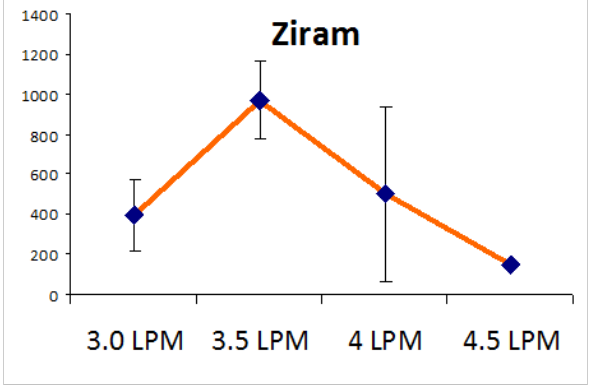
- **Optimisation of DART–TOFMS instrumental parameters**
  - Gas beam temperature → **300°C** optimal





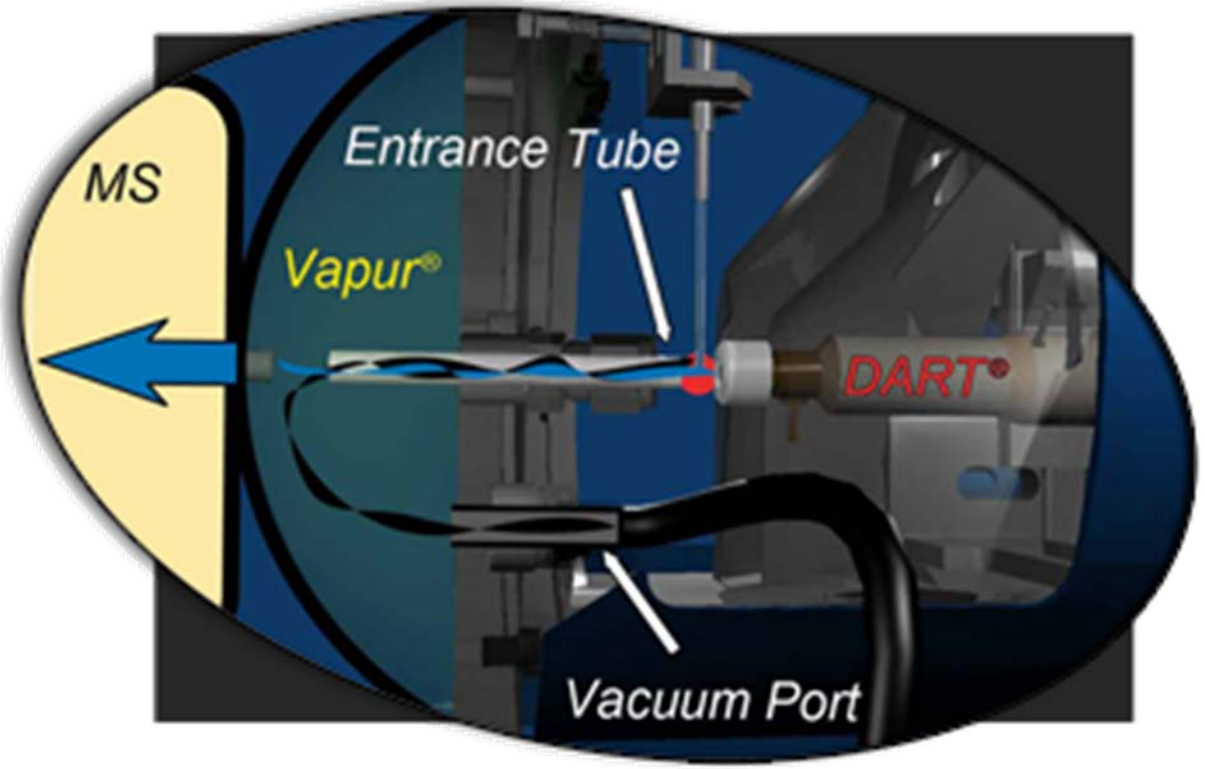
  - Helium flow → **3.5 litters per minute** optimal





Activities and achievements

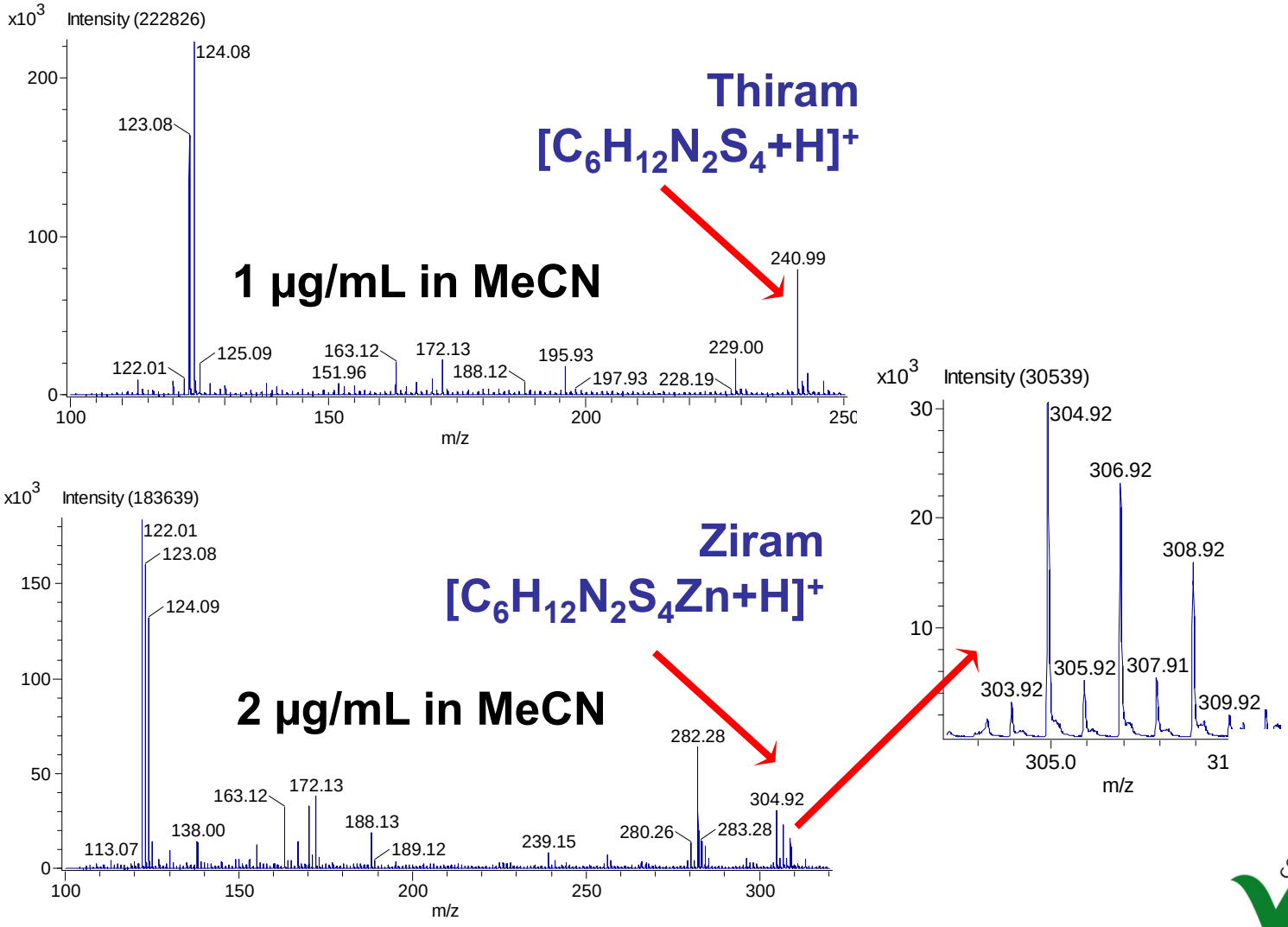
- **Optimisation of DART–TOFMS instrumental parameters**
  - VAPUR interface (only 20% increasing of signal intensity, but higher background) → **without VAPUR**



Source of figure: www.ionsense.com

Activities and achievements

- **DART[+]–TOFMS profiles of standards**



2007/57/EC

COMMISSION DIRECTIVE 2007/57/EC

of 17 September 2007

amending certain Annexes to Council Directives 76/895/EEC, 86/362/EEC, 86/363/EEC and 90/642/EEC as regards maximum residue levels for dithiocarbamates

(Text with EEA relevance)

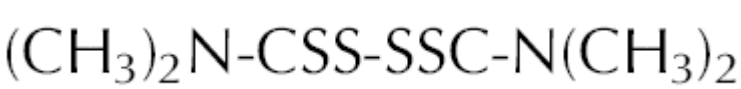
Groups and examples of individual products to which the MRLs apply	Dithiocarbamates, expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram (1), (2)	Propineb (expressed as propilendiammine) (3)	Thiram (expressed as thiram) (3)	Ziram (expressed as ziram) (3)
Others	0,05 (*)			
(iii) **POME FRUIT**	5 (ma, mz, me, pr, t, z)	0,3		
Apples			5	0,1 (*)
Pears			5	1
Quinces				
Others			0,1 (*)	0,1 (

mg/kg

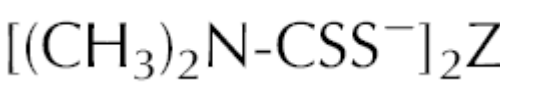
Sample preparation

- **First considerations for the determination of thiram and ziram in fruits (pears) using DART–TOFMS**
  - Both compounds soluble in acetonitrile (this information not available in literature!)
  - Possibility to use acetonitrile for sample extraction (QuEChERS approach)
  - Internal standard needed for reliable quantification (triphenyl phosphate, TPP)

Thiram



Ziram

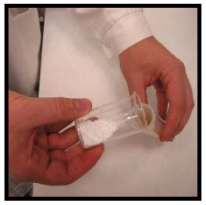


Sample preparation

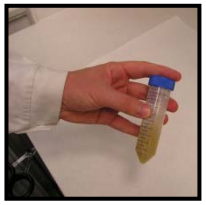
- **QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe)**

(1) 

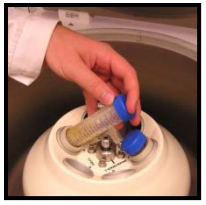
10 g sample (pears)
10 mL acetonitrile
Shaking – 1 min

(2) 

4 g $MgSO_4$ + 1 g NaCl

(3) 

Shaking – 1 min

(4) 

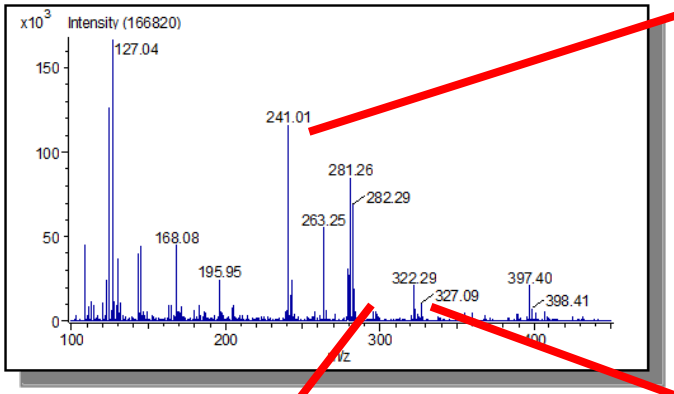
Centrifugation – 5 min, 11,000 rpm

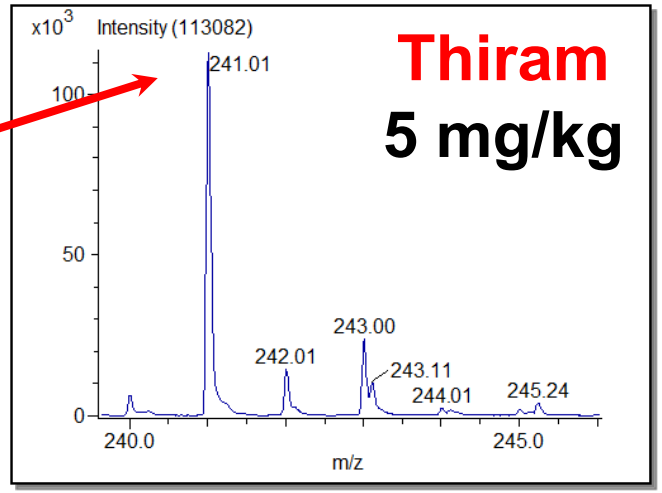
(5) 

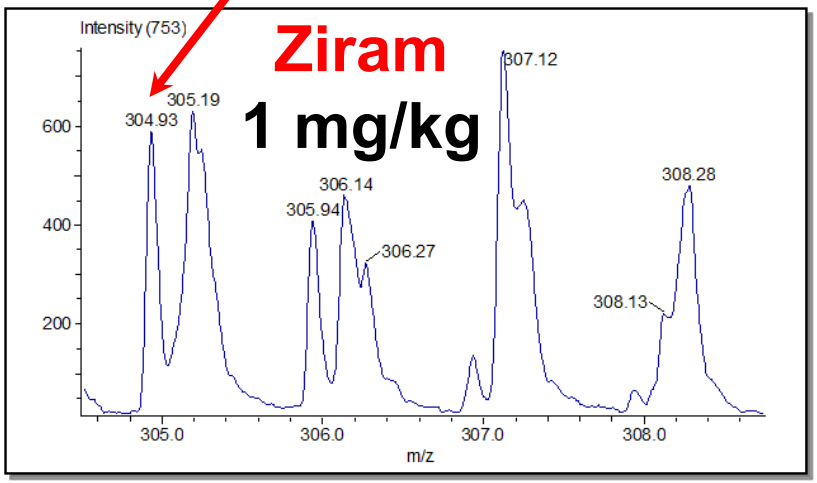
DART–TOFMS analysis

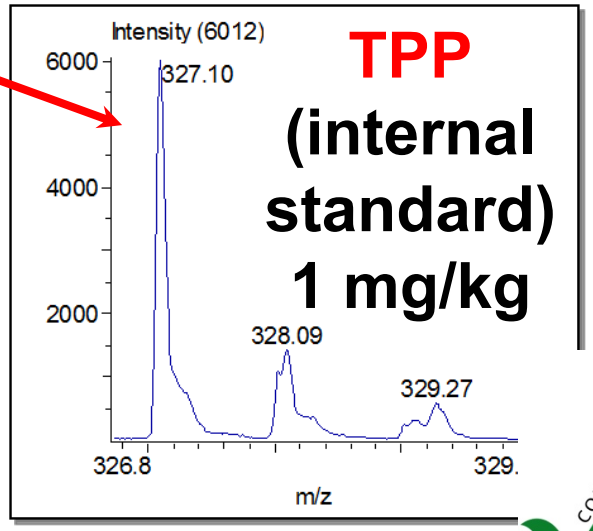
Activities and achievements

- **DART–TOFMS spectrum of matrix-matched standard (pear extract)**



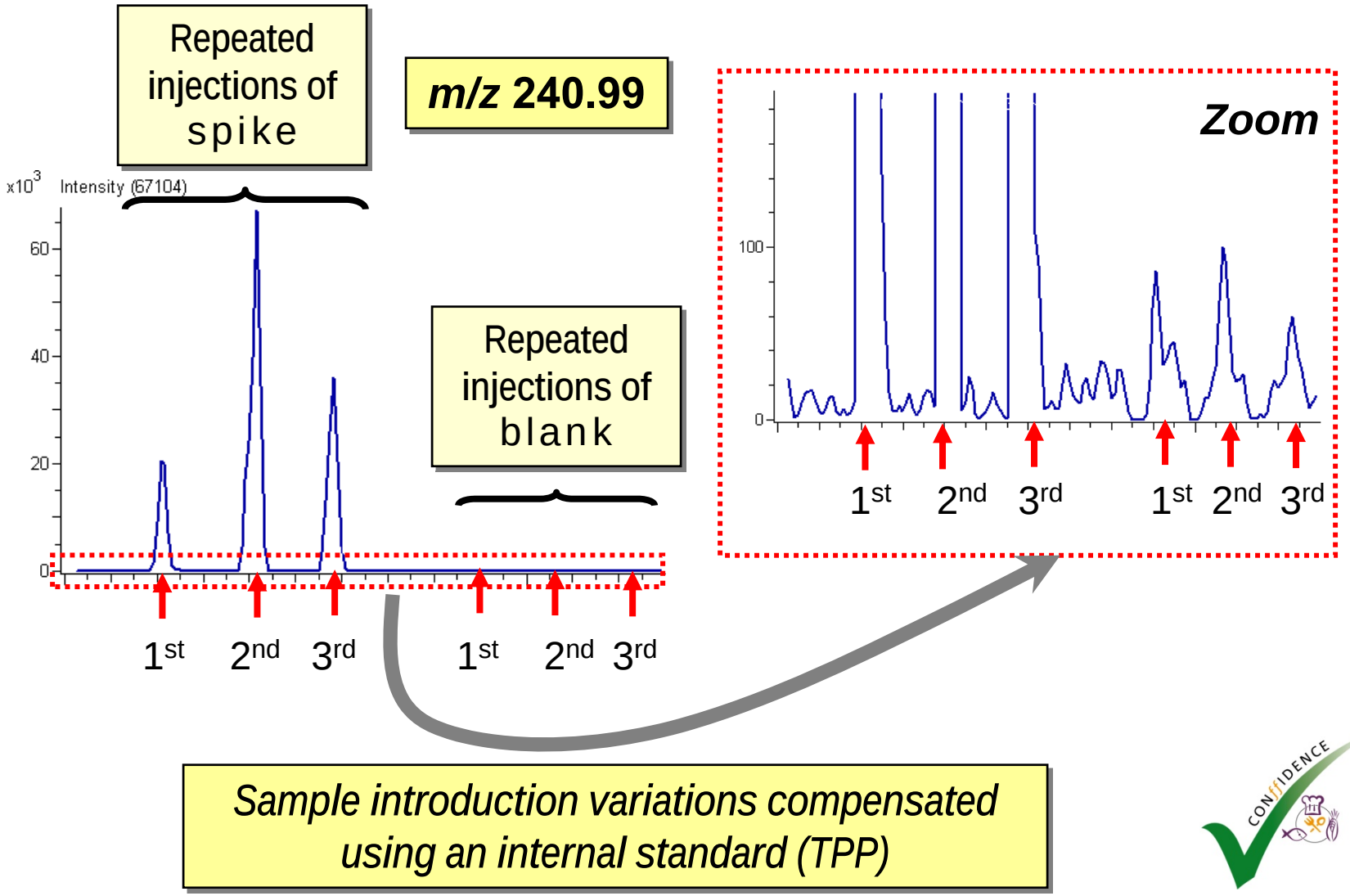






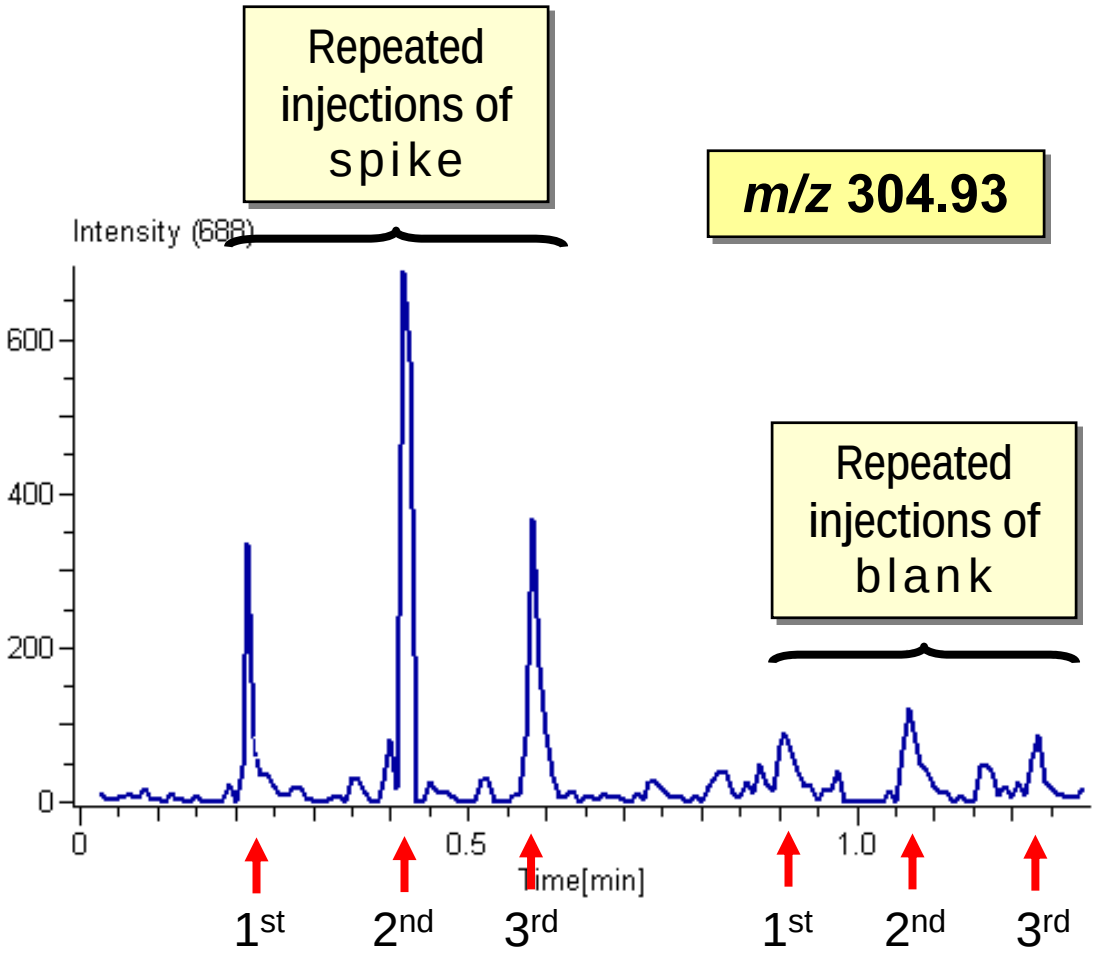
Activities and achievements

Thiram — 5 mg/kg (MRL)



Activities and achievements

Ziram — 1 mg/kg (MRL)



Sample introduction variations compensated using an internal standard (TPP)

Activities and achievements

- **Validation study**
- **Matrix: pears**

Analyte	MRL (mg/kg)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOQ (mg/kg)
Thiram	5	5	85.2	6.7	0.1
Ziram	1	1	82.7	8.9	0.5

*) *Note: Quantification performed using matrix-matched standards with internal standard (TPP) correction*

CONCLUSIONS

DART offers a lot of challenges in food analysis

- **Qualitative screening**
- **Quantitative analysis**
- **Metabolomics (non-target) profiling**
- **Rection dynamics monitoring**
- ***Method development***