



**Advances of Quantitative DART®-MS for Direct and Sensitive  
Analysis in Real-Time**

**定量 DART® 最新进展**



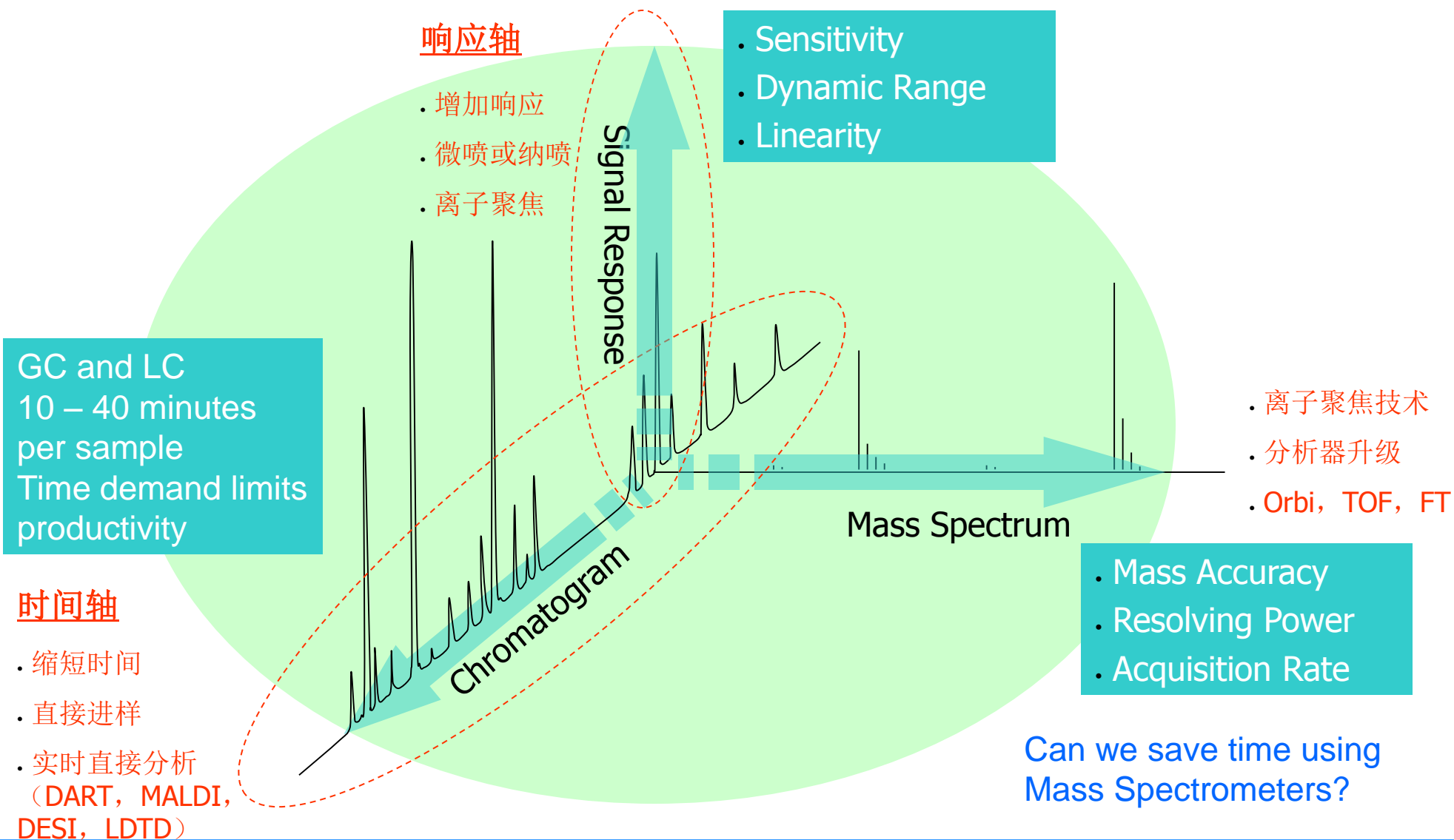
**Charles C Liu, Ph.D.**

刘春胜 博士

**ASPEC Technologies**

华质泰科生物技术（北京）有限公司

# MS-based Technique 质谱相关技术

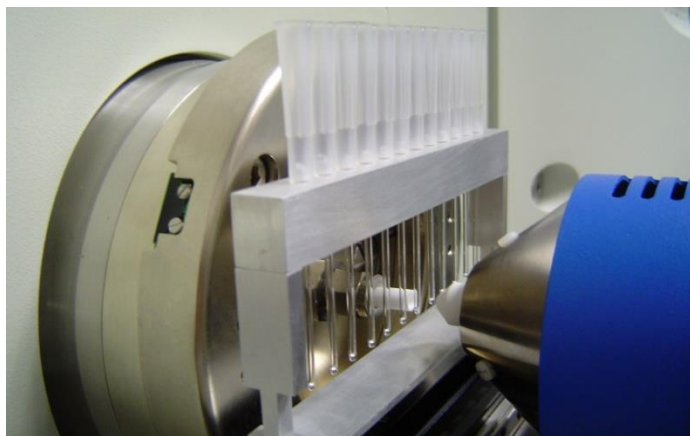


# Operational and Safety 可操作性及安全性不同

## DART

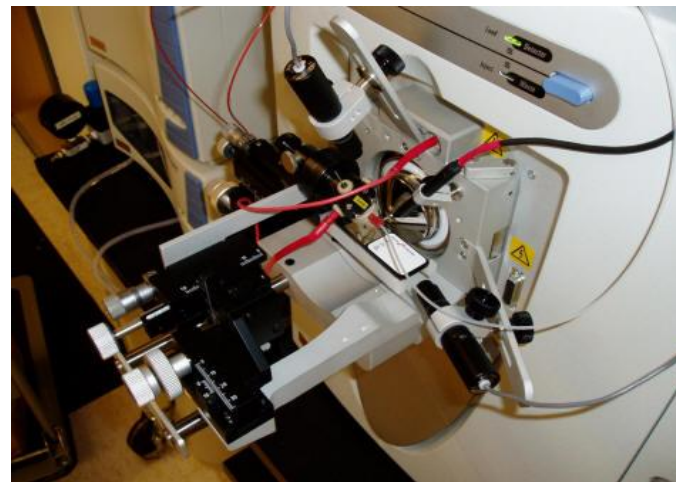


安全

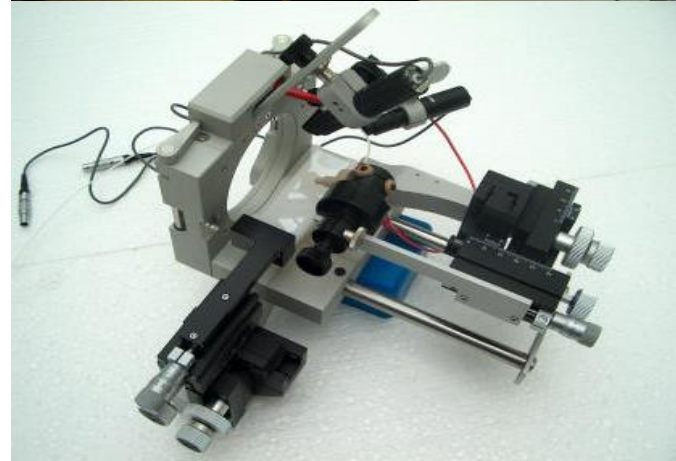


自动

## DESI & Similar

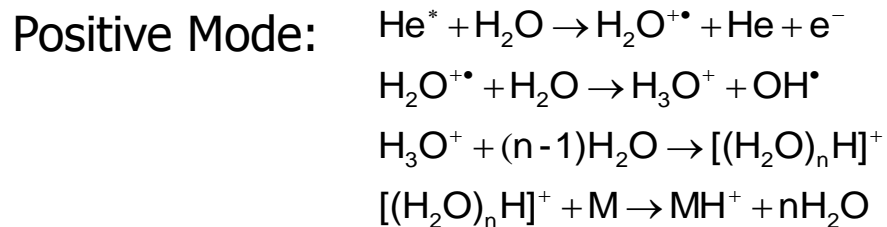
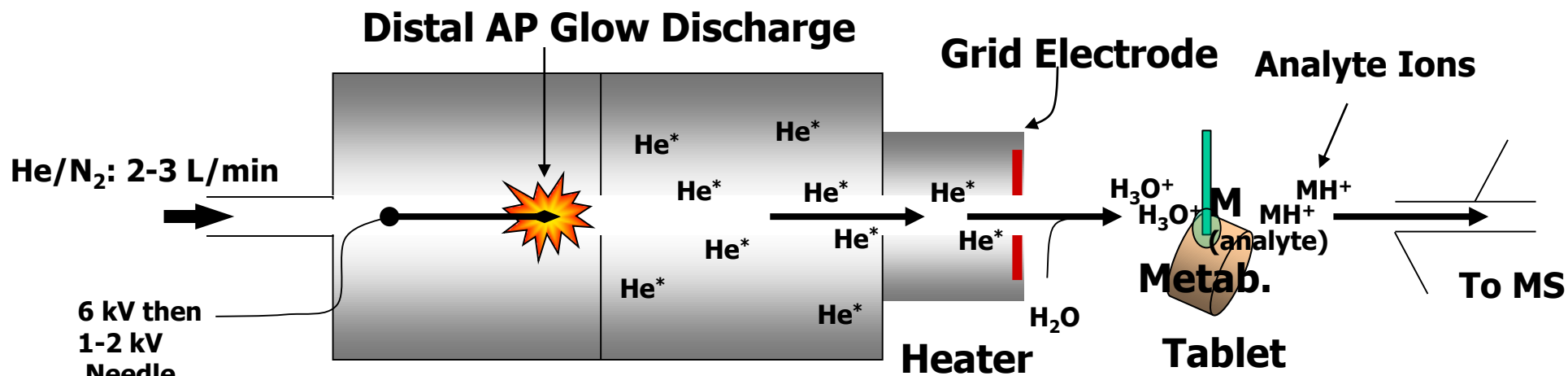


暴露



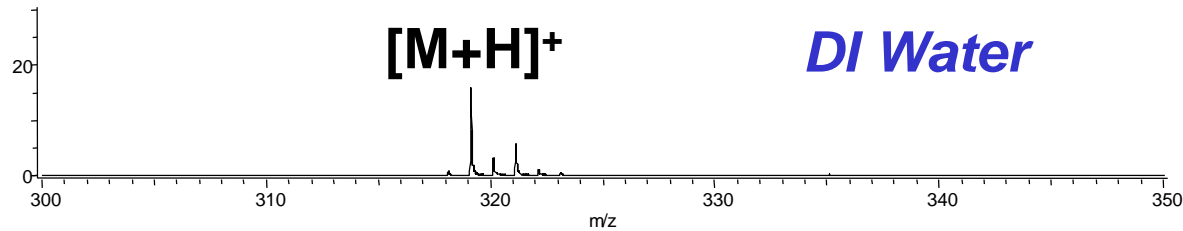
手动

# DART<sup>®</sup> 原理图

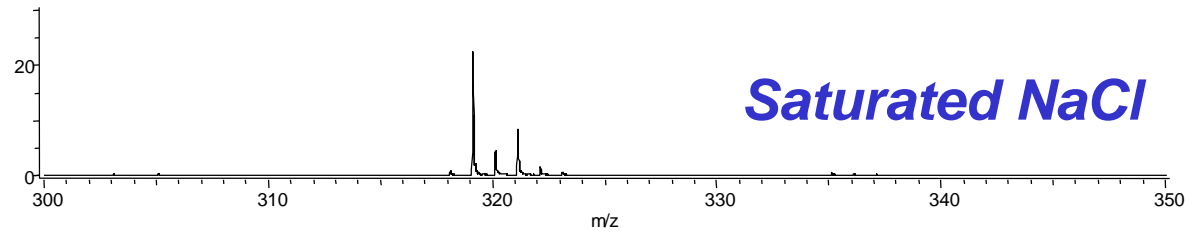


Cody, R., et al., *Anal. Chem.*, **2005**, 77, 2297.

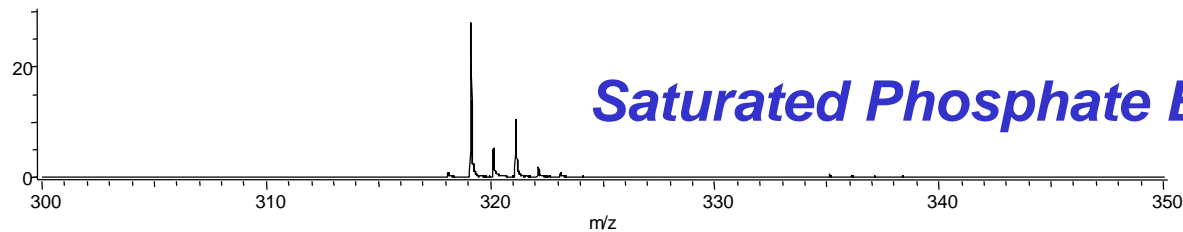
# Contamination Resistance 无离子抑制



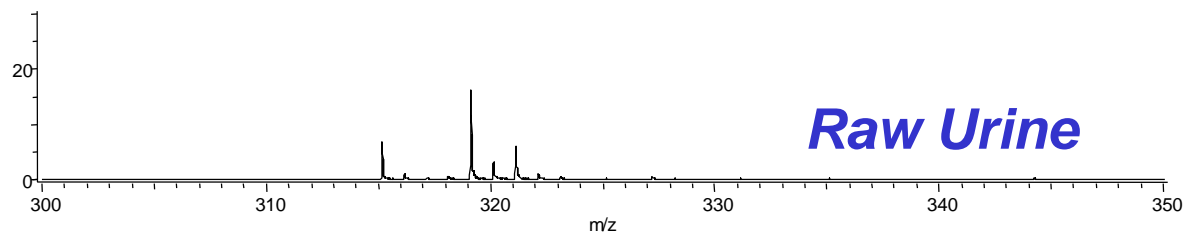
谱图简单  
**Chlorpromazine**  
 $[M+H]^+$



无加合离子  
**No alkali metal**  
**cation adducts**

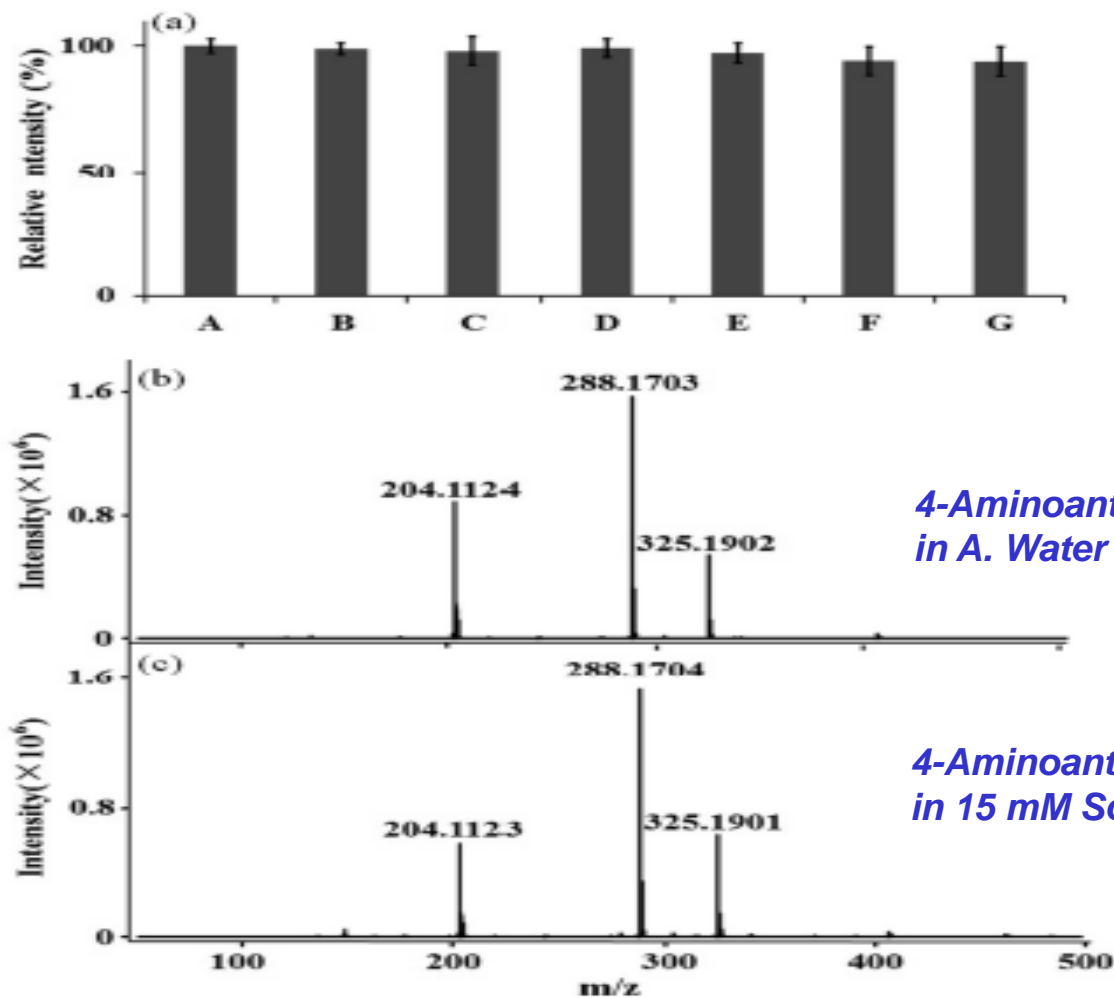


无多电荷产生  
**No multiple charging**



无明显离子抑制  
**No apparent**  
**suppression**

# Contamination Resistance 无离子抑制



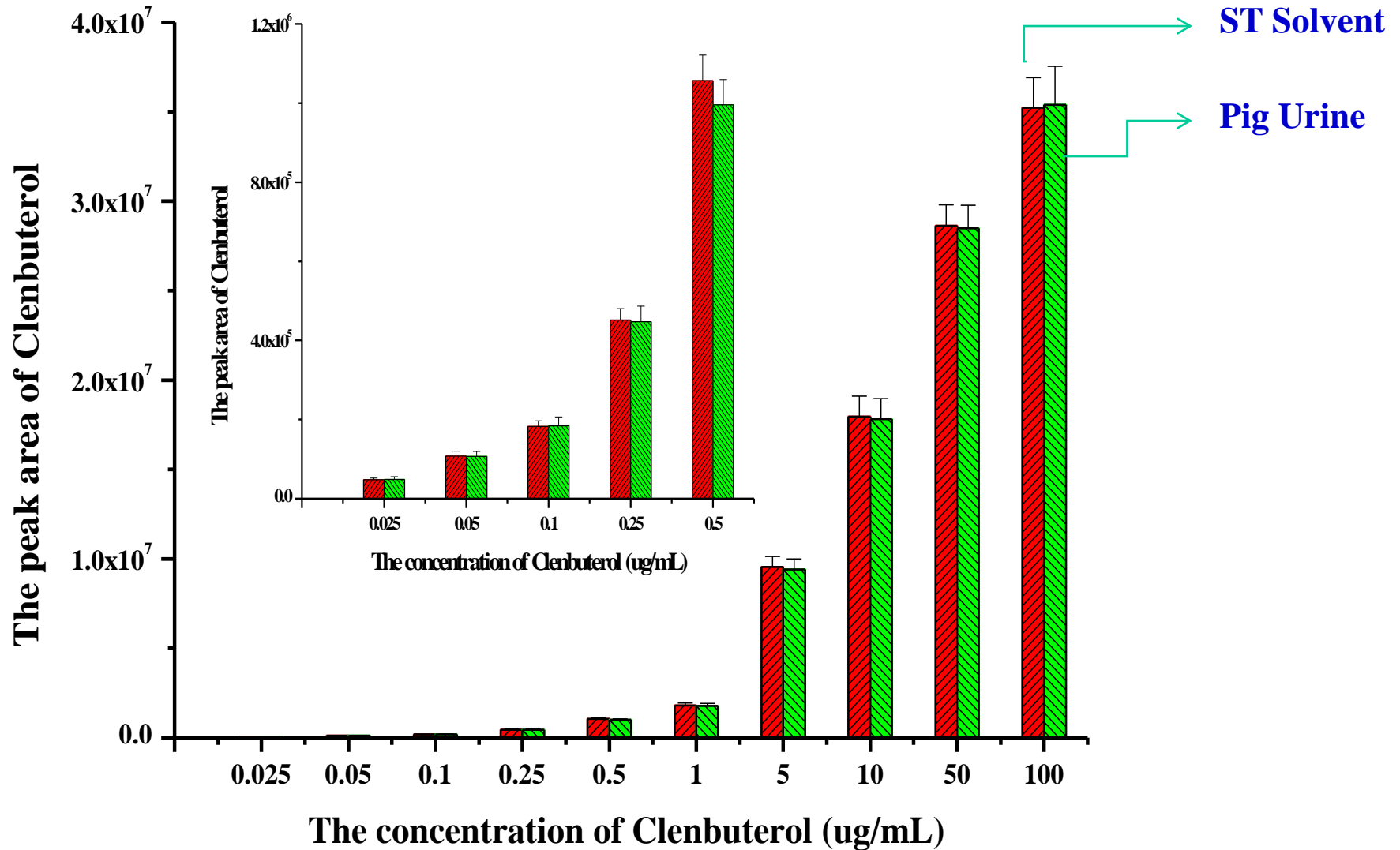
- A. Water
- B. 15 mM Sodium Borate
- C. 30 mM Sodium Borate
- D. 50 mM Sodium Borate
- E. 100 mM Sodium Borate
- F. 15 mM SDS in 15 mM Sodium Borate
- G. 30 mM SDS in 30 mM Sodium Borate

4-Aminoantipyrine 4-氨基安替吡啉 100ppm  
in A. Water

4-Aminoantipyrine 100ppm in F. 15 mM SDS  
in 15 mM Sodium Borate

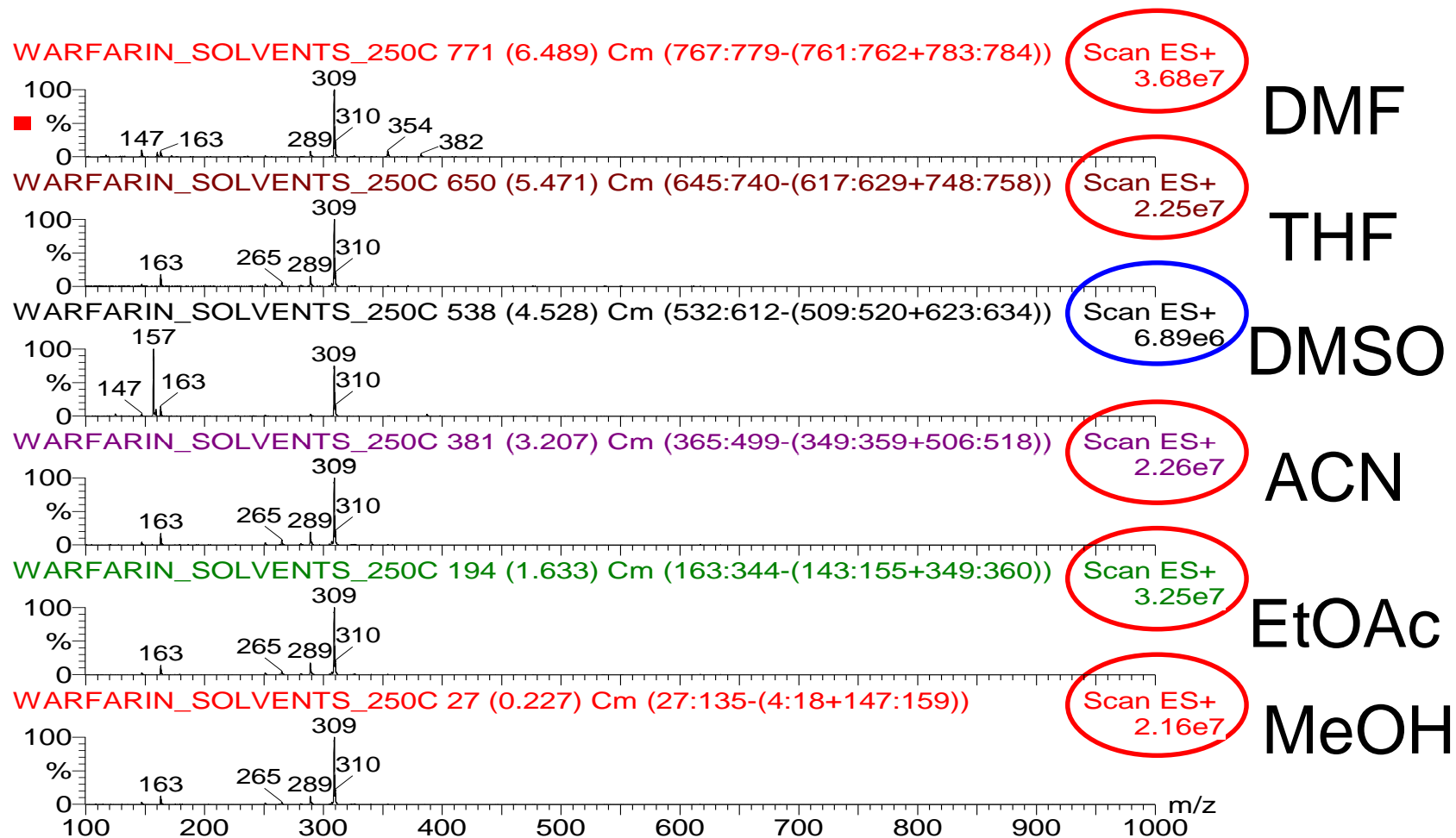
*Anal. Chem.* 2013, 85, 170–176

# No Matrix effect 无基质效应





# Solvents Friendly 无溶剂效应



Regardless of solvent type, DART yields protonated molecules

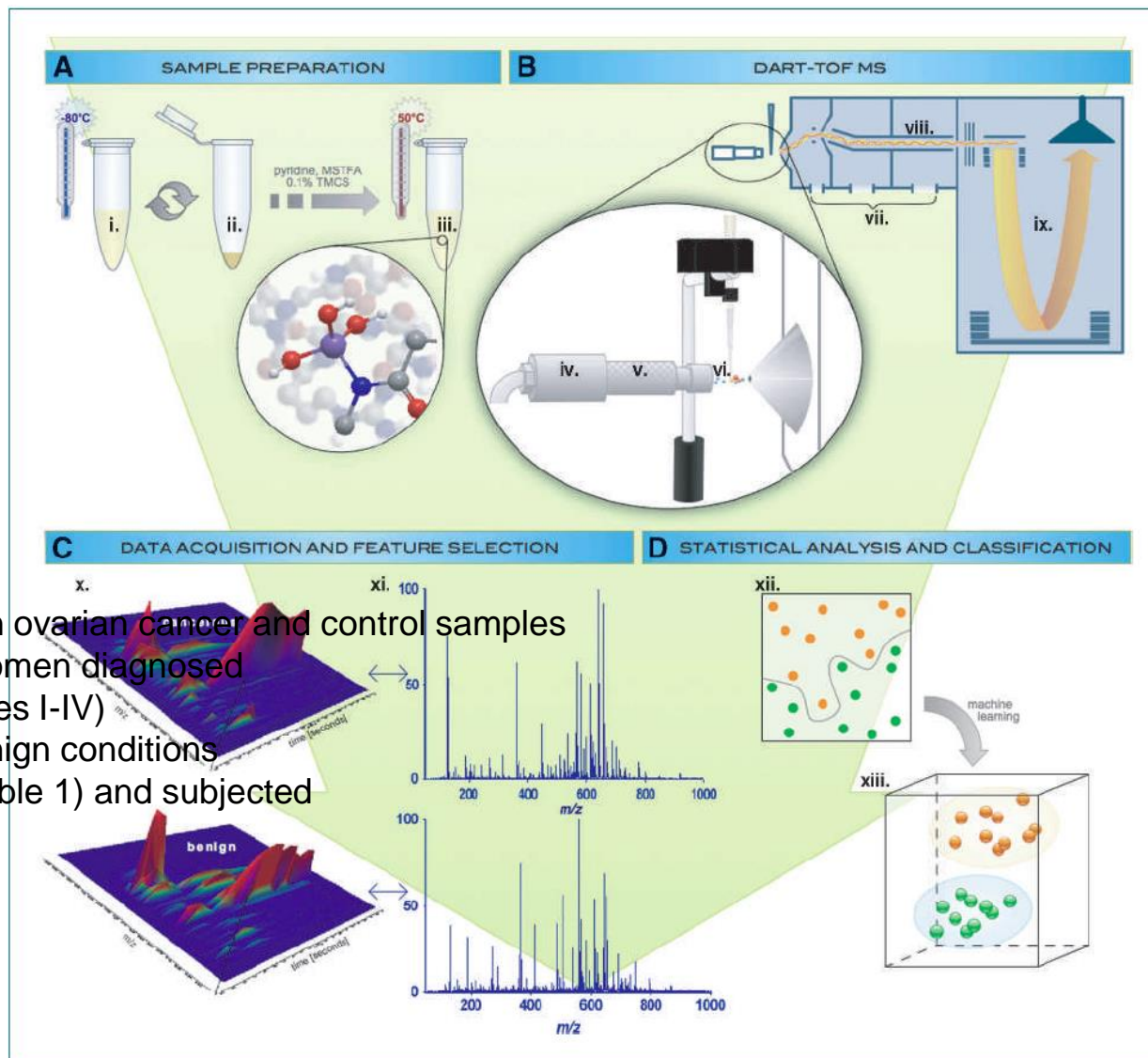


# DART 准确检测卵巢癌患者血清代谢谱

- Cancer and Control Groups
- 99% to 100% accuracy
  - 100% sensitivity
  - 98-100% specificity
- Two different data evaluation approaches

Metabolic profiles can distinguish between ovarian cancer and control samples. Serum samples were obtained from 44 women diagnosed with serous papillary ovarian cancer (stages I-IV) and 50 healthy women or women with benign conditions (e.g., serous, simple, or follicular cysts; Table 1) and subjected in triplicate to DART MS profiling.

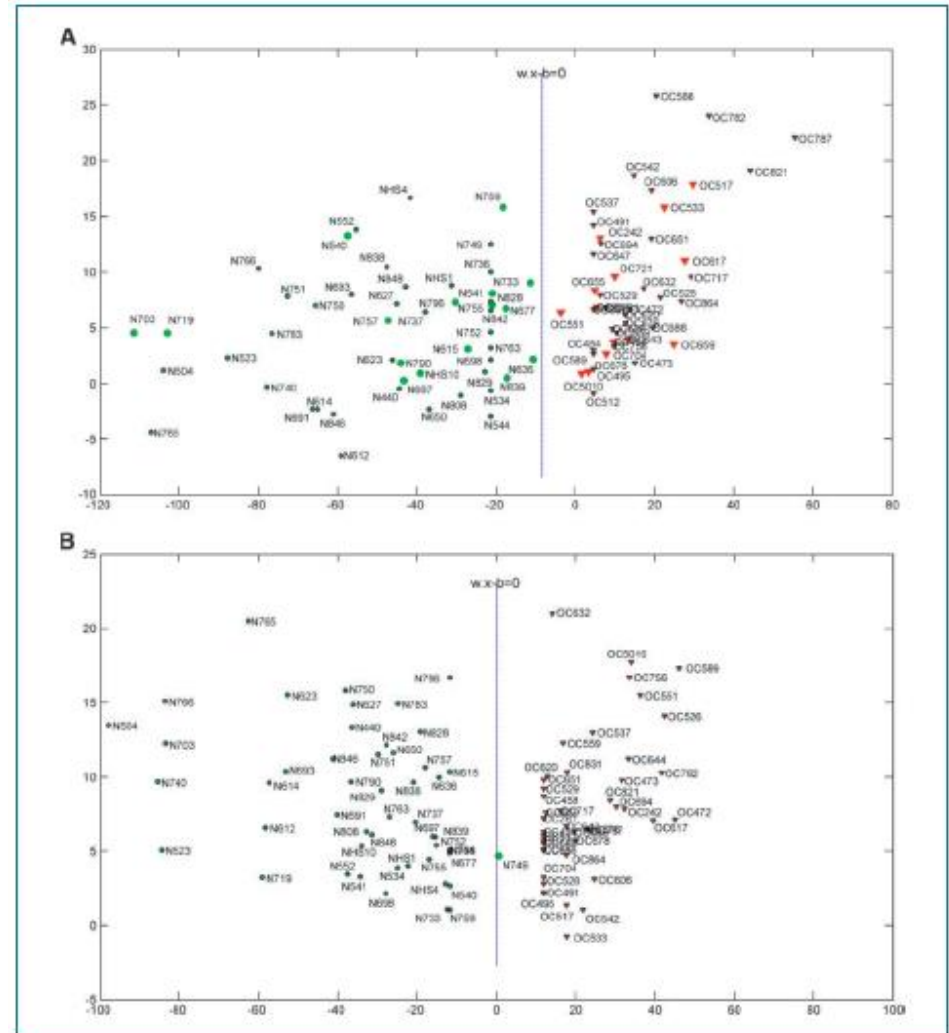
Zhou, Fernández, et al.  
Ovarian Cancer Institute, Georgia Tech., etc.  
*Cancer Epidemiology, Biomarkers & Prevention*,  
2010



# DART 准确检测卵巢癌患者血清代谢谱

- Metabolic profiles can distinguish between ovarian cancer and control
- 44 women diagnosed with serous papillary ovarian cancer (stages I-IV)
- 50 healthy women or women with benign conditions
- Subjected in triplicate to DART MS profiling.

Zhou, Fernández, et al.  
Ovarian Cancer Institute, Georgia Tech., etc.  
*Cancer Epidemiology, Biomarkers & Prevention*,  
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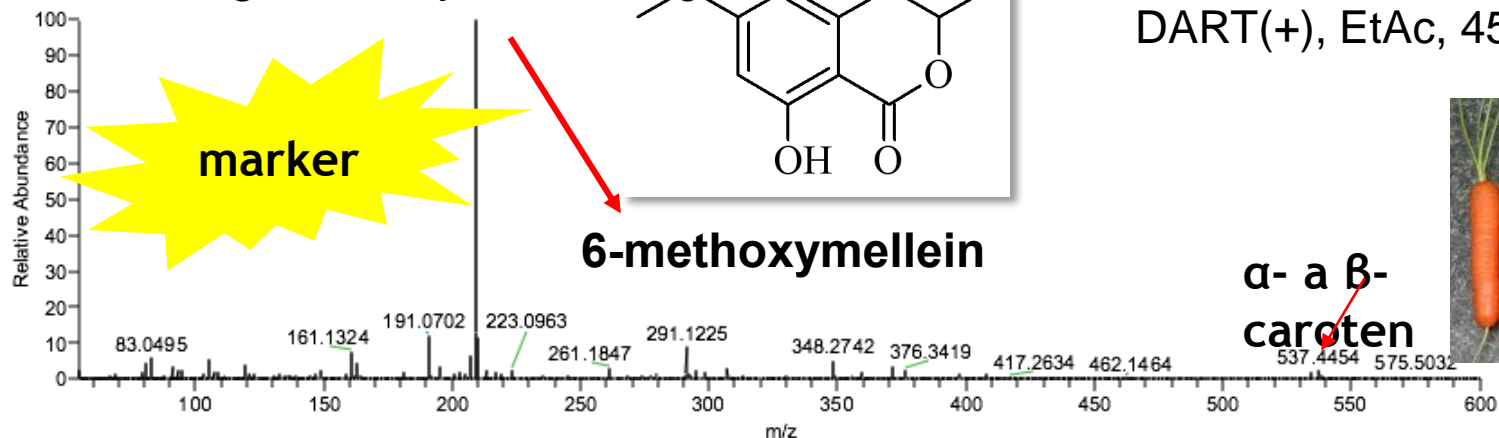


# Metabolomics based non-target screening

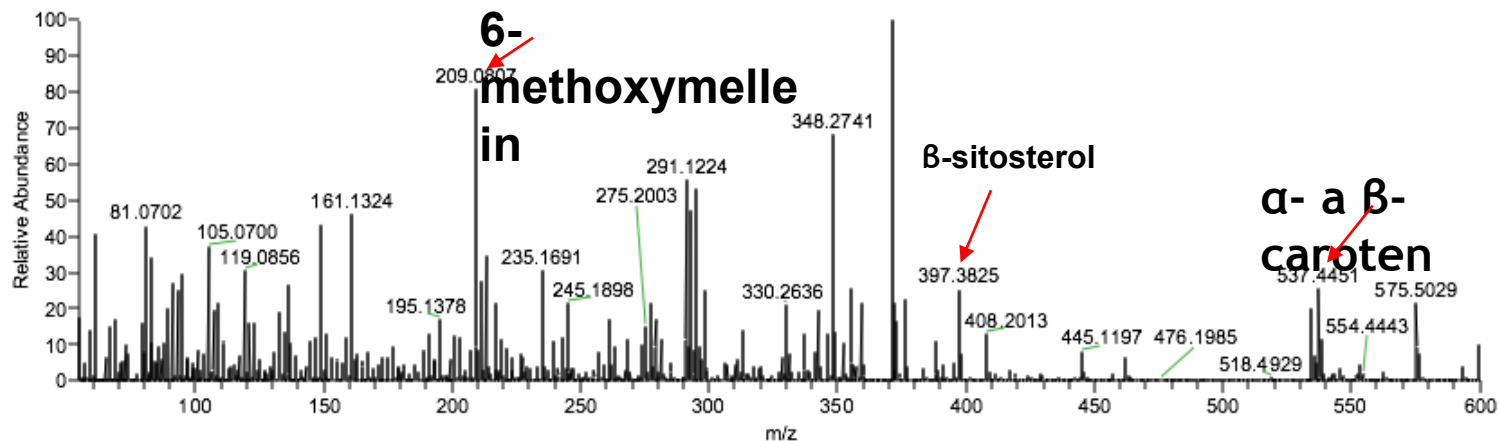
Methods for Organic Food Authentication, BioFach 2013

DART 有机食品认证

Cortina, organic, Troja



Cortina, conventional, Suchdol



Locality Troja - no treatment (Ortiva) against *Alternaria Dauci*  
→ induction of phytoalexine **6-methoxymellein**

# DATA ANALYSIS: way of farming

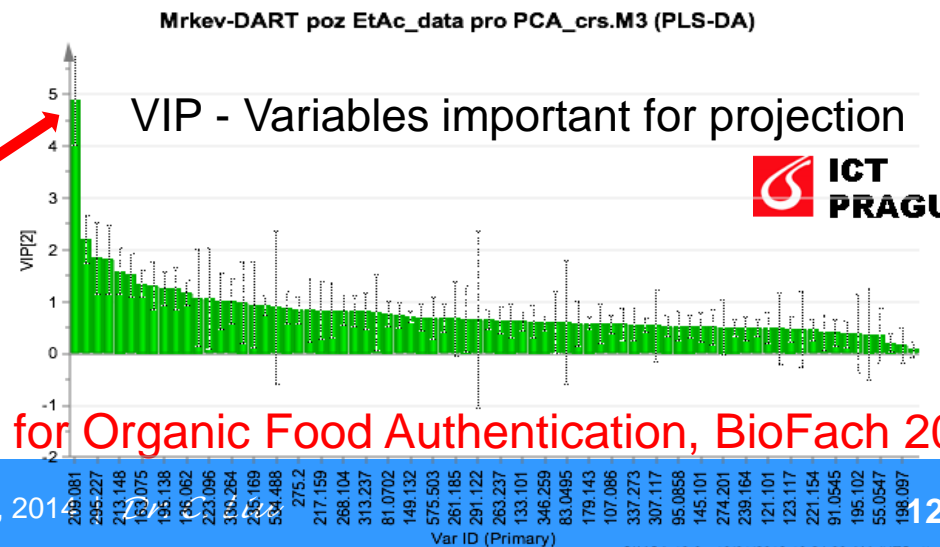
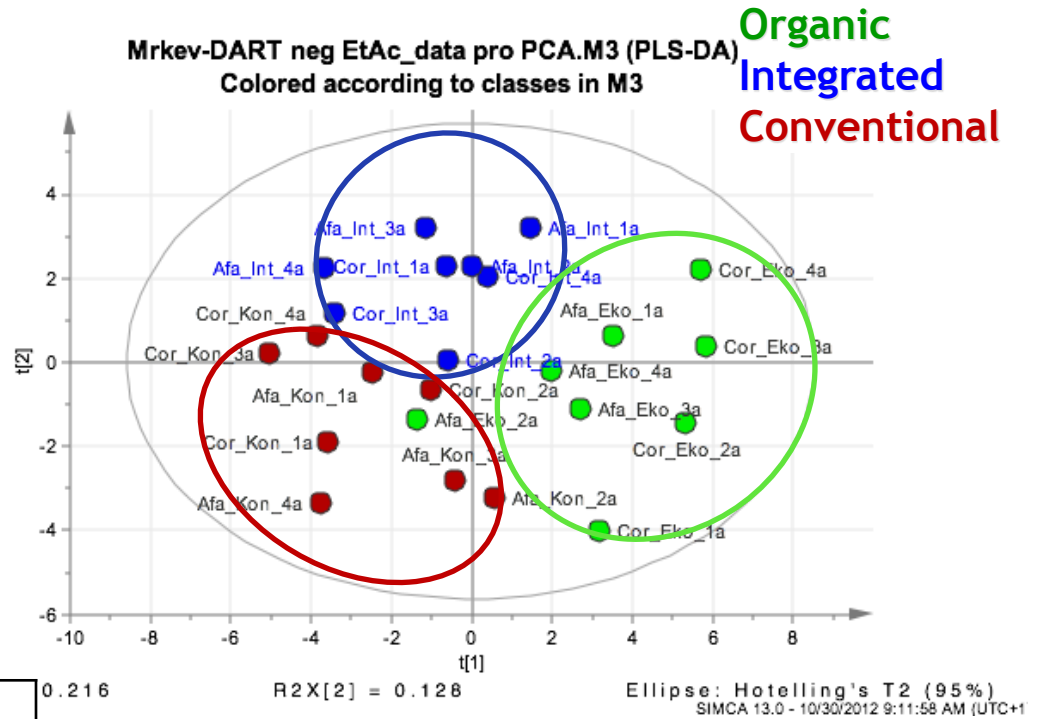
## Data processing:

- Principal Component Analysis (PCA)
- Partial Least Squares Discriminant Analysis, PLS-DA

Prediction and recognition abilities between **organic**, **integrated** and **conventional** crops, obtained by PLS-DA model

Variables	Recognition ability	Prediction ability
24	91.7 %	62.5 %

**6-methoxymellein** discrimination between organic, integrated and conventional farming



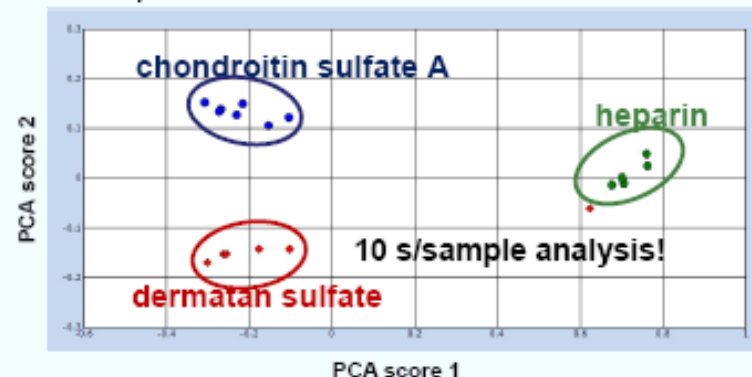
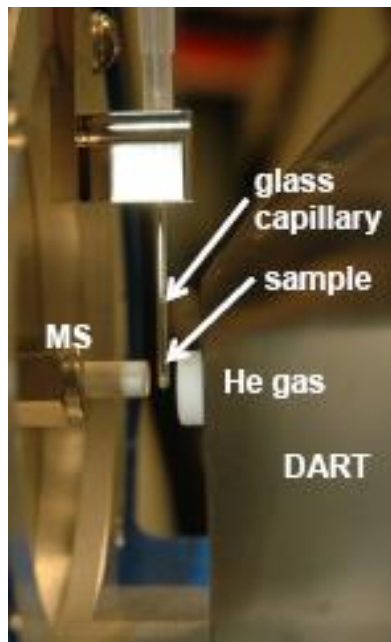
Methods for Organic Food Authentication, BioFach 2013

DART 有机食品认证

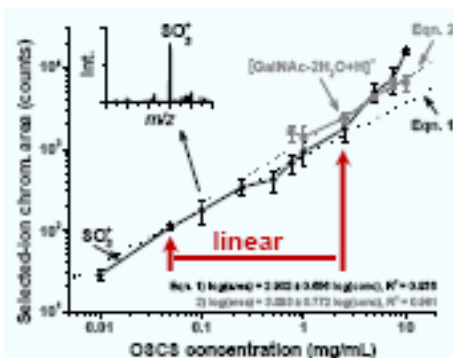


# DART 快速识别肝素素及多硫酸软骨素污染

- GAGs degrade at elevated temperatures in DART MS
- Studied: chondroitin sulfate, dermatan sulfate, OSCSs, and heparin
- Degradation products help to screen for contaminants
- Conjoin *real time* multivariate data analysis to discriminate samples
- Limit matrix interference on quantitation
- Measure OSCS-contaminated samples from industry
- Combine with portable MS to mobilize screening to sites of need

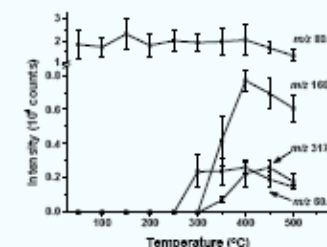
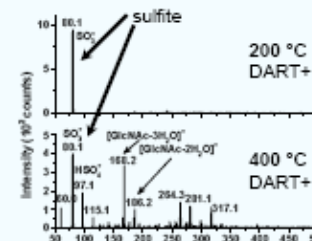
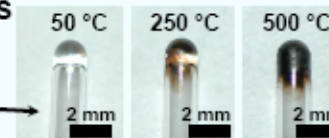


→ Thermal degradation in DART with PCA of the data capable of differentiating major GAG types in high throughput.



## OSCS samples by DART MS

- 10 mg/mL OSCS in water
- discoloration in line with thermal degradation



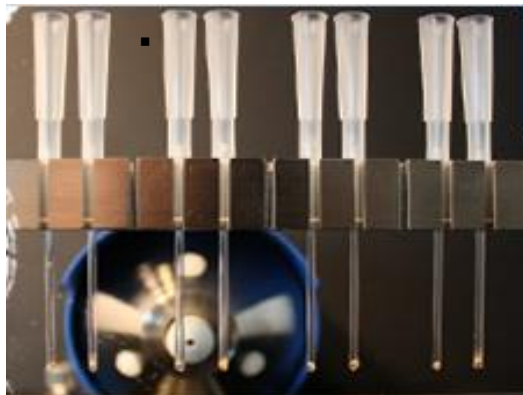
## In DART MS, OSCSs

- decompose in a temperature-dependent manner,
- yield fragments different from those of heparin, and
- show feasibility for diagnosing contamination.

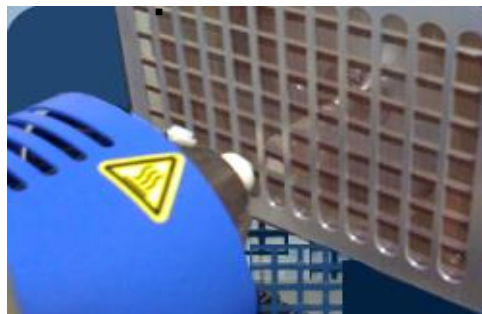
Peter Nemes and Dinesh V. Patwardhan  
 FDA OSEL/CDRH/Division of Chemistry and  
 Materials Science, Silver Spring, MD, USA  
 ASMS 2012

# DART Modules 进样方式多样化

1 中通量液体进样



2 高通量液体进样



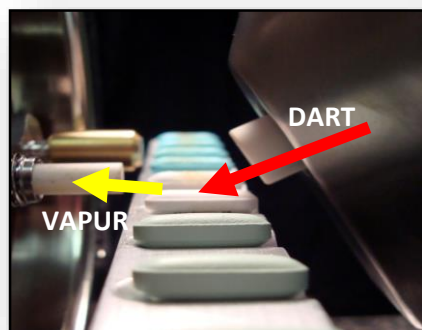
6 手动单一样品进样



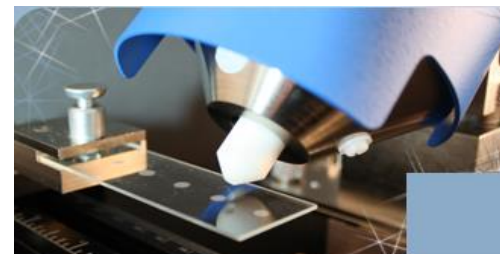
4 连续自动进样



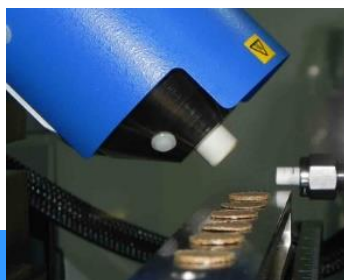
5 药片自动进样模块



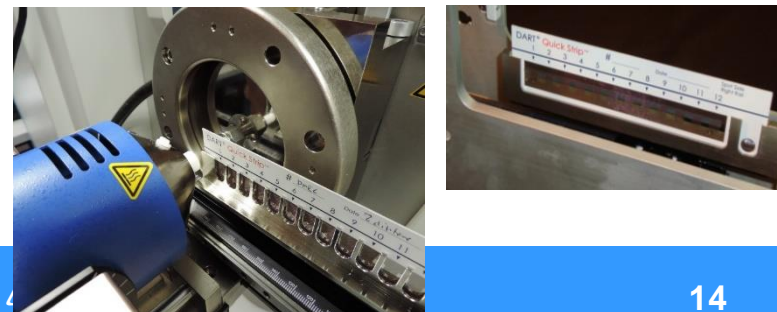
3 薄层板进样



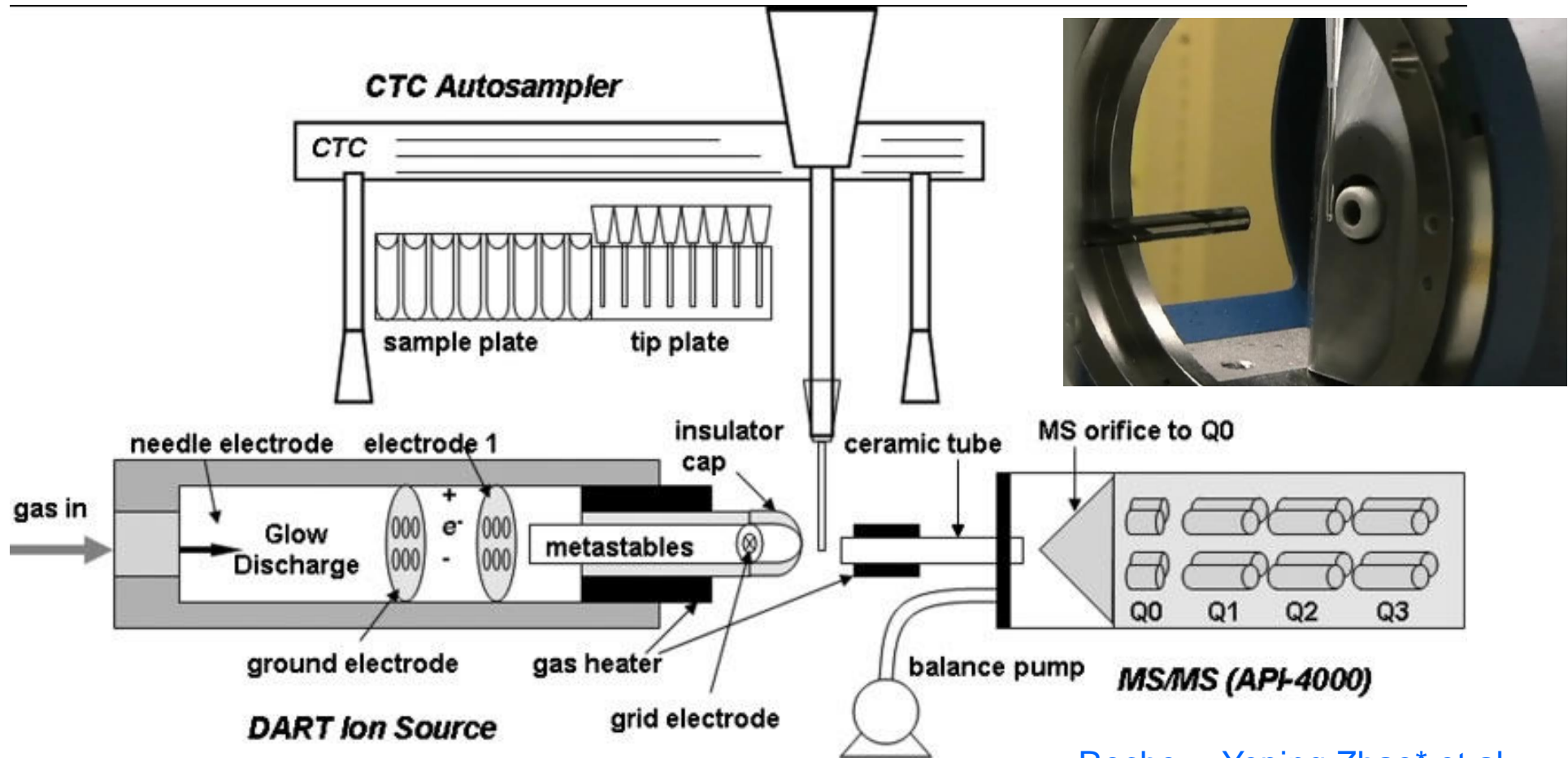
7 压片自动进样模块



8 QS 中通量自动进样模块



# DART in ADME 药代及药分：定量

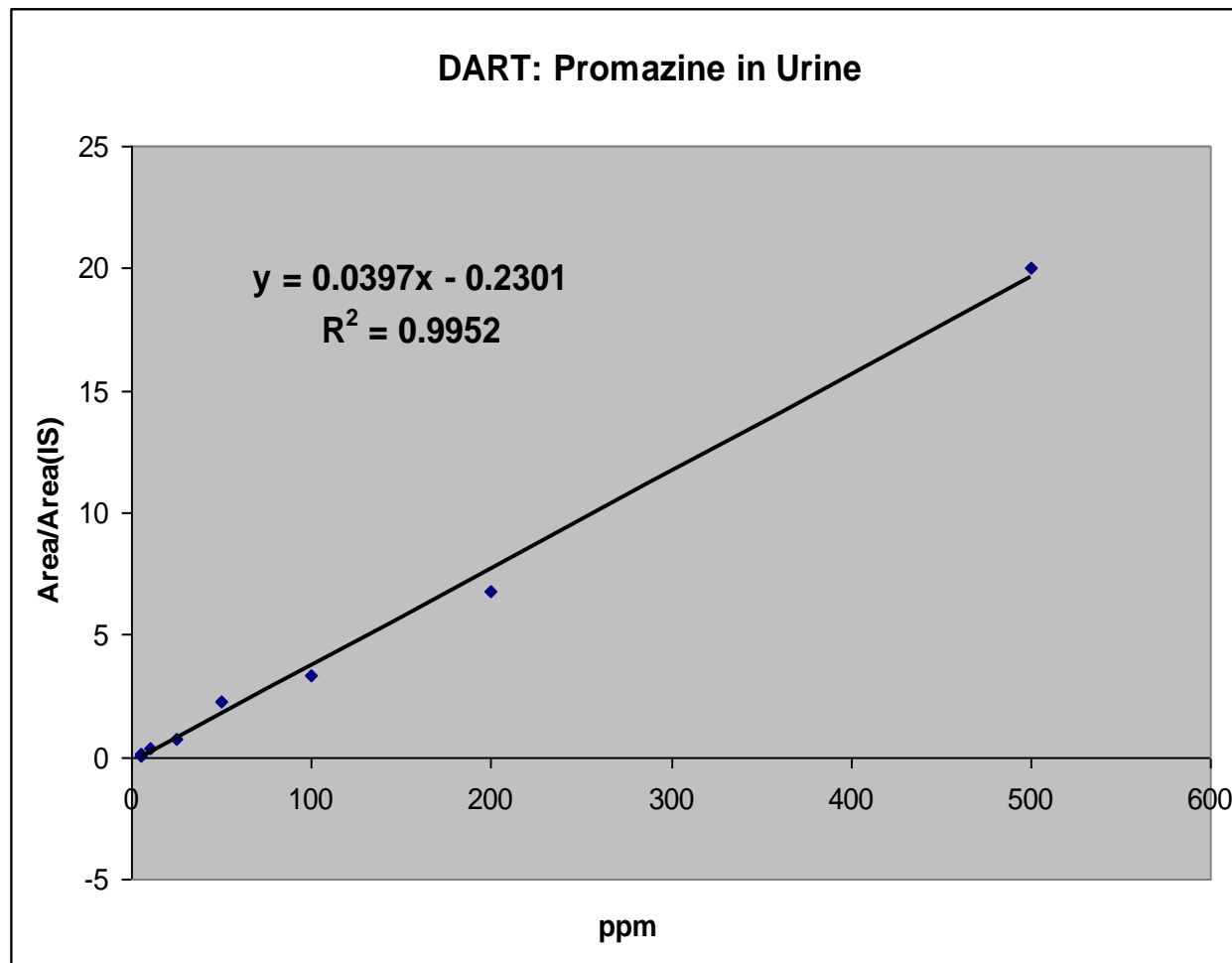


Roche, Yeping Zhao\* et al  
*Rapid Commun. Mass Spectrom.* 2008; 22: 3217–3224



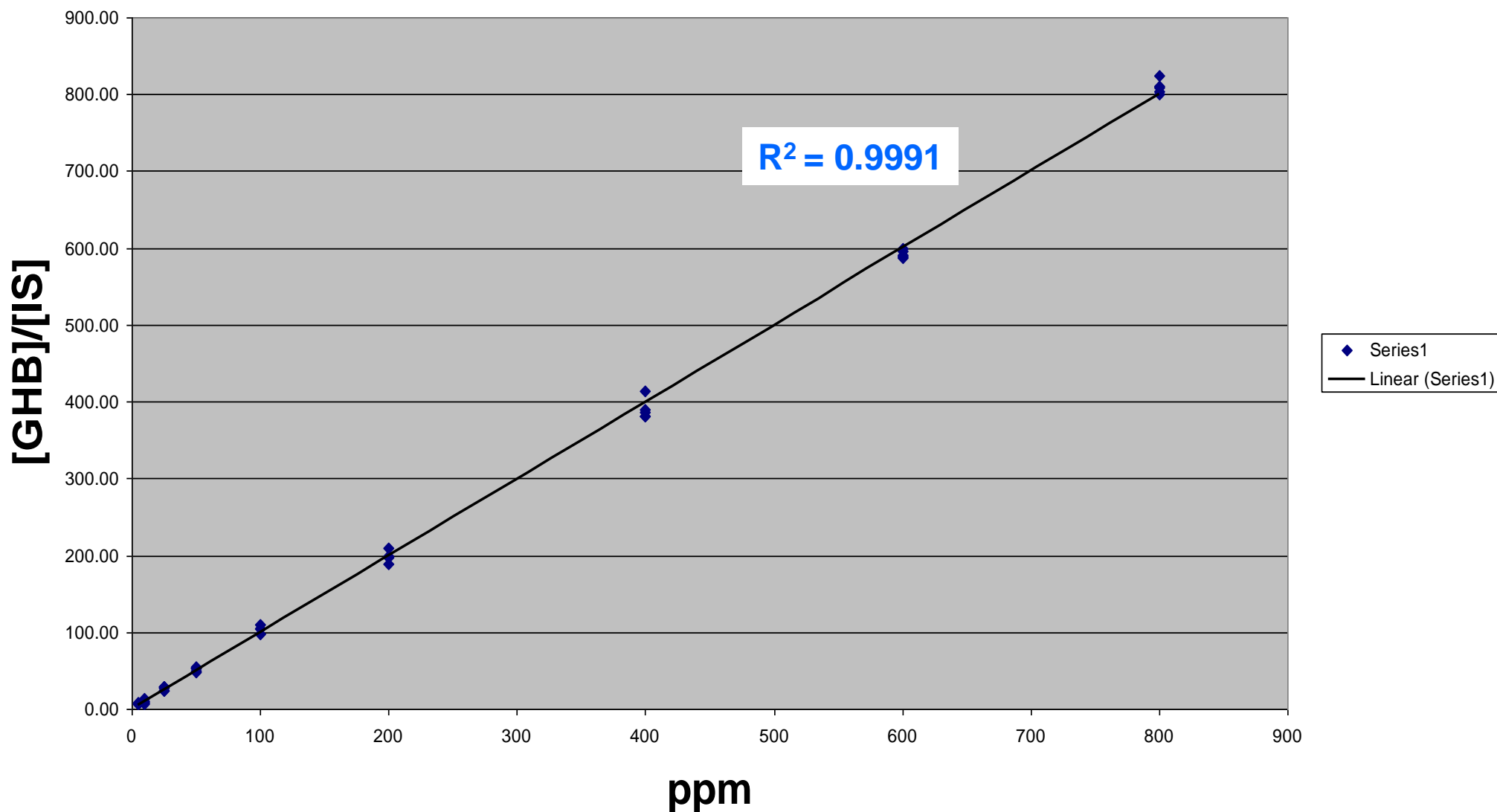
# Promazine in Urine 内标定量

## Chlorpromazine internal standard

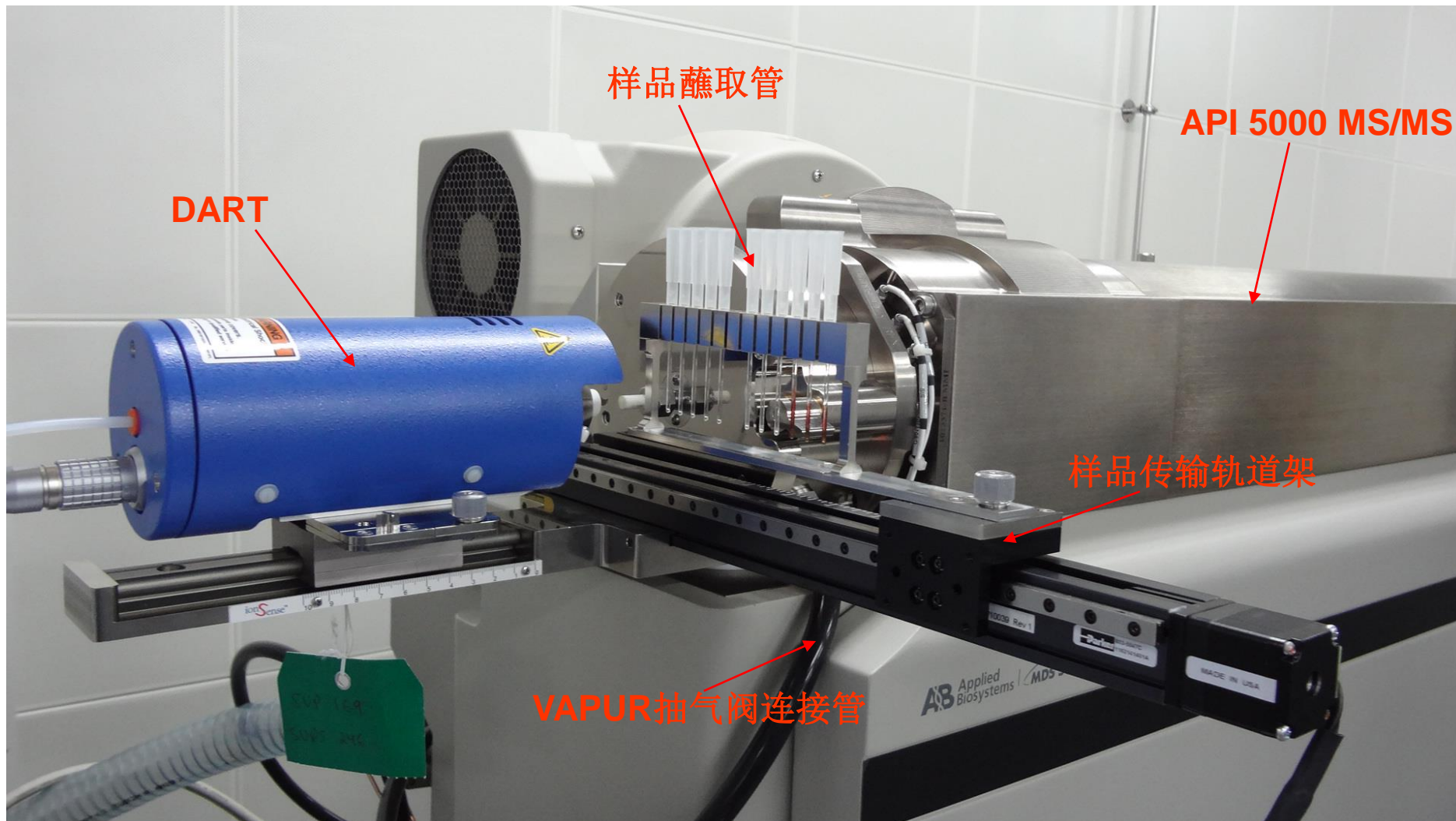


Typical LLOD  
0.25 – 5 ng/mL  
in plasma  
22 compounds

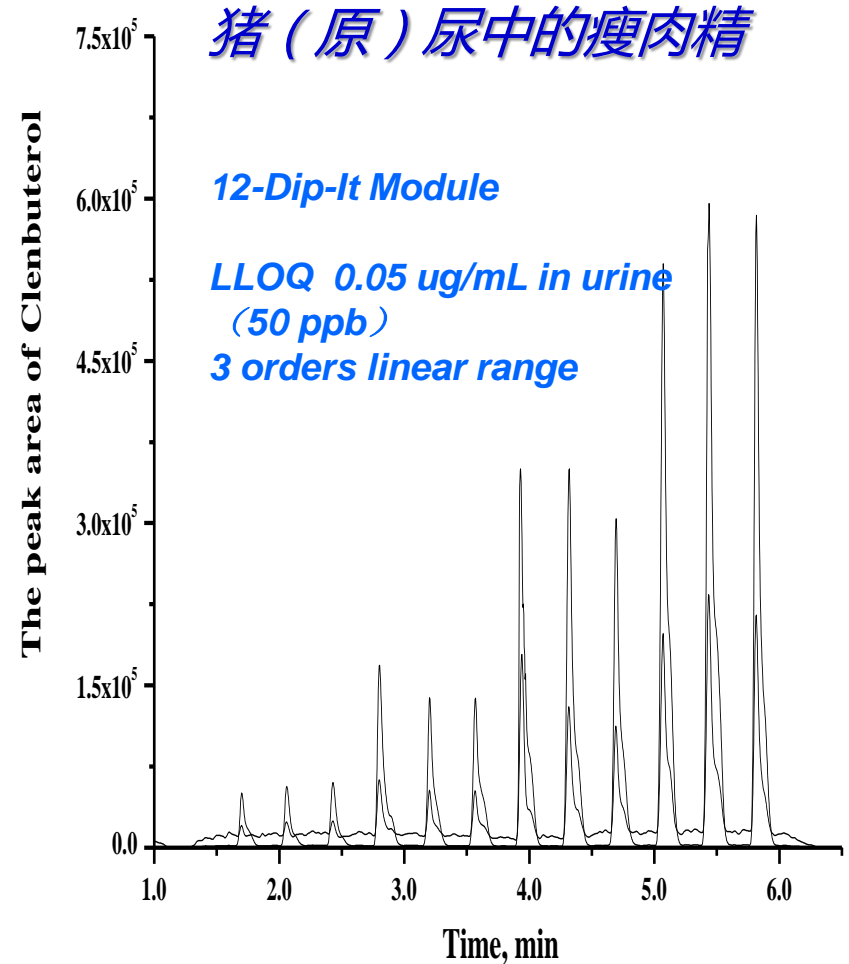
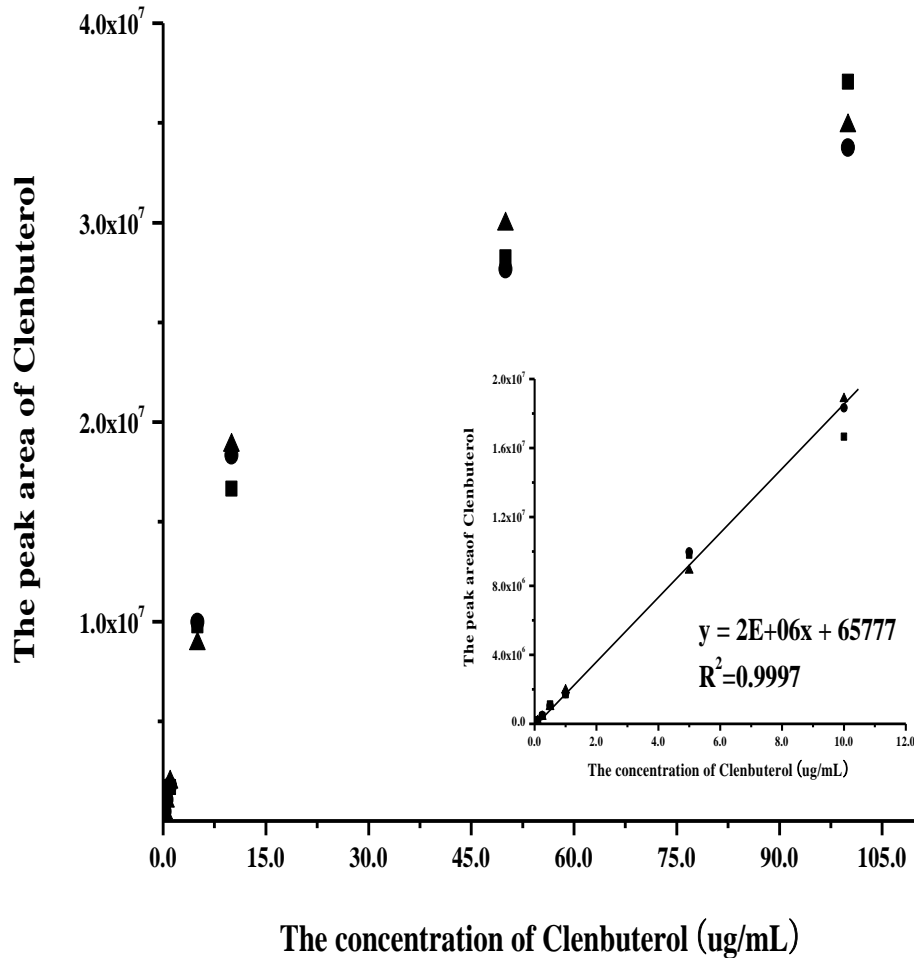
# GHB in Urine 氘代内标定量 (Deuterated I.S.)



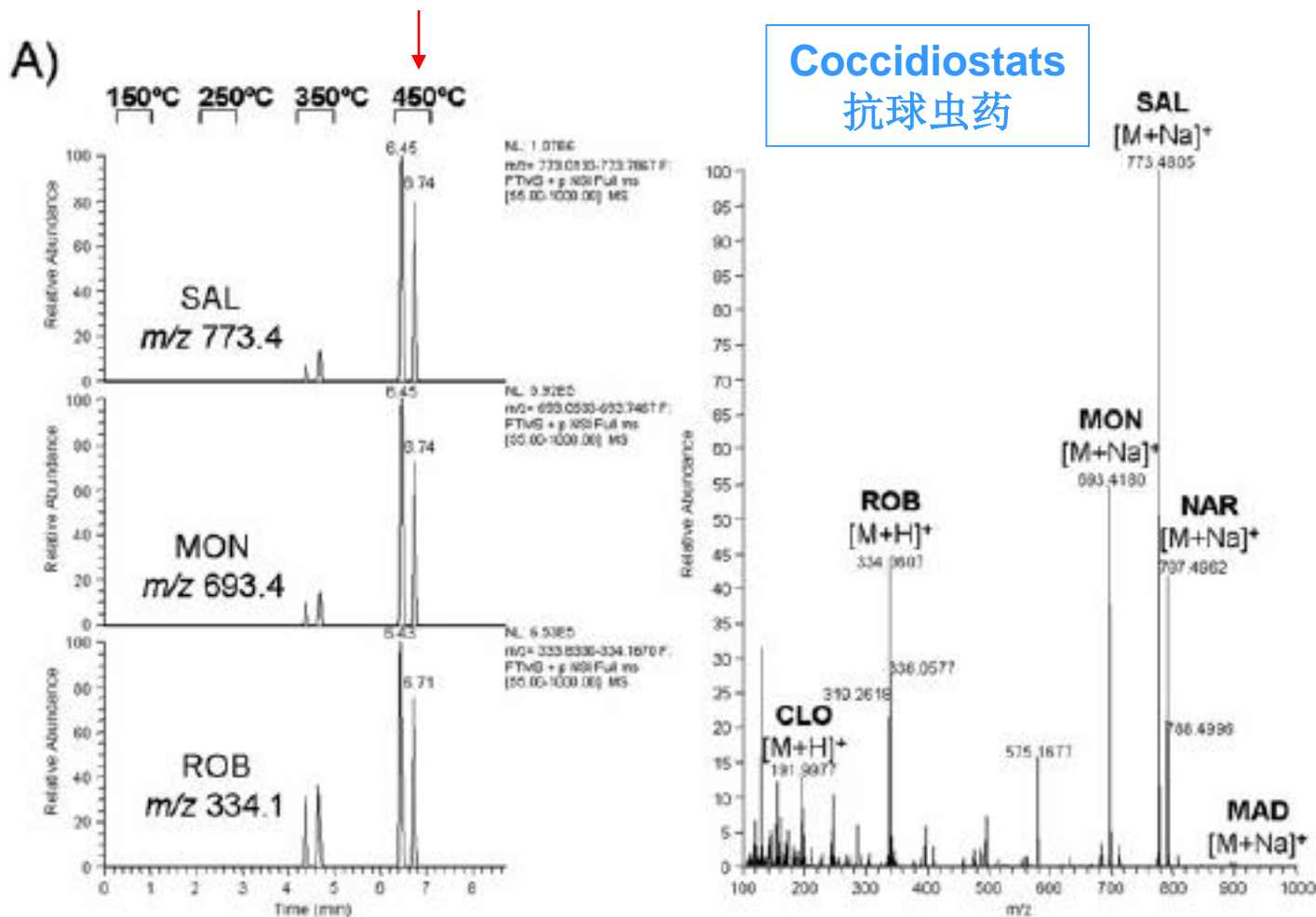
# DART - API 5000 MS/MS 质谱系统



# DART - 5000 MS/MS MRM 定量



# DART 快检饲料食品中的抗寄生虫兽药

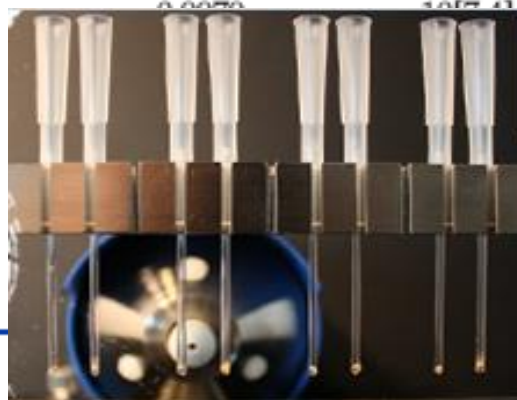


Rapid Commun Mass Spectrom. 2013 Feb 15;27(3):467-75.

# DART 快检饲料食品中的抗寄生虫兽药

Table 2. Quality parameters of the method for the determination of benzimidazoles in milk and authorized MRLs in milk

Compound	LCL ( $\mu\text{g kg}^{-1}$ )	Recovery (% RSD)	Linearity (r)		Run-to-run (% RSD) [Accuracy (rel. error %)]		MRL ( $\mu\text{g kg}^{-1}$ )
			External calibration	Internal standard calibration	Low level ( $10 \mu\text{g kg}^{-1}$ )	Medium level ( $100 \mu\text{g kg}^{-1}$ )	
ABZ	1	92 (5.1)	0.9968	0.9993	19 [2.5]	11[2.0]	100
ABZ-SO <sub>2</sub>	5	87 (3.4)	0.9949	0.9986	25[8.3]	22[5.4]	100
ABZ-SO	1	86 (6.3)	0.9911	0.9991	21[8.5]	13[6.1]	100
NH <sub>2</sub> -ABZ-SO <sub>2</sub>	5	82 (5.7)	0.9920	0.9994	25[7.9]	18[6.3]	100
TBZ	1	95 (2.4)	0.9937	0.9960	17[5.3]	14[3.3]	100
TBZ-OH	1	89 (4.8)	0.9969	0.9997	15[6.2]	13[4.2]	100
FBZ	1	82 (6.2)	0.9960	0.9978	13[5.4]	9[4.2]	10
FBZ-SO <sub>2</sub>	5	84 (5.7)	0.9942	0.9970	20[9.3]	15[6.8]	10
MBZ	1	88 (4.3)	0.9991	0.9990	18[6.2]	16[5.3]	-
NH <sub>2</sub> -MBZ	5	85 (6.7)	0.9937	0.9985	25[9.2]	20[7.6]	-
MBZ-OH	1	84 (5.4)	0.9968	0.9984	22[6.8]	5[4.2]	-
FLU	1	79 (3.4)	0.9953	0.9979	18[7.4]	6[3.7]	-
NH <sub>2</sub> -FLU	10	77 (7.2)	0.9957	0.9979	18[7.4]	18[5.3]	-
OFZ	5	89 (5.6)	0.9952	0.9979	17[6.4]	17[6.4]	10
OXI	1	87 (6.1)	0.9981	0.9979	13[5.2]	13[5.2]	-
CBZ	1	90 (3.4)	0.9994	0.9979	11[5.3]	11[5.3]	-
TCZ	1	76 (7.2)	0.9994	0.9979	12[6.4]	12[6.4]	-
KETO-TCZ	1	65 (8.6)	0.9977	0.9979	14[7.5]	14[7.5]	-
FEB	1	92 (3.5)	0.9968	0.9979	14[3.8]	14[3.8]	10
LEV	1	94 (2.2)	0.9979	0.9979	16[5.4]	16[5.4]	-



Rapid Commun Mass Spectrom. 2013 Feb 15;27(3):467-75.



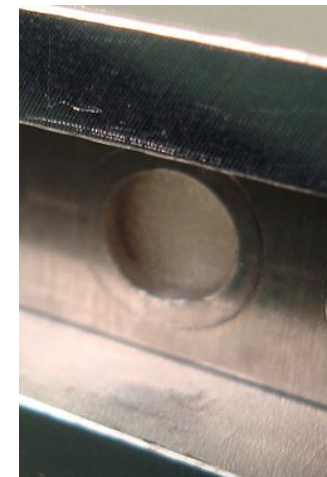
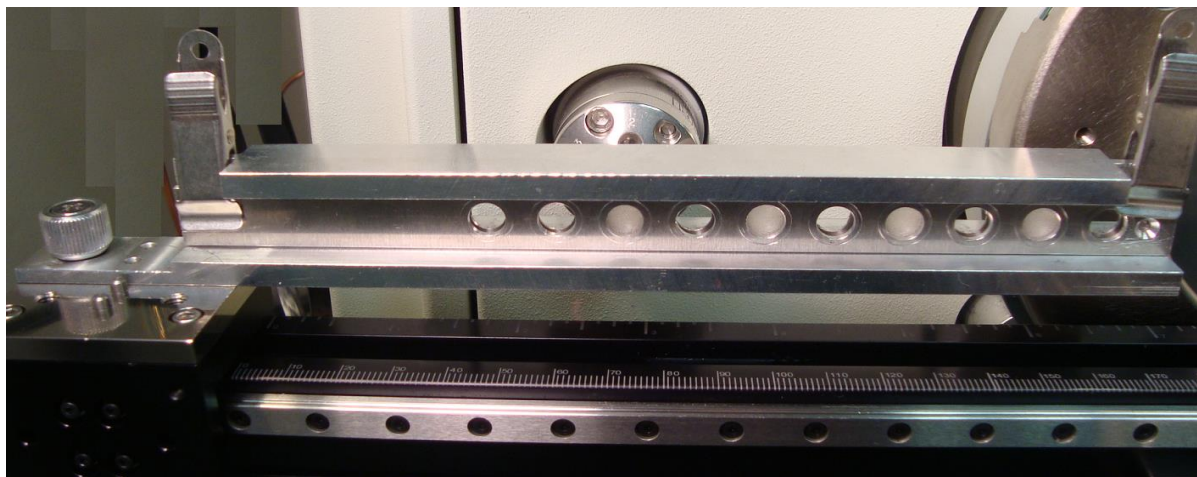
# Transmission Module 透过式 DART

Rapid Screening for Pesticides

## DART and High Resolution

FDA Forensic Center Results

April 2010

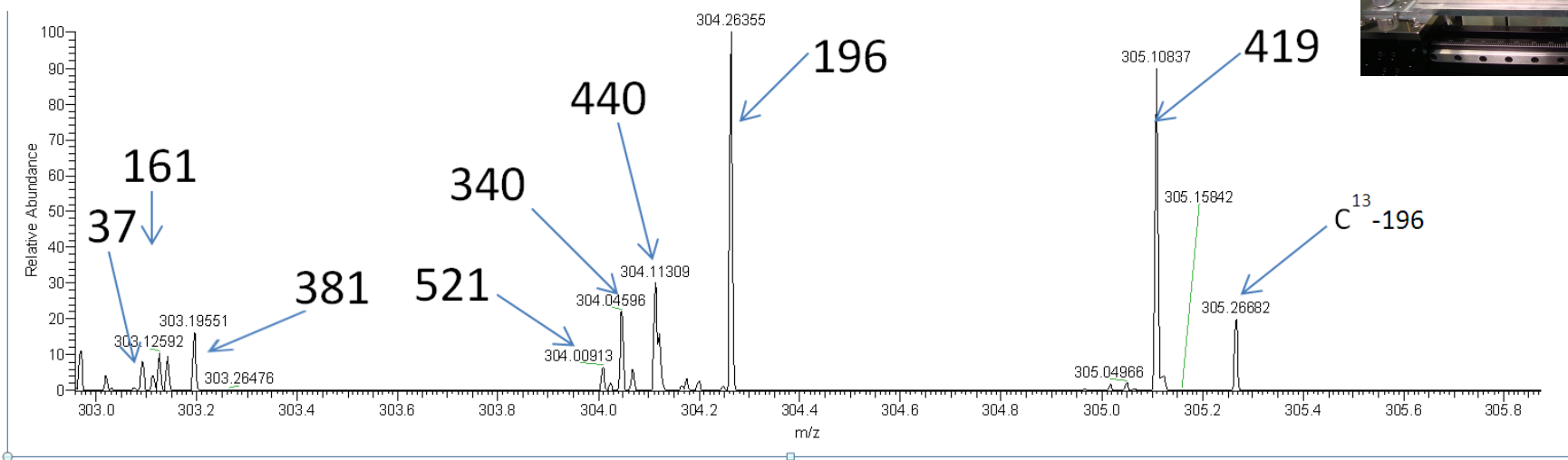




# Transmission Module 穿透式 DART

1.8 min Screening for 529 Pesticides

## Simultaneous Detection of 8 Pesticides in 3 dalton mass range



Clofentezine #37  
Norflurazon #340

Cumyluron #161  
Fenamiphos #440

Allethrin #381  
Diazinon #419

Tri-allate #521  
Fenpropimorph #196

# DART Apple Juice: DART 苹果汁

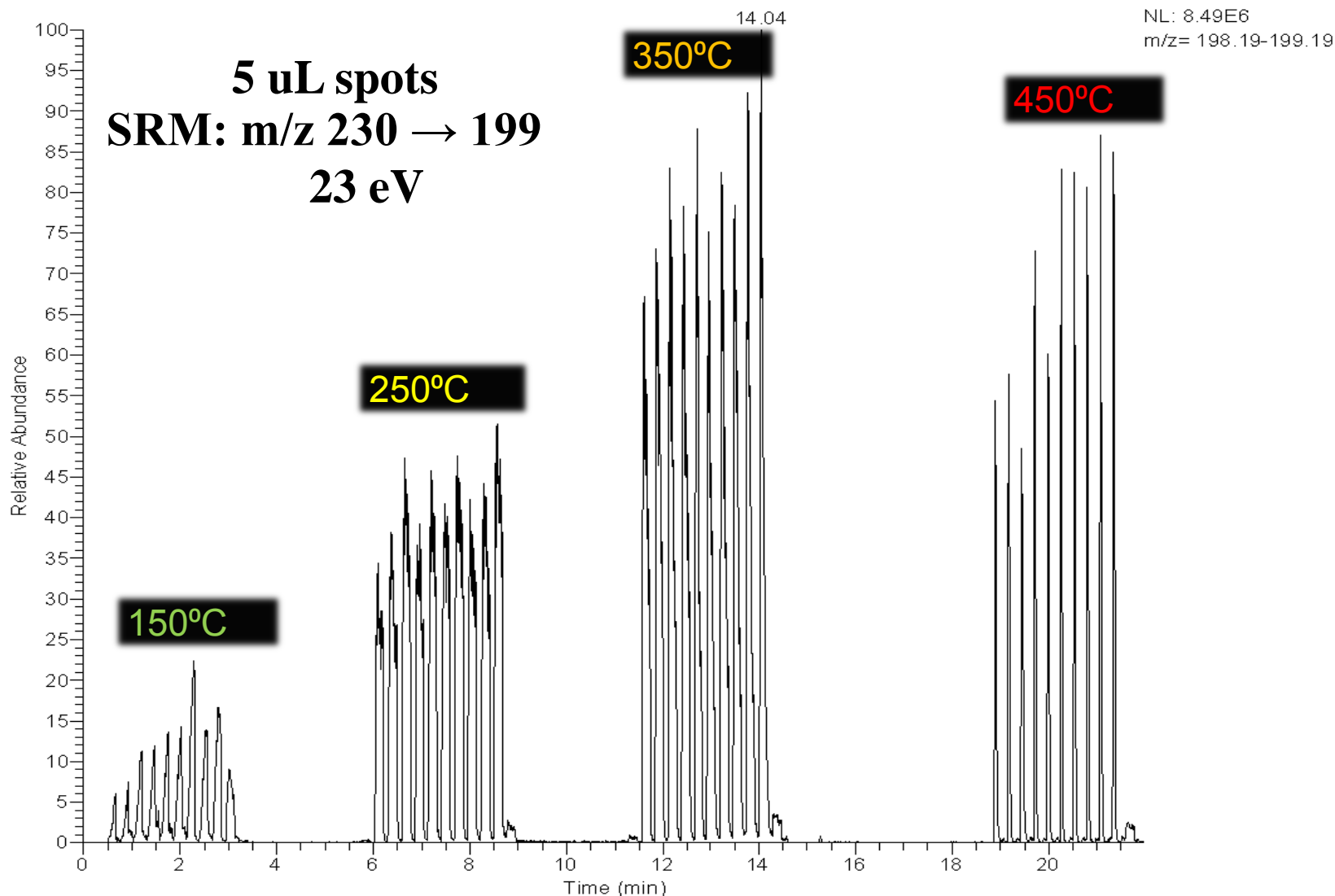


## Dimethoate Spiked at:

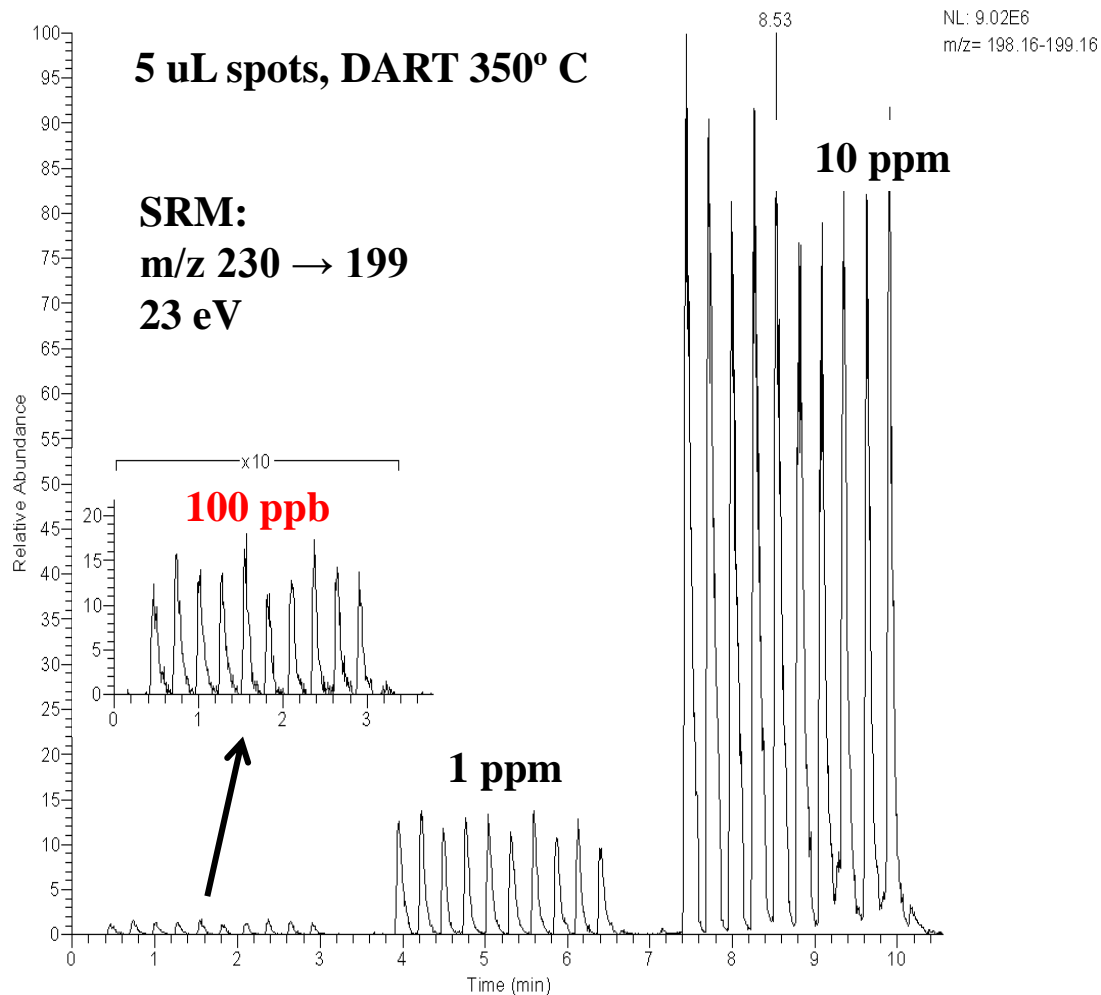
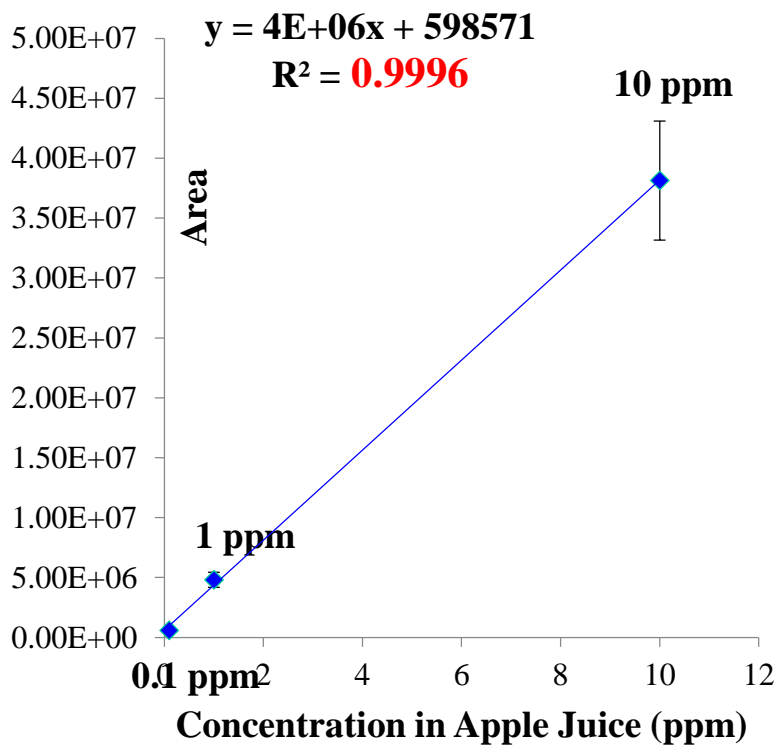
- 100 ppb
- 1 ppm
- 100 ppm

# Temp Ramp 3+D: Dimethoate in Apple Juice

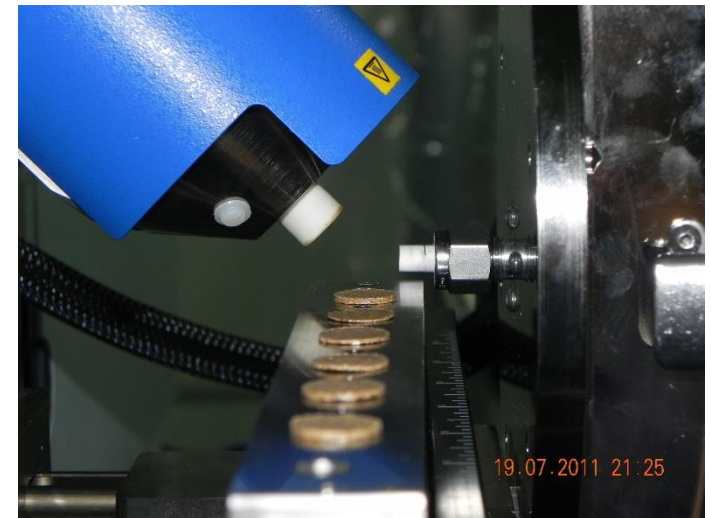
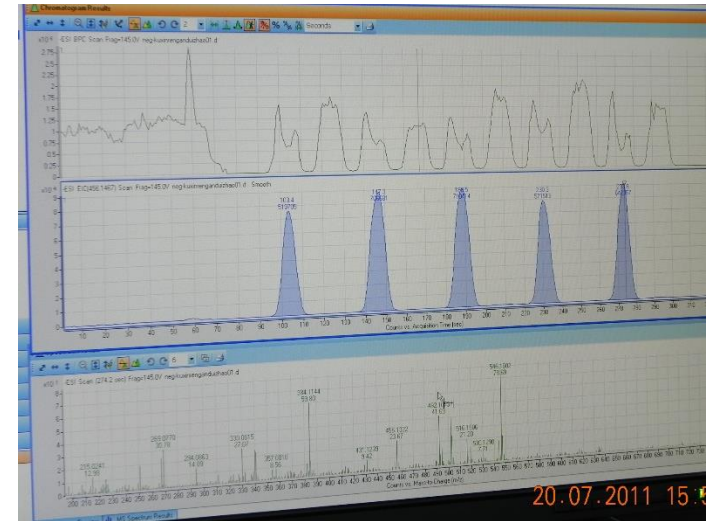
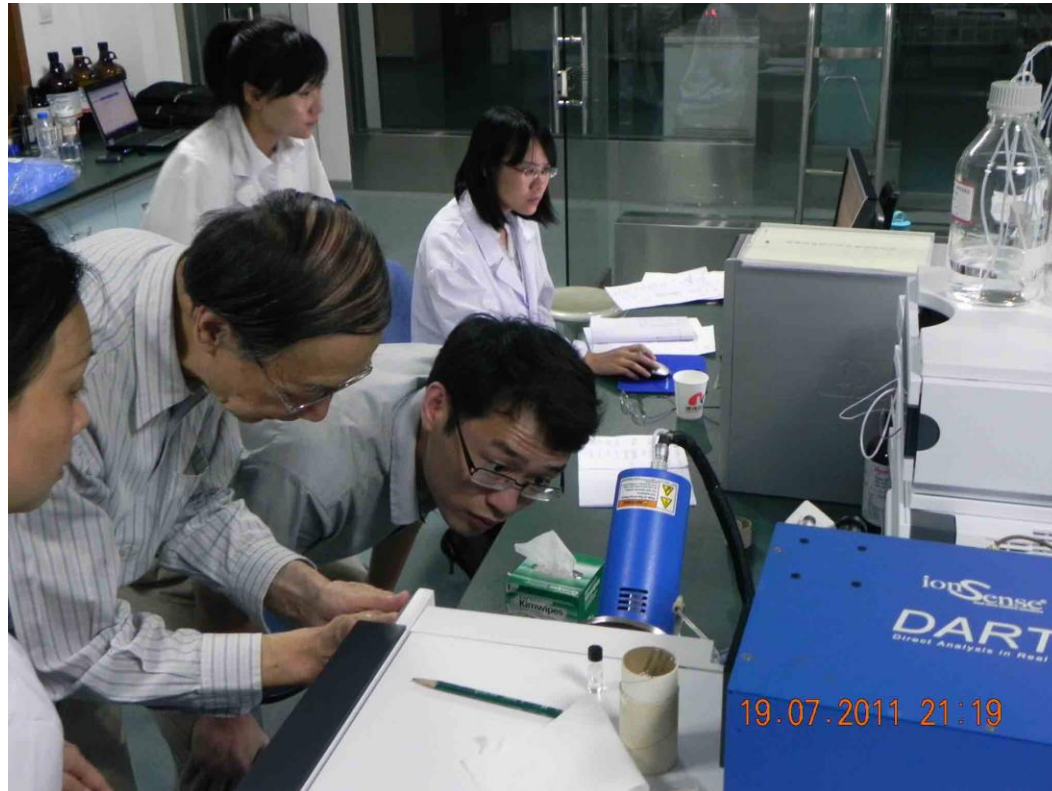
10 ppm



# Dimethoate in Apple Juice 苹果汁中乐果

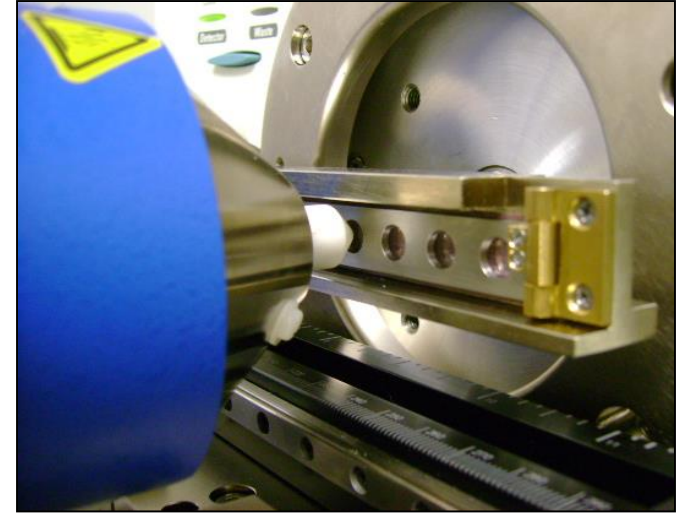
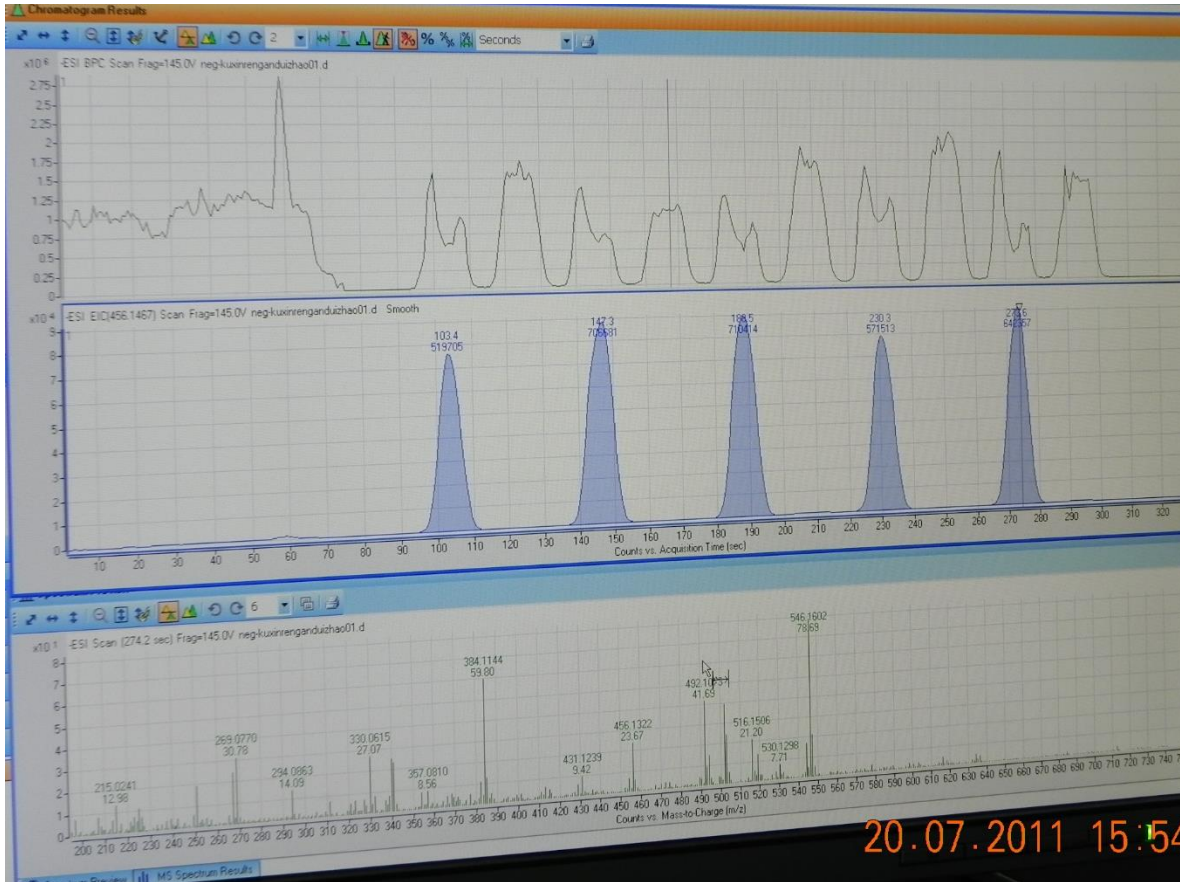


# DART - TOF 中药制剂分析



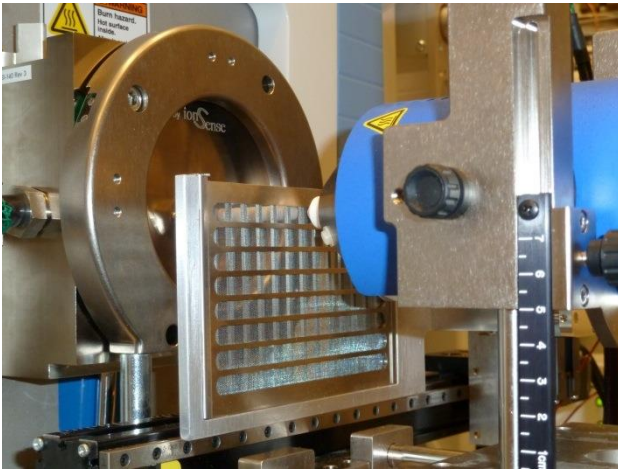
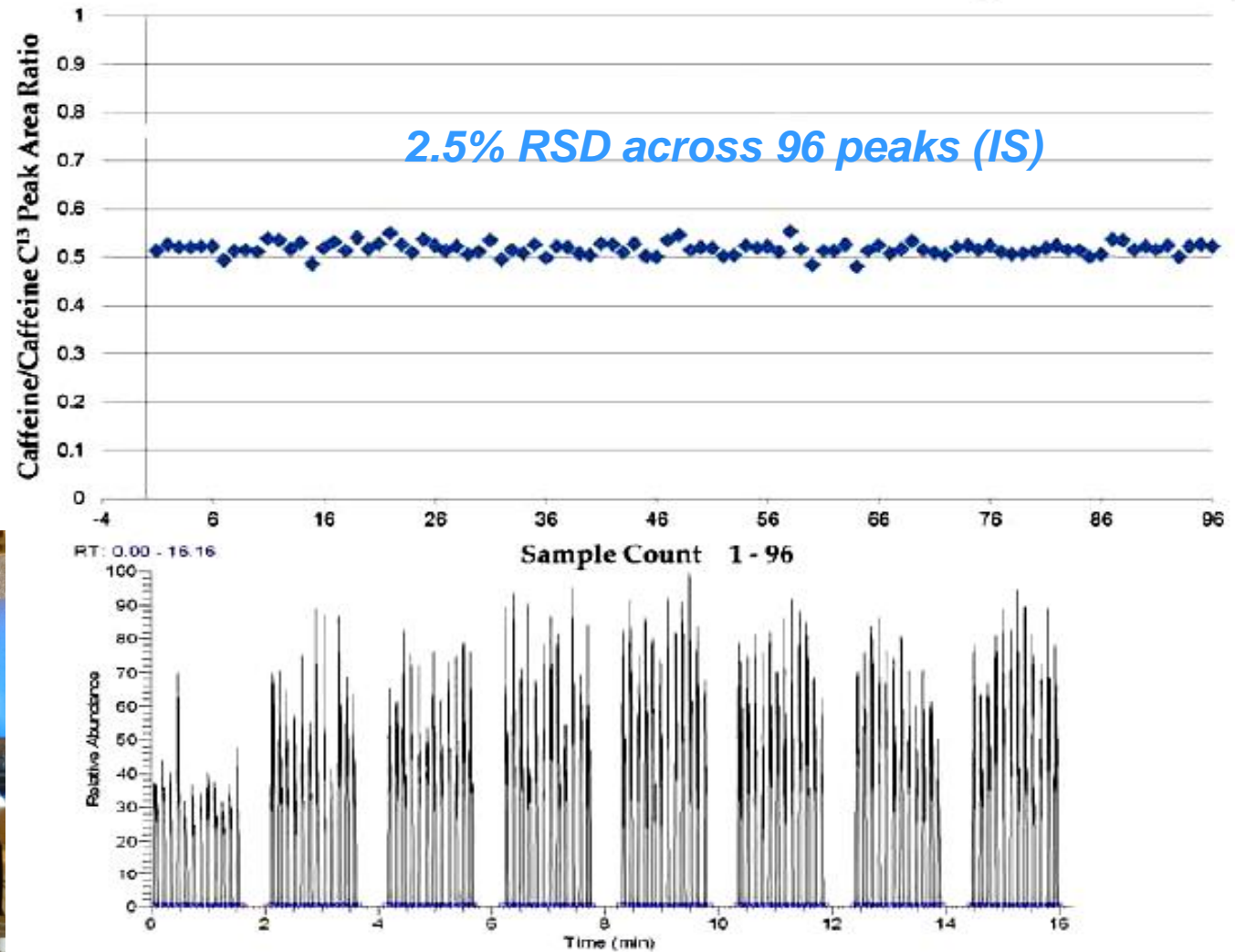


# Transmission DART: 透过式



# X-Z Transmission: 透过式

- XZ Scanner
- 96 samples in 16 minutes
- Caffeine standards





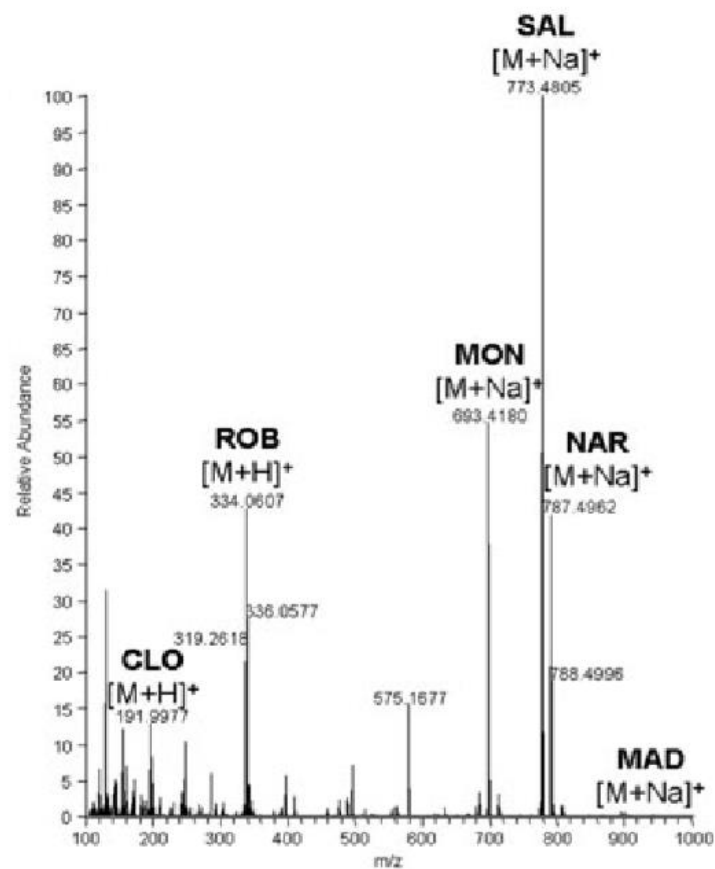
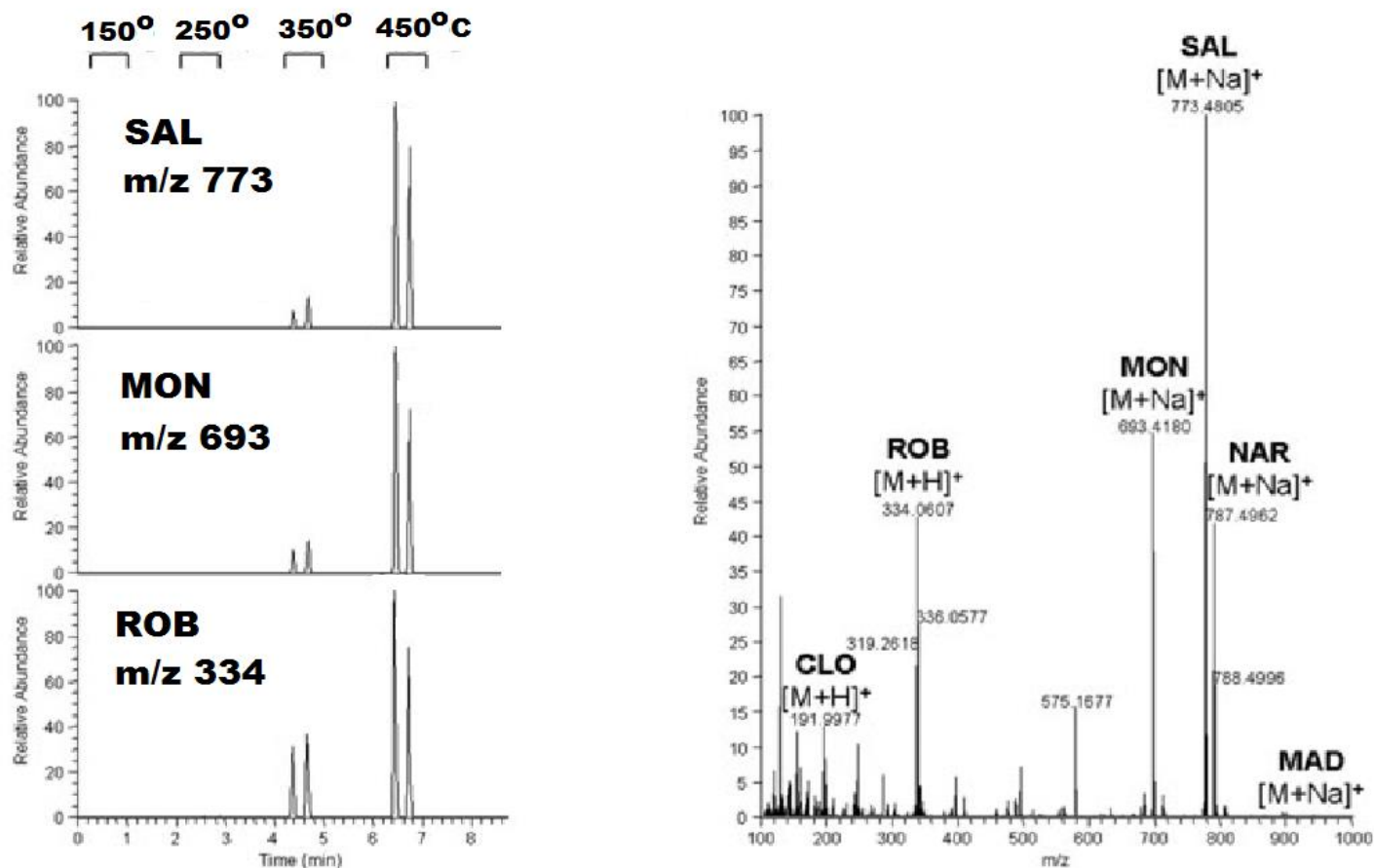
# Antiparasitic Veterinary Drugs in Feed and Food

## DART-MS Analysis with QuEChERs

- Utilize commercially available QuEChERs kit
  - Good for complex food matrices, bulk food and those containing high fat content
  - Enhances transfer of small polar molecules into the organic solvent phase of the extraction
- Antibiotics in milk example:
    - Milk 15 gm
    - Add 0.1% Formic acid to create more acidic solution for acidic antibiotics
    - Add Dispersive Sorbents
      - 50mg PSA and 50 mg C18
      - 1ml Acetonitrile
    - Add Mg salt and mix
    - Analyze organic phase by DART-MS

Hajsolva, J., et al. Institute Chemical Tech., Prague, CZ.  
Rapid Comm. Mass Spectrom. 2013, 27, 467

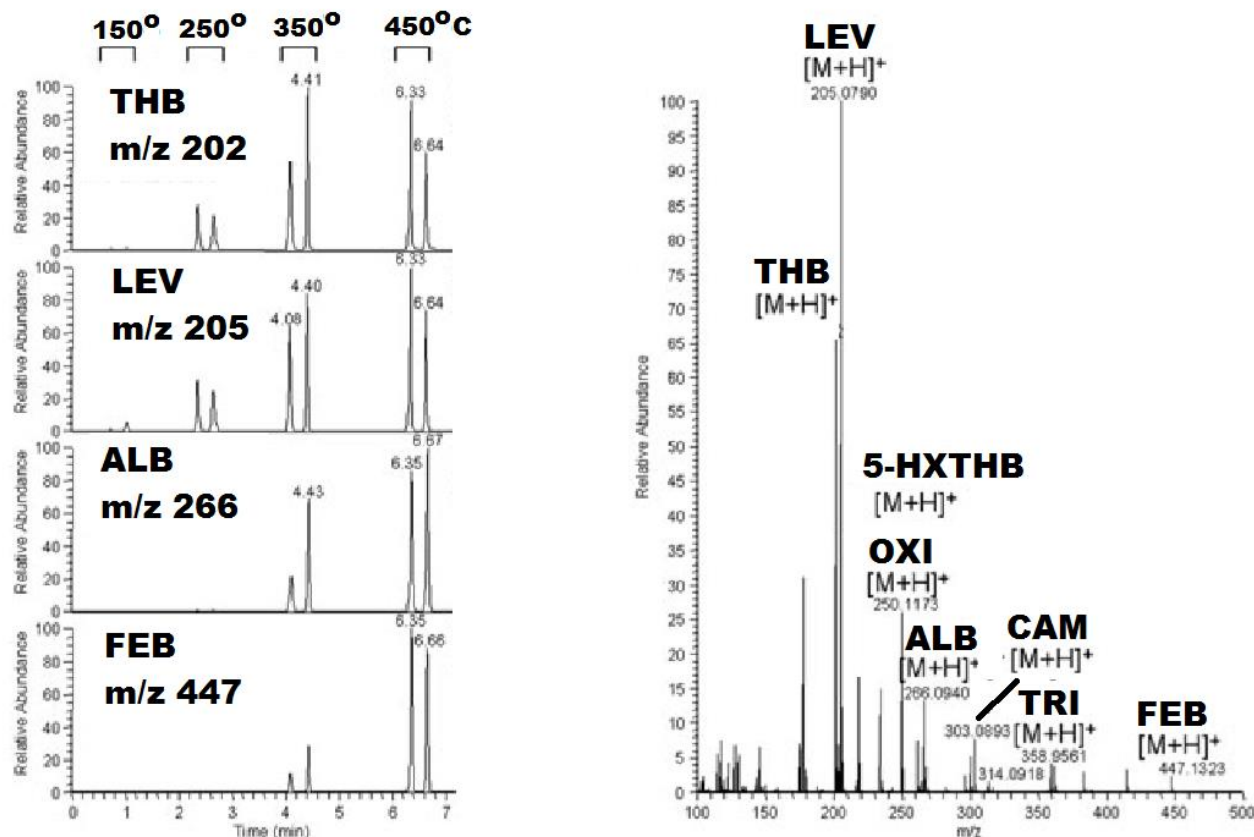
# Analysis of QuEChERS extracts of milk for antibiotics



Effect of gas temperature on DART-HRMS sensitivity for coccidiostats

Hajsolva, J., et al. Institute Chemical Tech., Prague, CZ. Rapid Comm. Mass Spectrom. 2013, 27, 467

# Analysis of QuEChERS extracts of milk for antibiotics

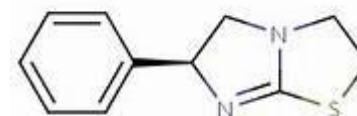
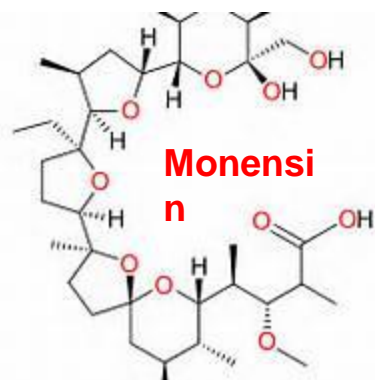


Effect of gas temperature on DART-HRMS sensitivity for benzimidazoles.

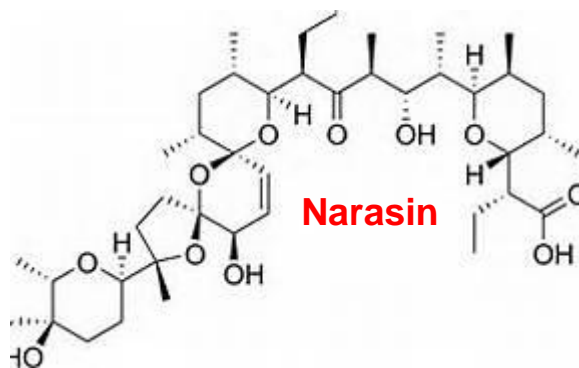
Hajsolva, J., et al. Institute Chemical Tech., Prague, CZ. Rapid Comm. Mass Spectrom. 2013, 27, 467

# Rare occurrence of $[M+Na]^+$ produced by DART

Compounds	Ion assignment	Detected ions Exact mass (Da)
ABZ	$[M+H]^+$	266.0958
ABZ-SO <sub>2</sub>	$[M+H]^+$	298.0857
ABZ-SO	$[M+H]^+$	282.0907
NH <sub>2</sub> -ABZ-SO <sub>2</sub>	$[M+H]^+$	240.0802
TBZ	$[M+H]^+$	202.0434
TBZ-OH	$[M+H]^+$	218.0383
FBZ	$[M+H]^+$	300.0802
FBZ-SO <sub>2</sub>	$[M+H]^+$	332.0700
MBZ	$[M+H]^+$	296.1030
NH <sub>2</sub> -MBZ	$[M+H]^+$	238.0975
MBZ-OH	$[M+H]^+$	298.1187
FLU	$[M+H]^+$	314.0936
NH <sub>2</sub> -FLU	$[M+H]^+$	256.0881
OFZ	$[M+H]^+$	316.0751
OXI	$[M+H]^+$	250.1187
CBZ	$[M+H]^+$	303.0911
TCZ	$[M-H]^-$	356.9428
KETO-TCZ	$[M-H]^-$	326.9500
FEB	$[M+H]^+$	447.1333
LEV	$[M+H]^+$	205.0794
MON	$[M+Na]^+$	693.4185
NAR	$[M+Na]^+$	787.4967
SAL	$[M+Na]^+$	773.4811
LAS	$[M+Na]^+$	613.3711
MAD	$[M+Na]^+$	939.5288
AMP	n.d.	
ROB	$[M+H]^+$	334.0621
CLO	$[M+H]^+$	191.9978
ETH	$[M+H]^+$	238.1074
DIC	$[M-H]^-$	404.9718
DNC	$[M-H]^-$	301.0578
TOL	$[M-H]^-$	424.0584
TOL-SO <sub>2</sub>	$[M-H]^-$	440.3737
TOL-SO	$[M-H]^-$	456.3731



e



Structures with significant hydrogen bonding facilitate capture of the cation

# Solid Phase Extraction (ITSP SPE)

Instrument top sample prep (ITSP) solid phase extraction is a procedure that utilizes a small cartridge with C-18 sorbent.

## Procedure

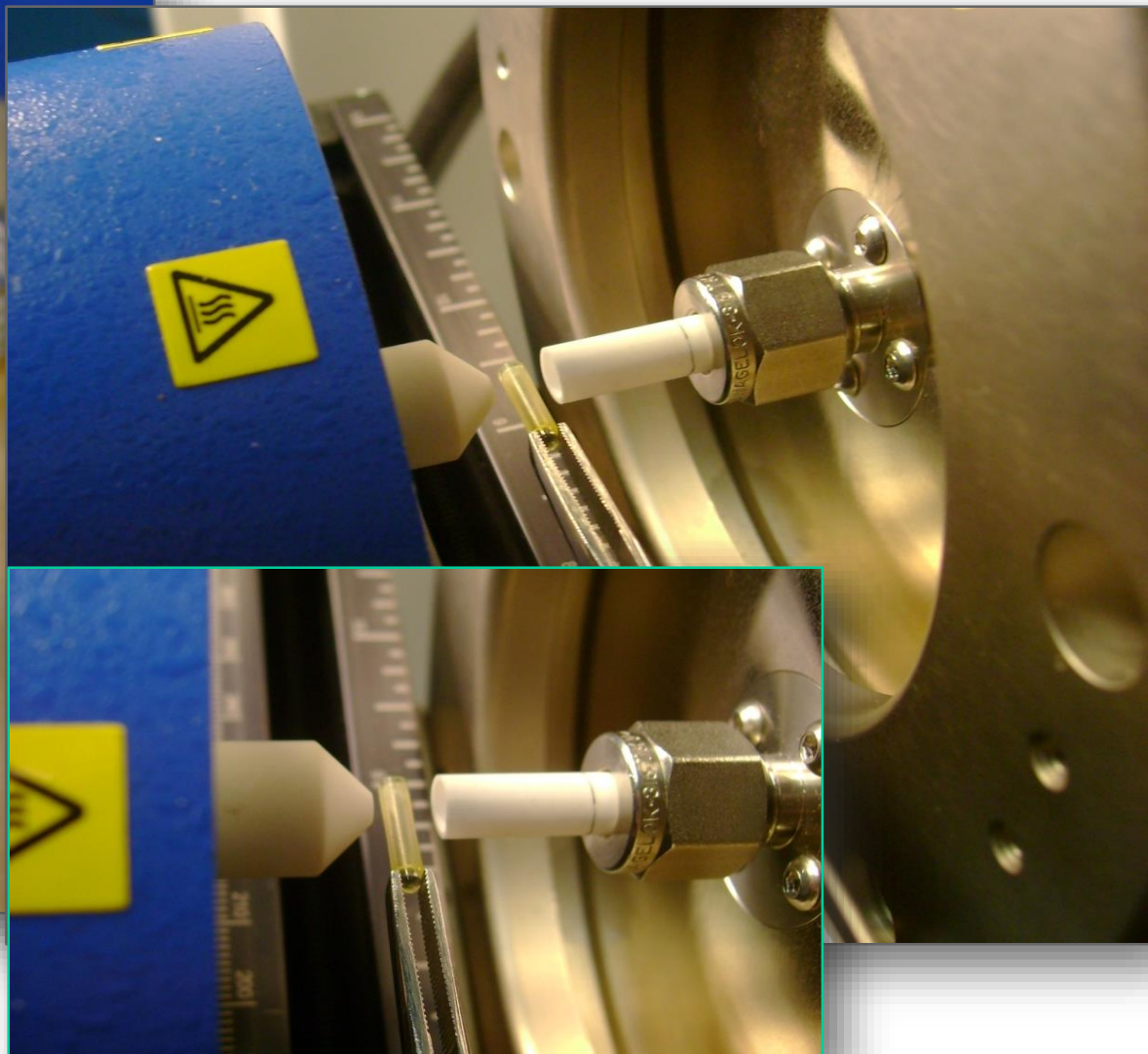
- The initial sample preparation was done by extracting 200 mg of sample in 5 ml of water at 90° C for 5 minutes.
- The cartridge was first conditioned with methanol and water.
- 100µl of sample was applied to the column.
- A 100µl portion of water was used to elute interfering molecules.
- A 100µl portion of methanol was used for the elution of more polar compounds.
- The sample and two elutions were collected in separate vials for analysis.



[info@itspsolutions.com](mailto:info@itspsolutions.com)



# Gerstel Twister Spin Bar: Sample Concentration

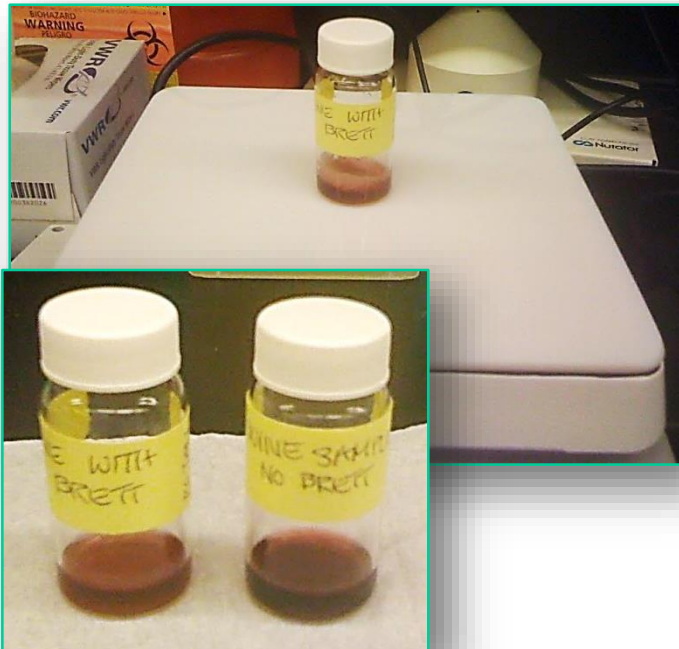


**Twister was spun overnight in orange juice with 50 ppb level of 10 pesticides**

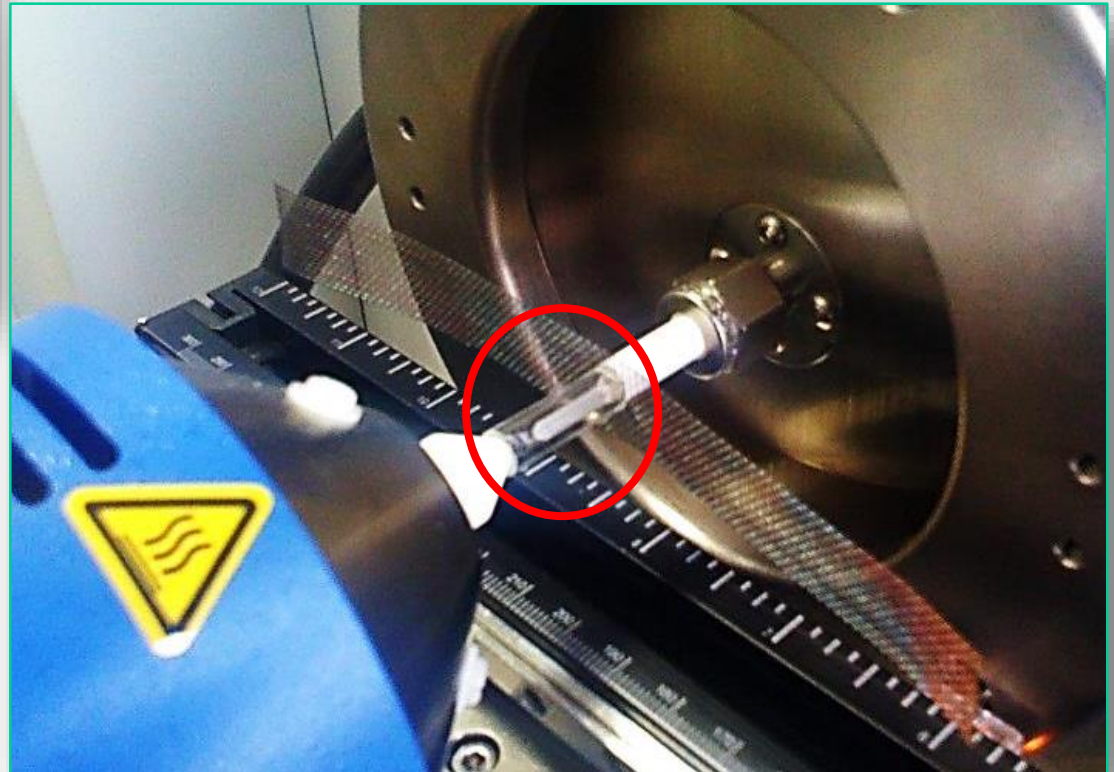
# Wine Sampled with PDMS Twister

Minimum 30 minutes  
unattended stirring

Twister placed in glass chamber = COMPLETE  
desorption



Twister stir bar  
(PDMS, 0.5 mm thickness)  
introduced into 2 mL wine



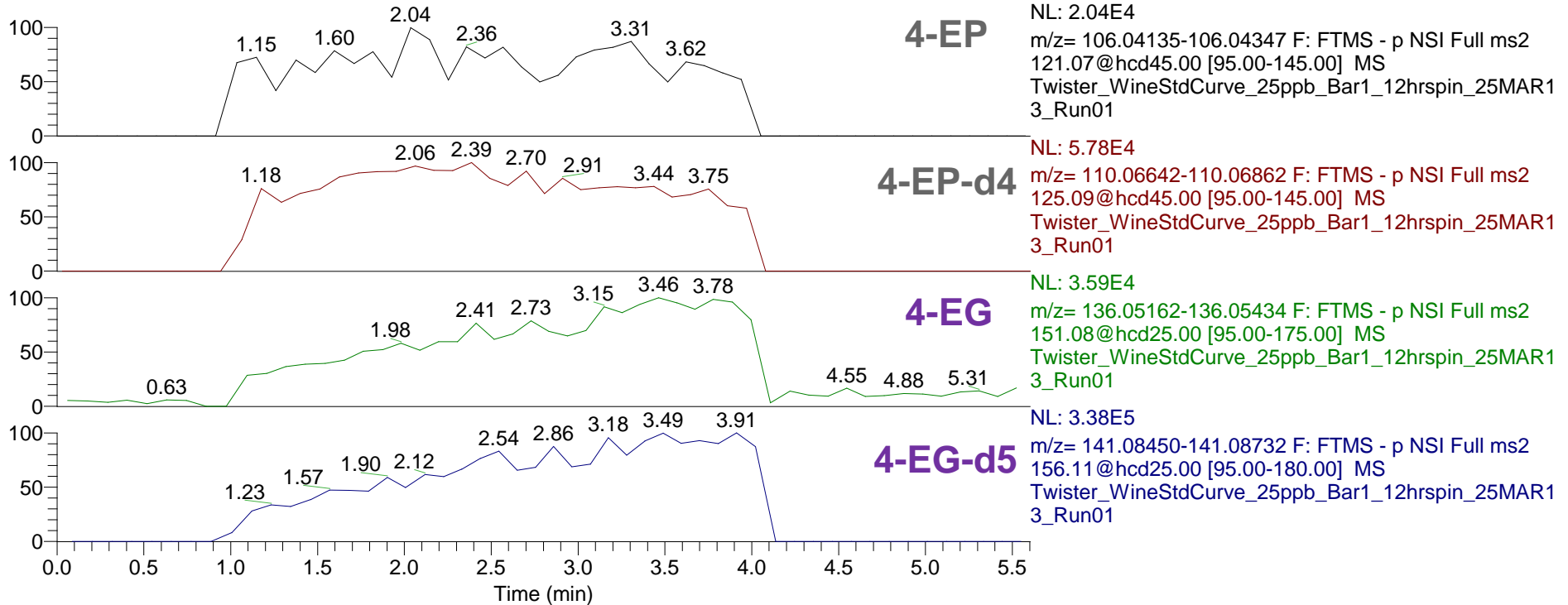


# Typical DART-MS Chronogram from Stir Bar

## Glass Chamber: Much Improved Reproducibility

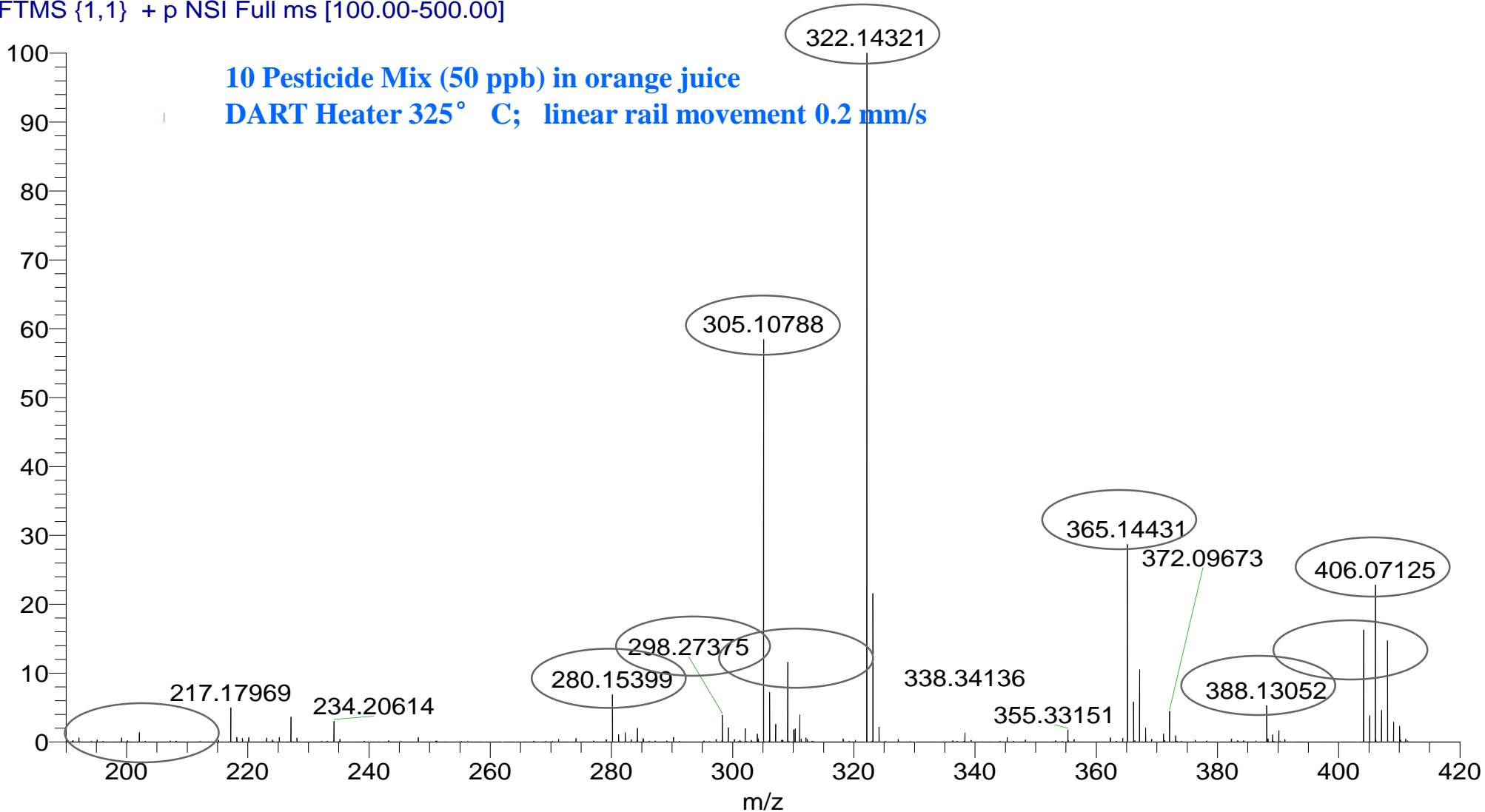
### 25 ppb Spiking Level of Phenolics

RT: 0.00 - 5.60



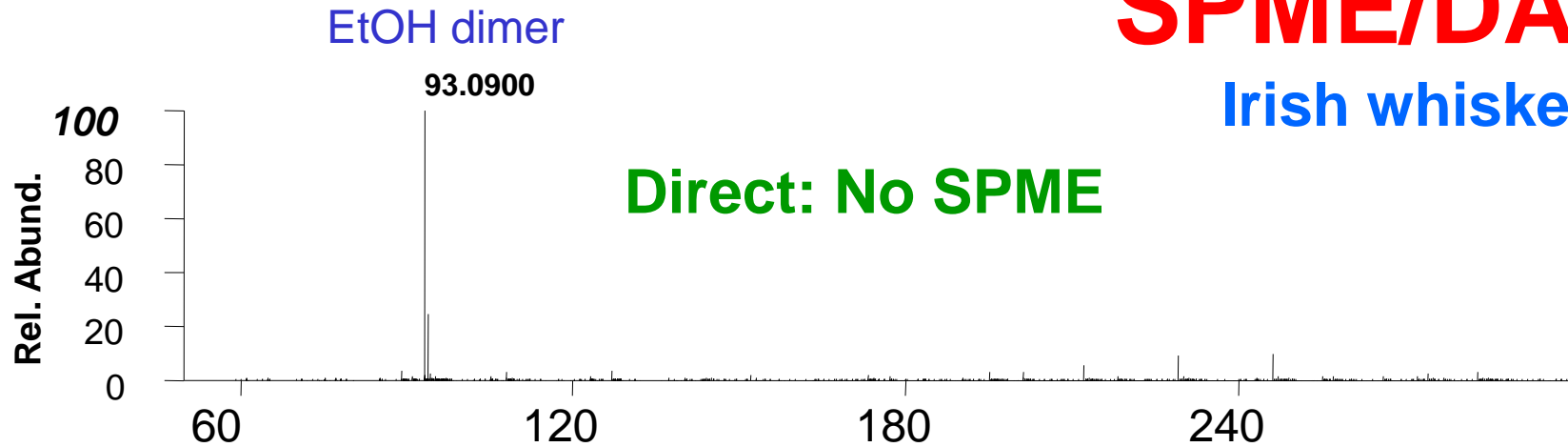
# Direct Twister DART-MS Analysis

120424-01\_Twister19&20\_OSCranLt\_Blank&50ppbSpin #598-654 RT: 4.99-5.41 AV: 57 SB: 116 0.46-1.46 NL: 1.34E6  
T: FTMS {1,1} + p NSI Full ms [100.00-500.00]

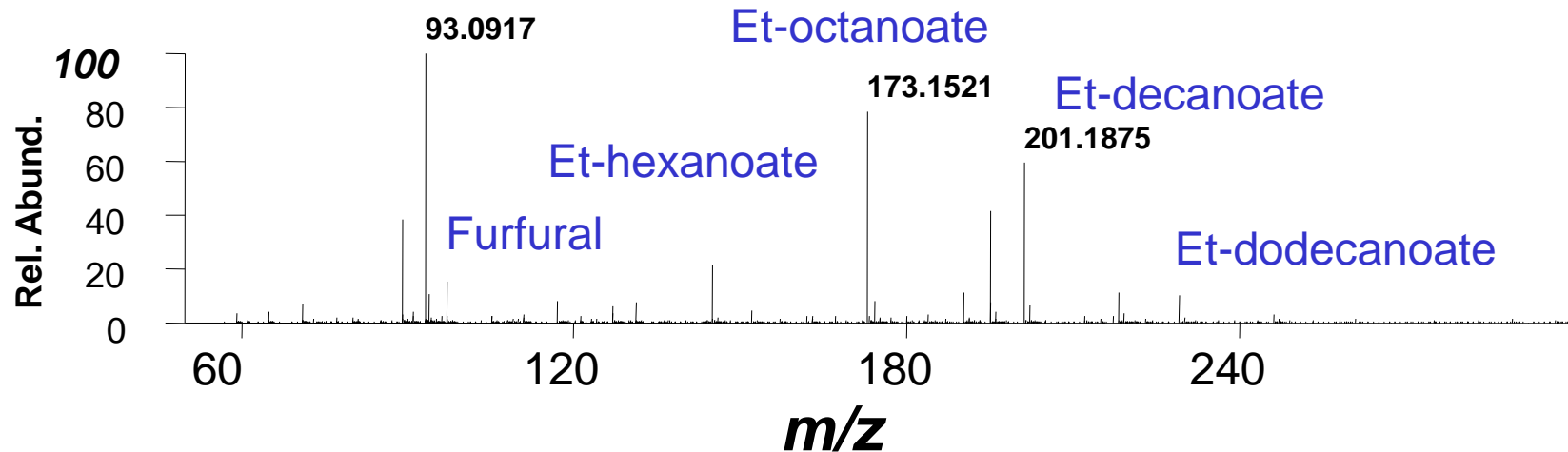


# SPME/DART

Irish whiskey

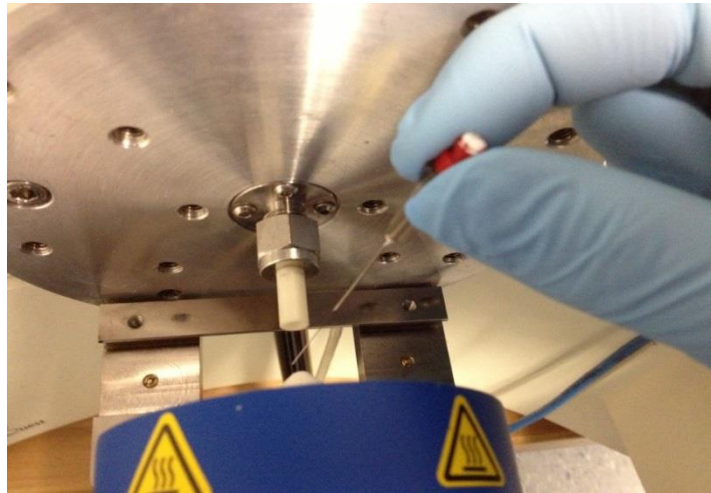
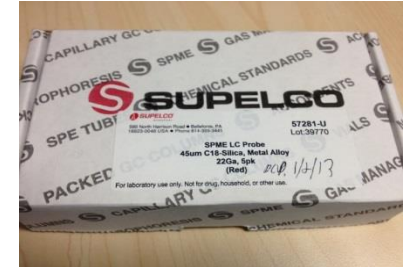


## Carboxen/DVB/PDMS SPME Fiber



# New Technology Solid Phase Micro Extraction (SPME) Probes

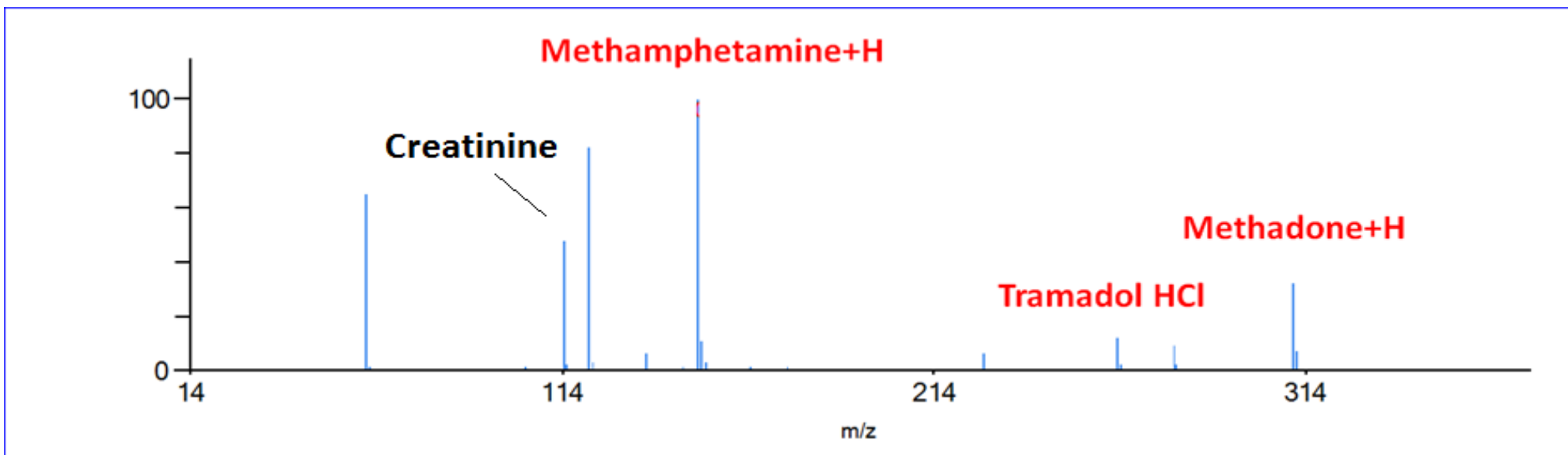
- Supelco LC-Probes are 45 micron SPE coated fibers
- Designed to collect samples for LC/MS analysis
- DART-MS probe to urine for rapid 15 minute extraction
- C-18 coating retains drugs and small molecules
- Remove probe, rinse with water to remove solubles like creatinine
- Position between DART source and MS inlet with results in seconds
- Also works with foods and forensic samples



Sorbent coated portion of the probe

# LC-Probe (SPME) Analysis of Urine (HR-MS)

Drugs concentrate on the fiber reducing effect of creatinine which normally causes matrix interference

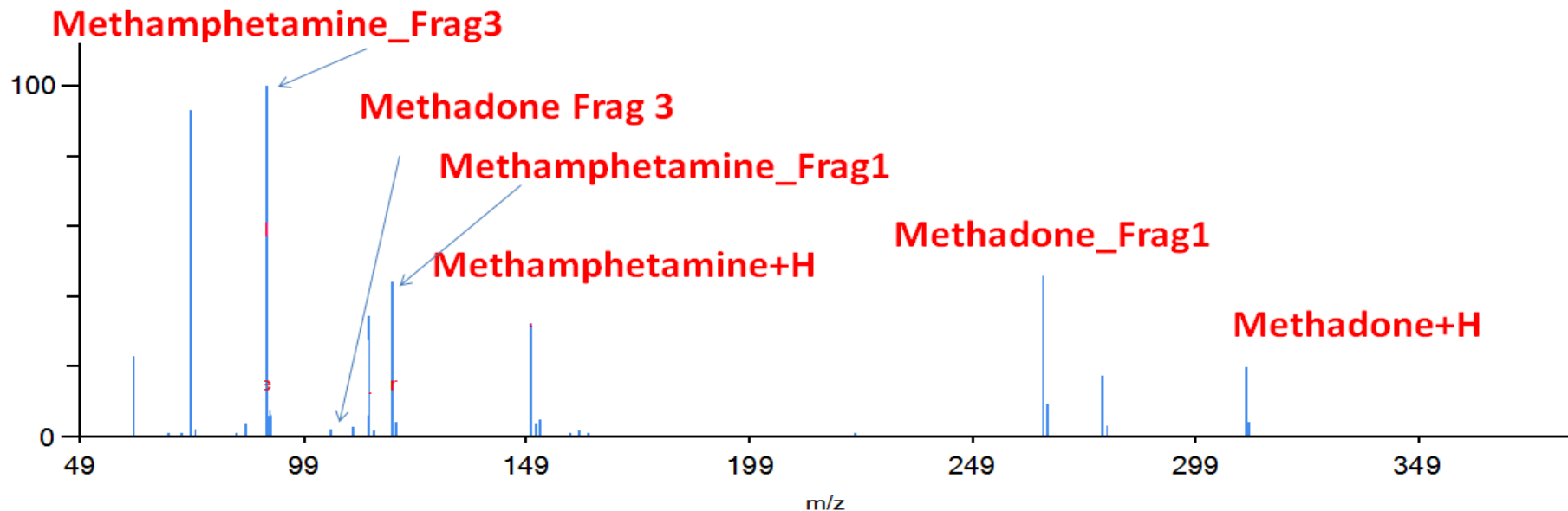


Name	Composition	Adduct	Measured	Calculated	mmu	Abund.
Tramadol HCl	C <sub>16</sub> H <sub>25</sub> NO <sub>2</sub>		263.186	263.188	1.83	12
± Methadone	C <sub>21</sub> H <sub>27</sub> NO	+H	310.215	310.217	1.48	32
Methamphetamine	C <sub>10</sub> H <sub>15</sub> N	+H	150.128	150.128	-0.22	100



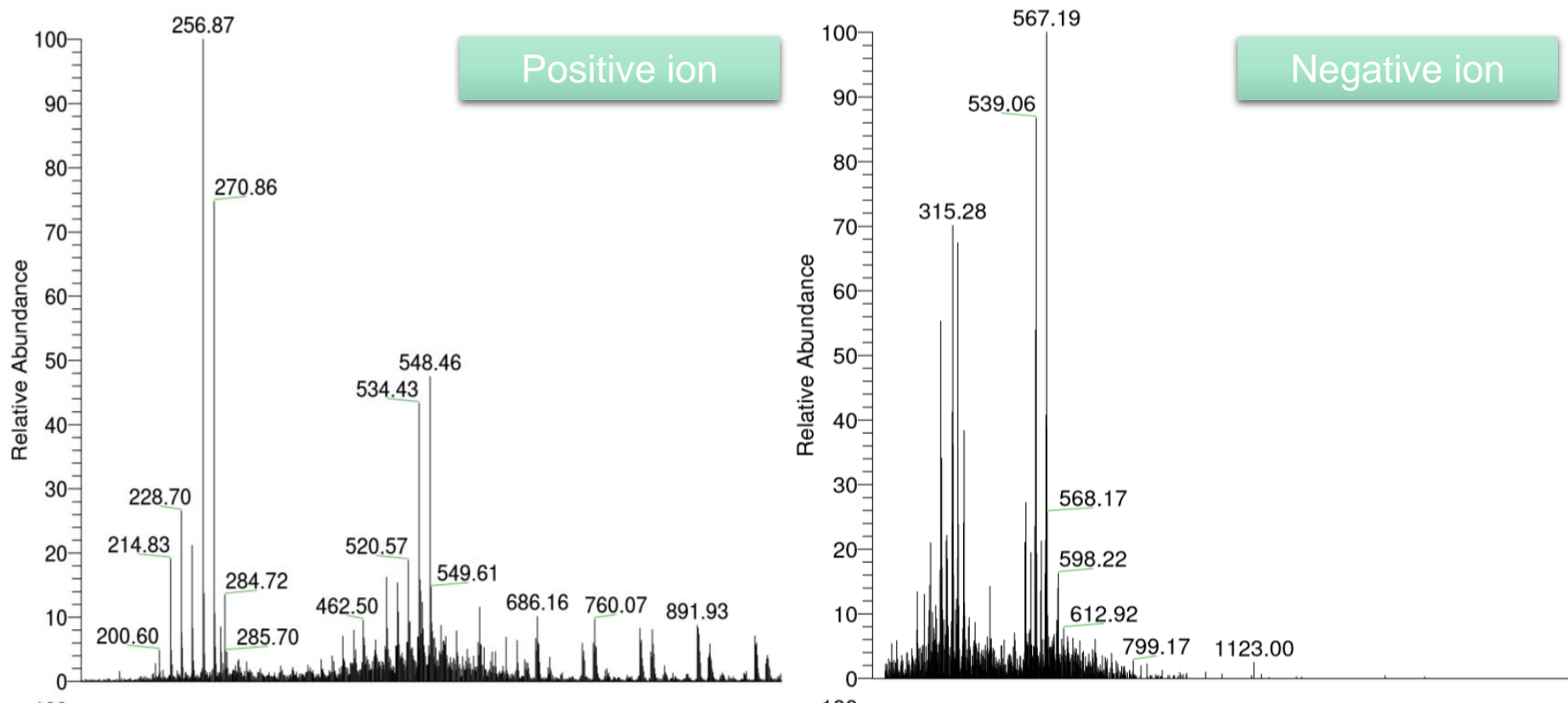
# LC-Probe (SPME) Analysis of Urine (HR-MS)

## Drug confirmed with in-source fragmentation



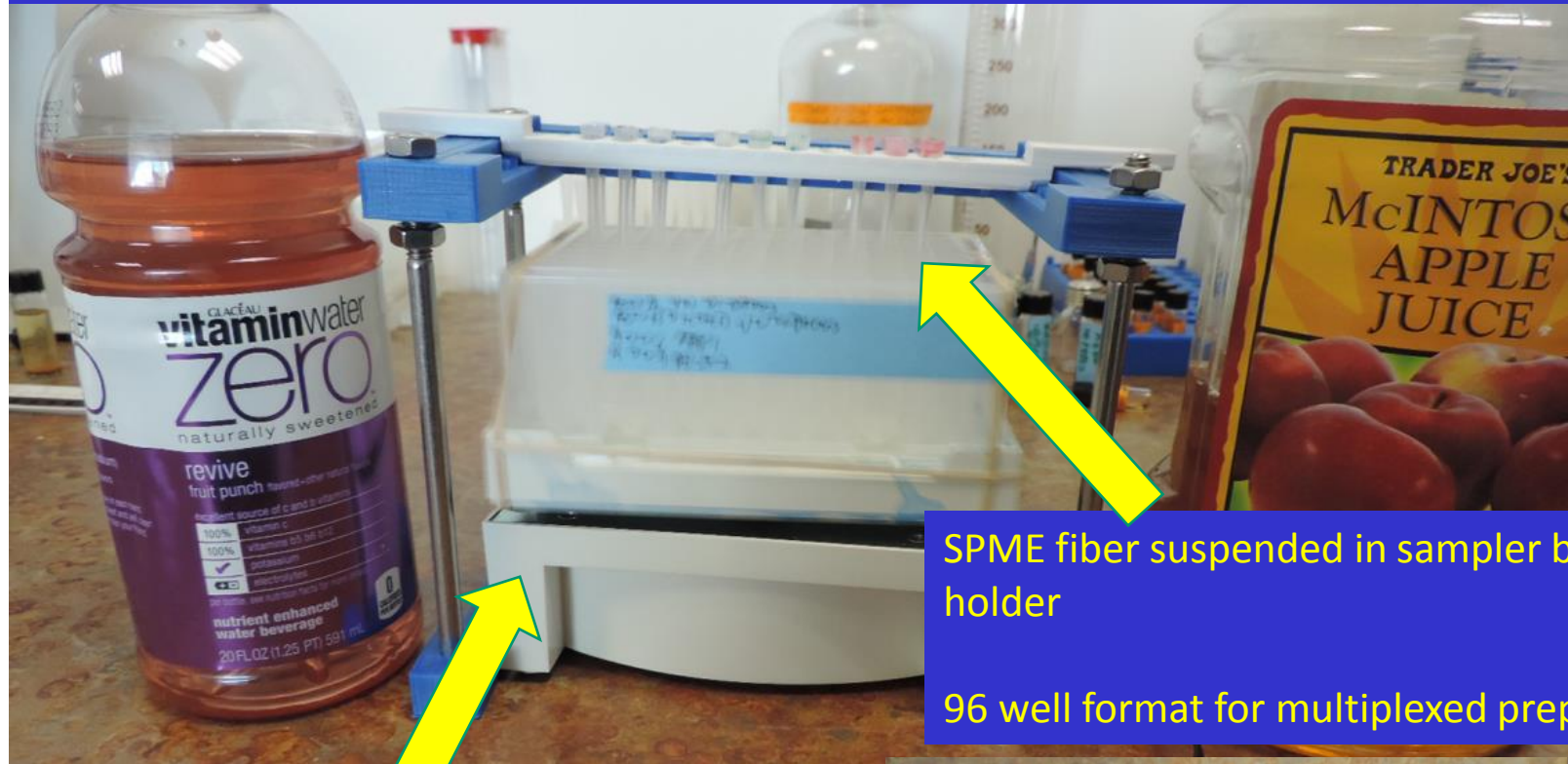
Name	Composition	Adduct	Measured	Calculated	mmu	Abund.
± Methadone	C <sub>21</sub> H <sub>27</sub> NO	+H	310.217	310.217	-0.11	19
± Methadone_Frag1	C <sub>19</sub> H <sub>21</sub> O		265.159	265.159	-0.55	45
± Methadone_Frag3	C <sub>7</sub> H <sub>5</sub> O		105.033	105.034	0.44	2
Methamphetamine	C <sub>10</sub> H <sub>15</sub> N	+H	150.127	150.128	1.08	36
Methamphetamine_Frag1	C <sub>9</sub> H <sub>11</sub>		119.083	119.086	2.57	45
Methamphetamine_Frag2	C <sub>7</sub> H <sub>7</sub>		91.054	91.054	0.77	100

# SPME DART of Green Tea



SPME extraction with PDMS DVA showing positive ion mass spectrum and same sample extracted with SCX fiber (right). Most likely different chemical entities are collected by the different fibers as evidenced by many different mass values

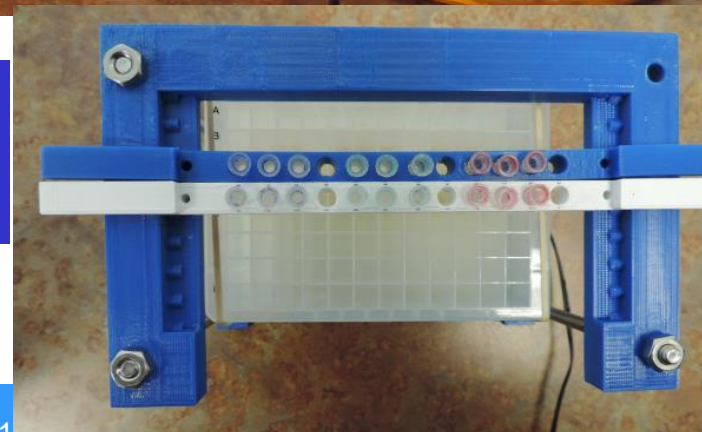
# Sample Apparatus



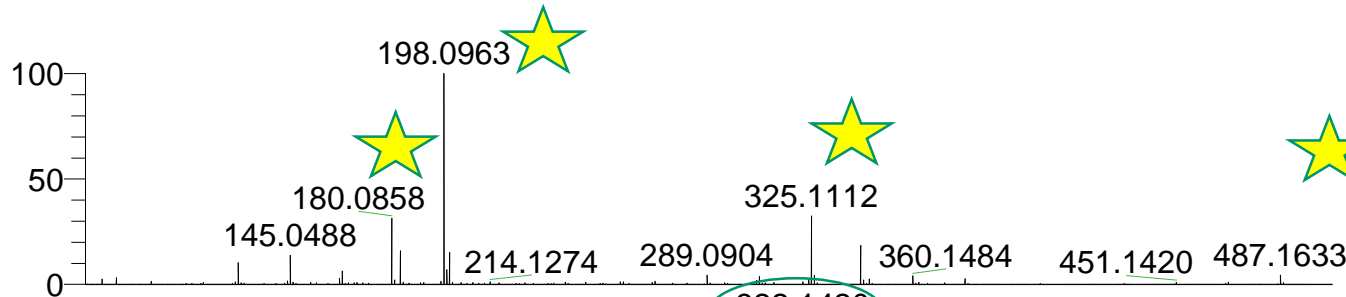
SPME fiber suspended in sampler by holder

96 well format for multiplexed prep

Plate shaker used for sustained sample agitation while SPME fiber is immersed in liquid sample



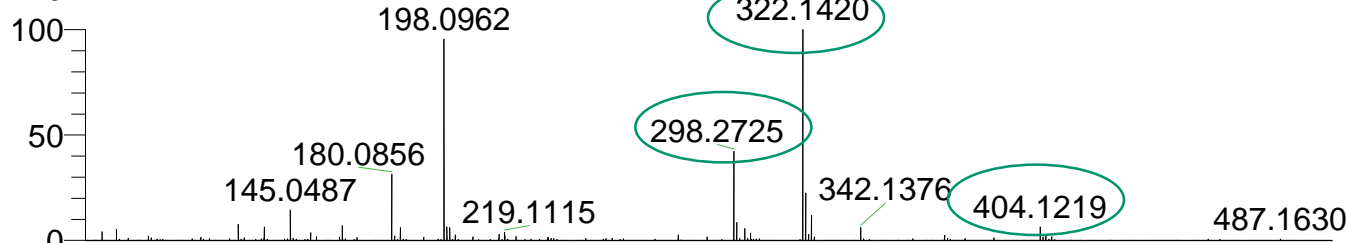
# Apple Juice with 6 Pesticide Mix



NL: 3.84E8

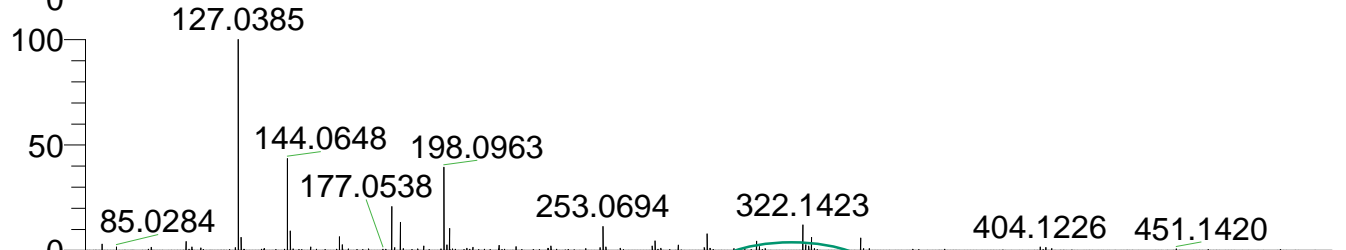
**Glass Capillary**

★ Carbohydrates dominate signal



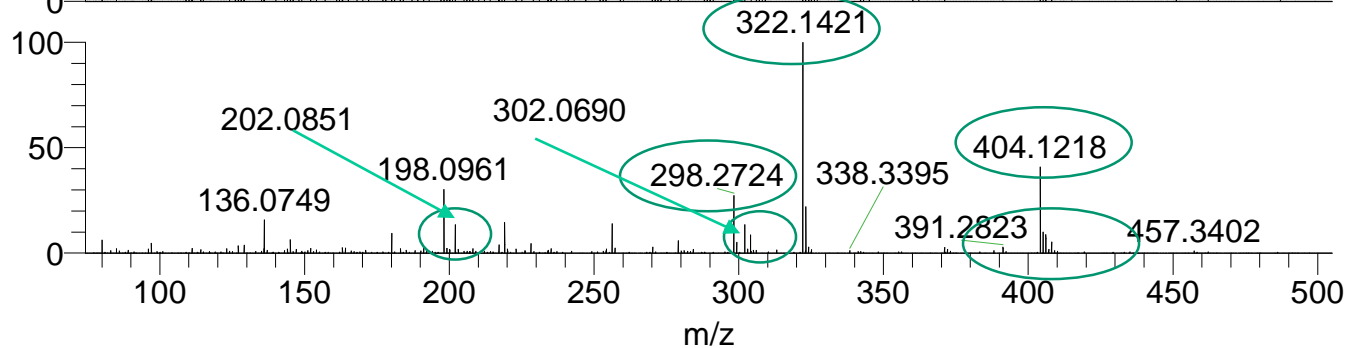
NL: 3.51E8

**C18 SPME Fiber**



NL: 5.62E8

**SCX SPME Fiber**



NL: 1.69E8

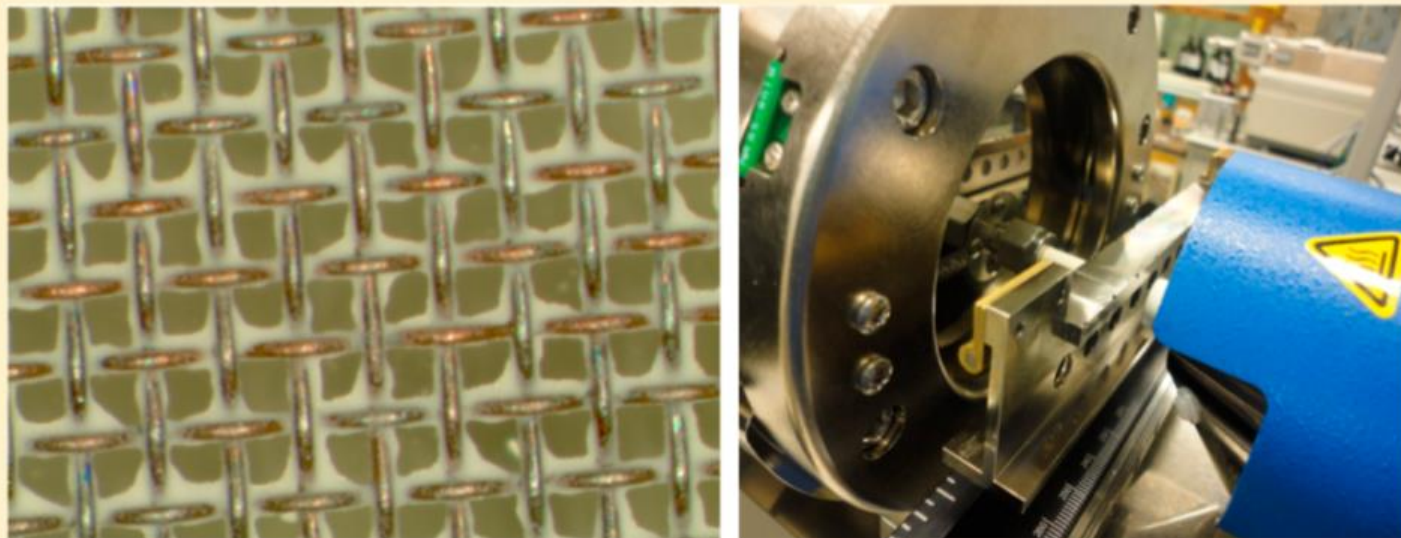
**PDMS/DVB SPME Fiber**

Pesticides and m/z of [M+H]<sup>+</sup>  
 Carbaryl 202,  
 Spiroxamine 298,  
 Pyriproxyfen 322  
 Fenhexamid 302,  
 Azoxystrobin 404  
 Difenoconazole 406,

# Reusable Solid-Phase Microextraction Coating for Direct Immersion Whole-Blood Analysis and Extracted Blood Spot Sampling Coupled with Liquid Chromatography–Tandem Mass Spectrometry and Direct Analysis in Real Time–Tandem Mass Spectrometry

Fatemeh S. Mirnaghi and Janusz Pawliszyn\*

Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada



C18 PAN coated  
screen (left) mounts  
in Transmission  
Module



# SPME-TM-DART 高灵敏度DART定量

ChemComm

RSC Publishing

COMMUNICATION

## Solid phase microextraction (SPME)-transmission mode (TM) pushes down detection limits in direct analysis in real time (DART)<sup>†</sup>

/Cite this: DOI: 10.1039/x0xx00000x

Germán Augusto Gómez-Ríos and Janusz Pawliszyn

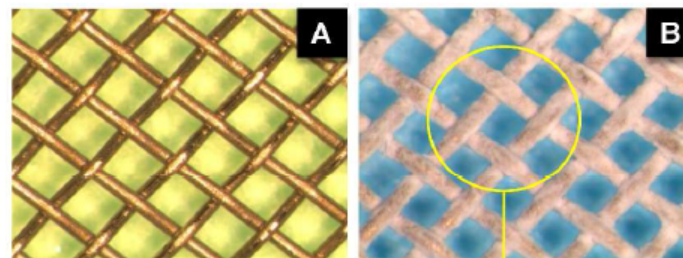
Received 00t **2014**  
Accepted 00t

DOI: 10.1039/x0xx00000x

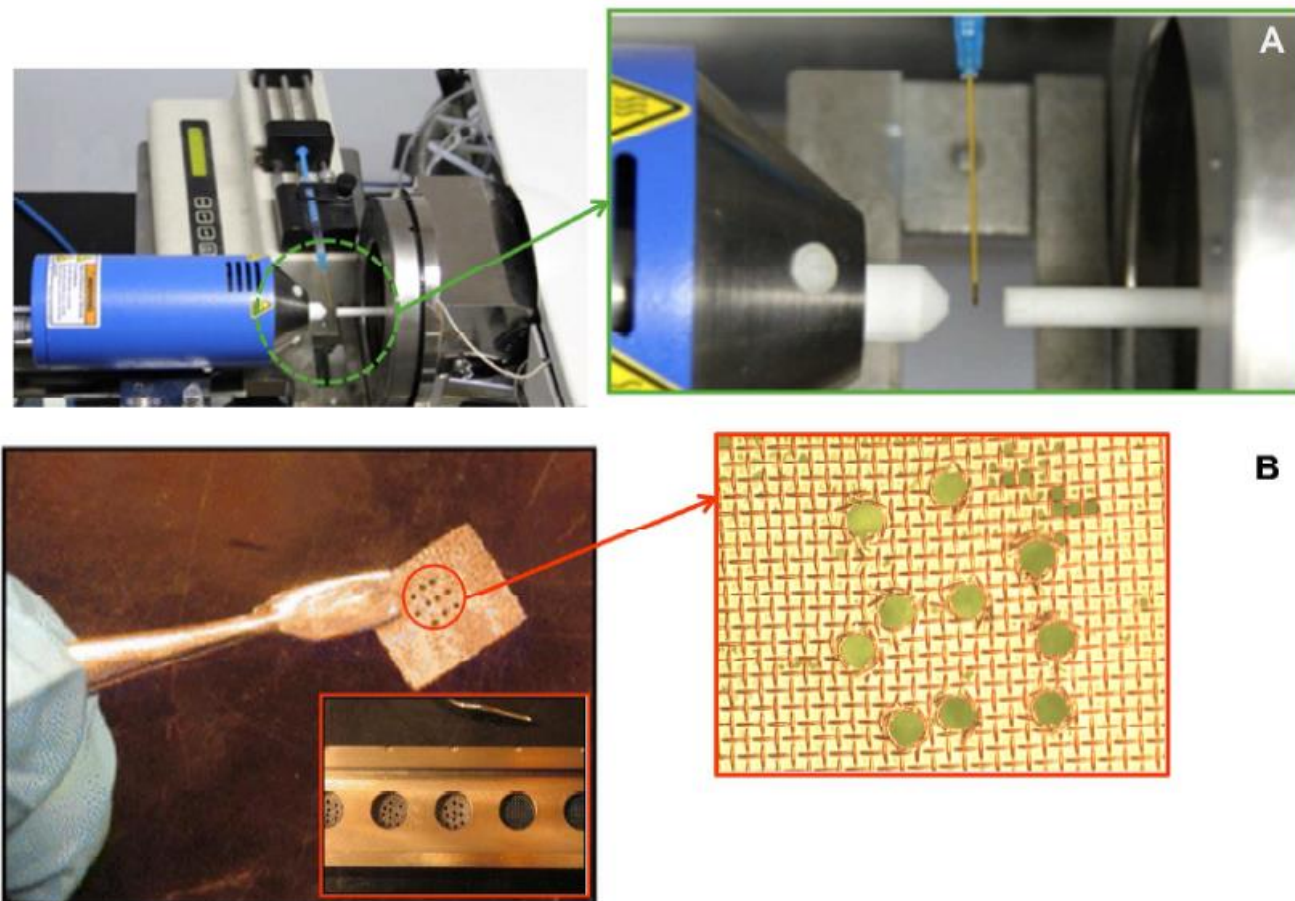
www.rsc.org/

***RSD < 5%***  
***LLOD ~ 10 - 100 ppt***  
***3 min per sample***

A new SPME device was developed and applied for quick solventless extraction/enrichment of small molecules from complex matrices. Subsequently, the device was coupled as a transmission mode substrate to DART resulting in limits of detection in the low pg/mL level in less than 3 minutes with reproducibility below 5% RSD.



# SPME-TM-DART 高灵敏度DART定量

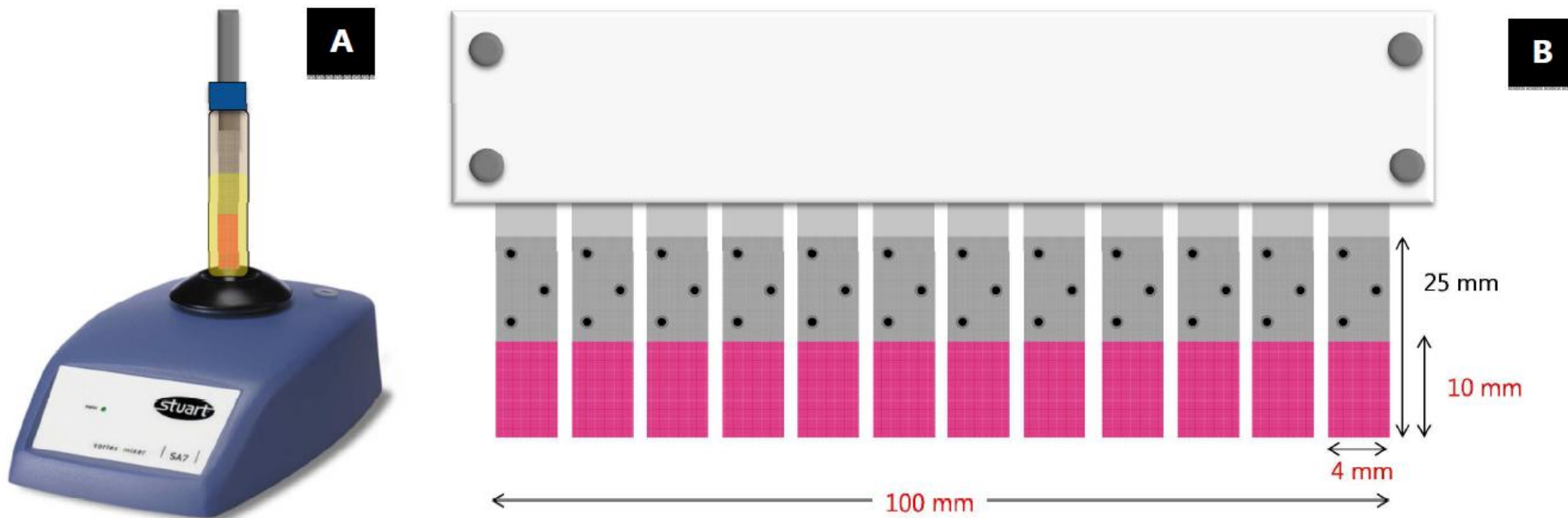


X. Wang, X. Li, Z. Li, Y. Zhang, Y. Bai, H. Liu, *Anal. Chem.* 2014, **86**, 4739-4747.

A. Rodriguez-Lafuente, F. S. Mirnaghi, J. Pawliszyn, *Anal. Bioanal. Chem.* 2013, **405**, 9723-9727.

**Figure S2A.** In-Tube Solid-Phase Microextraction with Direct Analysis in Real Time Mass Spectrometry; image was adapted from the original source published by Wang and collaborators [2]. **B.** Thin-film solid-phase microextraction and direct analysis in real time; image was adapted from the original source published by Rodriguez-Lafuente and collaborators [3].

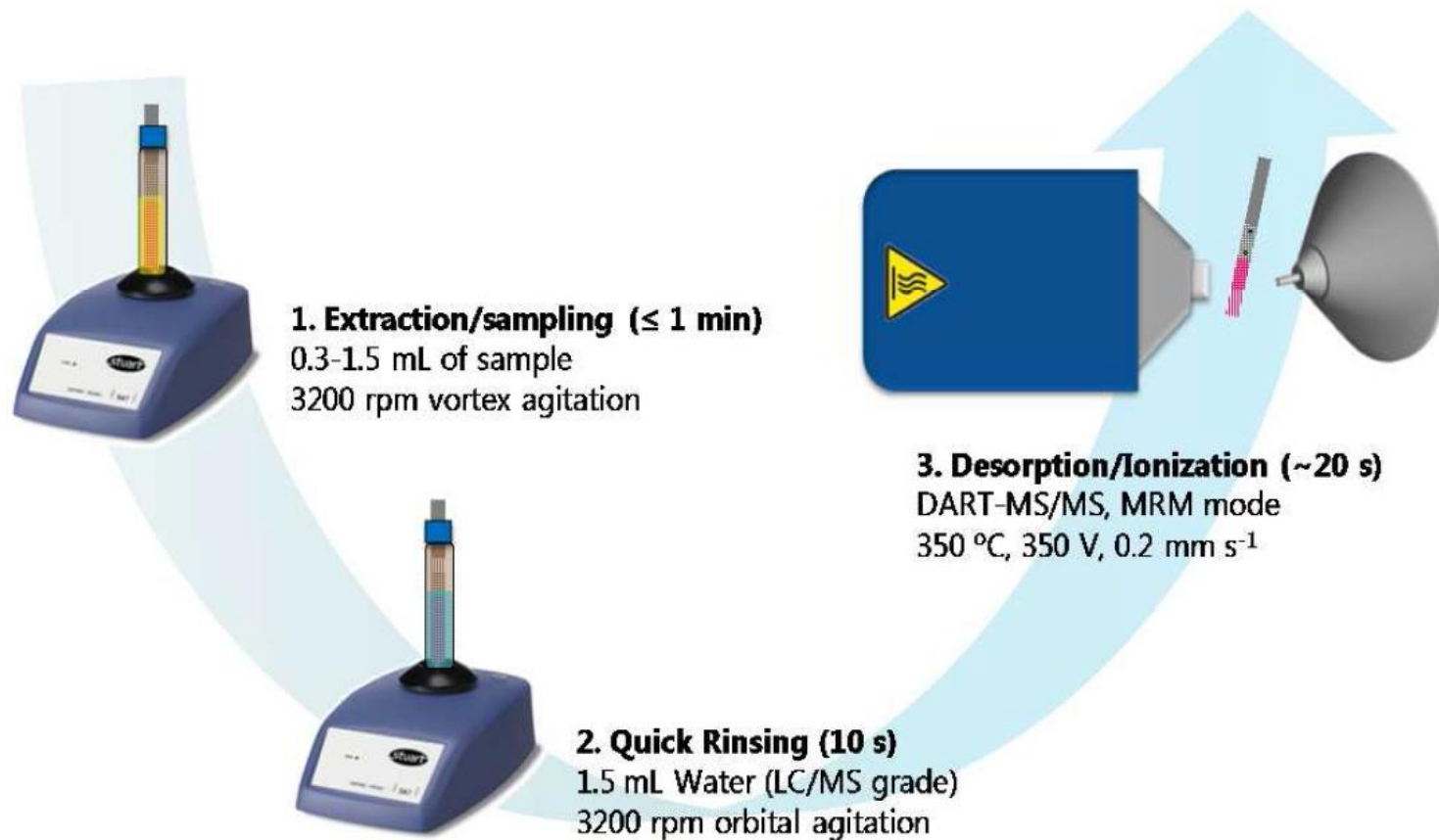
# SPME-TM-DART 高灵敏度DART定量



**Figure S10** A. SPME-TM configuration for individual extractions and B. SPME-TM 12-strips configuration for high-throughput analysis using 96-Concept autosampler (PAS Technologies) [1].

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ChemComm 2014

# SPME-TM-DART 高灵敏度DART定量

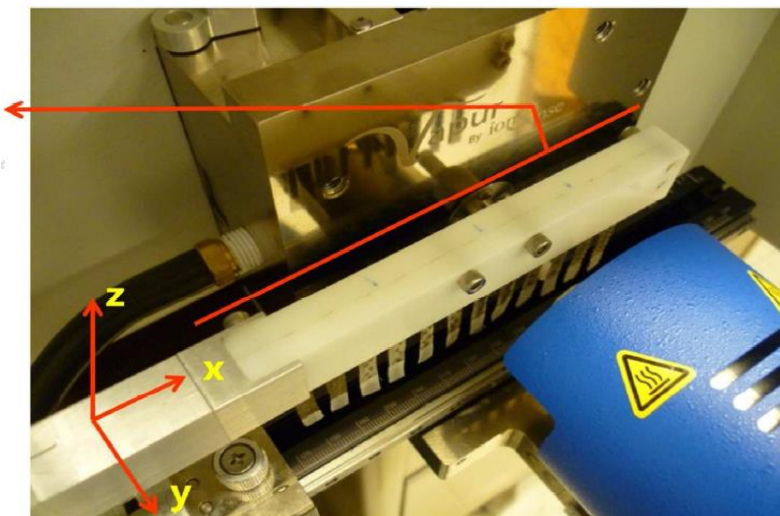
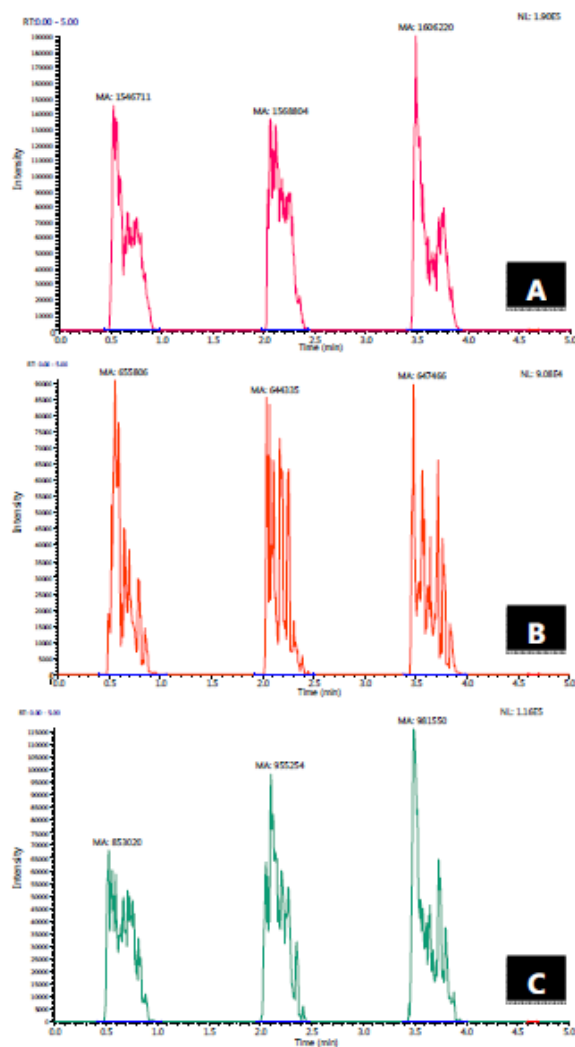


**Scheme 1** Experimental set up for SPME-TM extraction from complex matrices and desorption/ionization using DART-MS/MS.

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# SPME-TM-DART 高灵敏度DART定量

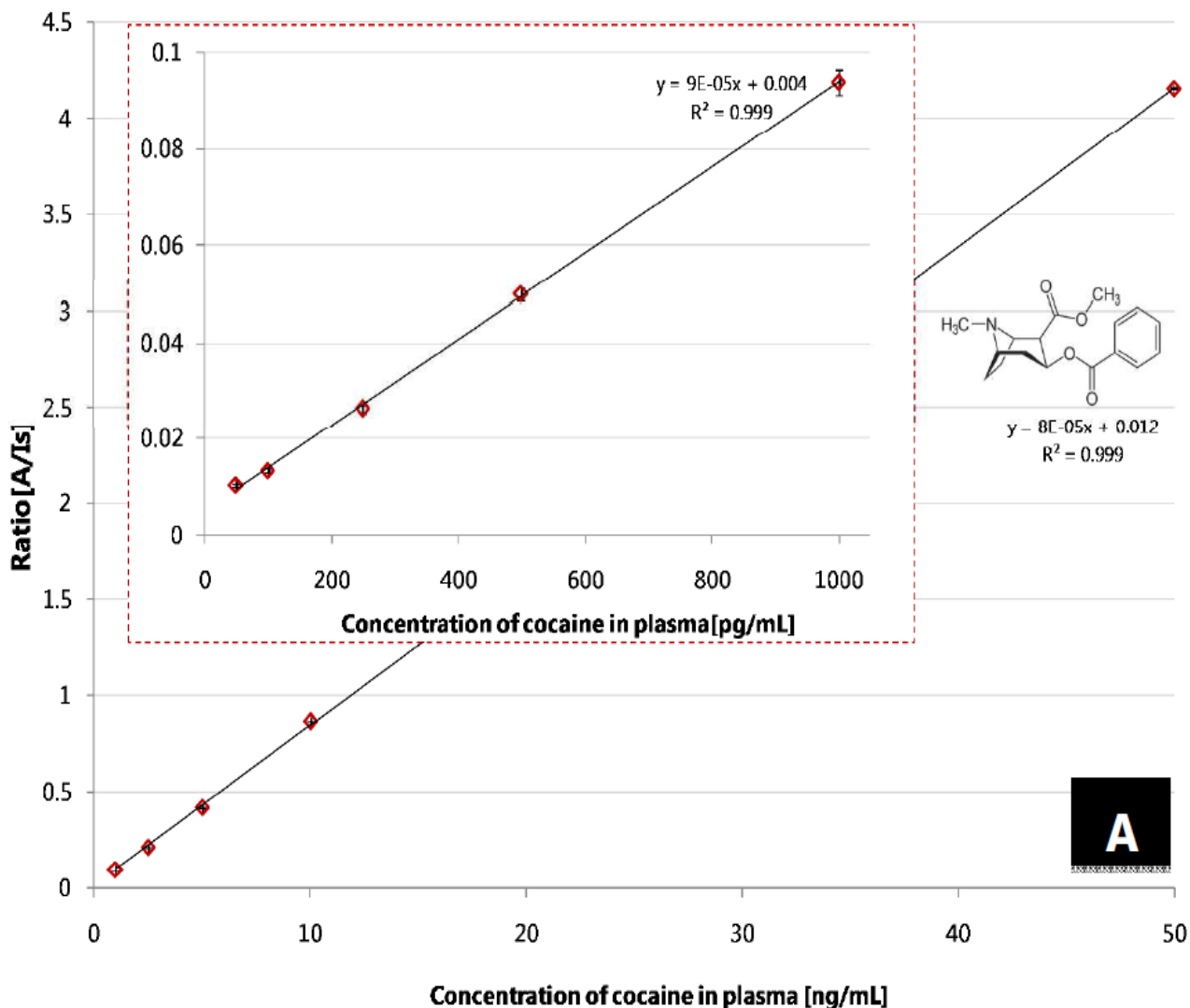


**Figure S9** Ion chromatograms of three controlled substances: heroin (**A**), propranolol (**B**), and stanozolol (**C**). 1 min extractions were performed using vortex agitator set-up at maximum speed (3200 rpm). Simultaneous extraction from 1.5 mL of PBS spiked with 20 ng mL<sup>-1</sup> of 21 substances described on **Table S2**. Analyses were performed using a Thermo TSQ on MRM mode.

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# SPME-TM-DART 高灵敏度DART定量



**Figure S7-1 A.** Quantitative analysis of plasma spiked with cocaine (50 pg mL<sup>-1</sup> to 50 ng mL<sup>-1</sup>) and its isotopomer [D3] cocaine (12 ng mL<sup>-1</sup>). **B.** Quantitative analysis of urine spiked with cocaine (50 pg mL<sup>-1</sup> to 50 ng mL<sup>-1</sup>) and its isotopomer [D3] cocaine (12 ng mL<sup>-1</sup>).

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Janusz Pawliszyn\*  
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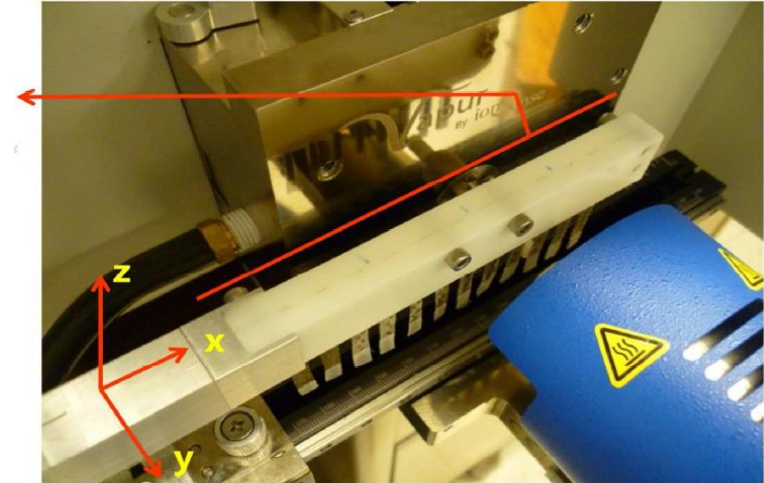
# SPME-TM-DART 高灵敏度DART定量

#	Compound name	Log P	Parent ion (m/z)	Product ion (m/z)	S-lenses	Collision energy	Polarity	LOD* (ppt)
1	Amphetamine	1.76	136.099	91.114	17	36	+	112
2	Methamphetamine	2.07	150.112	91.120	19	45	+	20
3	Nikethamide	0.33	179.100	108.102	18	76	+	17
4	Salbutamol	0.64	240.143	148.103	18	59	+	1474
5	Propranolol	3.48	260.123	116.138	17	89	+	31
6	Metoprolol	1.60	268.140	116.146	18	94	+	108
7	Trenbolone	2.27	271.133	165.106	56	97	+	31
8	Clenbuterol	2.61	277.068	203.049	15	70	+	13
9	Testosterone	3.32	289.157	97.123	21	91	+	10
10	Exemestane	3.70	297.173	121.118	19	72	+	17
11	Codeine	1.20	300.105	152.092	64	104	+	46
12	Cocaine	2.30	304.142	182.173	18	87	+	2
13	Bisoprolol	2.14	326.160	116.135	17	102	+	45
14	6-acetylmorphine	0.42	328.126	165.092	37	122	+	21
15	Stanozolol	5.53	329.229	81.108	44	130	+	22
16	Strychnine	1.93	335.155	184.129	36	136	+	33
17	6-acetylcodeine	2.08	342.124	165.092	45	165	+	7
18	Formoterol	2.20	345.133	121.090	32	85	+	831
19	Heroin	1.52	370.133	165.097	48	119	+	13
20	Toremifene	6.80	406.210	72.167	24	108	+	42
21	GW501516	6.29	454.091	257.068	29	108	+	352

**Table S3** MS/MS parameters used for the analysis of 21 WADA controlled substances in positive mode, as well as instrumental response of C18-PAN SPME-TM tandem mass spectrometry analysis. Integrated peak area obtained for a 20 ng mL<sup>-1</sup> solution in PBS. Average peak area (n=3). LOD\*, limit of detection estimated.

*Germán Augusto Gómez-Ríos and Janusz Pawliszyn\**  
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# Summary 总结



## Direct Analysis in Real Time

### DART 原位电离与实时直接分析

- **2-3 sec analyses time** 几秒钟定性定量
- **Fully automated** 自动、高通量
- **No sample prep** 无需样品制备
- **Nondestructive** 非接触、无损分析
- **Solvents friendly** 无溶剂效应
- **Salts compatible** 耐盐、无基质效应
- **Universal Ionization** 广谱、中能量电离

## Sensitive and Quantitative DART-MS

### 高灵敏度的 SPME 结合 DART 定量分析

- **3 min per sample** 几分钟定量
- **<5% RSD** 高通量、高精度
- **10-100 ppt LLOD** 检出下限在 ppt 级别
- **3-5 Orders Linearity** 线性范围宽
- **Compatible with all MS** 兼容
- **Comprehensive** 应用范围广谱
- **Simple and Fast** 实施简便、分析快速