The New Agilent 7200 Q-TOF for GC/MS

The benefits of accurate mass GC/MS for the analysis of targets and unknowns

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Content

- Product introduction – why a GC-Q/TOF?
- Features
- Instrumental aspects
- Benefits of accurate mass MS and MS/MS for Quantitative analysis
- Benefits of accurate mass MS and MS/MS for Qualitative analysis
- Conclusions and Summary
The Agilent Portfolio of Benchtop GC/MS Systems

5975E SQ
5975C SQ
5975T LTM SQ
7000 TQ
220 IT
240 IT

What’s next?
The New Agilent 7200 Series GC/Q-TOF

High Resolution, High Mass Accuracy, Fast Scanning and Sensitive GC-MS(MS)
What Will GC/Q-TOF Do For You?

- **TOF mode (full spectrum acquisition)**
  - High resolution full scan spectra
  - Accurate mass measurements
  - Fast scanning of full spectra

- **Q-TOF mode (MS/MS)**
  - Full spectrum of Product Ions (SIM-TOF)
    - With high resolution and accurate mass
  - Selectivity beyond any “triple quad” MRM method
    - Confirm TOF spectrum without interferences
  - High sensitivity structural elucidation tool

*Ideal tool for solving complex analytical problems*
GC/MS for Targets, Non-targets and Unknowns

- Targets, non-targets & unknowns
- Targets with higher sensitivity
- Targets with higher selectivity & sensitivity

SQ or IT: GC-MS scan → GC-MS SIM (SIS) → GC/MS/MS

TQ or IT
Why the Demand for High Resolution and Accurate Mass MS and MS/MS?

The Analytes Are the Same (MS or MS/MS)

Demand Is Driven by the MATRIX COMPLEXITY

High Res & MS/MS Increase Selectivity

Demand Is Driven by the ANALYSIS OF NON_TARGETS & UNKNOWNS

Accurate Mass, Especially with MS/MS, Greatly Facilitates Qualitative Analysis
GC/MS for Targets, Non-targets and Unknowns

Targets, non-targets & unknowns

Targets with higher sensitivity

Targets with higher selectivity & sensitivity

SQ or IT

GC-MS scan

GC-MS SIM (SIS)

GC/MS/MS

TOF has no SIM or SIS equivalent

TOF GC/MS ‘scan’

Q-TOF GC/MS/MS

Higher resolution
Accurate mass
Higher data rate
Better sensitivity

Product ion spectra
Higher resolution
Less sensitivity

Targets, non-targets & unknowns

Targets with higher selectivity & structural elucidation

Agilent Technologies
High Res Mass Spectrometry

The Agilent 7200 GC/Q-TOF is a high res instrument.

What does this mean?
Importance of Profile View for Mass Resolution

Most users view centroided spectra, but the MS operates in profile mode.
Zoom on MSD mass peaks: 0.1 u steps

Baseline resolution between m/z 614 and 615 not quite achieved
Similar plot from 7200 Q-TOF . . .

As high resolution holds great benefit for GC separations . . .

High resolution hold benefits for mass spectra . . .
Resolving Power & Mass Accuracy

Resolving Power:
\[ R = \frac{m_z}{\text{FWHM}} \]

Mass Accuracy:
\[ \Delta m_z = \frac{d_m}{m_z} \times 10^6, \text{ parts per million (ppm)} \]

PFTBA mass 614
C12F24N=613.964203

\[ R = \frac{614}{0.68} = 903 \]
\[ \Delta m_z = \frac{0.1}{614} = 160 \text{ ppm} \]

\[ P_w = 0.68 \]

\[ R = \frac{614}{0.0423} = 14522 \]
\[ \Delta m_z = \frac{0.0004}{613.96} = 0.7 \text{ ppm} \]
Comparing Quad & TOF

Quads operate with constant peak-width (Resolving Power changes with mass)

TOF has constant Resolving Power (peak-width changes with mass)
High Res TOF to increase mass selectivity
Appears as **Single** 240 u Mass Peak for Any Unit Mass Resolution MS

\[ \Delta m/z = 0.0433 \]

Flurenol methyl ester
\[ m/z = 240.0781 \]
Mass error = 1.7 ppm

Dimetilan
\[ m/z = 240.1217 \]
Mass error = 0.4 ppm

\(~13,500\) resolution FWHM
No Internal Reference Mass (IRM) corrections applied
TOF Accurate Mass to Eliminate Matrix Interferants

Okra QuEChERS Extract
Matrix interferant ion (b-Tocopherol)  
150.06839 Da
Analyte Indoxacarb ion (100pg)  
150.01195 Da (fragment ion)

$\Delta m = 0.05644$ Da.

If even more selectivity is needed, option of MS/MS MS/MS with high resolution and accurate mass!
Let’s have a look at the system first

It’s our newest GC/MS . . . built upon many well proven parts:

Almost one thousand 7000 TQs
Over one thousand 6500 TOFs and Q-TOFs
Many thousand 7890 GCs
GC/Q-TOF: Combining 7000 & 6500 Technologies

- Increased selectivity from accurate mass measurements
- Rapid screening of targets with high data rate MS
- Structural elucidation of unknowns by MS/MS

**Target applications:** Metabolomics, Natural Products, High End Research, Environmental/Food contaminants screenings, Doping control, Petrochemical
The merging of two platforms
7200 Q-TOF Component

NEW Removable Ion Source

7000B TQ

NEW Optics

6500 Q-TOF

Four stages of pumping

Two 300 L/s Turbos
New GC/Q-TOF System . . . Yet Totally Proven

**4GHz ADC electronics** enable a high sampling rate (32 Gbit/s) which improves the resolution, mass accuracy, and sensitivity for low-abundance samples. Dual gain amplifiers simultaneously process detector signals through both low-gain and high gain channels, extending the dynamic range to 105.

**Dual-stage ion mirror** improves second-order time focusing for high mass resolution.

**Proprietary INVAR flight tube** sealed in a vacuum-insulated shell eliminates thermal mass drift due to temperature changes to maintain excellent mass accuracy, 24/7. Added length improves mass resolution.

**Analog-to-digital (ADC) Detector:** Unlike time-to-digital (TDC) detectors which record single ion events, ADC detection records multiple ion events, allowing very accurate mass assignments over a wide mass range and dynamic range of concentrations.

**New Internal Reference Mass** can be delivered to the source at a low and high concentration for mass axis “locking” and mass correction.

**Two 300L/s turbos** pump the focusing optics and flight tube.

**Split-flow turbo** differentially pumps the ion source and quadrupole analyzer compartments.
Removable Ion Source (RIS)
30 Minute Source Swap with RIS

Manual Steps – Automated Steps

Install extraction tool
  Rinse the chamber with nitrogen
  Pump out chamber
  Open gate valve/retract transfer line
Withdraw source into chamber
  Close gate valve/re-engage transfer line
  Vent chamber and cool ion source
Open chamber
Replace/maintain source components
Close chamber
  Rinse chamber & new source with N₂
  Pump out chamber
  Open gate valve/retract transfer line
Insert source into the manifold
  Close gate valve/re-engage transfer line
  Pressurize the chamber
Remove extraction tool
Load appropriate tune (heat source)
Removable Ion Source (RIS)

- RIS Standard on Q-TOF
- Allows fast EI/CI source swapping without venting
- Allows swap of complete ion source, including filaments, in ~30 minutes without venting

• video
Internal Reference Mass (IRM)

- Engineering goal: minimize source of drift
  - Proprietary INVAR flight tube
    - Sealed in a vacuum-insulated shell eliminates thermal mass drift due to temperature
  - IRM correction often not needed
    - IRM ions may be an interference with analyte ions
- Proprietary IRM delivery system is “backup” correction
  - “Locks” mass axis to known background ions
    - Tris(pentafluoroethyl)-s-triazine
  - “On the fly” mass axis correction
## IRM correction example

Mass accuracy of 2-formyl thiophene and 2-acetyl thiazone in spiked Whiskey

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<th>2-formyl thiophene</th>
<th>2-acetyl-thiazole</th>
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<td>Average ABS Error</td>
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<td>Good: &lt; 10 ppm</td>
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<tr>
<td>Excellent: &lt; 5 ppm</td>
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<td>Good: &lt; 10 ppm</td>
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Average mass error < 2 ppm over X1000 concentration range
Large dynamic range detection system
ADC is important for chromatographic peaks

ADC has greater linear range and is quantitation over a larger concentration range.

TDC has limited linear range and is quantitative over a small concentration range.
Response linearity and mass accuracy

ADC advantages

5 Hz acquisition, RIS

LOD about 0.01 pg
What about TOF SPEED?

TOF always collects full mass range
Q-TOF always display full product ion spectrum

• Spectral Rate:
  • Typical max rate: 25-200 spectra/sec (Hz) to disk
  • Usable rate is limited by signal level (ion count)
• New analysis opportunities for GC/MS:
  • Fast GC and Ultra high resolution GC: ~ 20-40Hz
  • GCxGC: ~50-200 Hz
What about TOF SPEED?

Is high speed always better?

Speed may effect:

Sensitivity
Mass accuracy
Mass Stability
Data file size and data processing
And what about *Q-TOF Speed*?

- Typical file sizes for pesticide analysis
  - MSD SIM – 0.8-1 MB/18-min run
  - MSD scan – 3-5 MB/40-min run
  - TQ MRM – 5 MB/20-min run
  - TQ scan – 8 MB/20-min run
  - IT MS/MS – 2.5 MB/45-min run (99 compounds)
- **TOF or Q-TOF Typical run**
  - 800-1200 MB/20-min run at 5 Hz, profile
  - Centroid only reduces 5-10X

*Note: File size depends on the threshold, number of target compounds, number of masses/compound, and runtime etc.*
## GC/Q-TOF vs GCxGC/TOF

### GC/Q-TOF

- 3 stages selectivity
- Best chemical noise reduction
- Requires MS method set-up
- Conventional software
- Added value to structural elucidation:
  - 1-1 correlation precursor-product
  - neutral loss
  - Bonding strength correlated to CID voltage
- Suited for qualitative and quantitative analysis
- Use of deconvolution software to compensate for lacking chromatography

### GCxGC/TOF

- 3 stages of selectivity
- Moderate chemical noise reduction
- Requires GC method set-up
- Dedicated software
- Added value to chemically similar components
- Quantitation is more difficult

There are more differences, like robustness, data file size, sensitivity
High data rate = better deconvolution

Time

Slow data rate will not pick each peak apex

Time

Fast data rate will allow deconvolution of closely eluting peaks
High data rate = better deconvolution

The 7200 Q-TOF in TOF mode will have:

- Faster Data Rates
- Maintain Excellent S/N
- New MassHunter Deconvolution

Time

Slow data rate will not pick each peak apex

Fast data rate will allow deconvolution of closely eluting peaks
GC/Q-TOF Performance Specifications

- Resolving Power: > 12.5K at m/z 272
  - 13K to 15K typical
- Mass Accuracy: < 5 ppm at m/z 272
  - < 2 ppm typical
- MS Sensitivity >400:1 at m/z=272
- MS/MS Sensitivity is between SRM and Product Ion scan of a Tandem Quad MS
- Dynamic Range: 3-5 orders of magnitude
- Quad Mass range: 20-1050 Da (0.7-4.0 Da FWHM)
- TOF Mass range: 20-1700 Da
- Spectral Rate: up to 50 Spectra/sec
Quantitative Analysis

Target Confirmation and Selectivity of MS/MS
Pesticides in Okra Extract - TIC

1uL cold splitless injection
Internal Reference Mass Correction in Matrix
10 ppb pesticides in Okra extract

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<tr>
<th>Analyte</th>
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<th>Measured Accurate Mass (Da)</th>
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Quantification with excellent selectivity and confirmation

No IRM, -5.8
IRM, 2.5

Measured Accurate Mass and Mass Error (ppm)
Reduction of Matrix Interferences

Fludioxonil in Frozen Blueberry Extract, incurred 38 ppb in extract

- EIC: 248.0392 +/- 0.5 Da
  - Signal/Noise = 108

- EIC: 248.0392 +/- 10 ppm
  - Signal/Noise = 1154

[Graph showing TIC, EIC, and signal/noise ratios]
Low Concentration Analytes in Heavy Matrix

EIC (Leek extract)

drins 10 pg
262.8564 ±0.5 Da

drins 10 pg
262.8564 ±20 ppm

aldrin
isodrin
dieldrin
endrin

Data courtesy of Hans Mol, Rikilt Institute of Food Safety
Why Add ‘Q’ to TOF to Make Q-TOF?

Sometimes the combined power of GC Resolution (Agilent) + MS Resolving Power (Agilent)
Why Add ‘Q’ to TOF to Make Q-TOF?

Sometimes the combined power of GC Resolution (Agilent) + MS Resolving Power (Agilent) is not enough based upon:

Small ΔMass Defect (Nature) + Intense Matrix Ions (Sample)

Add ‘Q+CID’ to TOF solution

High resolution MS/MS can solve some of these problems
For Targets: Where and why is MS/MS Used?

- When high res TOF still has interferences
- 3 stages of selectivity
- Best chemical noise reduction
- Conventional software for qualitative and quantitative analysis
- Better Confirmatory data for identified targets
Qualitative Analysis

• What about non-targets and unknowns?
  • When no spectral / library match is seen
  • Or too many library matches
  • Or not confirmatory enough
Many possible formulas with an MSD or IT
But only a few with TOF

Possible Number of Chemical Formulas at m/z 272

Accurate mass reduces risk of investing effort on the wrong molecule

Formulas made of: C, H, N, O, F, & Cl

Octafluoronaphthalene (CAS 313-72-4)

C\textsubscript{10}F\textsubscript{8} = 271.98667

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In-built Formula Calculator in MassHunter

Determine all possible molecular ion or fragment ion formulas consistent with the measured mass and compare it with the calculated exact masses in order to known elemental compositions.

<table>
<thead>
<tr>
<th>Formula (M)</th>
<th>Score</th>
<th>m/z (Calc)</th>
<th>Diff (ppm)</th>
<th>DBE</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7H2Cl5</td>
<td>100</td>
<td>260.859365</td>
<td>-1.67</td>
<td>4.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C7Cl4[37Cl]</td>
<td>98.26</td>
<td>260.840765</td>
<td>72.97</td>
<td>5.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C10H14Cl4</td>
<td>97.54</td>
<td>260.882687</td>
<td>87.74</td>
<td>8.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C4H3Cl5</td>
<td>97.35</td>
<td>260.836043</td>
<td>-91.07</td>
<td>0.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C6H8Cl2[37Cl]3</td>
<td>93.61</td>
<td>260.897465</td>
<td>144.39</td>
<td>0.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C4H2Cl6</td>
<td>82.06</td>
<td>260.817443</td>
<td>-162.38</td>
<td>1.5</td>
<td>260.8598</td>
</tr>
<tr>
<td>C3H2Cl7</td>
<td>84.93</td>
<td>260.817443</td>
<td>-162.38</td>
<td>8.5</td>
<td>260.8598</td>
</tr>
</tbody>
</table>

The calculated m/z for the proposed formula C7H2Cl5 is 260.859365 with a difference of -1.67 ppm.
## Fragment Ion Mass with High Mass Accuracy

Helps unambiguously identify fragment ions

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>m/z</th>
<th>Formula</th>
<th>Calculated Molecular Ion</th>
<th>Measured Fragment Ions</th>
<th>Measured Fragment Ions</th>
<th>Measured Fragment Ions</th>
<th>Measured Fragment Ions</th>
<th>Δ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos -methyl</td>
<td>320.8944</td>
<td>C7H7Cl3NO3PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C7 H7 Cl [37Cl] N O3 P S</td>
<td>0.0</td>
<td>C7 H7 Cl2 N O3 P S</td>
<td>0.0</td>
<td>C2 H6 O2 P S</td>
<td>215.4</td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>219.9454</td>
<td>C4H7Cl2O4P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C4H7ClO4P</td>
<td>-0.9</td>
<td>C2H6O3P</td>
<td>3.7</td>
<td>C4 H7[37Cl] O4 P</td>
<td>336.5</td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>419.8112</td>
<td>C9 H6 Cl6 O4 S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C9 H6 Cl4[37Cl] O4 S</td>
<td>-0.7</td>
<td>C5 Cl5[37Cl]</td>
<td>0.0</td>
<td>C5 Cl4[37Cl]2</td>
<td>-220.9</td>
</tr>
<tr>
<td>Propachlor</td>
<td>211.0758</td>
<td>C11 H14 Cl N O</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C10 H11 Cl N O</td>
<td>1.1</td>
<td>C11 H14 N O</td>
<td>1.8</td>
<td>C8 H8 Cl N O</td>
<td>-3.9</td>
</tr>
<tr>
<td>Fluazifop-p-butyl</td>
<td>383.1339</td>
<td>C19 H20 F3 N O4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C19 H20 F2 N O4</td>
<td>-1.1</td>
<td>C14 H11 F3 N O2</td>
<td>-1.3</td>
<td>C12 H7 F3 N O</td>
<td>771.6</td>
</tr>
<tr>
<td>Triazophos</td>
<td>313.0645</td>
<td>C12 H16 N3 O3 P S</td>
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<td></td>
<td></td>
<td></td>
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<td>-1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C10 H12 N3 O3 P S</td>
<td>-2.7</td>
<td>C8 H8 N3 O3 P S</td>
<td>-0.6</td>
<td>C8 H7 N3 O</td>
<td>-494.2</td>
</tr>
</tbody>
</table>

Examples from building accurate mass pesticide library
NIST 2011 MS Interpreter with Accurate Mass
Software tools

NIST MS Interpreter (and MassHunter) tools to make routine operations easier

The most useful tools are:

• Empirical formula generator from measured mass with mass error estimates
• Isotopic abundance calculator
• Automatic listing of neutral losses and their empirical formulas
• Automatic listing of empirical formulas for each mass fragment

NIST MS Interpreter has some of these.
LC MassHunter has some of these and most are planned to be in GC MassHunter.
Where and how is MS/MS Used?

- To improve selectivity
  - When high res TOF still has interferences

- Structural elucidation from product ion spectra using high resolution and accurate mass

- Higher level of Confirmation for an identified unknown
  - Structural Elucidation from product ion spectra using high resolution and accurate mass
  - Start will full scan EI spectrum
  - Use CID on each fragment mass to confirm structure of fragment
    - Select Fragment 1 to be precursor 1 → Product ions
    - Select Fragment 2 to be precursor 2 → Product ions
Benefits of MS/MS for Structure elucidation

Ion molecular formula confirmed by accurate mass

Precursor-product ion relationship is documented with much better 1-to-1 correlation than fragments in an EI spectrum

Neutral losses confirmed by accurate mass

Bonding strength info vs CID voltage

Requires multiple analyses and much more sensitive than NMR
Will not replace NMR, but will complement nicely
**MS/MS product ion mass with high mass accuracy**

Helps unambiguously identify product ions

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>m/z</th>
<th>Formula</th>
<th>Fragment Ions 1</th>
<th>Fragment Ions 2</th>
<th>Fragment Ions 3</th>
<th>Fragment Ions 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos-methyl</td>
<td>320.8944</td>
<td>C7H7Cl3NO3PS</td>
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</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>419.8112</td>
<td>C9 H6 Cl6 O4 S</td>
<td>-2.1 C9 H6 Cl[53Cl] O4 S</td>
<td>-0.7 C5 Cl5[37Cl]</td>
<td>0.0 C5 Cl4[37Cl]2</td>
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</tr>
<tr>
<td>Propachlor</td>
<td>211.0758</td>
<td>C11 H14 Cl N O</td>
<td>-1.0 C10 H11 Cl N O</td>
<td>1.1 C11 H14 N O</td>
<td>1.8 C8 H8 Cl N O</td>
<td>-3.9 C6 H5</td>
</tr>
<tr>
<td>Fluazifop-p-butyl</td>
<td>383.1339</td>
<td>C19 H20 F3 N O4</td>
<td>-2.2 C19 H20 F2 N O4</td>
<td>-1.1 C14 H11 F3 N O2</td>
<td>-1.3 C12 H7 F3 N O</td>
<td>2.1 C6 H3 F3 N</td>
</tr>
<tr>
<td>Triazophos</td>
<td>313.0645</td>
<td>C12 H16 N3 O3 P S</td>
<td>-1.4 C10 H12 N3 O3 P S</td>
<td>-2.7 C8 H8 N3 O3 P S</td>
<td>-0.6 C8 H7 N3 O</td>
<td>-1.9 C8 H8 N3 O</td>
</tr>
</tbody>
</table>

Examples from building accurate mass pesticide library
Key Features of the 7200

1. Internal Reference Mass for routine sub 5ppm mass accuracy even in heavy matrix
2. Removable Ion Source for quick source cleaning, filament replacement and EI/CI swapping without breaking vacuum
3. Q-TOF MS/MS:
   • Chemical noise reduction
   • Selectivity
   • Structural information
   • Method development
4. Software tools – formula calculator
Summary

• The world about us is always changing and new problems are always emerging
• New problems often require new tools to find a solution
• The GC/Q-TOF offers capability to solve new problems in new ways
• Higher resolution (HR), better mass accuracy (MA), and faster scan speed always improves analytical results with improved selectivity and sensitivity
• Add High Res and Accurate Mass to MS/MS product ions and structure elucidation is possible

Thus more confirmatory data

• Agilent offers the largest range of GC/MS tools – SQ, IT, TQ, & Q-TOF
7200 Series Q-TOF for GC/MS
A new analytical tool for solving complex analytical problems

Thanks to

Terry Sheehan,
Agilent GC/MS Marketing Manager, USA

Sofia Aronova,
Agilent GC/Q-TOF Application Chemist, USA

Hans Mol
RIKILT, NL

Nobuo Ochiai and Kikuo Sasamoto
Gerstel, Japan