About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Pharma scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

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Analytical Methodology Centre

Recent Advances in the Applications of Chromatography-Mass Spectrometry to Environmental Matrix Analysis

Peter J Baugh

Coordinator of the EMSSIG

(The BMSS)

www.analyticalmethodologycentre.co.uk

BMSS
BRITISH MASS SPECTROMETRY SOCIETY

Analytical Methodology Centre

Typical Range of Applications (taken from 1)

1. **GC/MS: A workhorse of modern environmental analysis**
2. **LC/MS- Qualitative/quantitative analysis of environmental pollutants**
3. **MS/MS Approaches for the analysis of environmental pollutants**
4. **Informatics & mass spectral data bases in evaluation of environmental mass spectral data**
5. **Advanced methods for GC/MS including GC/GC/MS**
6. Ambient MS- environmental analysis without sample preparation.
7. Desorption electrospray MS
8. Miniaturised MS for environmental analysis Graham Cookes, Purdue University
9. ICPMS in environmental analysis
10. MS- role in studies of VOPs
11. MS- ID & quantification of toxicologically important drinking water disinfection by-products
12. **Emerging contaminants in the environment**
13. **Pesticide residue analysis by GC & LC/MS**
14. **Analysis of persistent halogenated compounds- DBDs & DBFs**
15. MS of Atmospheric aerosols
16. MS in the study of interactions of environmental pollutants with DNA
17. Petroleomics- complex organic mixtures using FTICR MS
18. Ultrahigh resolution FTICR for the analysis of natural organic matter
19. MS Imaging in environmental science
20. ICR MS, e.g., earth sciences

***1. Comprehensive Environmental Mass Spectrometry,* Advances Topics in Environmental Science, Albert T. Lebedev, ed. (2012), ILM Publications (St Albans, England ; Glerndale, AZ, USA),**

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Schedule of Presentation

1. Introduction
2. 3. 4. & 5 Sample Preparation ; yes or no matrix dependent
6. Chromatography – GC, LC
7. & 8. Mass Spectrometry – ionisation and analyser functions
9. & 10. LRMS & HRMS exemplified ; other instrumentation used
11. Applications Illustrated
12. Data System Software Capability exemplified

The focus is on selected examples of GLC & HPLC with LRMS and HRMS. There is insufficient time available to review extensively this extremely large field of analysis. Several areas are highlighted to illustrate the power and capability of the instrumentation and options available to the environmental analyst.

Sound bites and snapshots of the recent advances.

1. Introduction- general comments

The ever increasing sophistication in instrumentation means yesterday's data can be somewhat obsolete and there is continuing need to refine acquired information. Particularly, important are the sensitivity, specificity and detection limits obtainable, which enable ever decreasing levels of pollutants to be detected, and quantified. Also the regulations on permissible levels are ever-changing in parallel.

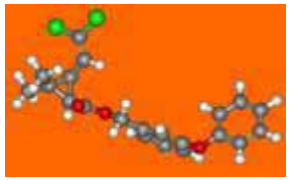
It is important to emphasise where the problems lie in relation to ensuring that the data obtained reflect accurately the integrity of the sample and what it originally contained. It is not a case hopefully, of **GI & GO** as it has frequently been when characterising a complex polluted sample. Remember what occurred in 1976 when the first packed column GC/MS analysis attempted by the EPA (USA) where the introduction of one dirty sample totally clogged up the instrument, even though GC/MS was selected as the facility of choice for environmental analysis.

To this end the introduction of the sample-
front end, through **separation & analysis** to the **back end- data acquisition, handling and processing** must be considered in sequence and integrally.

1. Introduction- Sample analysis regime

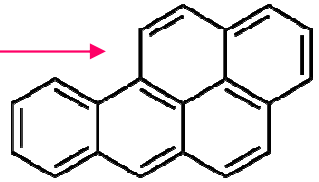
A Simple Flow Diagram of the Process for Environmental Matrix Analysis

1. Sample matrix from the environment (preservation of sample integrity)
2. sample preparation (liquid or solid dependent)
3. sample clean-up (clean or contaminated sample dependent)
4. sample introduction (physico-chemical property dependent- finite vapour pressure, involatile, labile, neutral or polar)
5. Sample analysis - selection of chromatography (physico-chemical property dependent as above)
6. Sample analysis – selection of MS ionisation & analyser with options
7. Analysis of data – identification- ms database search, mass accuracy (elemental composition & structure) & quantitation including calibration



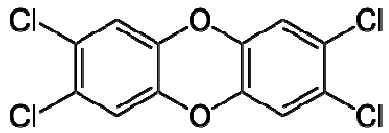
Chemical Pollutants Exemplified

- Priority Pollutant list (EPA) – PAHs,



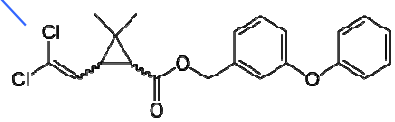
benzo-a-pyrene

Dioxins

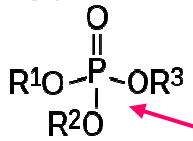


2,3,7,8, TCDD

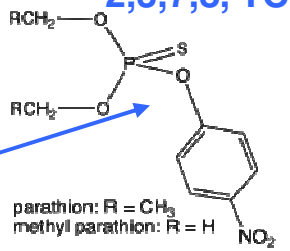
- Pesticides



Pyrethroid- permethrin

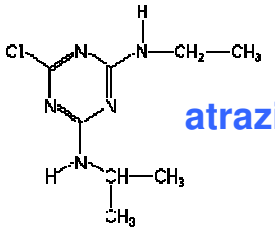


organophosphate structures



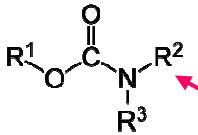
carbaryl

- Herbicides

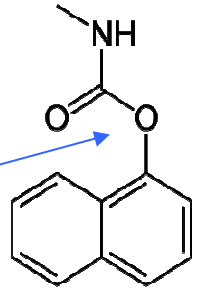


atrazine

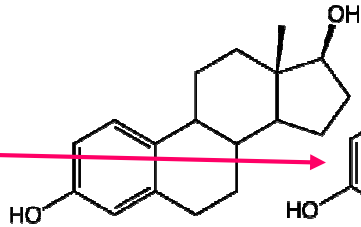
- Insecticides



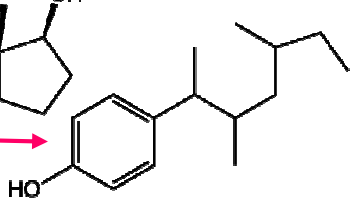
carbamate structures



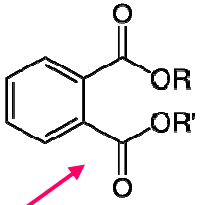
- Emerging Contaminants including Endocrine disruptors



Oestradiol



Nonylphenol



phthalate

2. Sample Preparation

It may be that sample preparation still commands as important a place as ever in the analysis when taking a finite amount of the raw matrix through a number of stages to obtain the final residue in a specific volume, in which extraction, separation via RP and NP column chromatography modes with the addition of standards (isotopically labelled) having the same chemistry as the target compounds are involved.

A good example of the rigour required is in the sample preparation and work up for dioxin analysis

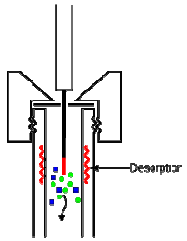
There has been a strenuous effort to render sample preparation largely unnecessary but a considerable element of clean up still remains. The availability of high resolution MS/MS which allows an increase in specificity can largely remove the need for matrix treatment thus avoiding the ever present problem of false positives. Limitations here can revolve around the number of MS/MS ion programs (precursor to product ion transitions) that can be accommodated when confronted with a multi-component mixture. Obviously MS/MS LRMS is of less value for unknown components.

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3. Sample Preparation methods

Sample preparation can be conducted off-line or on-line depending on the nature of the matrix and the extent to which clean-up and concentration are Required.

Off-line or On-Line ?
Essentially, the extent to which sample preparation is necessary from the raw matrix depends on the physical nature, liquid or solid (or gaseous atmosphere).



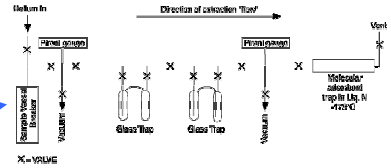


On-Line SPME

Water as a matrix (river system/effluent) can be solvent (LLE) or solid phase extracted (SPE) and the resulting sample pre-concentrated prior to analysis.

Large volume Injection (& headspace) is also possible for a water based matrix (direct or on-line preconcentration injection)

SolidPhaseMicroExtraction can be conducted off-line or on-line. (VOCs & SVOCs)
Purge & trap for HVOCs can be conducted on-line (lost in LLE).



Purge & Trap

Soil or fly ash as matrix may be solvent extracted (direct, soxhlet or microwave digestion) but the resultant liquid will require extensive clean-up involving a number of steps (classic case- dioxins) PFE can replace soxhlet extraction
Note: Fauna & flora also will require a similar sample treatment



Microwave digestion/extraction

SPME Oct 1, 2012 By: John Hinshaw LCGC EUROPE Volume 25, Issue 10, pp. 570-575

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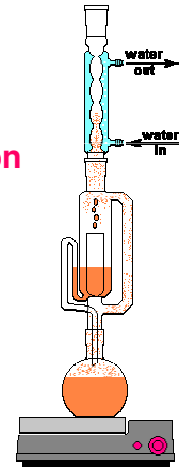
4. Sample Clean up exemplified

Clean waters relatively free of particulates can be filtered through solid-phase extraction (SPE) discs that, for example, quantitatively retain dioxins & furans. The EPA Methods 8260 and 8270 are the basis of the sample preparation for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and PCBs in surface and ground water.

Typical sample clean-up for Dioxins & Furans Analysis post soxhlet extraction

- Removal of lipids by sulphuric acid treatment
- Removal of interfering components by acidic/basic silica gel
- Separation of PCBs and similar interferences by activated alumina
- Separation of non-planar molecules by activated charcoal

Basic Soxhlet extraction unit ; automated multi-extraction systems are available.

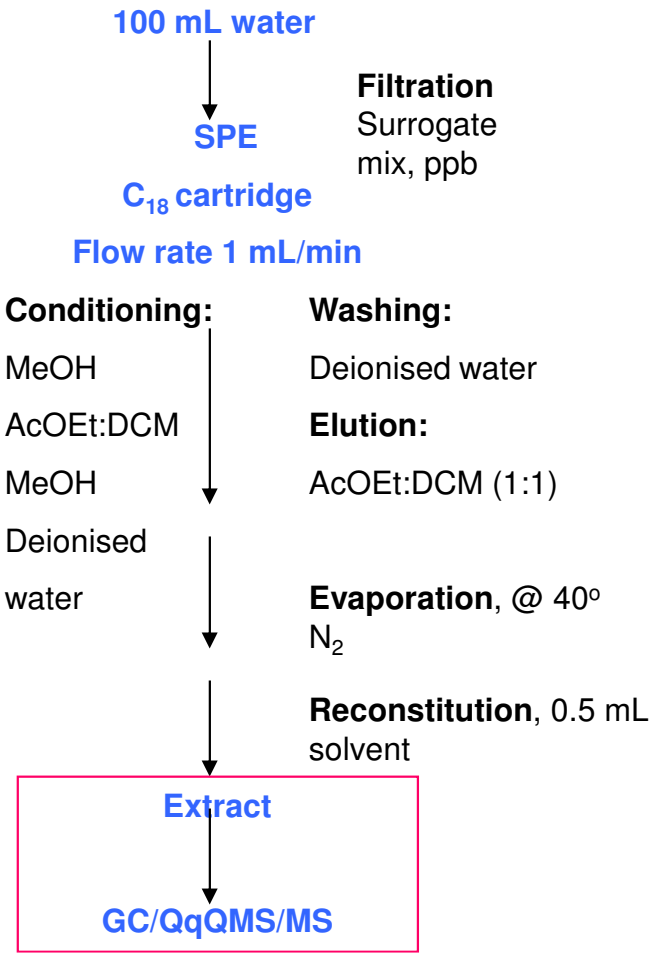


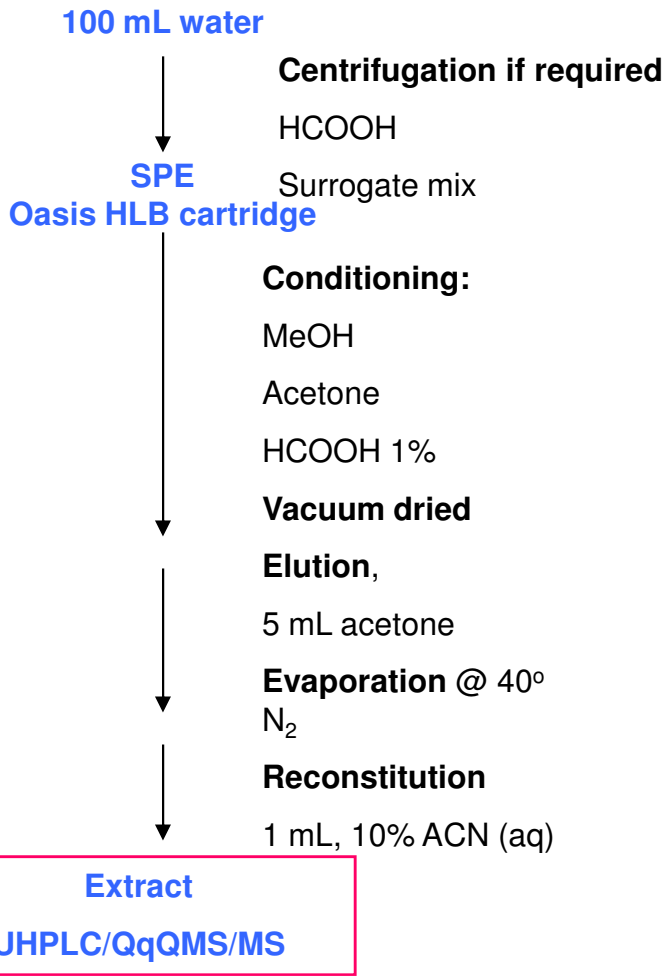
Pressurised fluid extraction (PFE) recently introduced requires less solvent use and reduced extraction time (EPA method 3545).

See later for details of GC/HRMS for ultra-trace analysis

4. Sample Treatment/Clean up exemplified

Flow Diagrams for the determination of pesticides in water





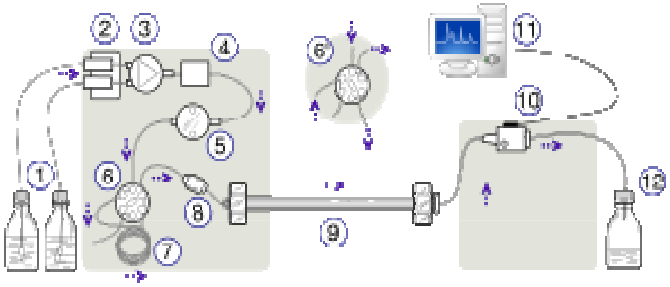
For examples see 11. Applications illustrated, later

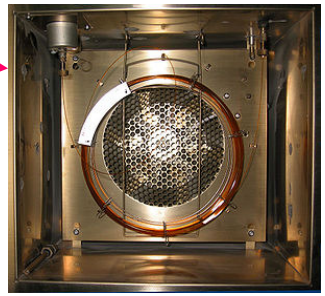
5. Sample Preparation, Injection Modes & Instrument Alternatives

Matrix	Extraction	Clean-up	Injection Modes	Instrument Alternatives/preferences	
water	LLE/SPE	No (Preconcent-ration)	Automated On-line SPME Purge & Trap or Headspace	**LC/MS-** Q, QqQ, TOF, QTOF SIM,MS/MS,MRM	**GC/MS** IT, Q, QqQ, TOF, QTOF SIM,MS/MS,MRM
waste water	LLE/SPE	Yes (Preconcent-ration)	Automated On-line SPME Purge & Trap or Headspace	Q, QqQ, TOF, QTOF SIM,MS/MS,MRM	IT, QMS, QqQMS, TOF, QTOF SIM/ MRM
Soil sediment	Soxhlet PFE	yes	Automated Injection, (headspace for HVOCs)	QqQ QTOF	GC/HRMS) SIM (dioxins)
Flyash (Incinerator)	soxhlet PFE	yes	Automated injection	QqQ MS/MS	GC/HRMS SIM (dioxins)
Pressurised fluid extraction (PFE) recently introduced requires less solvent use and reduced extraction time (EPA method 3545).					
Comments				MS/MS more selective for CDDs/CDFs than PCBs	10,000 resoluion in SIM

6. Chromatography

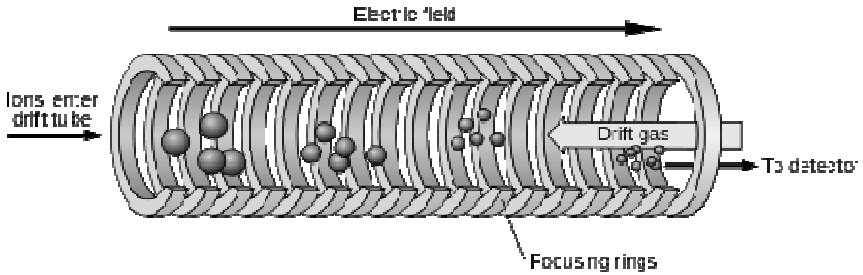
- **Capillary GLC: c.30-40% of pollutants with finite vapour pressures (including GC x GC, heart cut variations). Fast GC (MS) is capable of reducing analysis times by a factor of 3 - 10 using small diameter thin film capillary columns typically- 20 m x 0.15 mm i.d. x 0.12 µm film but with reduced sample capacity.**
- **HPLC/UHPLC: non-volatile, semi & polar pollutants**





Ultra high-performance liquid chromatography, UHPLC, uses columns packed with porous sub-2-µm particles (usually 1.8 µm) to vastly increase throughput and resolving power compared to conventional 5-µm columns (P ≤ 19000 psi). Important to avoid column overload.

- **IMS- Ion mobility coupled to MS**



$$K = \frac{3}{16}\sqrt{\frac{2\pi}{\mu kT}}\frac{Q}{n\sigma}$$

Ion mobility equation.

$$R = \frac{t}{\Delta t} = \sqrt{\frac{LEQ}{16kT\ln 2}}$$

Resolving power of drift tube

- **SFC: volatile & non-volatile (with polar additive to SF stream) not discussed**

6. Chromatography- GLC or HPLC & UPLC?

HPLC in gradient elution mode is increasingly used for Environmental Analysis with increase in elution strength of the solvent during separations to allow analysis of the more retained molecules.

LC/MS can be used for Environmental Analysis in many instances but GC/MS is still preferred for dioxin analysis.

Whereas coupling of capilllary GC to MS is relatively simple LC is more challenging for several reasons:

- Gas phase ions are required to be generated from either solvated molecules or ionised in liquid mobile phase. Nebulisation, desolvation, ionisation processes occur in the MS source at atmospheric pressure – API
- Ions formed in the source should be transferred efficiently into the optics of the MS while eliminating the huge volume of gas produced by evaporation of the MP
- Neutral compounds as contaminants should be eliminated as far as possible.

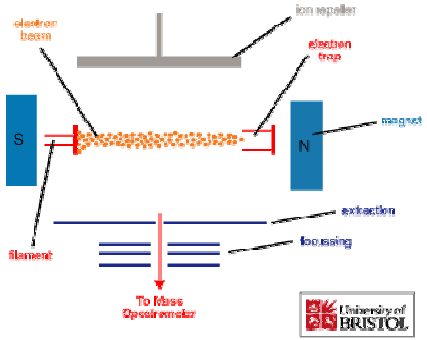
API covers a number of ionisation processes, which are soft ionisation modes unlike EI for GC/MS (Note though enhanced M+ applying lower ionisation energy for EI for GC x GC TOF without reduction in sensitivity)

Atmospheric Pressure Ionisation, API, APCI, APPI

Electrospray ESI, DESI

7. Ionisation/Scan Mode of choice

•EI full scan for ms data base search ; SIM for selected ion monitoring & higher levels of detection (GC-MS)



$AB + e^{-*} \rightarrow A^+ + B^- + e^-$

$AB + e^{-*} \rightarrow A^+ + B^* + 2e^-$

} fragment ion formation

$AB + e^{-*} \rightarrow [AB^{+**}] + 2e^-$

radical molecular ion formation

$[AB^{+**}] \rightarrow AB^{+*}$

$[AB^{+**}] \rightarrow$ secondary fragmentation

•EI/CI with MS/MS for M+ and precursor to product ion transition monitoring MRM

(a) $CH_4 + e^{-*} \rightarrow CH_4^{+*} + 2e^-$ methane molecular ion formation

(b) $CH_4^{-*} + CH_4 \rightarrow CH_5^+ + CH_3^*$ carbocation formation

(c) $CH_5^+ + AB \rightarrow CH_4 + [AB+H]^+$ protonated analyte formation

(d) $CH_4^{-*} \rightarrow CH_3^+ + H_2$ alternative carbocation formation

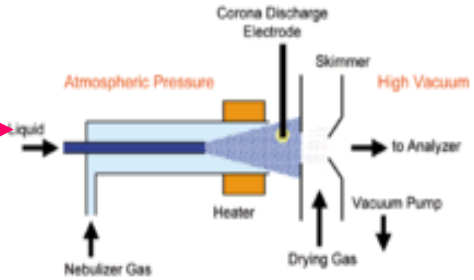
(e) $CH_3^- + M \rightarrow CH_4 + [AB-H]^+$ alternative analyte ion formation

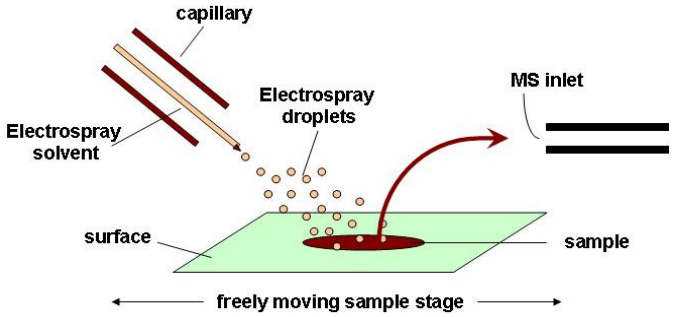
(f) $CH_5^* + CH_4 \rightarrow C_2H_5^* + H_2$ side reaction carbocation formation

(g) $C_2H_5^+ + AB \rightarrow [AB+C_2H_5]^+$ analyte adduct ion formation

DESI

•API/APCI with LC-MS/MS for M+ or M.-



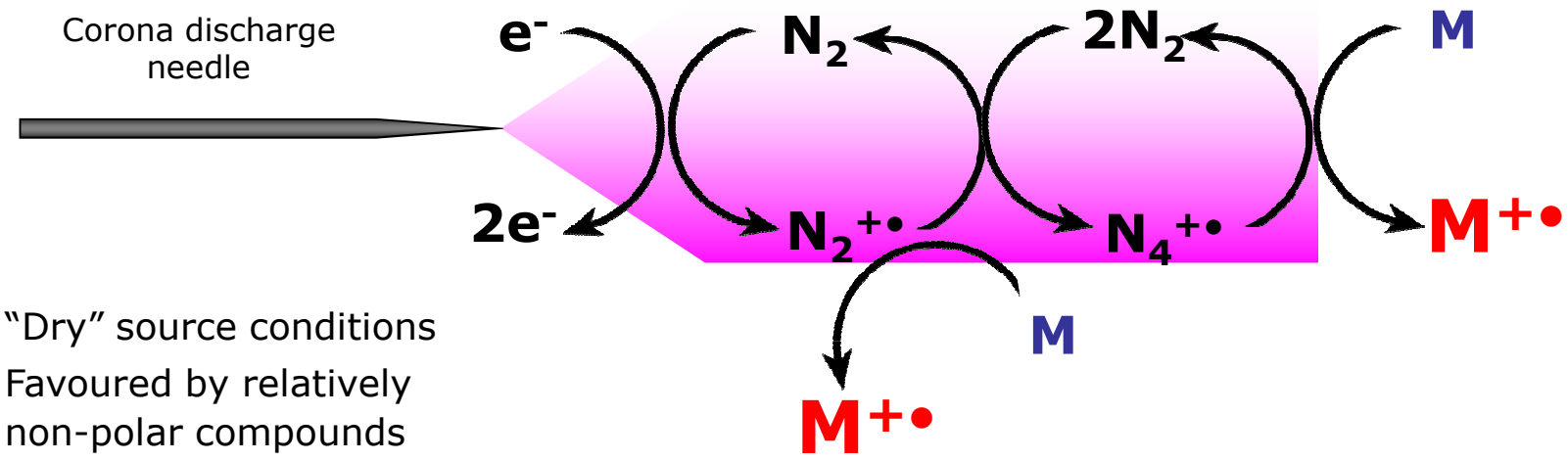


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7. Ionisation/Scan Mode of choice

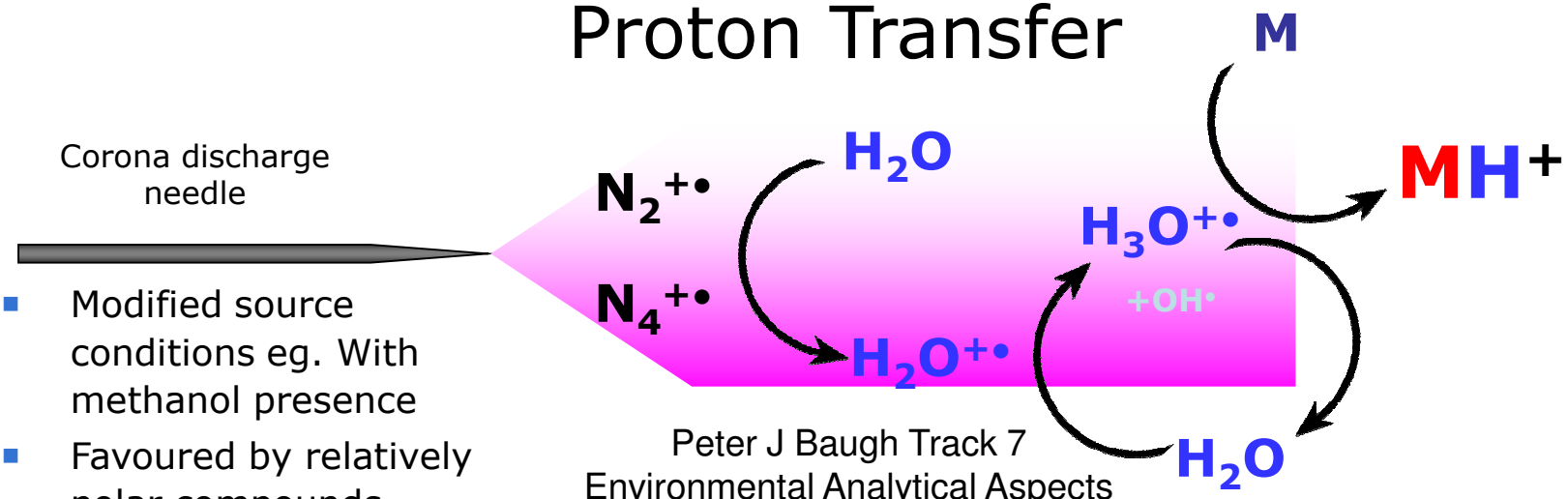
API Ionization processes

Charge Transfer



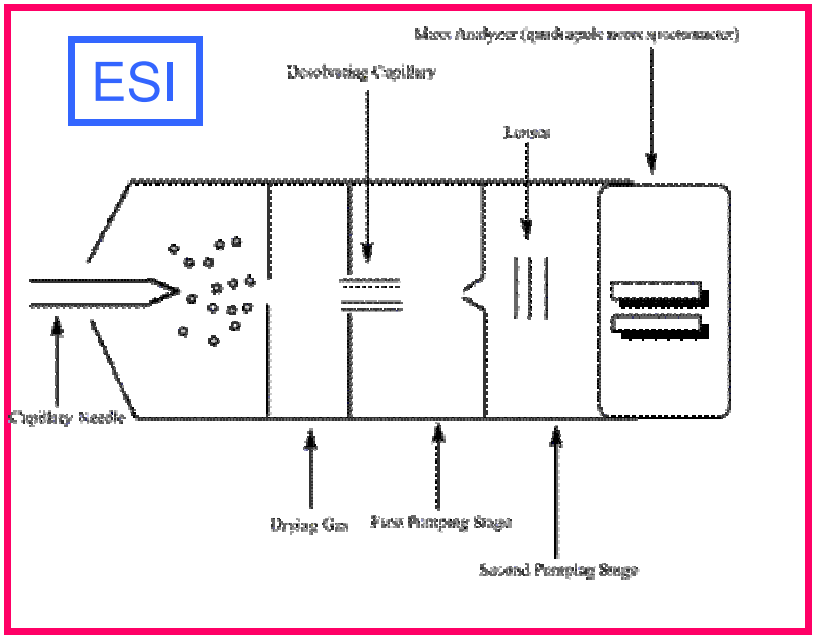
- "Dry" source conditions
- Favoured by relatively non-polar compounds

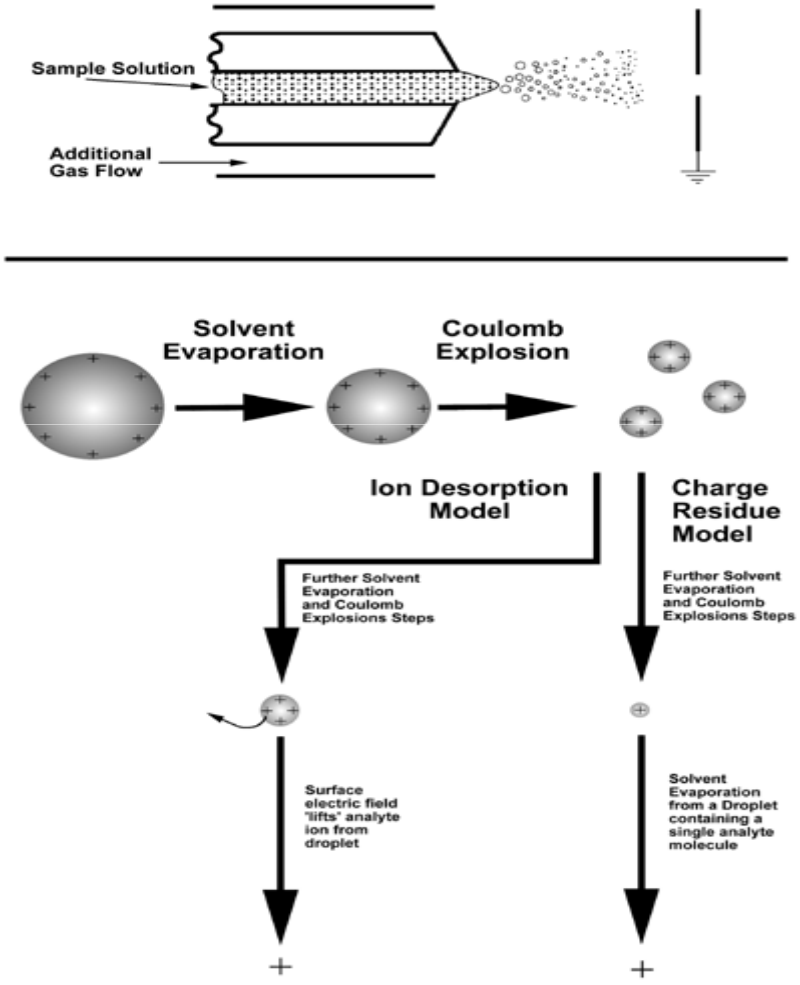
Proton Transfer



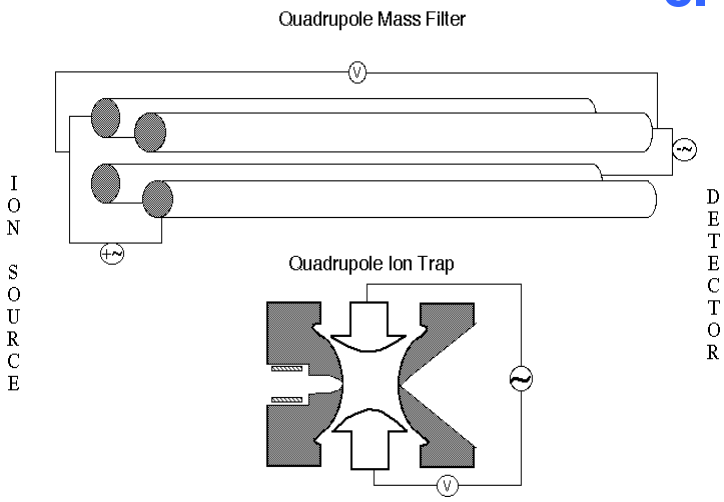
- Modified source conditions eg. With methanol presence
- Favoured by relatively polar compounds

7. Ionisation/Scan Mode of choice



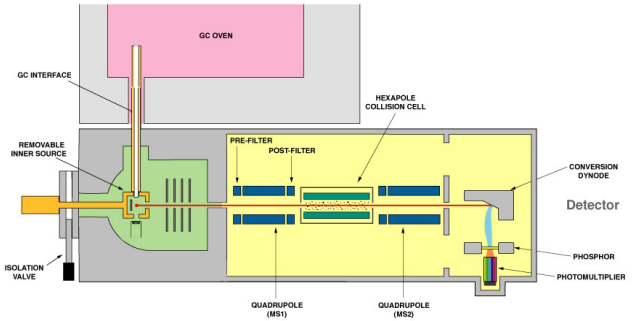


8. Mass Analysers



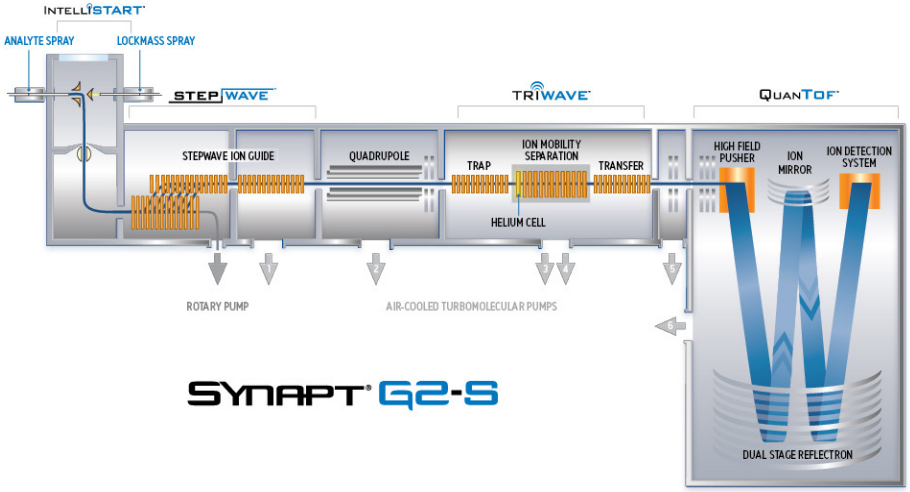
Single Quadrupole Mass Filter

Ion trap



Schematic of tandem mass spectrometry, QqQ

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

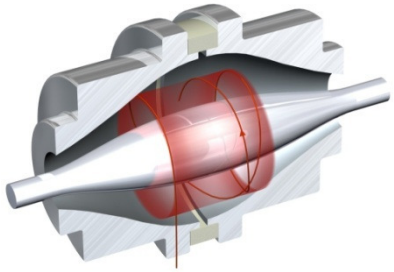


QTOF with ion mobility separator (or collision cell not shown here)

8. Mass Analysers- Orbitrap

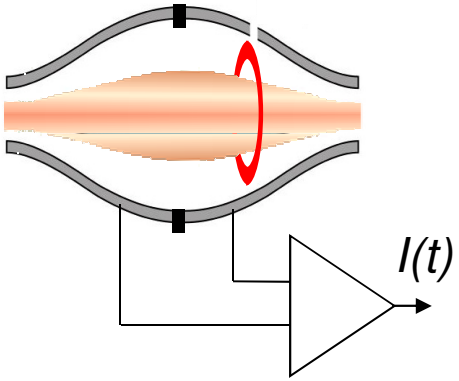
What is Orbitrap analyzer?

Orbitrap analyzer =

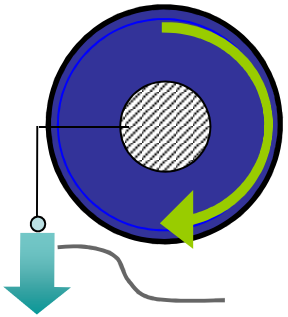


(Quadro-logarithmic potential)

+ Image current detection



(axial oscillations)



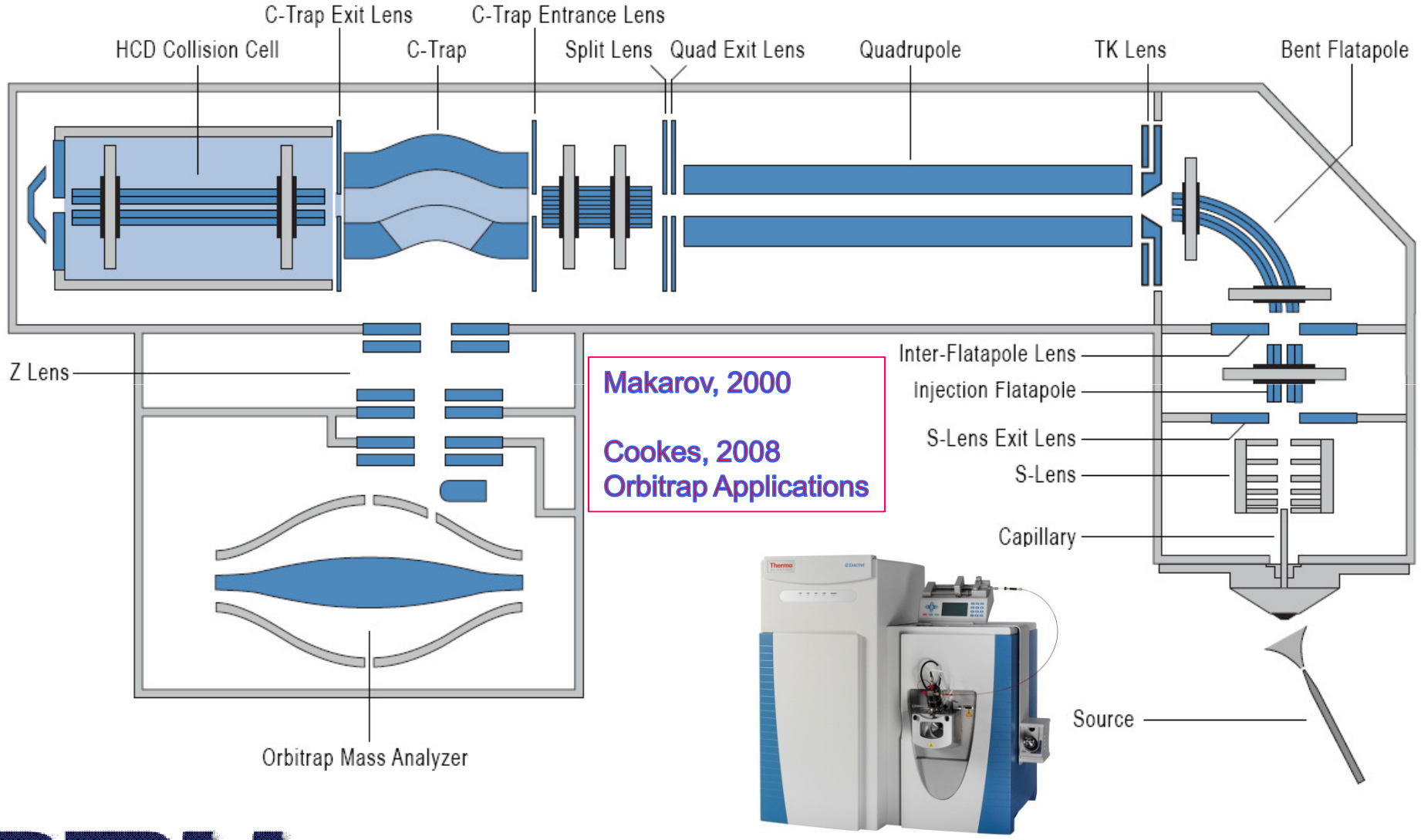
+ Electrodynamic squeezing

(time-dependent field during injection)

+ External pulsed ion source

(C-trap)

8. Mass Analysers- Orbitrap

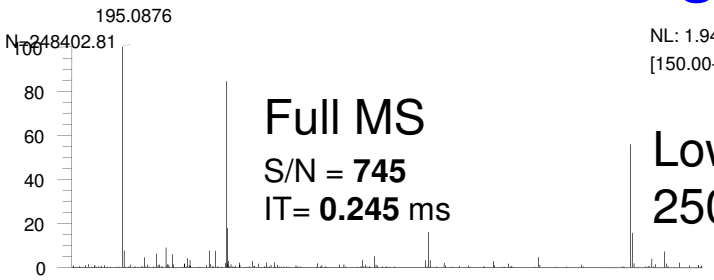


Makarov, 2000

Cookes, 2008
Orbitrap Applications

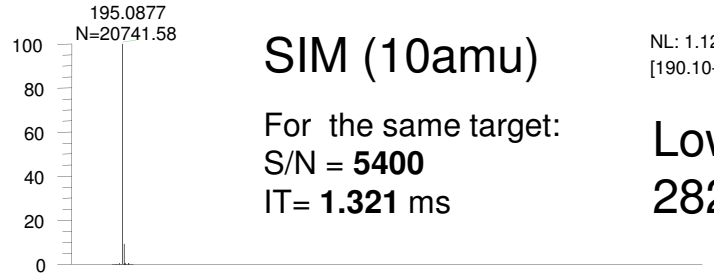
What do we gain by selected ion monitoring?

- Signal-to-noise ratio becomes dependent on the ratio of compound of interest to other analytes- much less so in SIM!
- In Full MS, total C-trap charge capacity is shared between multiple signals of different intensity
- In Orbitrap instruments, SIM could become MRM without any additional overhead!



Full MS
S/N = **745**
IT= **0.245** ms

Lowest signal 250330

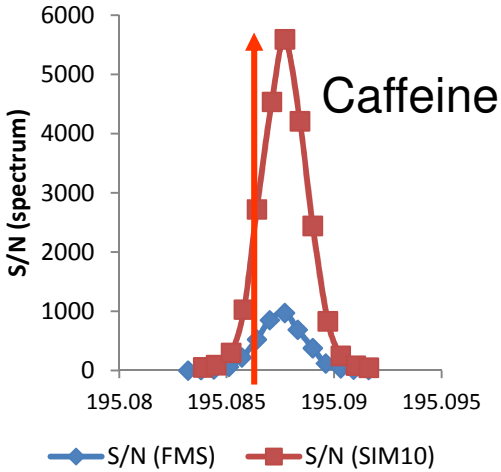


SIM (10amu)

For the same target:
S/N = **5400**
IT= **1.321** ms

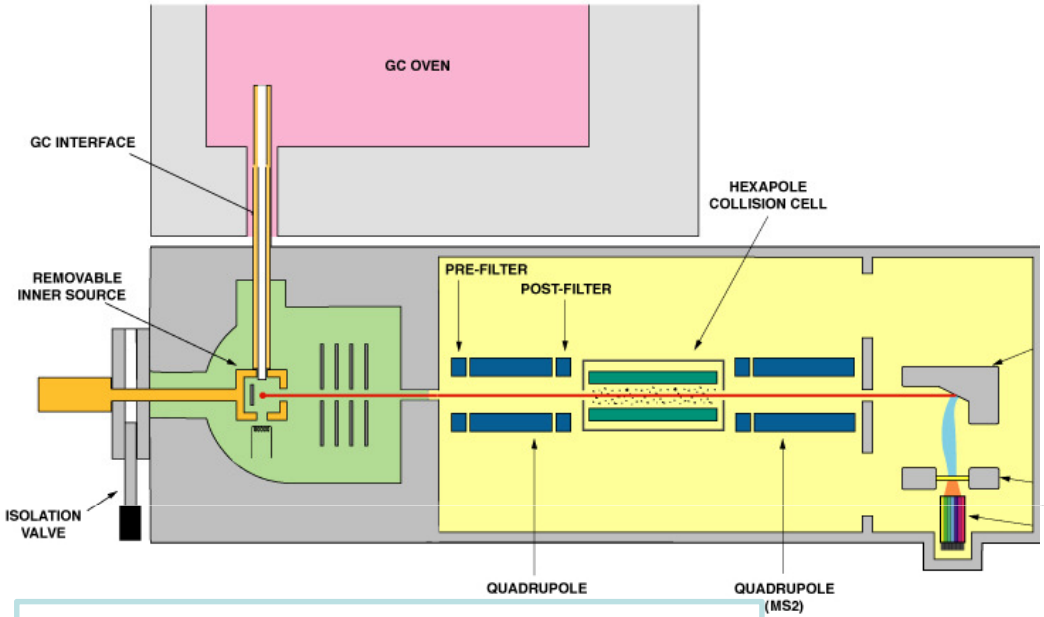
Lowest signal 28240

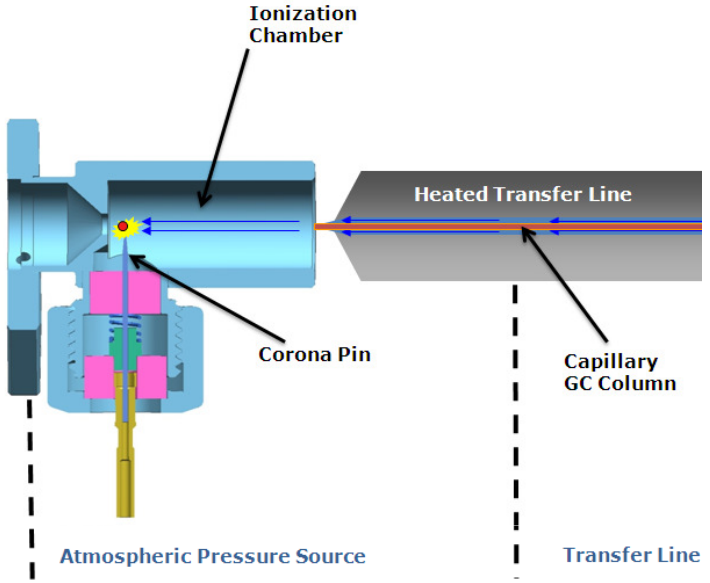
Gain in sensitivity (7x)



- **Sensitivity gain 5 – 10 x with SIM mode**
- **The gain will be higher in more complex matrices**

8. Mass Analysers- Conventional EI/CI vs APGC





- **Under vacuum source constraints**
- **Gas flow and chromatography and resolution limitations**
- **Specific source design optimization. LC to GC switch limitations**
- **Source cleaning**
- **EI fragmentation, molecular ion? EI library search**

- **API source**
- **FID like chromatography**
- **API design optimization. Easy LC to GC switch**
- **VERY easy source cleaning**
- **NO EI fragmentation, soft ionization molecular ion, CID**

8. Mass Analysers- Sensitivity & Parameters

Analyser	Mass Range [*10^{-3}]}	Resolution, [Δm/z]	Resolving Power FWHM [*10^{-3}]	Mass Accuracy [ppm]	MS/MS	Scan Rate [Scans/s]
Q	3	0.1 - 0.7	-	Low	-	0.5 - 4
QqQ	3	0.1 - 0.7	-	Low	MS/MS	0.5 - 4
IT	4 - 20	0.1 - 0.7	-	Low	MS^N	5 - 10
LIT	4 -20	0.1 - 0.7	-	Low	MS^N	1 - 10
Orbitrap	6	-	50 - 100	≤5	MS^N	0.5 - 2
oaTOF	20 - 40	-	15 - 20	≤5		20 - 30
QqTOF	10 - 40	-	15 - 25	≤5	MS/MS	20 - 30
Sector, EB hybrid	5 - 15	-	30 - 80	≤5	MS/MS	0.1 – 0.5

9. Low resolution instruments (IT, Q & QqQ/TSQ)

Single quadrupole or ion trap instruments are employed for environmental analysis where low cost is required. However, **tandem quadrupole systems** are preferred and for general quantitative analysis MS/MS. MRM is used providing selectivity, sensitivity and linearity over a wide range. Screening methods allow a large number of target compounds to be analysed and target pollutants to be confirmed and quantified. MRM is limited to detecting specified compounds selected.

Features/capabilities of TSQs are:

- **Acquisition speed: capability 10 ms per acquisition ;**
- **Multi residue methods require fast analysis with UPLC and 2MRMs (transitions) per compound and n x 2MRM, where n = 50 – 200, the number of target compounds.**
- **Time programmed methods are used with time windows to select a number of MRMs for compounds expected (retention time related) as for single quadrupoles in SRM mode**
- **Linearity: TSQ 5 – 6 orders of magnitude**

Only the most recent/sensitive LC/TSQ can achieve required Detection Limits (DLs) in drinking water by direct sample injection.

NOTE Ion traps can be used as low cost alternative to TSQs and Qtrap (quadrupole + linear trap) can be employed in EA as a conventional TSQ, enabling good sensitivity.

9. TandemQ continued

Applications of interest include, pesticides, drug residues and oestrogenics, drugs of abuse, residues from personal care products, halogenated compounds having domestic and industrial applications and ECDs are required (EC directive). An LC/MS/MS method with 2 MRM transitions is confirmatory if the quantification and confirmation are in the expected ratio and the retention time is within the expected time window.

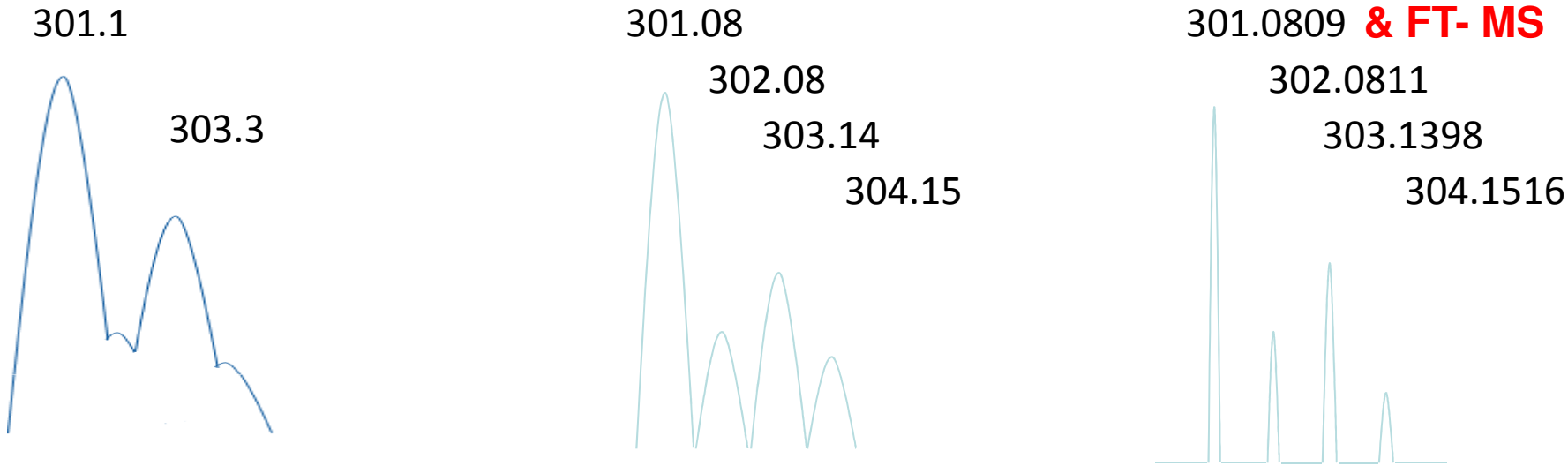
Targeted methods are also employed to detect and quantifiy a known list of compounds in an environmental matrix, such as, surface water. Targeted screening is the descriptive term for a more extensive list of compounds. The ID can be confirmed using a second transition and the amount can be calculated.

Pre-concentration 500x to 1 ml (GC/MS) or to sample volumes of 50 ml with an increase in instrument sensitivity (LC/TQ) can be applied. Alternatively on-line pre-concentration can be used as for SPME where the total sample is injected ; usually used for a class of compounds, such as acidic herbicides because of the problems associated with general method development. Surface contaminated waters can reduce column lifetime because of the possibility intractable materials (particulates) present.

10. High Resolution Instruments

Isotopic patterns, mass accuracy and resolution

Quadrupole MS e.g. IT/SQ/TQ → **Accurate MS e.g. TOF, Orbitrap, Sector & FT- MS**



$C_{15}H_{14}ClN_4O$
$C_{16}H_{14}ClN_2O_2$
$C_{12}H_{10}ClN_8$
$C_{14}H_{18}ClO_5$
$C_{10}H_{14}ClN_6O_3$
$C_{21}H_{14}Cl$
$C_9H_{18}ClN_2O_7$
$C_6H_{10}ClN_{12}O$

$C_{15}H_{14}ClN_4O$
$C_{16}H_{14}ClN_2O_2$
$C_{12}H_{10}ClN_8$
$C_{14}H_{18}ClO_5$

$C_{15}H_{14}ClN_4O$

Increasing mass resolution
Increasing mass accuracy
Improved isotopic distributions

PerkinElmer® For the Better

10. High Resolution Instruments

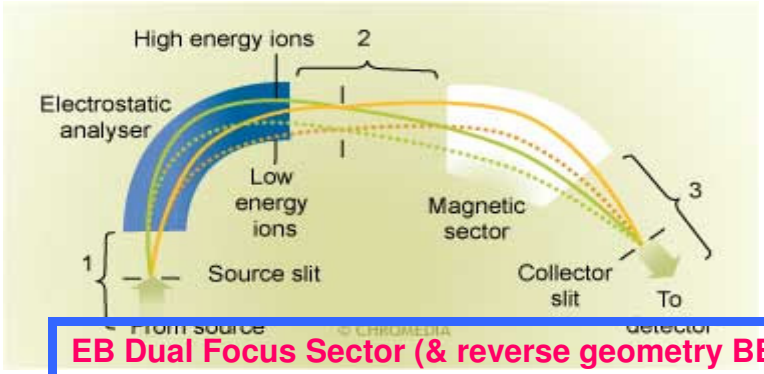
Double Focusing HR Mass Spectrometer for ultra-trace analysis

GC/HRMS operated in SIM mode is almost universally employed for ultra-trace analysis to selectively distinguish pollutant masses from the background. The advent of high sensitivity electron multipliers allows low femtogram detection of ions separated by HRMS and to distinguish between isotope-labelled analogues and the native compounds. There are a number of criteria for positive ID

1. Elution correct time window
2. Peak must be Gaussian
3. Intensity > 3:1 (S/N)
4. For CDDs, the 2,3,7,8 congeners must elute within ± 2 s of labelled analogues (LIS)
5. Isotope ratios must be within 15% of theoretical values

Isotope dilution MS allows ability to monitor recovery, recovery of LIS can be used to monitor sample extraction efficiency, LIS can be used as GC RT markers, IS can be used to enhance sensitivity at low concentrations by acting as carriers through the clean up stages and analysis

QC requirements are rigorous to avoid false positives and negatives and involve- extensive use of blanks, dedicated facilities, use of isotope dilution, replicate analyses, interlab comparison, certified reference material, validation of chromatography, multi-point HRMS calibration, validation of peaks- GC & MS, trained staff.



EB Dual Focus Sector (& reverse geometry BE

10. High Resolution Instruments, continued

Summary of the QTOF as preferred LC/MS instruments for Environmental Analysis

Because of the versatility of the QTOF from the standpoint of scan rate, sensitivity, resolution (mass accuracy) and MS/MS capability, since its inception, QTOF has become a workhorse for LC/MS for environmental analysis comparable to GC/MS and can analyse what GC/MS cannot. The attributes are as follows:

- Qualitative & quantitative analysis
- TOF chromatogram results from post-acquisition data processing to generate an XIC (tandem quadrupole MRM chromatogram results from direct data acquisition of mass filtered ions)
- Designed to acquire a comprehensive data set allowing a non-targeted compound to be detected (TandemQ is designed for targeting a predetermined list of compounds)
- Compound ID can be performed by using a library search on the MS accurate mass data by isotopic pattern comparison (and the expected RT).
- Reprocessing of the sample data to check for the presence of compounds possibly missed initially, which is not possible with a TQ.

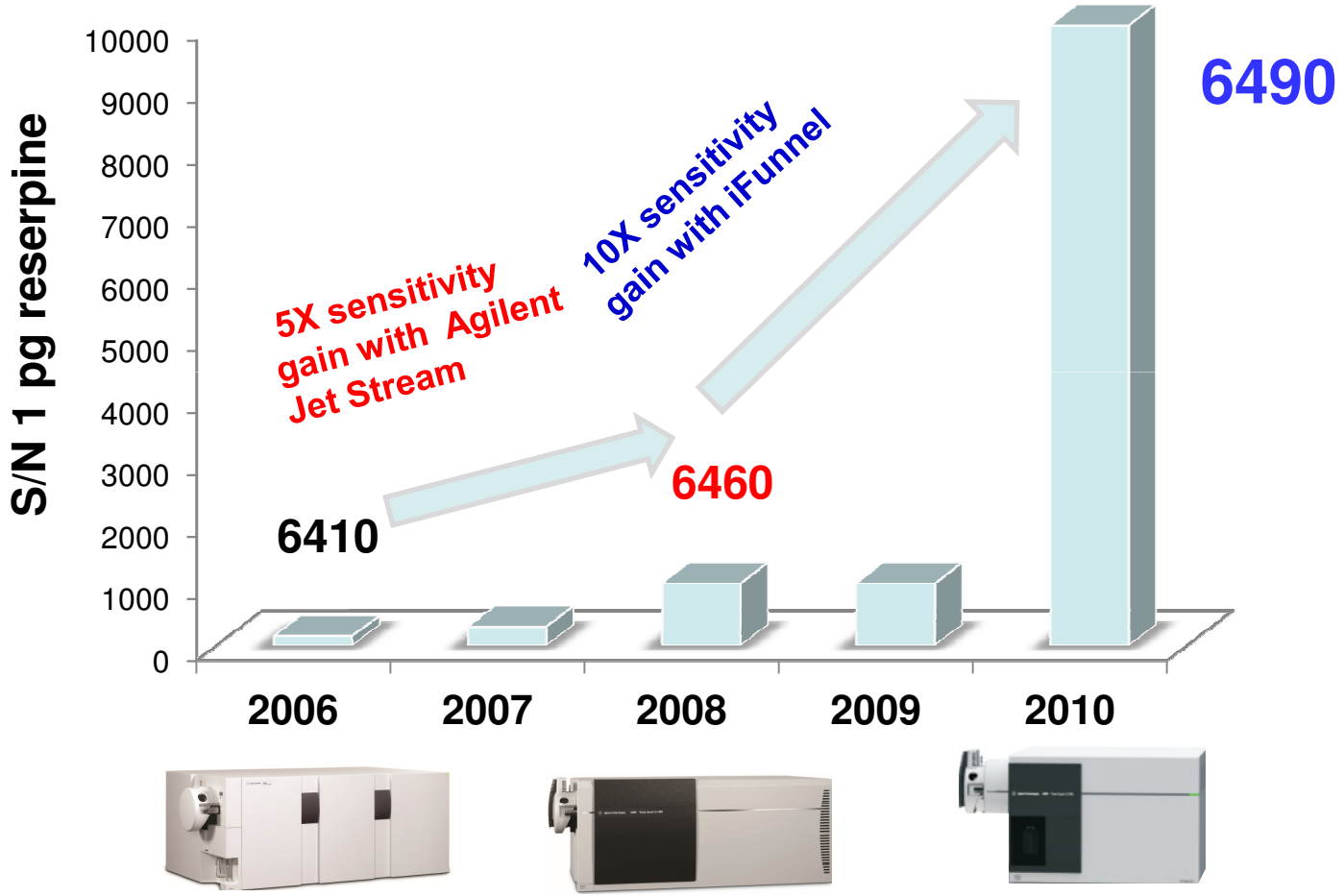
Fast screening is possible with UPLC resolution and speed because of the fast acquisition rate of TOFs providing compound ID based on accurate mass, isotope patterns and on MS/MS data and RT with selective XIC set for a narrow mass window.

Other attributes relate to the investigative capability of TOF (ref. Technical information, Waters 2010)

NOTE: The fast acquisition rate makes TOF analysers ideal for fast GC/MS applications. Deconvolution algorithms can be used to effect ID of overlapping peaks resulting from the decrease in GC separation

11. Applications illustrated 1. TandemQuad Sensitivity progression

6490 Advances Sensitivity 50 Fold in 4 Years



11. Applications illustrated 1. Inter-comparison of MS Instrumentation

GC/MS, LC/MS, GC/QQQ, LC/QQQ, LC/Q-TOF, LC/TOF, ICP/MS



Trace metals

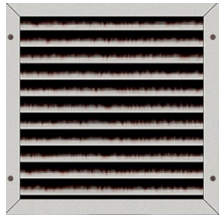
•Identification/quantification of elements such as **arsenic**, **lead**, and **mercury** at ppt levels



Persistent organic pollutants (POPs)

•Monitoring trace-level residues in the environment

•PCBs, Dioxins, and prefluorinated compounds



Indoor air testing

•Fast screening for solvents, paints, and other volatile organics (sick building syndrome)

•Thermal desorption techniques for monitoring air inside vehicles



Hormones in water

•Identification/quantitation of compounds and metabolites, which can affect marine organism physiology



Disinfection by-products

•Balancing the benefits of disinfection (microbial control) with the creation of possible carcinogenic compounds



Nutrients in water

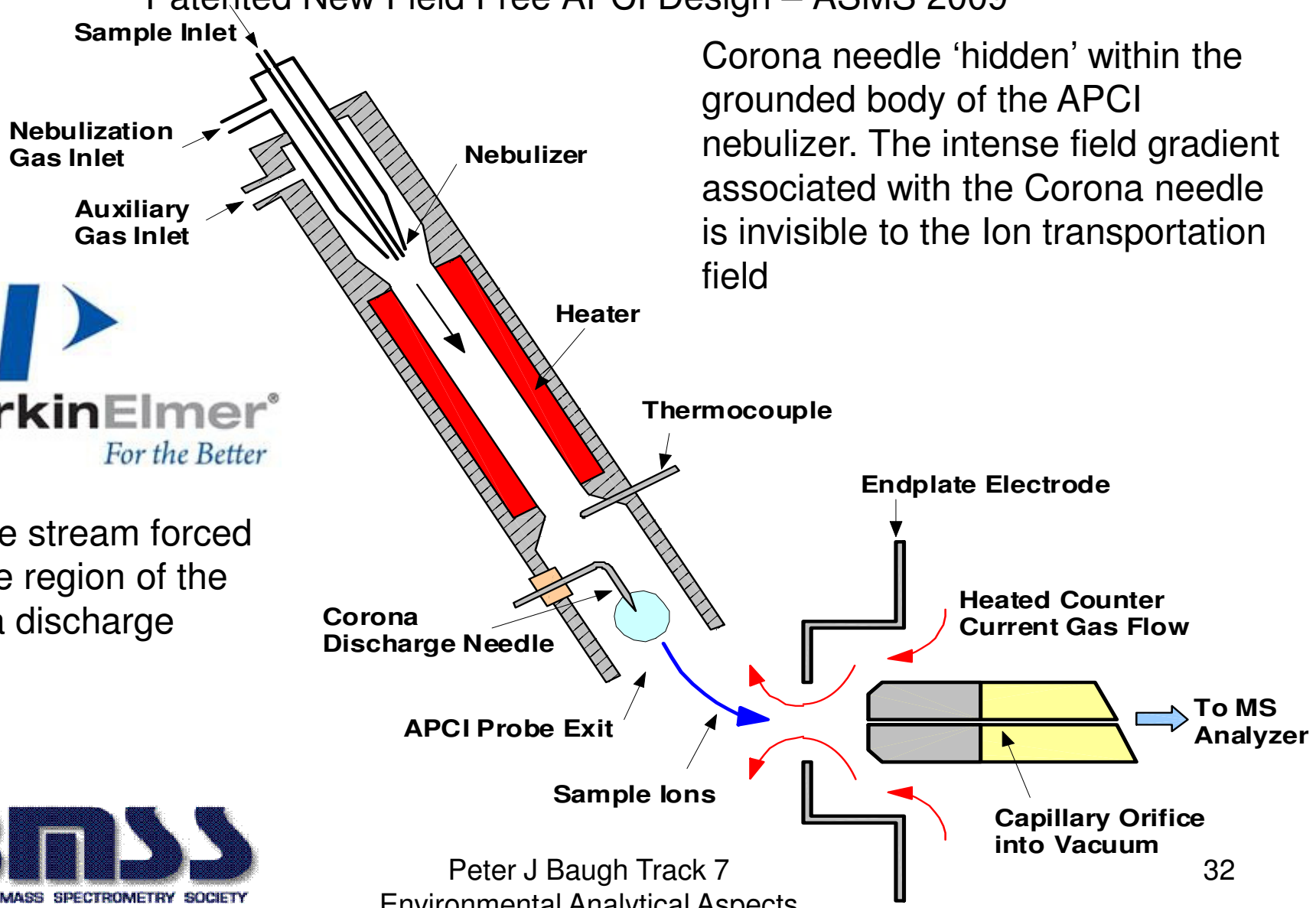
•UV/VIS and fluorescence solutions for nitrites, phosphates

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11. Applications illustrated 2. Direct Sampling Injection

Patented New Field Free APCI Design – ASMS 2009

Corona needle 'hidden' within the grounded body of the APCI nebulizer. The intense field gradient associated with the Corona needle is invisible to the Ion transportation field



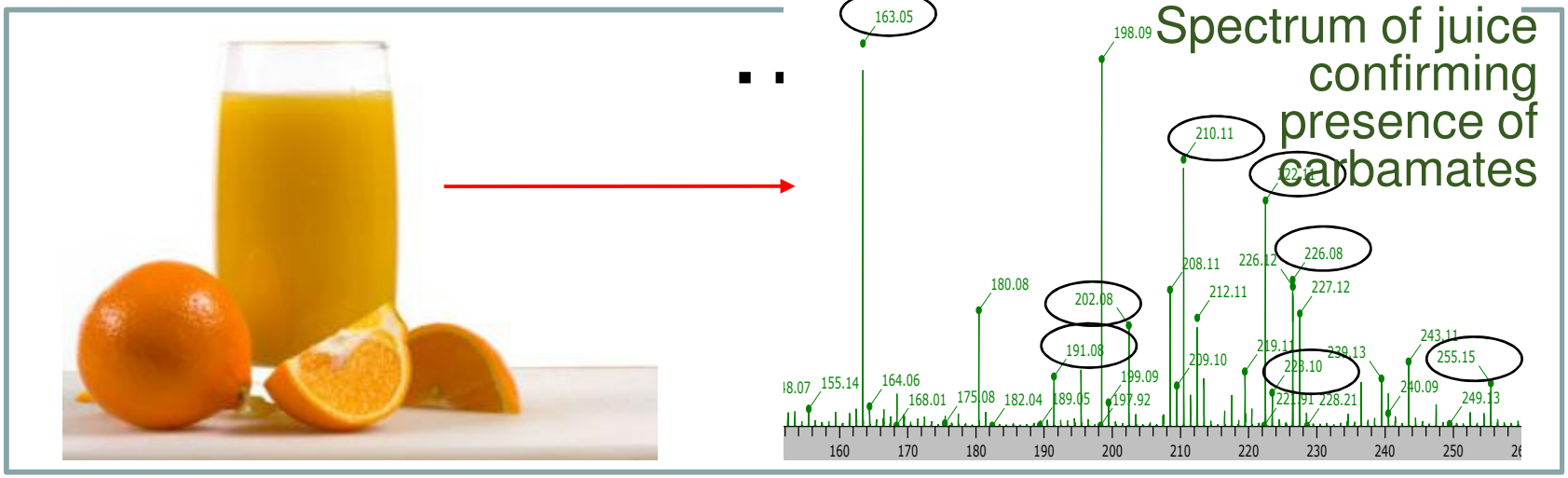
PerkinElmer® For the Better

Sample stream forced into the region of the corona discharge

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11. Applications illustrated 2. Direct Sampling Injection

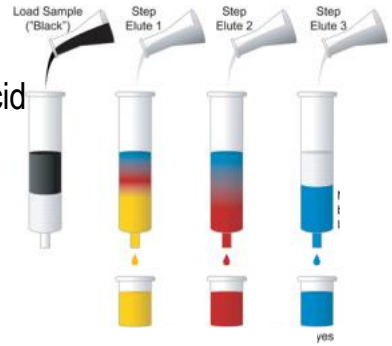
DSA IS Pesticides in orange juice - by the time you read workflow 1



1

- Wetting a SPE cartridge with MeOH
- Conditioning a SPE cartridge with Phosphoric acid
- Loading Orange juice sample in a pipette
- Putting sample in the SPE cartridge
- Washing salts away with Phosphoric acid
- Eluting with water/ MeOH
- Collecting eluant
- Putting eluant in a vial
- Run HPLC/MS analysis (15 min)
- Get confirmation carbamates are present

25 min



2

Loading Orange juice sample in a pipette (5 sec)

1 Pipette stroke on AxION DSA special mesh (5 sec)

Acquire spectra (15 sec)

Get confirmation carbamates are present

25 sec

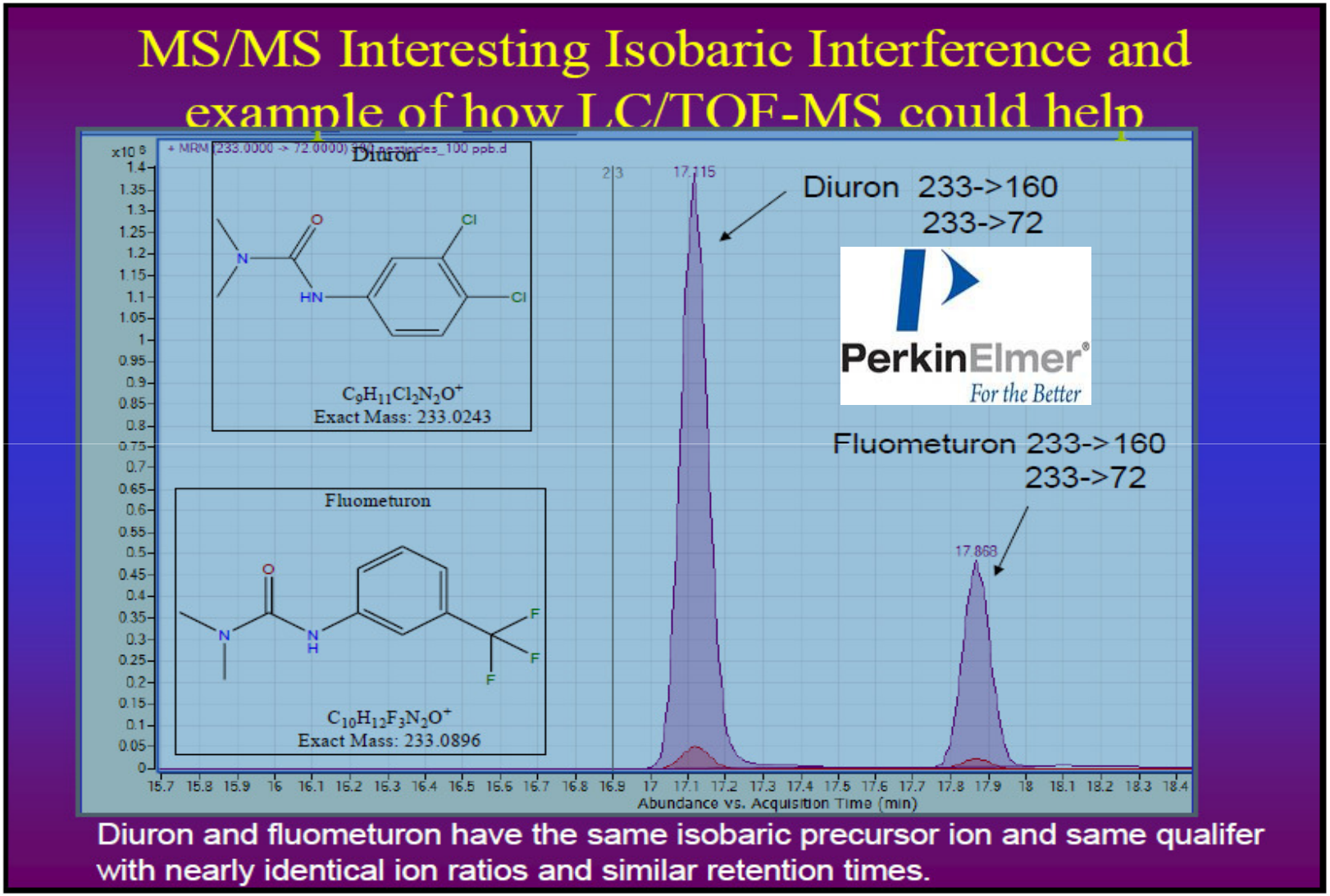
PerkinElmer® For the Better

Peter J Baugh Track 7
Environmental Analytical Aspects

...workflow 2 is probably complete!

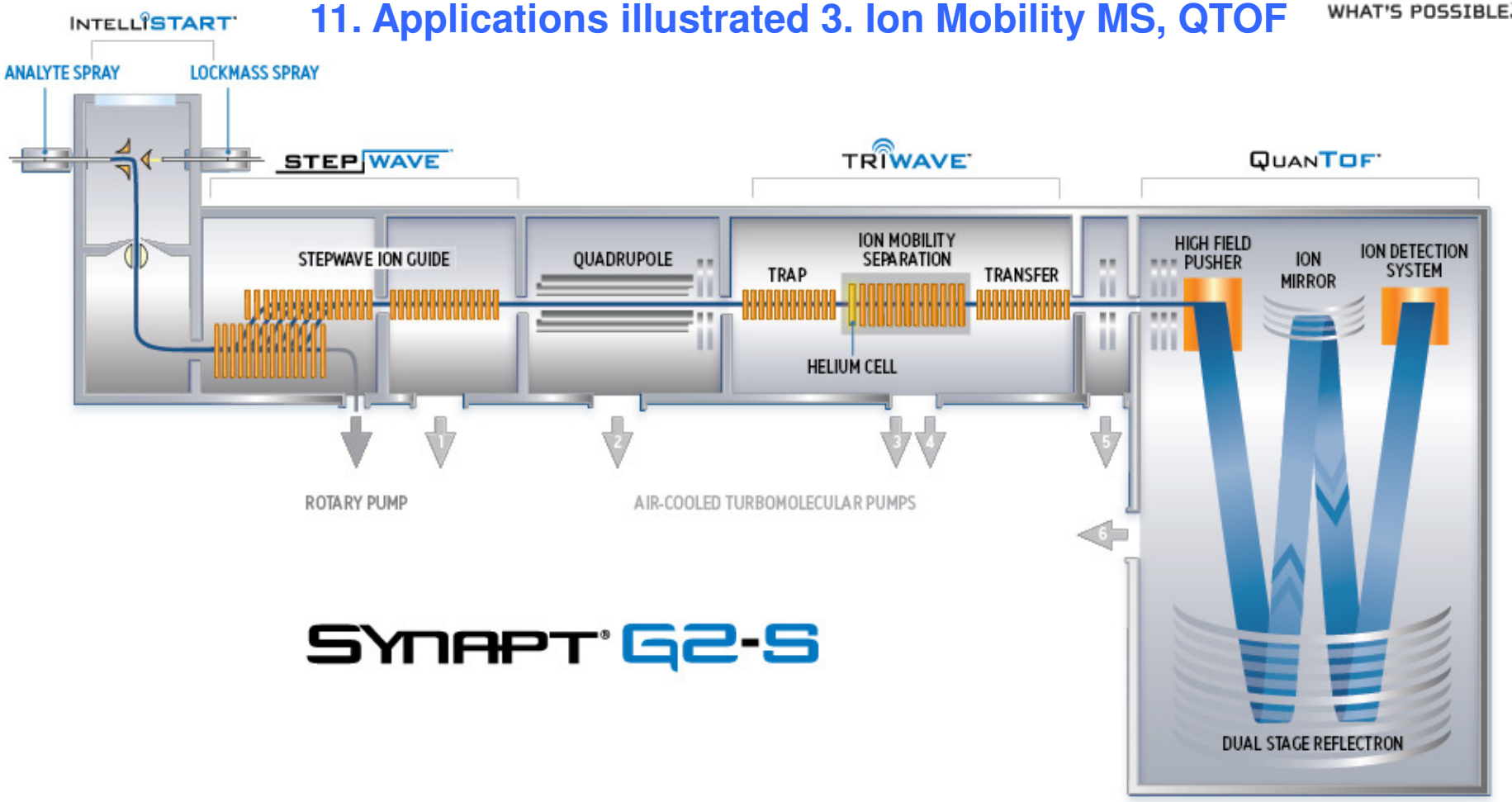
11. Applications illustrated 2 . LC/TOF-MS

When do you need a TOF for the correct results?



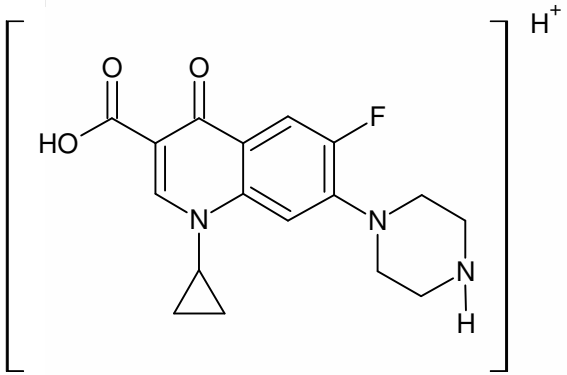
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

11. Applications illustrated 3. Ion Mobility MS, QTOF

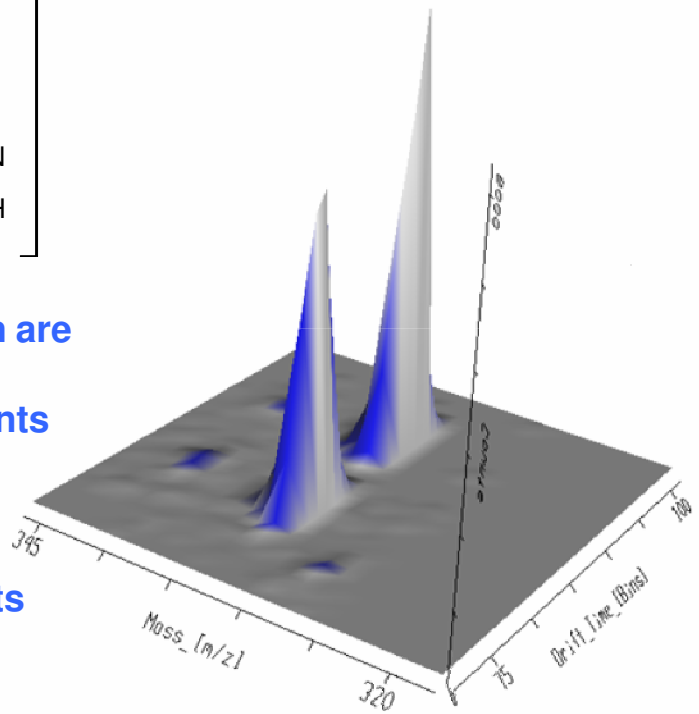


11. Applications illustrated 3. Ion Mobility MS

3D view of mobility separated co-eluting isobaric masses at 1.92 mins



Ciprofloxacin (M+H=m/z 332.1410)



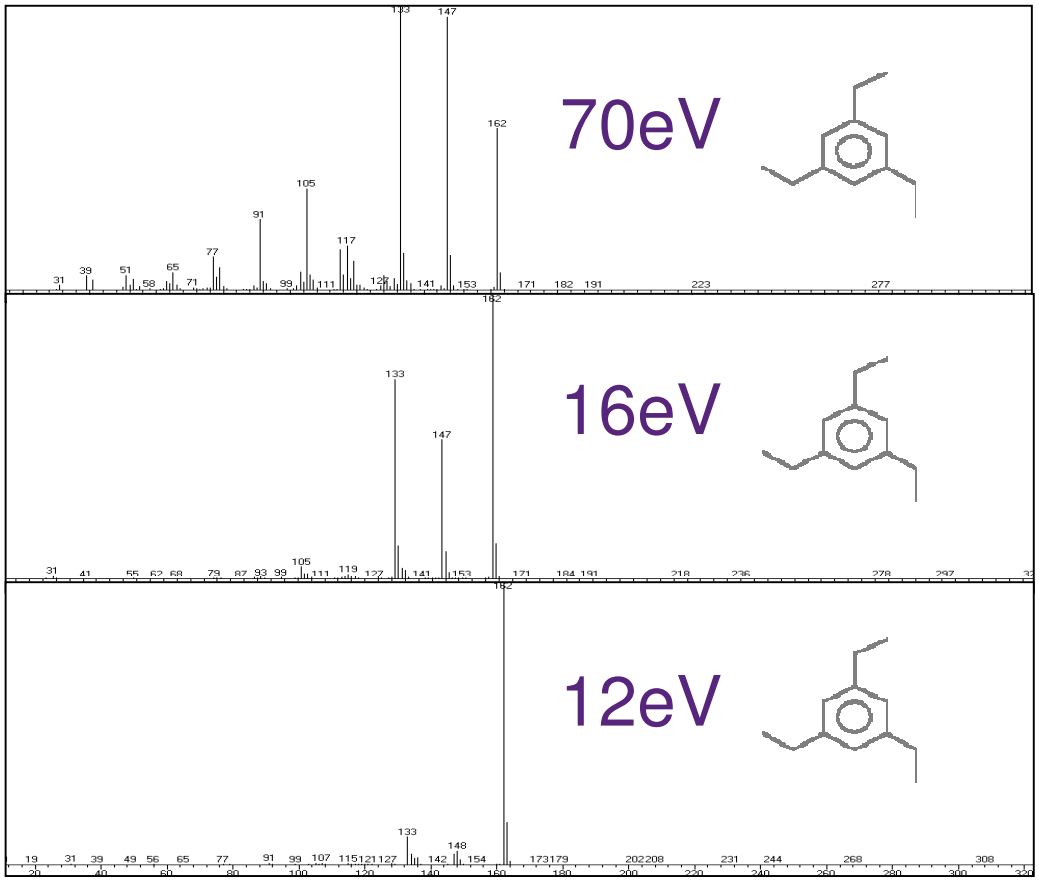
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

The two components of ciprofloxacin are shown here.
How is it certain that these components are ciprofloxacin.
Well, by generating accurate mass measurement and fragmentation information for these two components after separation by ion mobility.
The components identified are empirically isobaric.

Variable Electron Ionisation

11. Applications illustrated.

4.Variable EI for GCx GC TOFMS



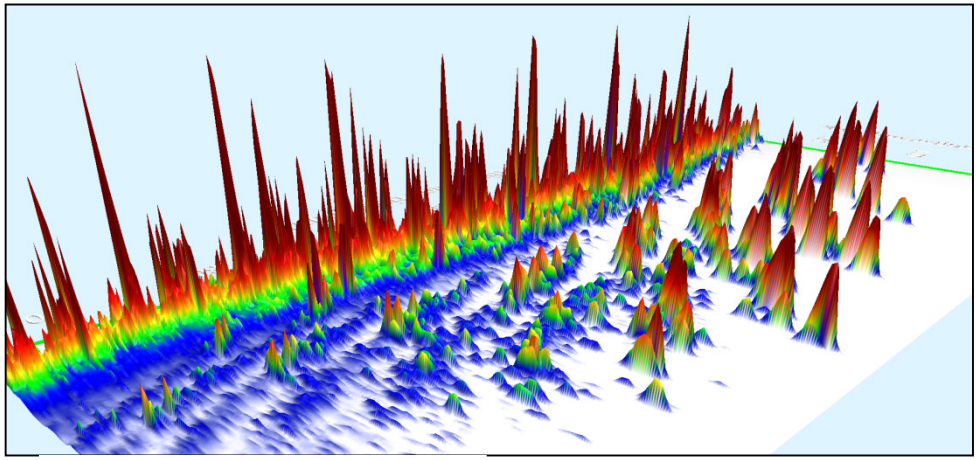
- Transition of fragmentation pattern with ionisation energy to assist structural elucidation

MARKES international

11. Applications illustrated. 4. GCx GC TOFMS

- *Comprehensive* two-dimensional gas chromatography
- Two columns of different selectivity connected in series.
- A modulator pulses 1st column eluents onto the 2nd column in narrow bands.





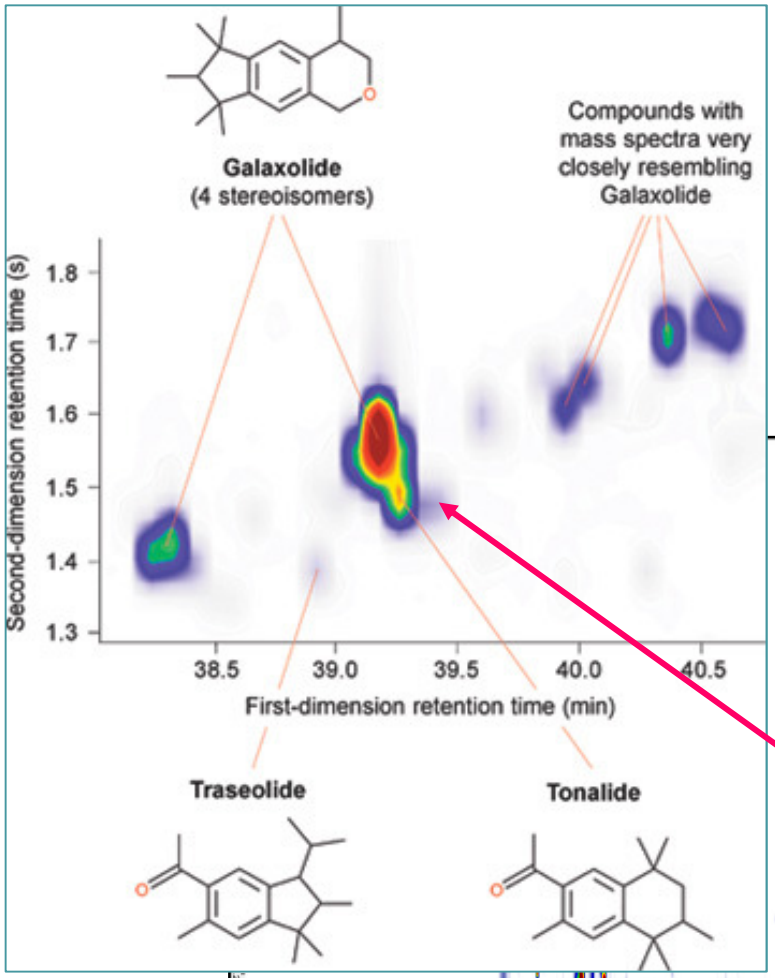
Enhanced separation for analysis of complex mixtures!

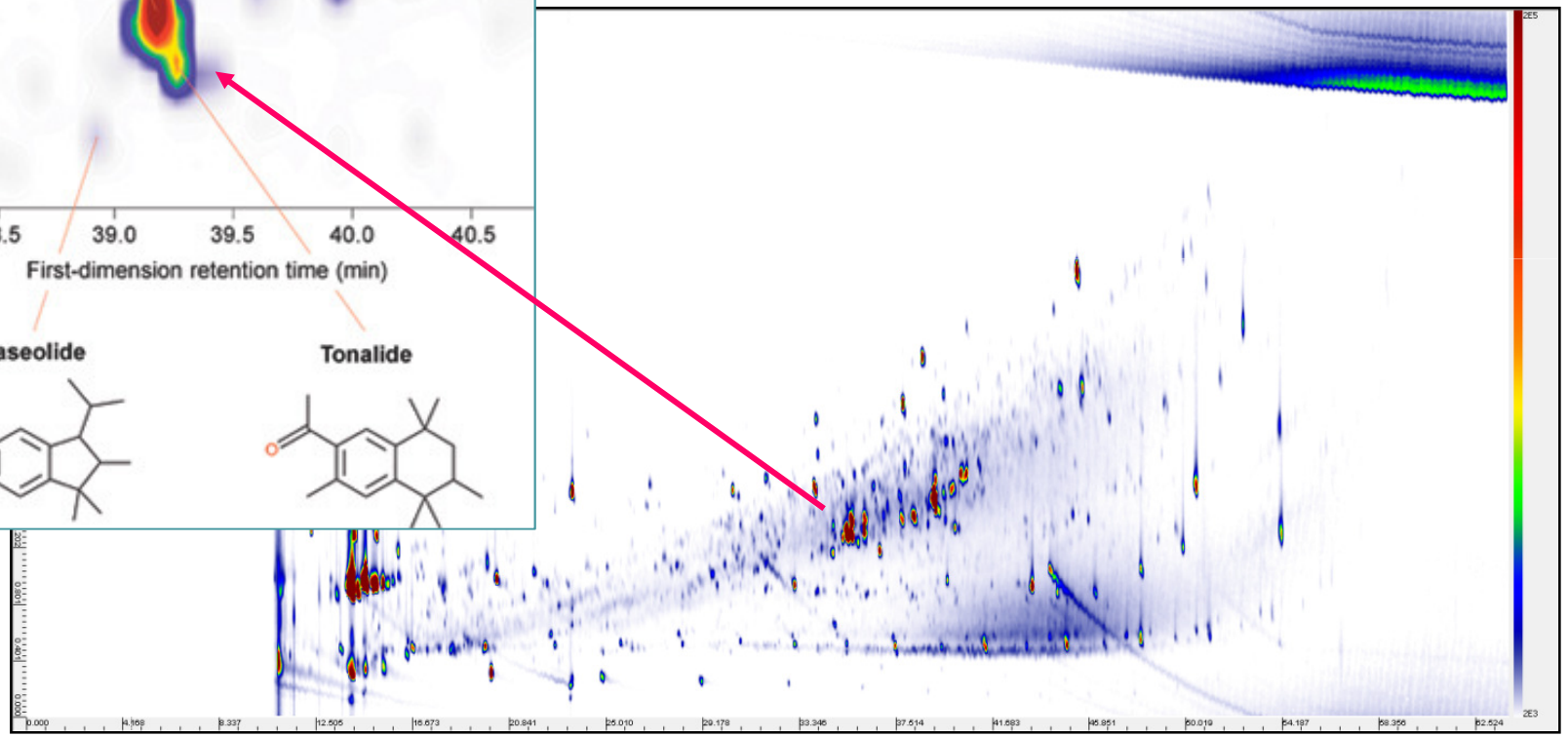
Analytical Methodology Centre

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11. Applications illustrated.
4. GCx GC TOFMS

Analysis of emerging contaminants

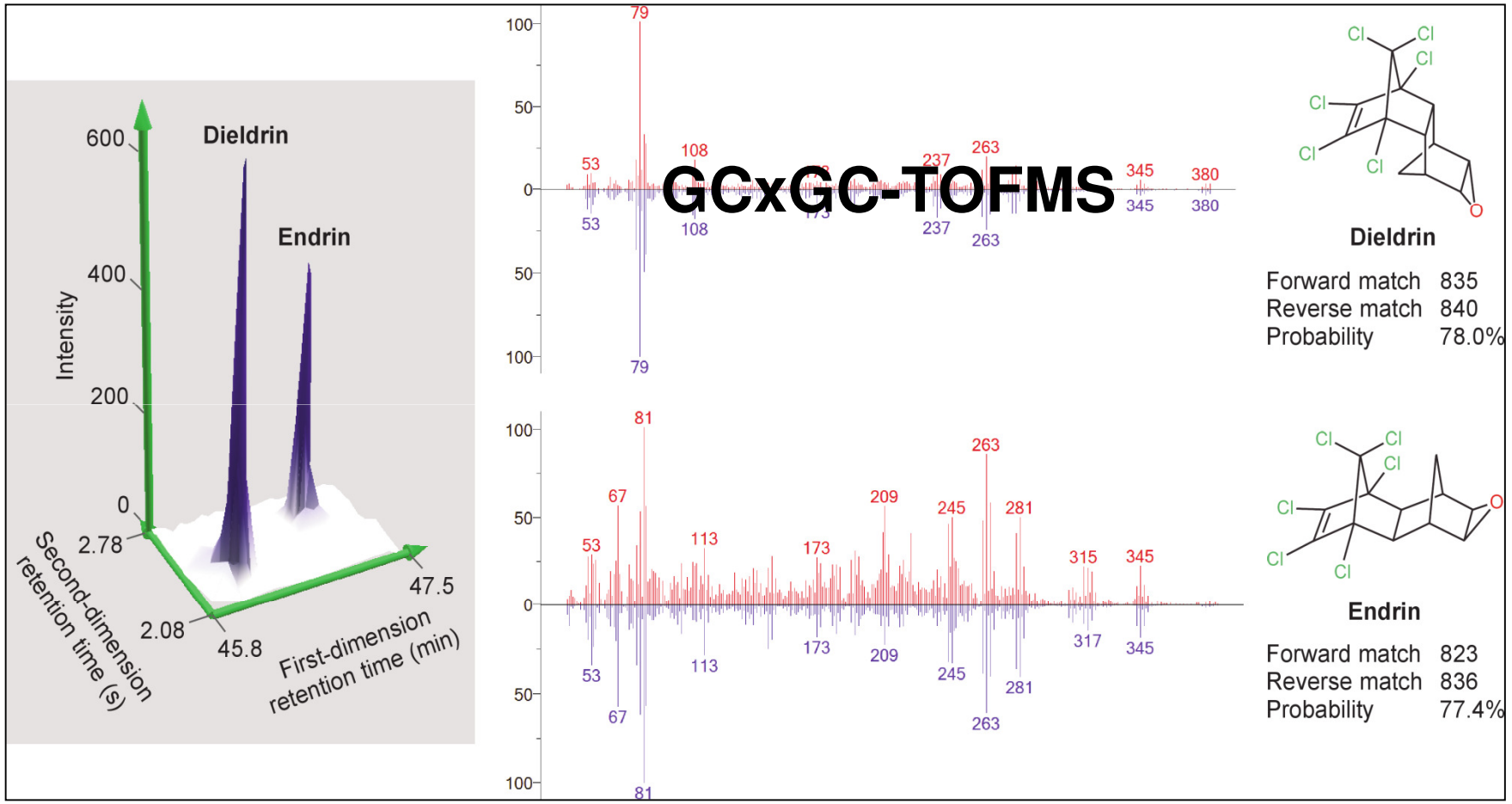




A. Gravell, P. Kutty, G.Mills, D. Barden and S. Smith, LCGC: Current Trends in Mass Spectroscopy, March 2013, 8-15.

MARKES international

11. Applications illustrated. 4. Analysis of pesticides by GCx GC TOFMS



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11. Applications illustrated. 5. PesticideScreener

- **Complete LC-QTOF solution based on high resolution, accurate mass data for multi-target screening in food and feed samples.**



Sample

Pesticides
food, feed, water



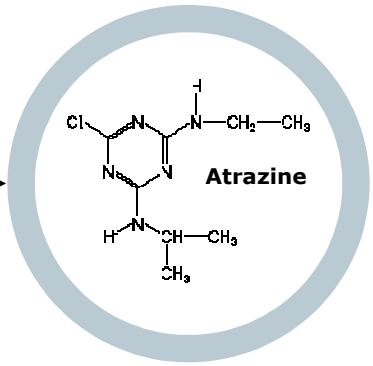
LC-QTOF-MS

RSLC +maXis impact
High sensitivity
high resolution
accurate mass data
true isotope pattern



Processing

TargetAnalysis
High Quality
Pesticide Database

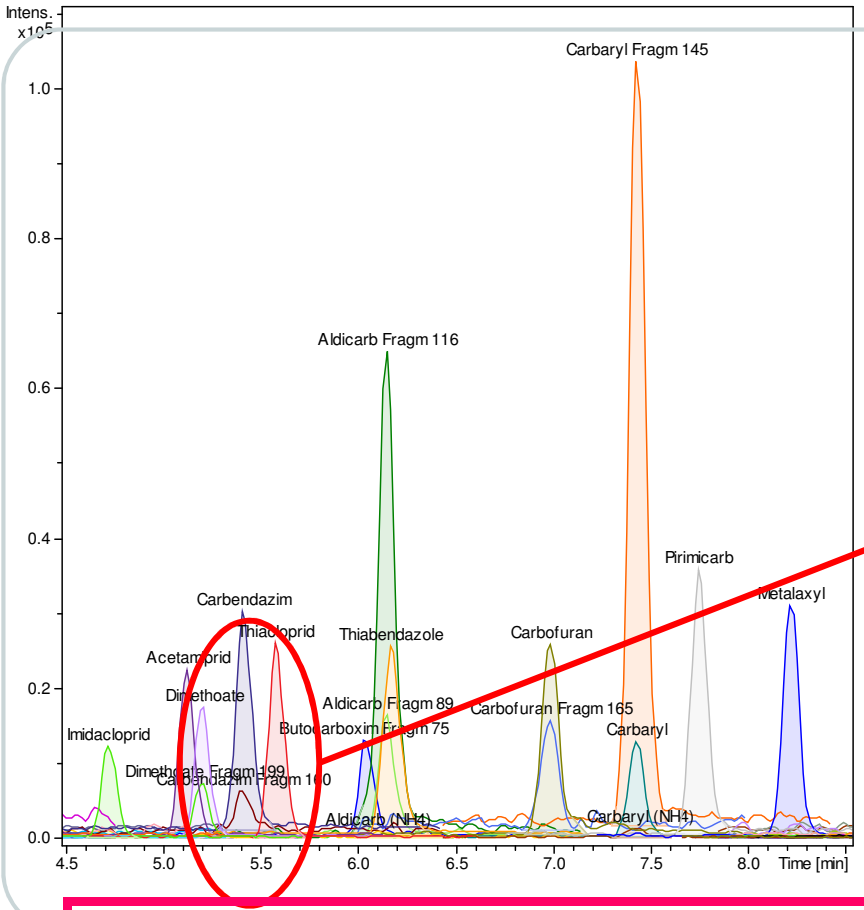


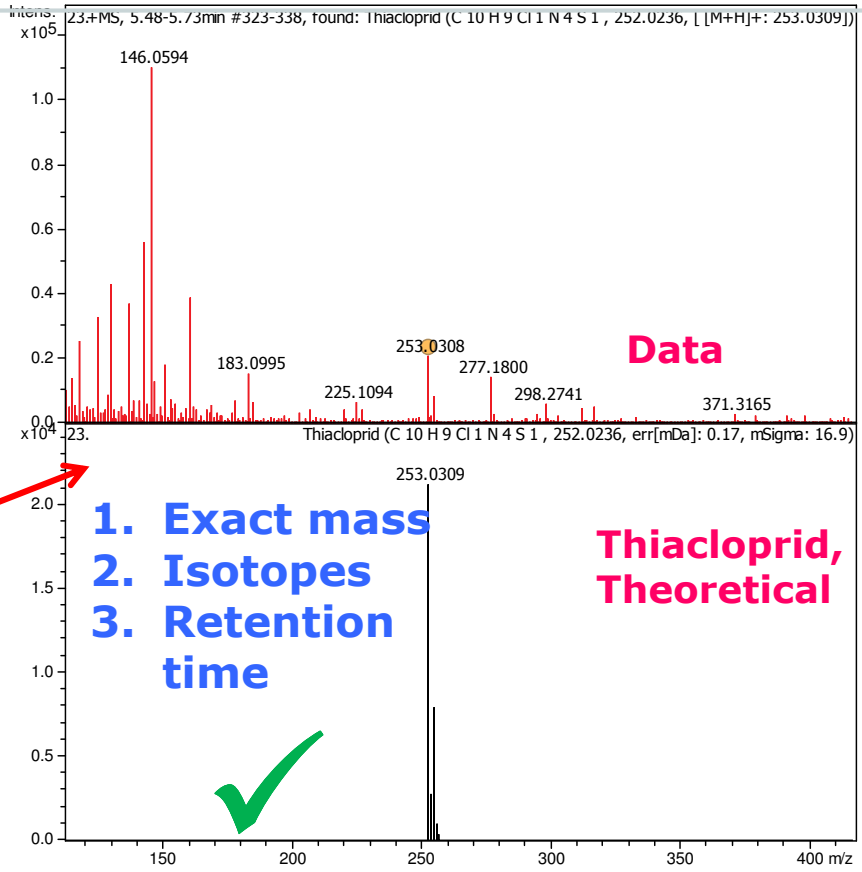
Identification
Confirmation
Report

11. Applications illustrated. 5. PesticideScreener

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Complete Data





One-click link back to the original data – full ability to examine chromatograms and spectra.

12. Data System Capabilities in brief

The acquisition of data (and rate) has reached enormous proportions and one file can have a capacity as great as 1Gb, for example, for a QTOF in which all ions are detected over the time period of the analysis. The data acquisition has several purposes.

1. To generate EI mass spectra which can be search via a mass spectral data base. GC/MS primarily

- NIST/EPA/NIH spectral database ; 244k compounds
- Wiley Registry of Mass Spectral Data, 9th edition (McLafferty, 2010) ; 666k compounds

All relevant information relating to each compound is included in the data base – mass spectra, primary name, synonyms, structure, elemental composition, nominal mass formula, CA Servcie Registry number (CASrn) and a number identifying the position in the database. There are a number of other DBs – viz. pesticides, pollutants and metabolites and organisation generated DBs.

2. NIST MS DB with LC/MS Data. With the advent of TOF MS accurate mass measurements are available to environmental analysts, which with isotope peak intensities can enable development of elemental compositions for unknowns. The large DBs can be searched to determine if compounds have identified elemental compositions.

3. NIST DB with the search program can also be used with data obtained by collision activation, CAD or MS/MS, for neutral loss searches determine the losses from a specified precursor.

12. Data System Software Capability exemplified

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- **ACD/Labs provides the ability to link interpreted analytical data with its chemical and geographical context and store in a database**
  - Stores the chemical profile of a sample point or product
  - Spot changes via chemo-metrics
  - Compare good or normal conditions with bad or emergency conditions and identify differences
  - Do spectral searching to see what other samples or sample points have a specific compound of interest
  - Also useful for environmental fate studies but drawing degradation pathways and characterizing the degradants by spectroscopy
- **Automated full scan GC-MS screening**
  - De-convolute a chromatogram and identify compounds from a library
  - Blank subtraction and single point quantitation against internal standards
  - Automated boiling point predictions to help identify the correct library hit in full scan GC-MS
  - Compare two samples and spot differences
- **Automated LC-MS screening**
  - De-convolution and formula searching against a library
- **Toxicity predictions for identified chemical structures**
  - Acute Toxicity
  - Aquatic Toxicity
  - Genotox
  - **Predicted health effects**

  + others
- **Automated archiving of raw data files retrievable via a database search**
  - Full audit trail
- **Chromatography method development**
  - Prediction of where a compound will elute within a method (also useful for identification)

Advanced Chemistry Development, Inc.
ACD/Labs

BMSS
BRITISH MASS SPECTROMETRY SOCIETY

12. Data System Software Capability exemplified

An example of a fully automated GC-MS automated screening system

Sample data

Run Full Scan GC-MS (and SIM if required)

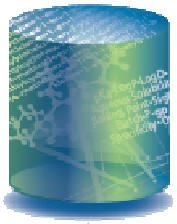


Analyst runs instrument

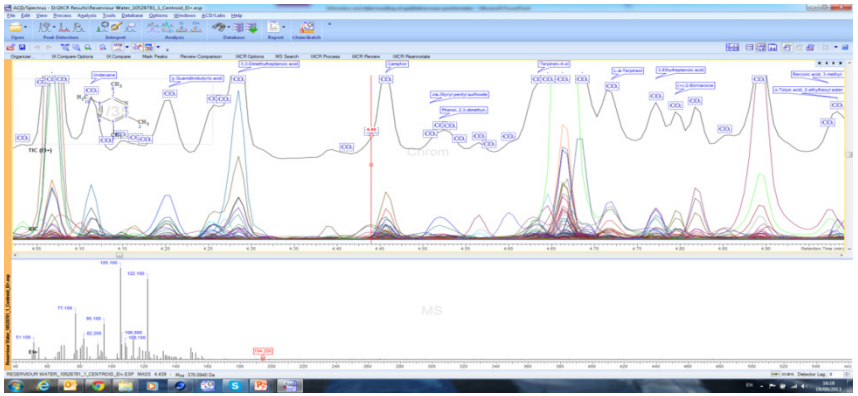
Raw file sent to archive Location stored in database

Data sets automatically picked up from the instrument directory

Auto-deconvolute the chromatogram and store extracted components



Chemo-metrics



Toxicity predictions
Boiling point predictions

ACD/Labs

Advanced Chemistry Development, Inc.

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Acknowledgements

1. The British Mass Spectrometry Society for support.
2. The Organising Committee, OMICS, for assistance with registration & accommodation expenses.
3. Mark Upton, PERKIN ELMER, for illustration of Direct Sampling Analysis using New Field Free APCI Design & applications.
4. Simon Stevens & Laura McGregor, MARKES INTERNATIONAL., for GCxGC-TOFMS illustration and examples.
5. Daniel McMillan, Waters, for illustration of Q-IM-TOFMS & GC-TOFMS instrumentation and example applications.
6. Tony Drury, BRUKER, for LC-Q-TOFMS and applications.
7. Tim Steele, AGILENT Technologies for TandemQ applications.
8. Claudia C. B. Martins, THERMO FISHER SCIENTIFIC, for LC/orbitrap-MS illustration & applications.
9. Peter Russell, ACDLabs for software capability & applications.
10. Chromedia for illustration of instrumentation diagrams.
11. ILM Publications for text & information from articles in reference 1.

Thank you for your attention and for listening