



Advantages in testing:

Possibilities with
quadrupole mass spectrometry
at
Institute for Testing and
Certification-Zlín



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Analytical chemistry for clients:

Define problem/directive

Selecting method

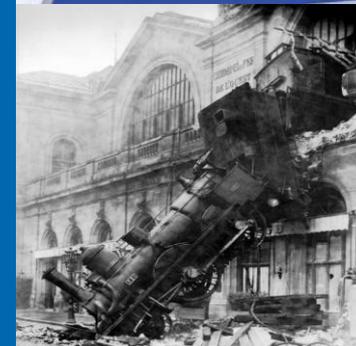
Analytical support

Evaluate data

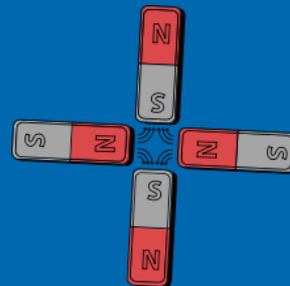
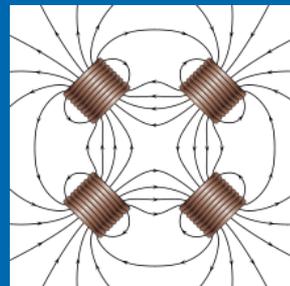
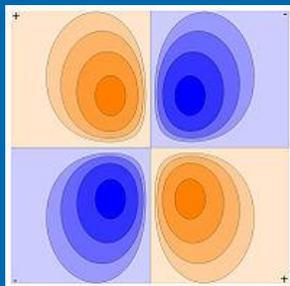
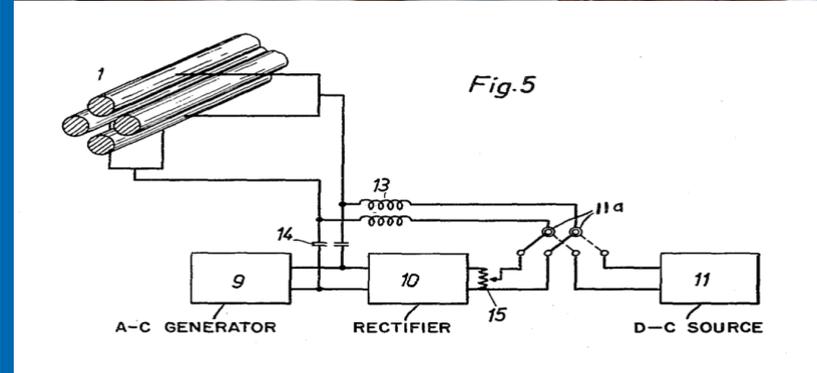
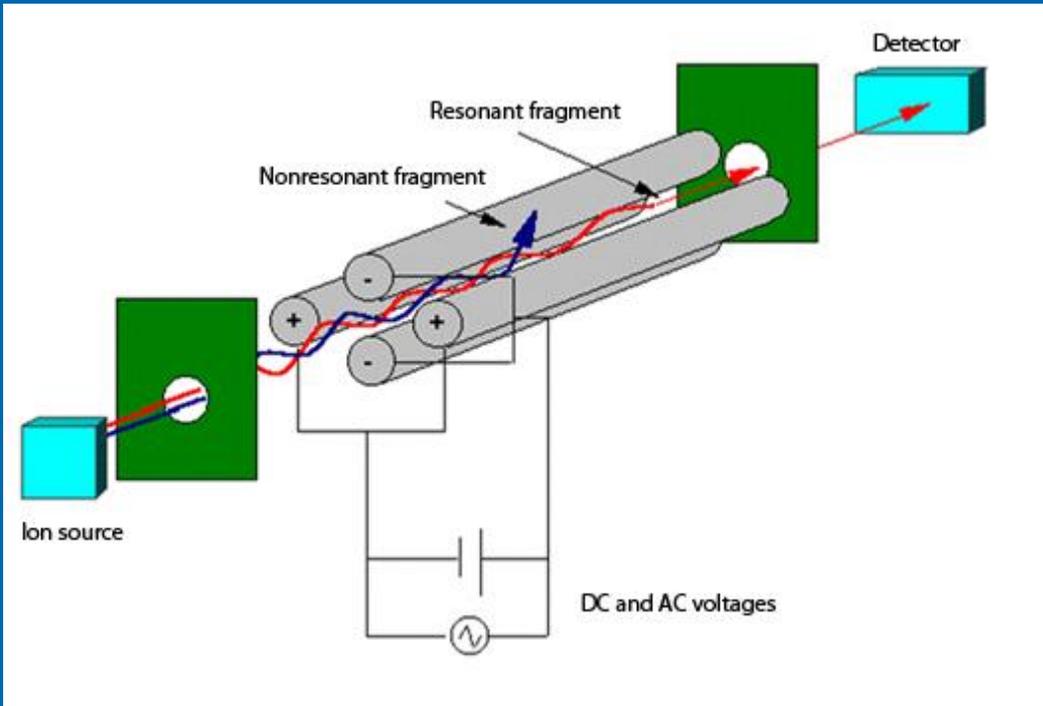
Working out cases scientifically

Working out cases technically

Prevention / Cost saving/ Market screening



Quadrupole - mass filter



Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Headspace-GC

Direct liquid injection-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

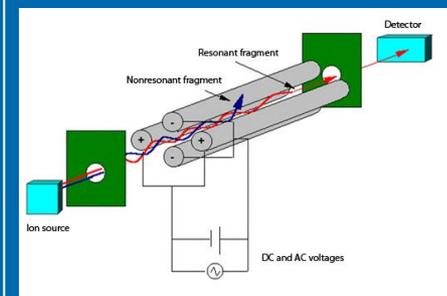
Pyrolysis-GC

Direct Inlet

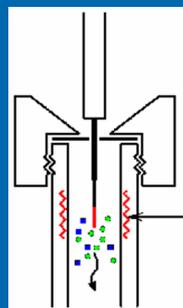
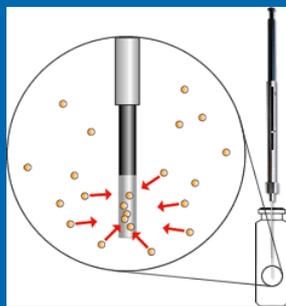
EI (70eV)

NCI

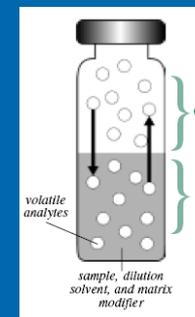
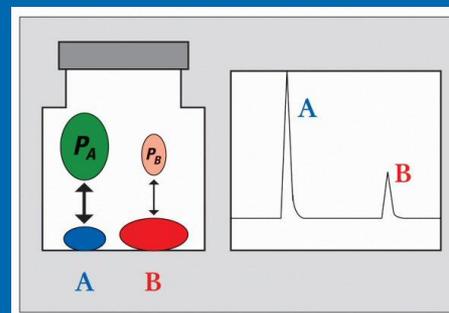
PCI



qMS

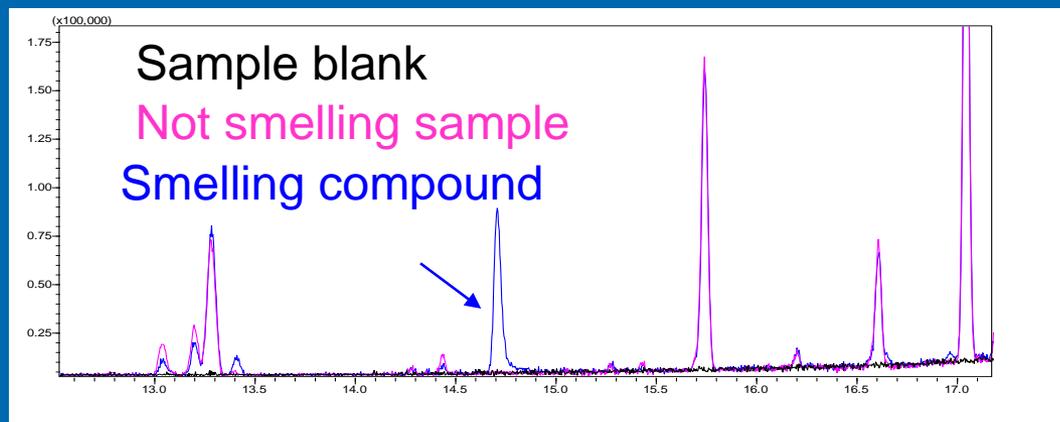
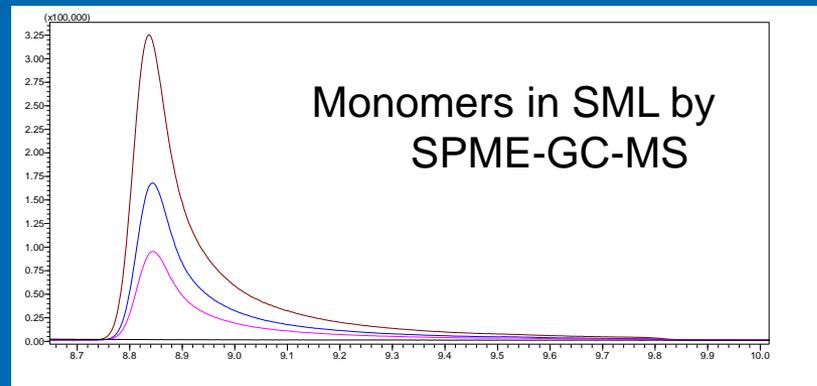


desorción



SPME-GC-MS and HS-GC-MS

- Volatiles in general (VOCs, VOCs)
- Free monomers
- Smell analysis, defect analysis
- Emission tests
- Automotive specific tests
- Food contact material



GMW8081:
car interior emissions
by static
headspace GC-MS

Identification report

Defect analysis for automotive industry – from the analytical point of view

Puype F., Samsoněk J. (2011) (4/2011) Chemické listy 105/370-373 -- ISSN 0009-2770

Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Headspace-GC

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Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

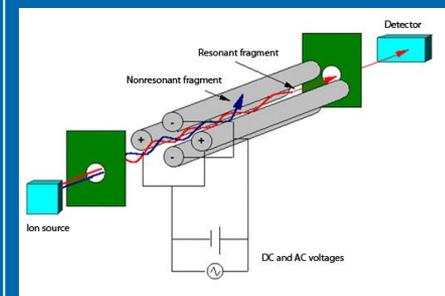
Pyrolysis-GC

Direct Inlet

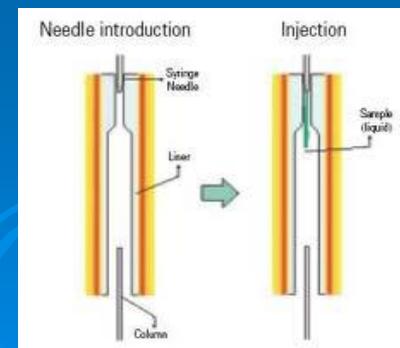
EI (70eV)

NCI

PCI



qMS



Quantification of allergens: Fungicide dimethylfumarate



Directive 2009/251/EC:DMF < 0,1 mg kg⁻¹ in consumer goods



Banning allergies, DMF screening of leather and textile products

Puype F., Samsonok J. (2010) Shimadzu News 1:12-13

Quantification of allergens: dimethylfumarate

iDNES.cz / Zprávy

IDNES.cz | Zprávy | Kraje | Sport | Kultura | Ekonomika | Finance | Bydlení | Cestování | Auto | Hobby | Mobil
 Domácí | Zahraniční | Černá kronika | Očima čtenářů | Kávárna | Kmetel | MF DNES | Počasí

V Česku se prodávají jedovaté boty

15. června 2009 2:29

Stovky svědivých puchýřků na nateklém chodidle. I tak může skončit koupě laciných bot neznámého původu. MF DNES zjistila, že v Česku se prodávají boty napuštěné dimethylfumarátem (DMF). Tato v Evropě zakázaná chemická látka se používá v některých asijských zemích proti plísni.



Uvalo, než jsem se jen zvedla.

Boty byly napuštěny dimethylfumarátem (DMF). Ukázaly to analýzy, jež nechala MF DNES udělat v Institutu pro testování a certifikaci ve Zlíně.

Látka chrání proti plísni.



MF DNES: 15.07.2009

Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Direct liquid injection-GC

Headspace-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

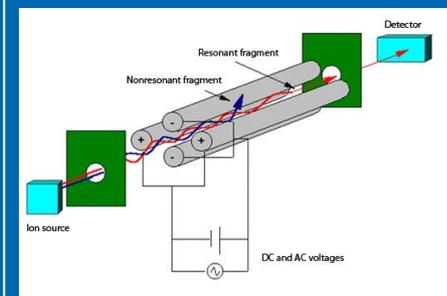
Pyrolysis-GC

Direct Inlet

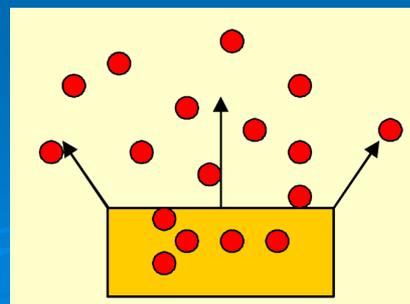
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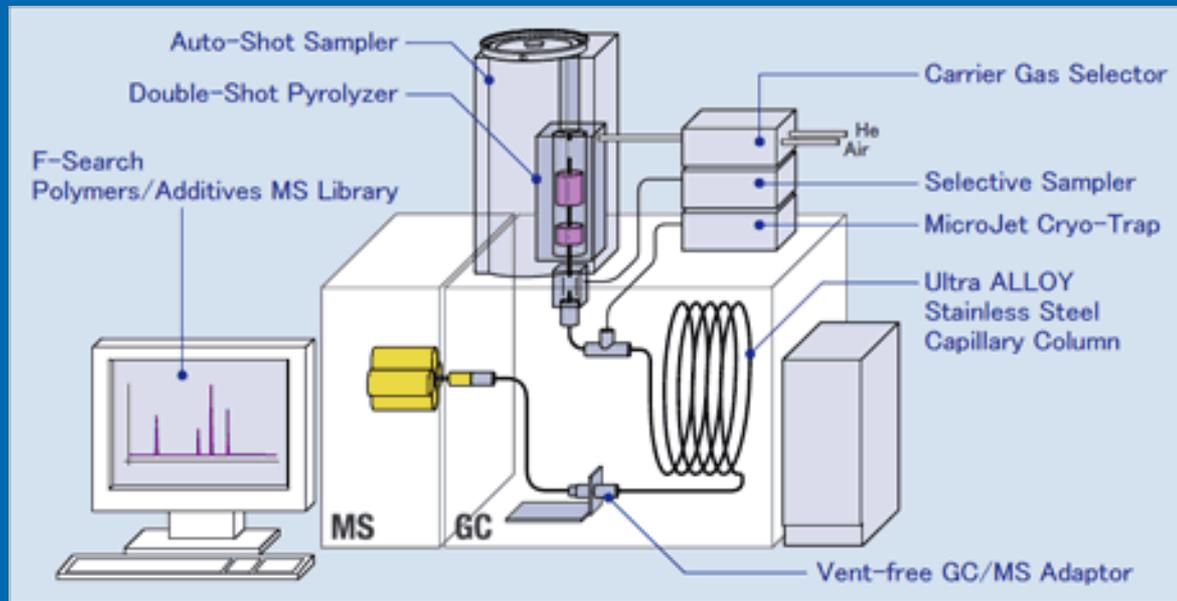
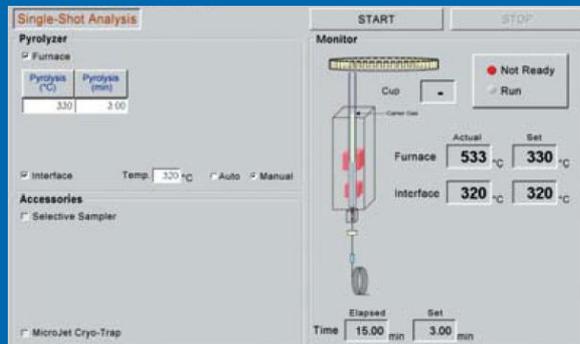
PCI



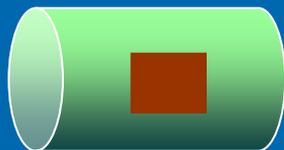
qMS



Direct thermal desorption-GC-MS



SSSS



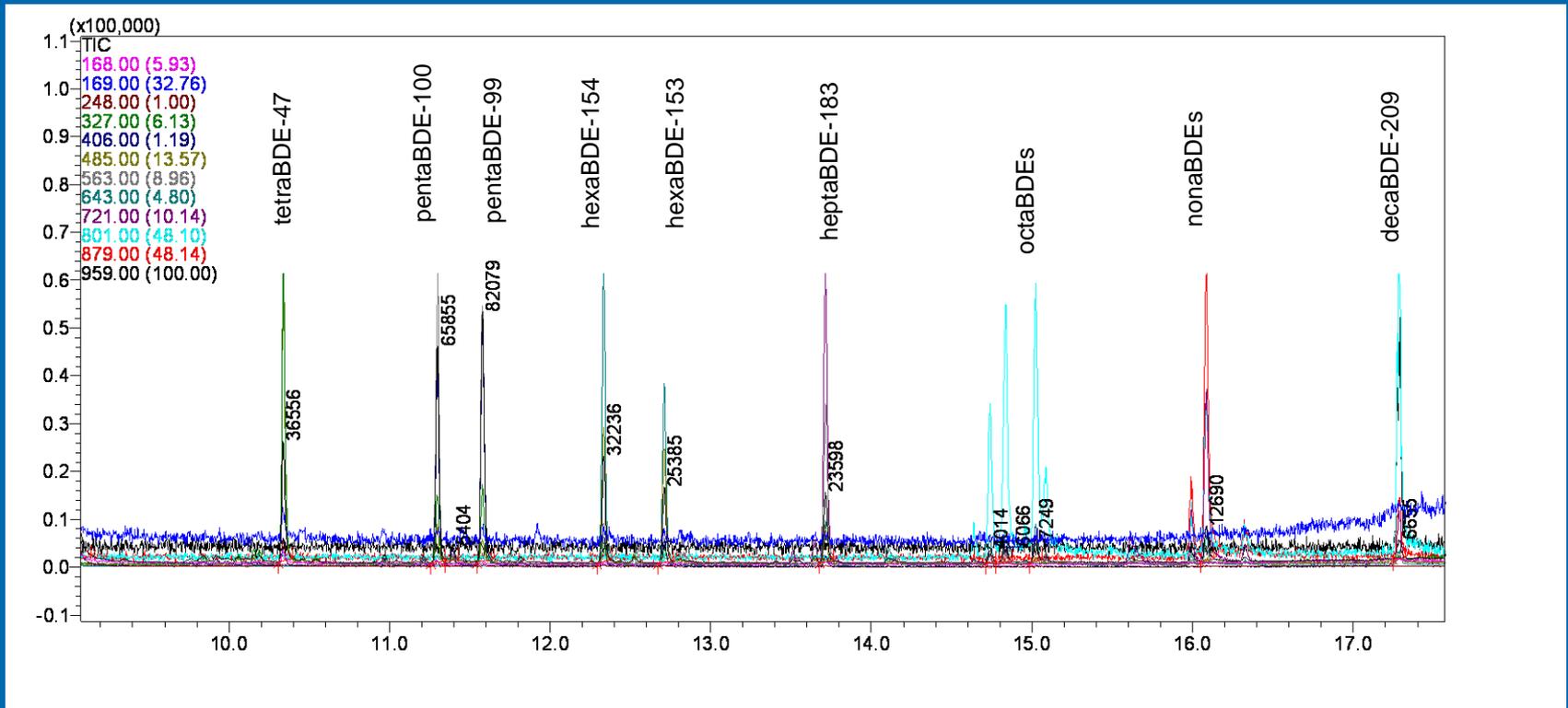
Sample Tube/Cup



Rapid determination of certain BFRs in plastics by thermal desorption GC-MS (TD-GCMS) for the RoHS directive

Puype F., Samsonok J., Vít D. (2007) Organohalogen Compounds, 69:2789-2792

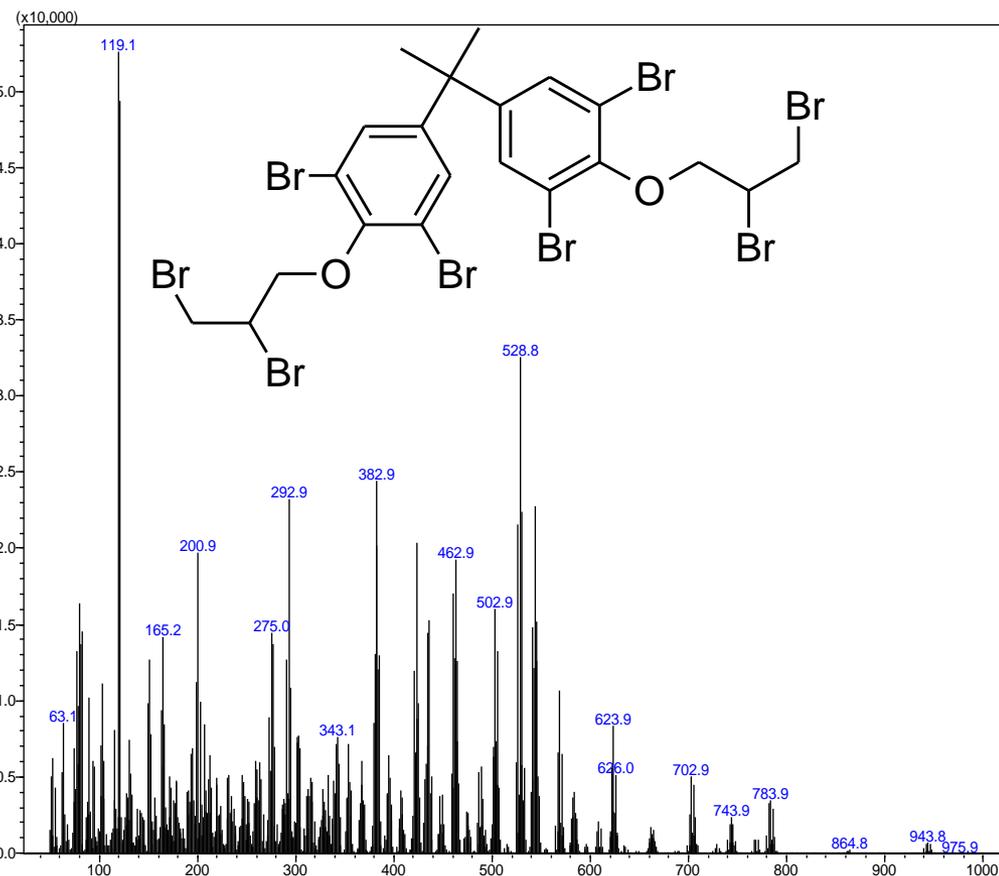
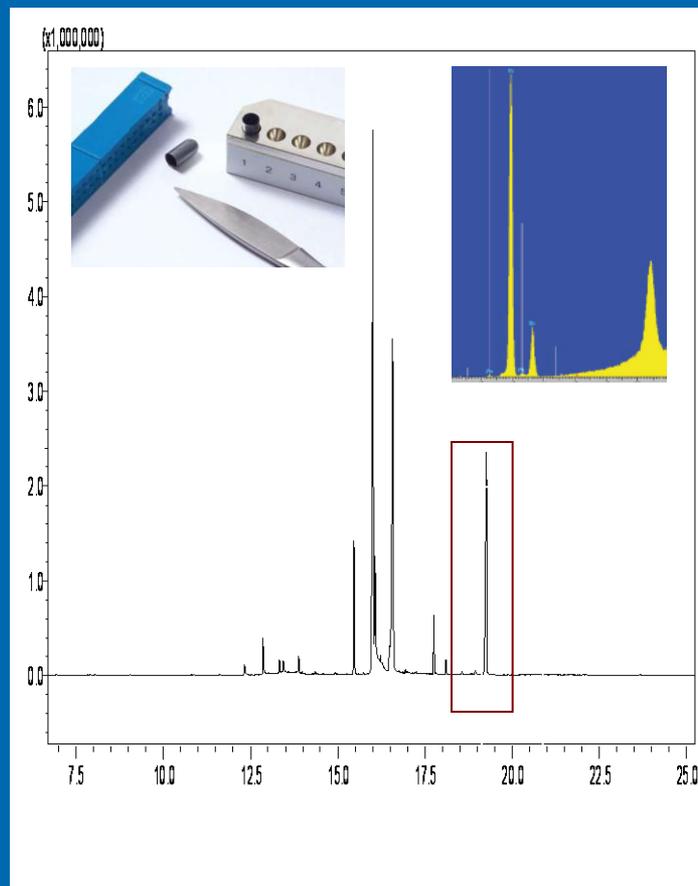
Direct thermal desorption-GC-MS



Evaluation of the quantitative analysis of PBDEs in plastics by thermal desorption GC-MS for soluble polymers

Puype F., Samsonok J. (2008) *Organohalogen Compounds*, 70;1522-1525

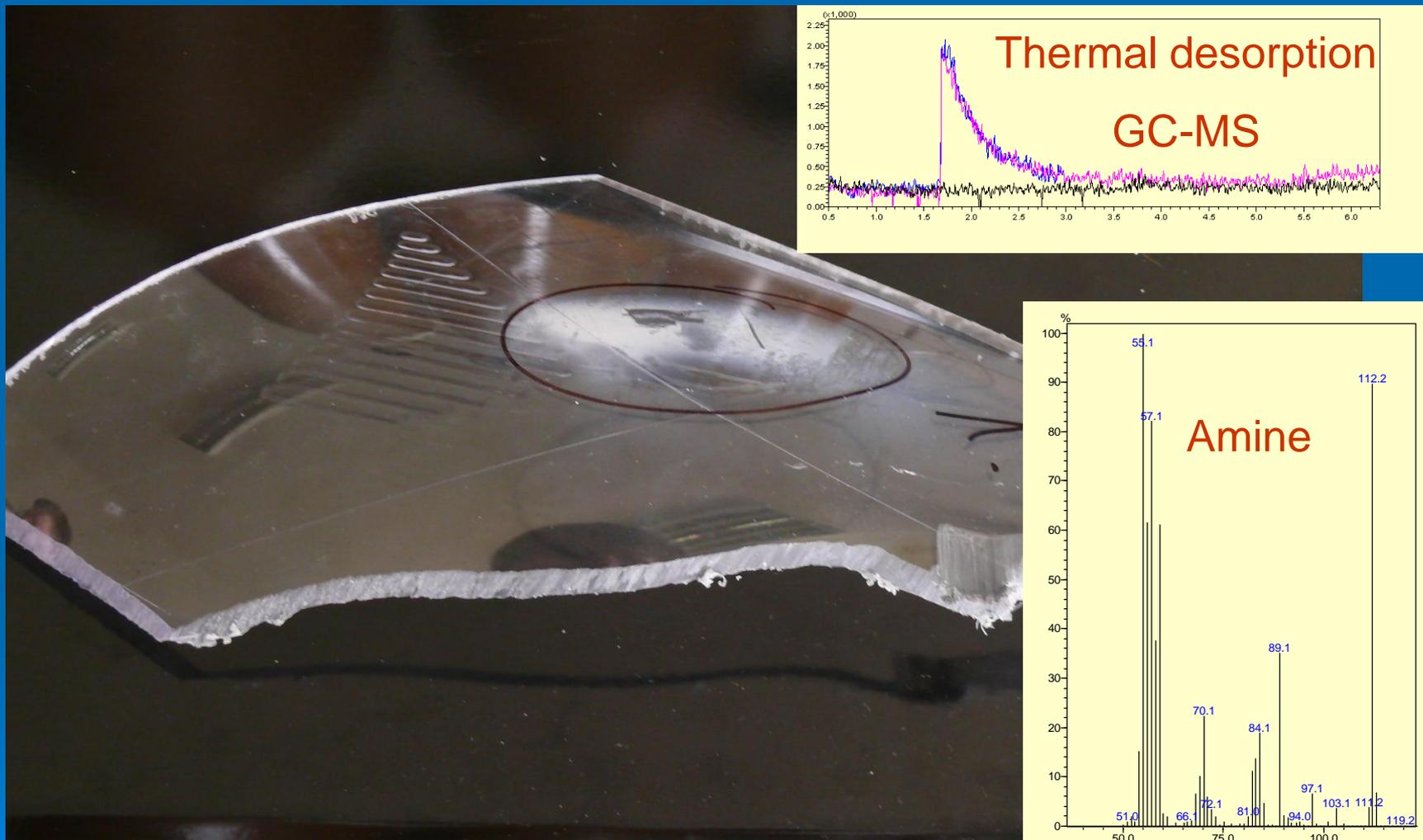
Direct thermal desorption-GC-MS



DIOXIN 2008 28th International Symposium on Halogenated Persistent Organic Pollutants (POPs)
 BIRMINGHAM ENGLAND UK
 17-22 August 2008

Identification of TBBPA-DBPE in plastics by direct thermal desorption-GC-MS
 Puype F., Samsonok J. (2008) Organohalogen Compounds, 70:000914-000917

Defect analysis - fogging



Defect analysis for automotive industry – from the analytical point of view

Puype F., Samsoněk J. (4/2011) Chemické listy, ISSN 0009-2770

Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Direct liquid injection-GC

Headspace-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

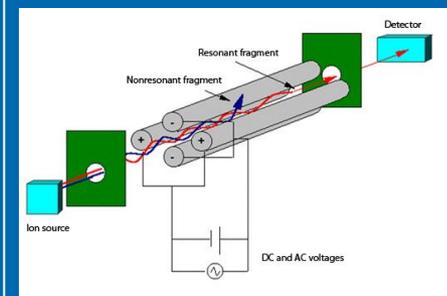
Pyrolysis-GC

Direct Inlet

EI (70eV)

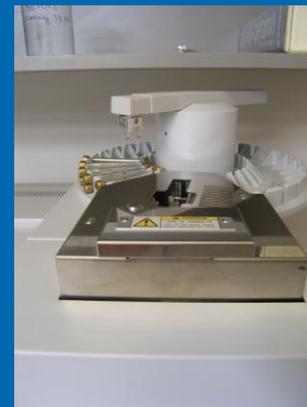
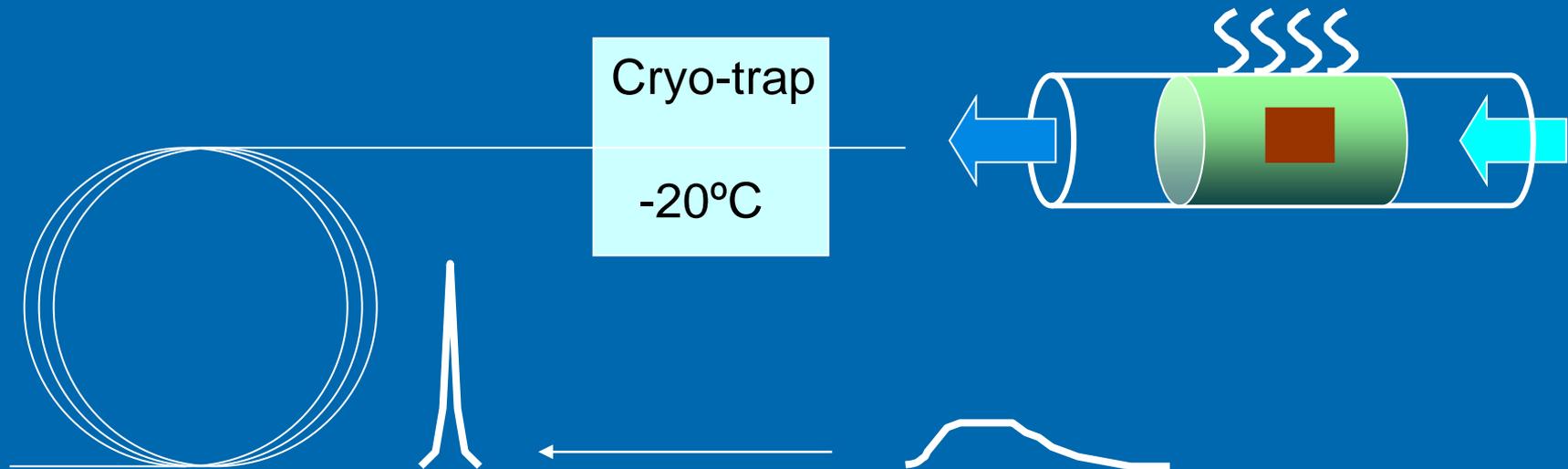
NCI

PCI

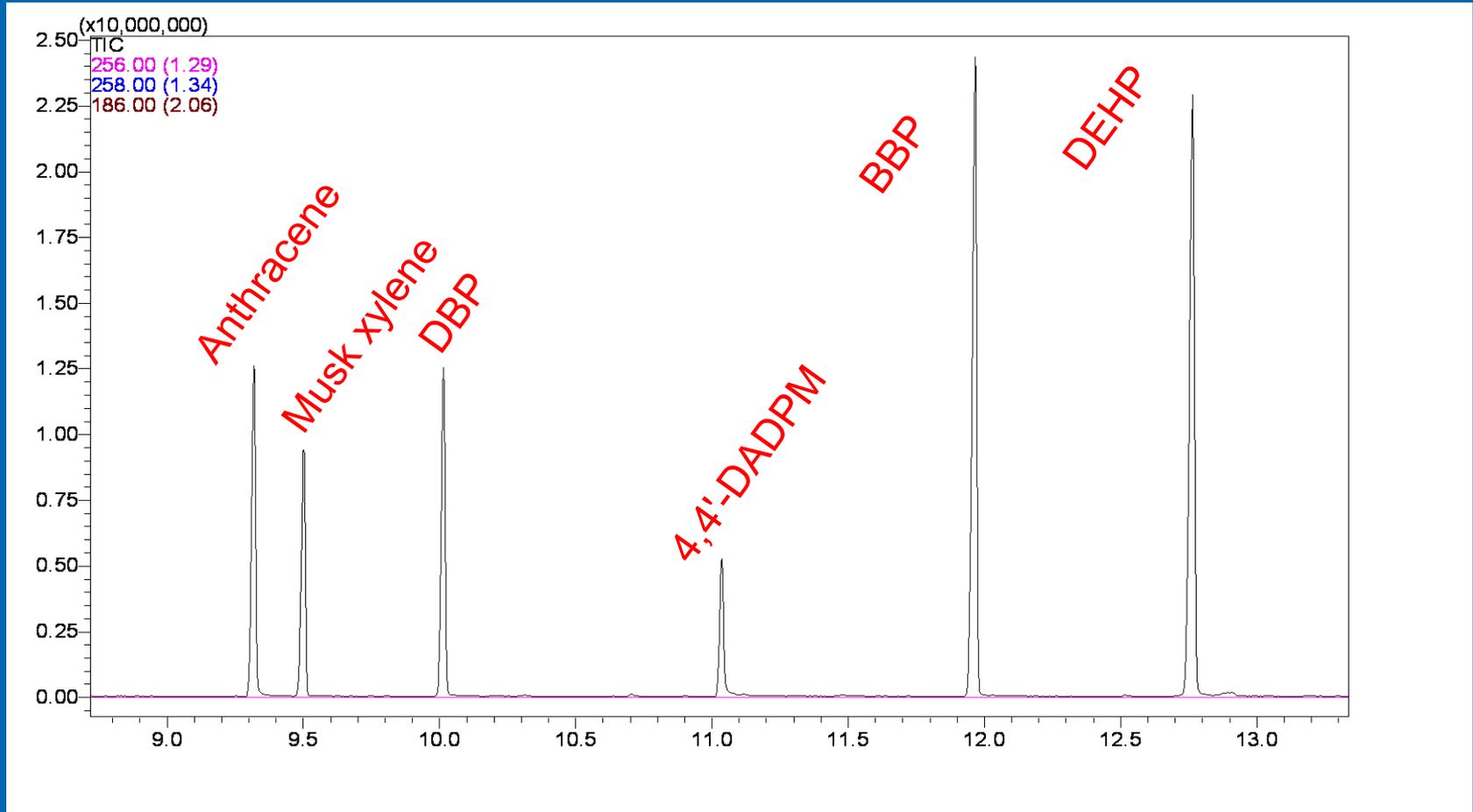


qMS

Thermal desorption with refocussation



Candidate List of Substances of Very High Concern (SVHC)



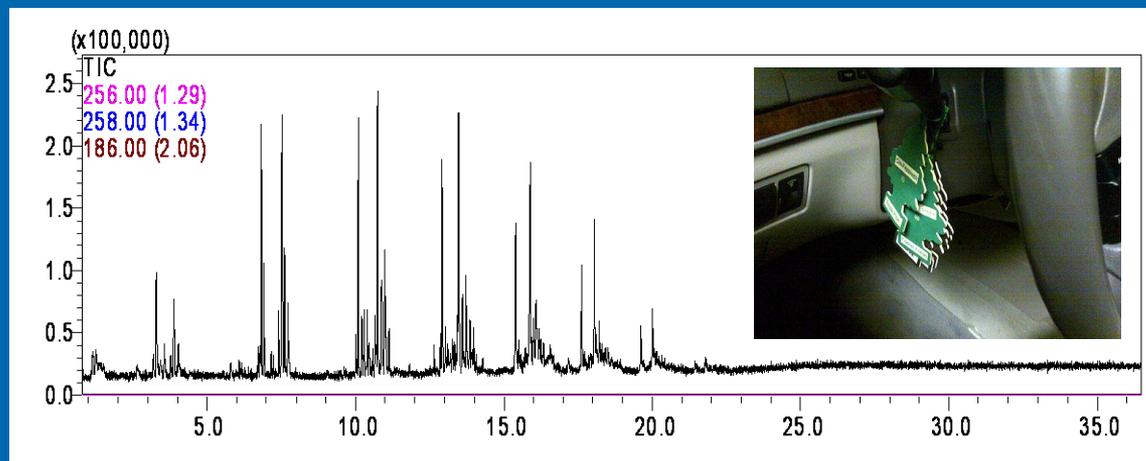
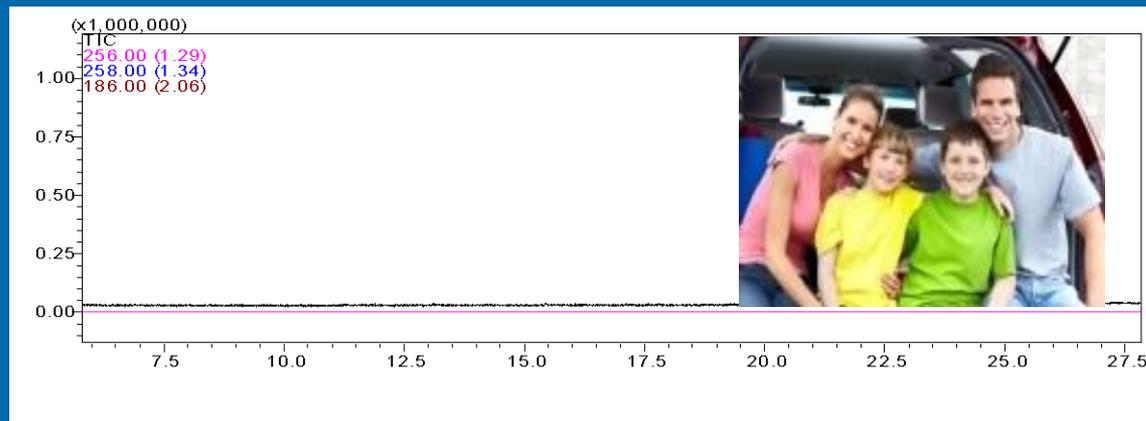
Possibilities with refocussing thermal desorption (TD-GC-MS) for the characterisation of synthetic polymers

Puype F., Samsoněk J. (2008) *Polymery* 2008, P-02 (ISBN 978-80-968433-5-0)

Emission measurements: indoor material / automotive-VDA 278

➤ Lifetime emissions of the product are simulated

➤ Quality requirements in automotive are getting higher !!



Emission testing of non-metal vehicle material according to VDA 278

Puype F., Samson J. (4/2011) Chemické listy 105/370-373 -- ISSN 0009-2770

Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Direct liquid injection-GC

Headspace-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

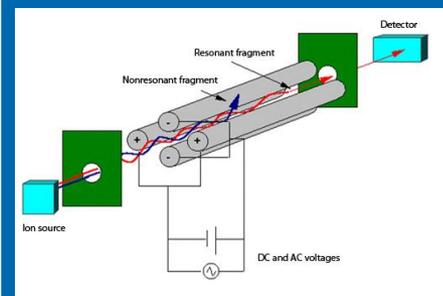
Pyrolysis-GC

Direct Inlet

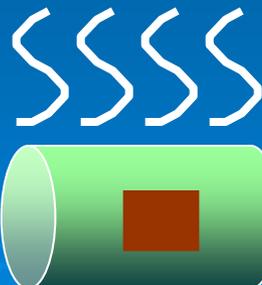
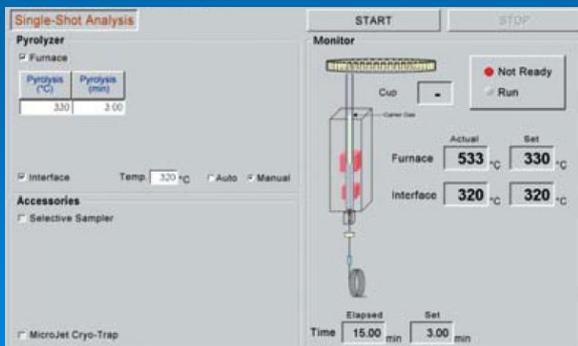
EI (70eV)

NCI

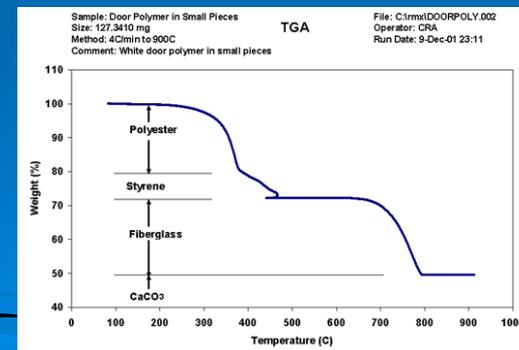
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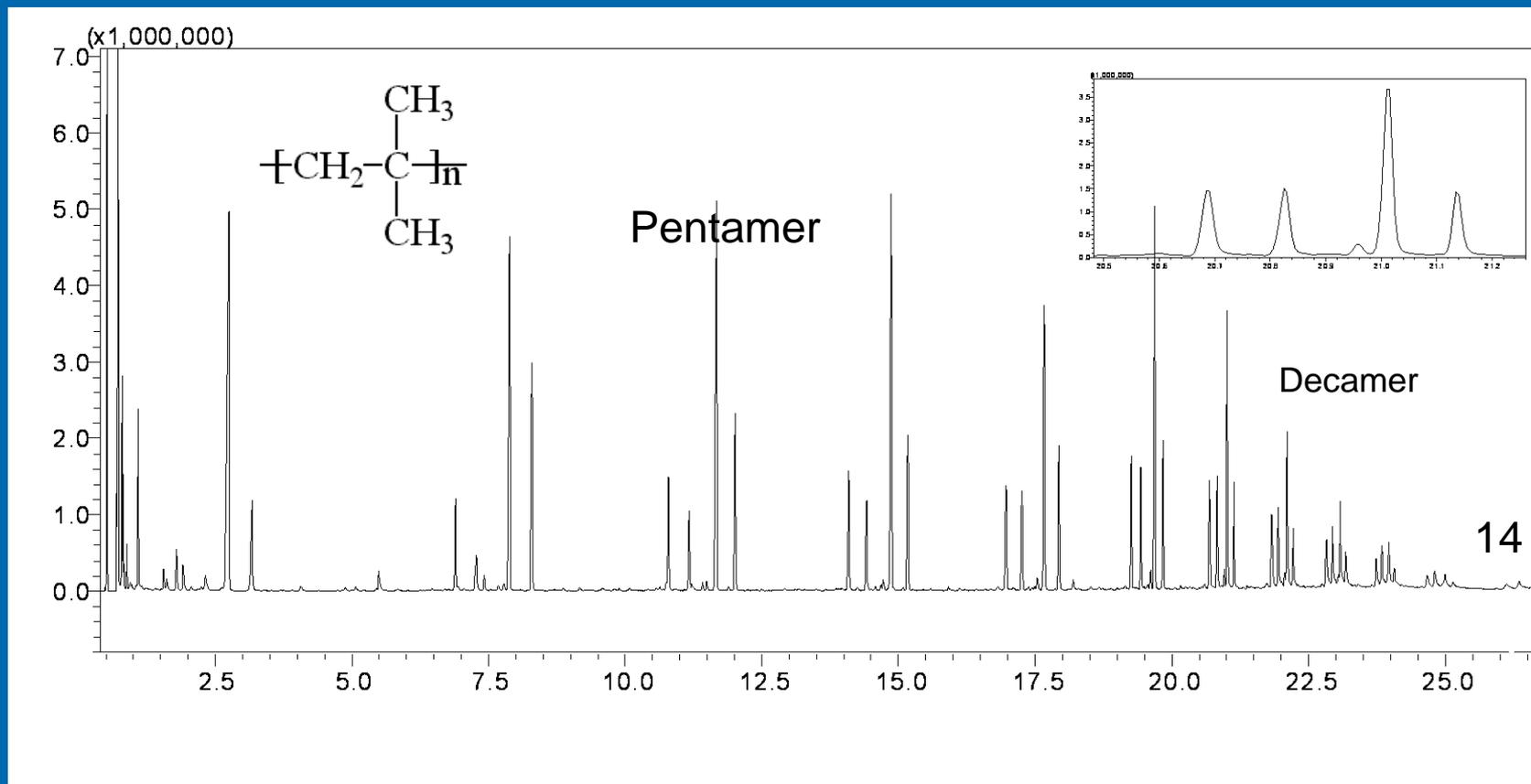
qMS



Sample Tube/Cup



Pyrolysis-GC-MS: Polyisobutylene

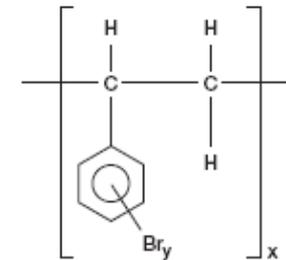


Pyrolysis coupled with gas chromatography and mass spectrometry (PY-GC-MS)
for the rapid characterisation of synthetic polymers

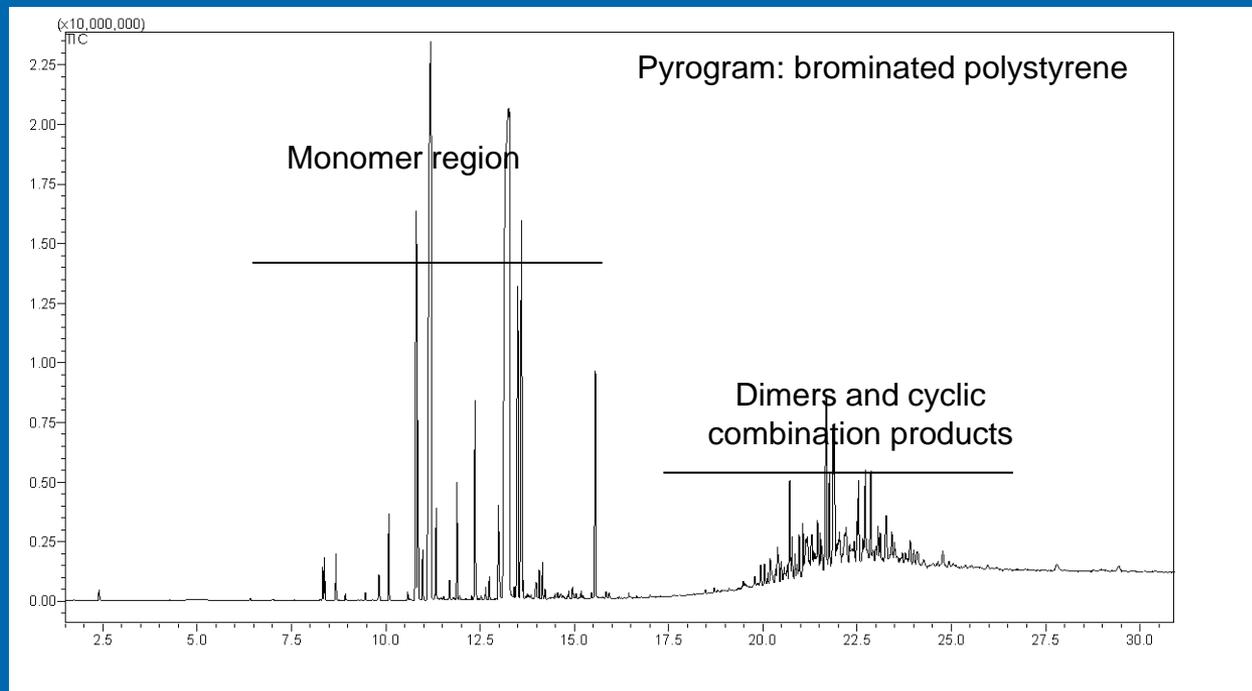
Puype F., Samsonok (2008) *Polymery* 2008,L-16 (ISBN 978-80-968433-5-0)

Brominated polymeric additives

- No migration/ non-blooming
- Some are restricted/limited – speciation required (PBDEs, PBBs, HBCD)
- Brominated polystyrene



where x and y are approximately 2000 and 2.7, respectively

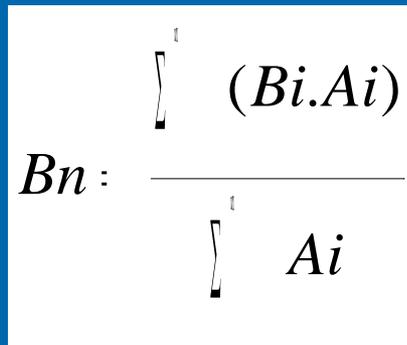


Brominated polymeric additives

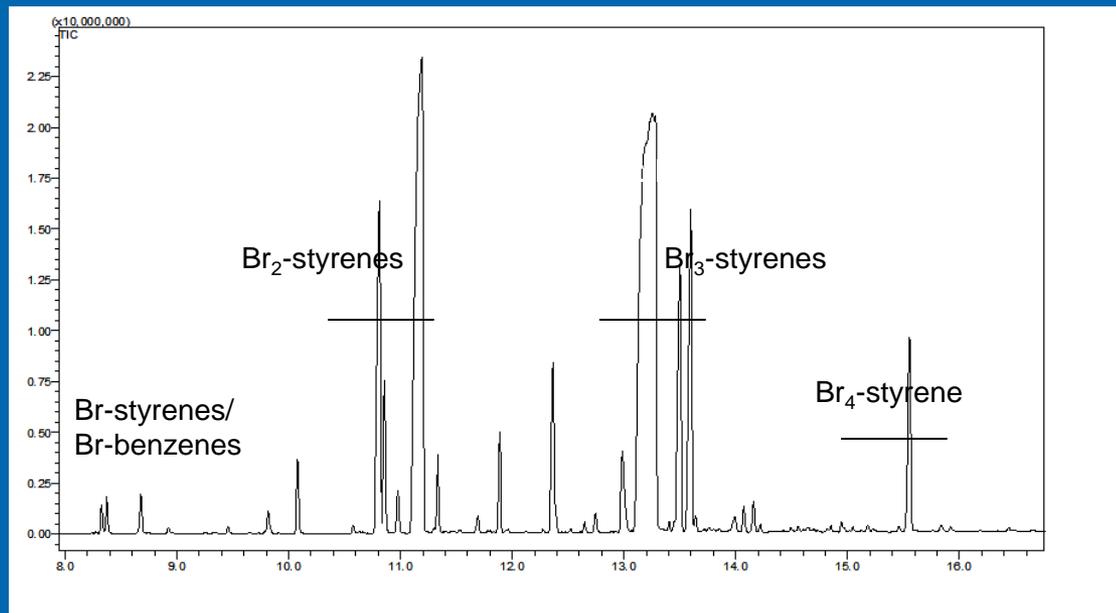
Radical unzipping – depolymerization PS



➤ Brominated polystyrene in PA6

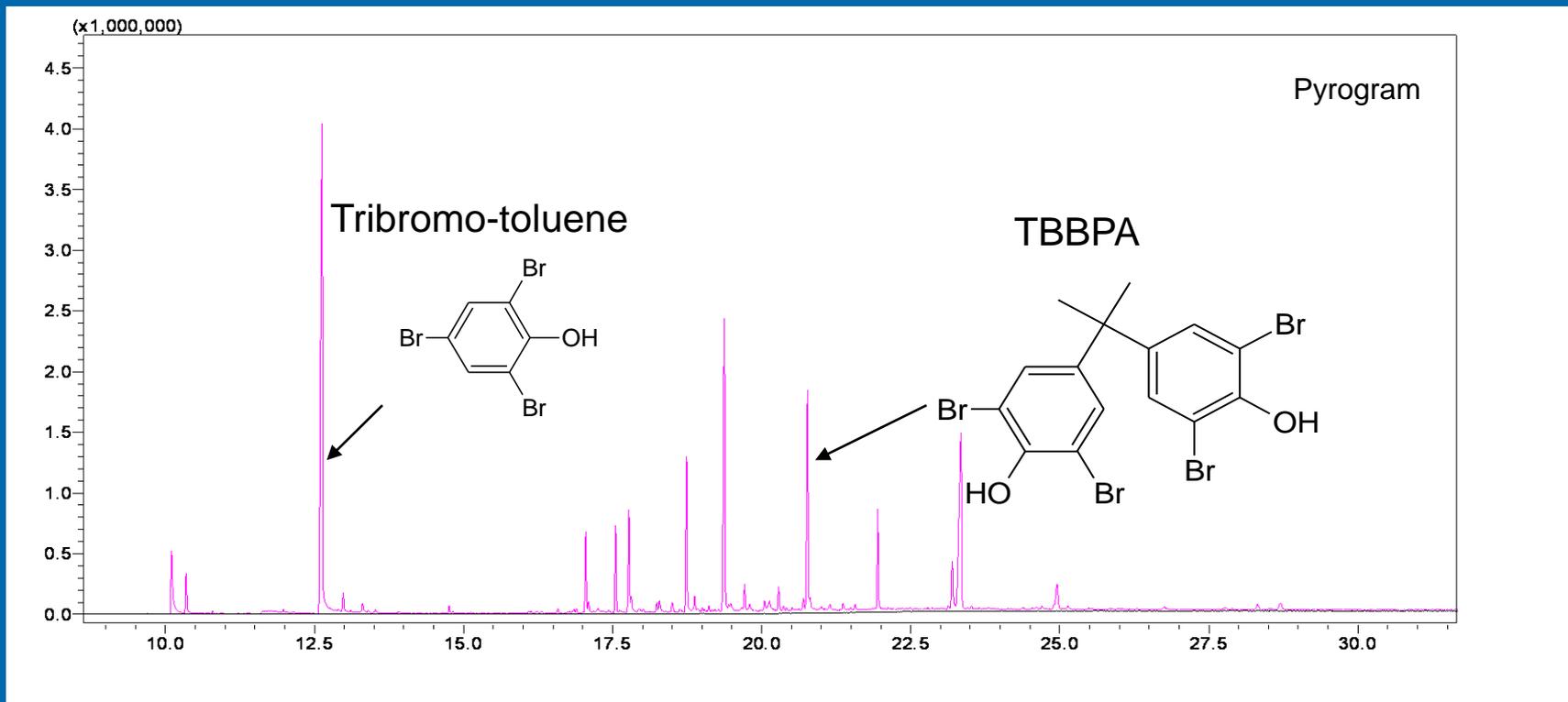


Bromination degree: 2,7 (2% RSD, n=3)



Brominated polymeric additives

- Unknown BFR in toluene extracts from PBT

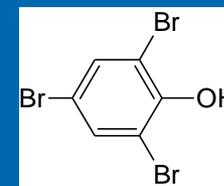
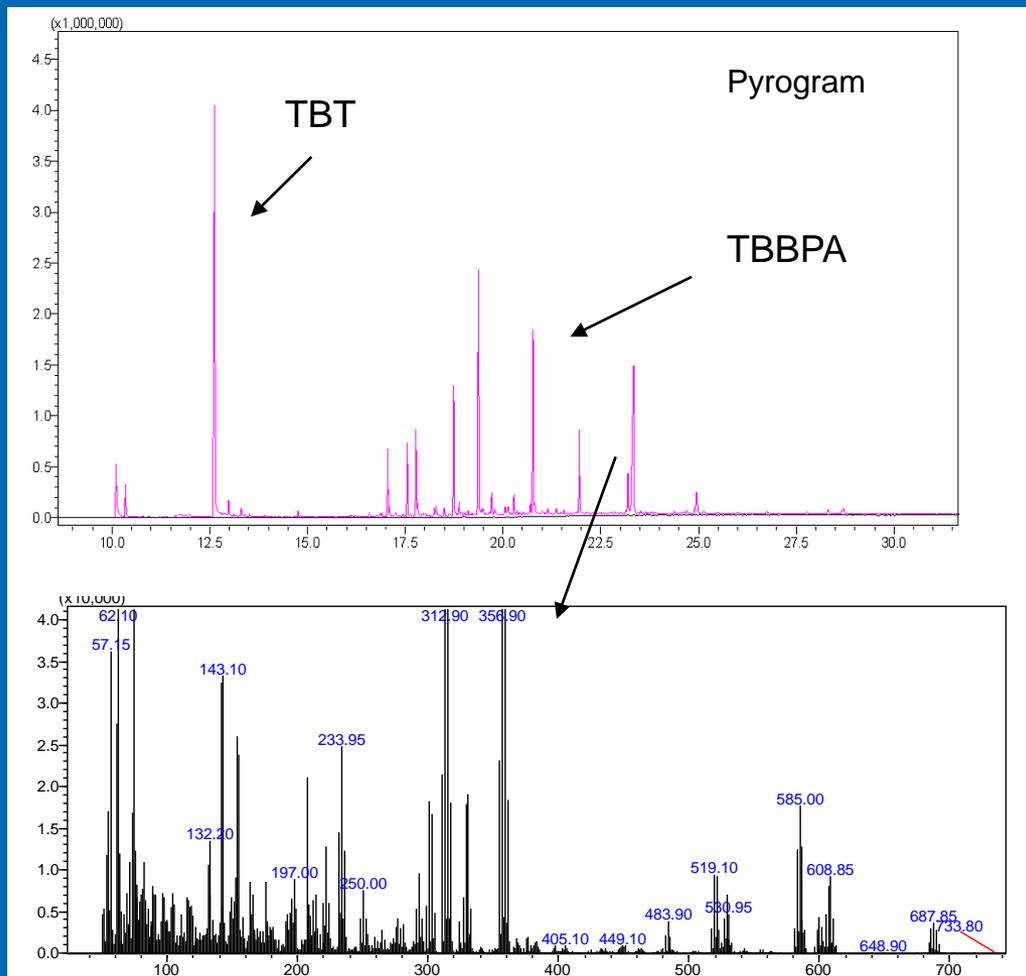


Mass spectrometric analysis of polymeric additives in polymer extracts by pyrolysis-GC-MS

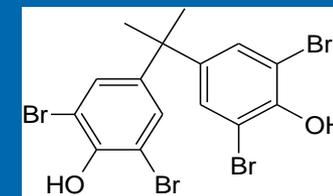
Puype F., Samsoněk J. (4/2011) Chemické listy, ISSN 0009-2770

Brominated polymeric additives

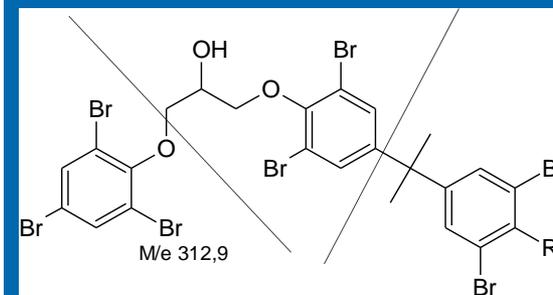
- Unknown BFR in toluene extracts from PBT



TBT

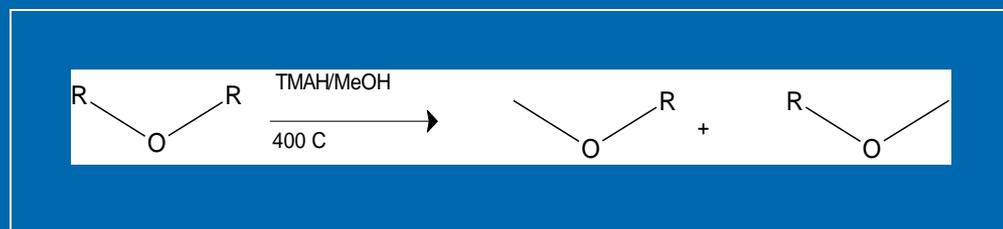
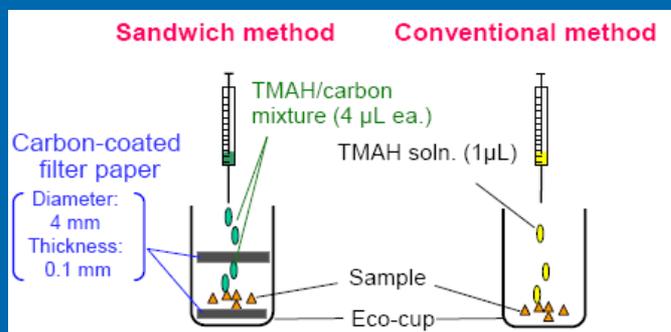


TBBPA

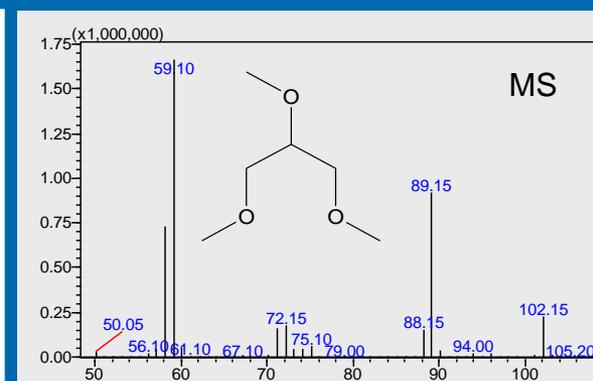
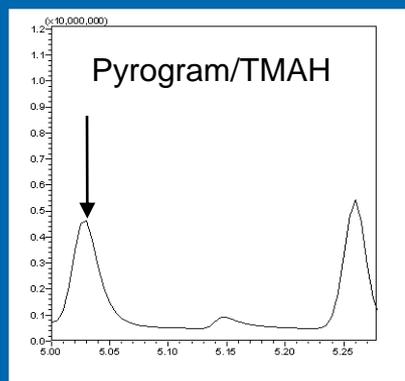
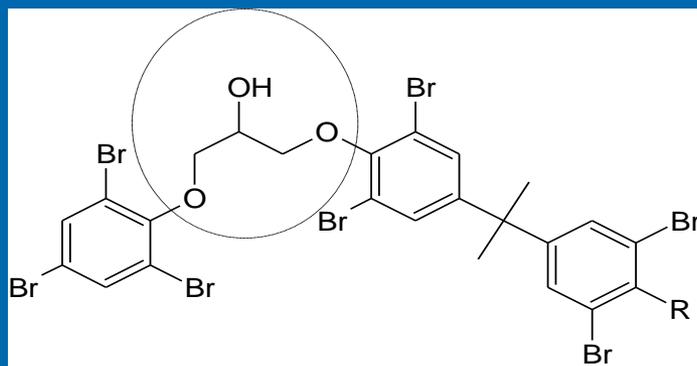


Brominated polymeric additives

- BFRs in toluene extracts from PBT – reactive pyrolysis

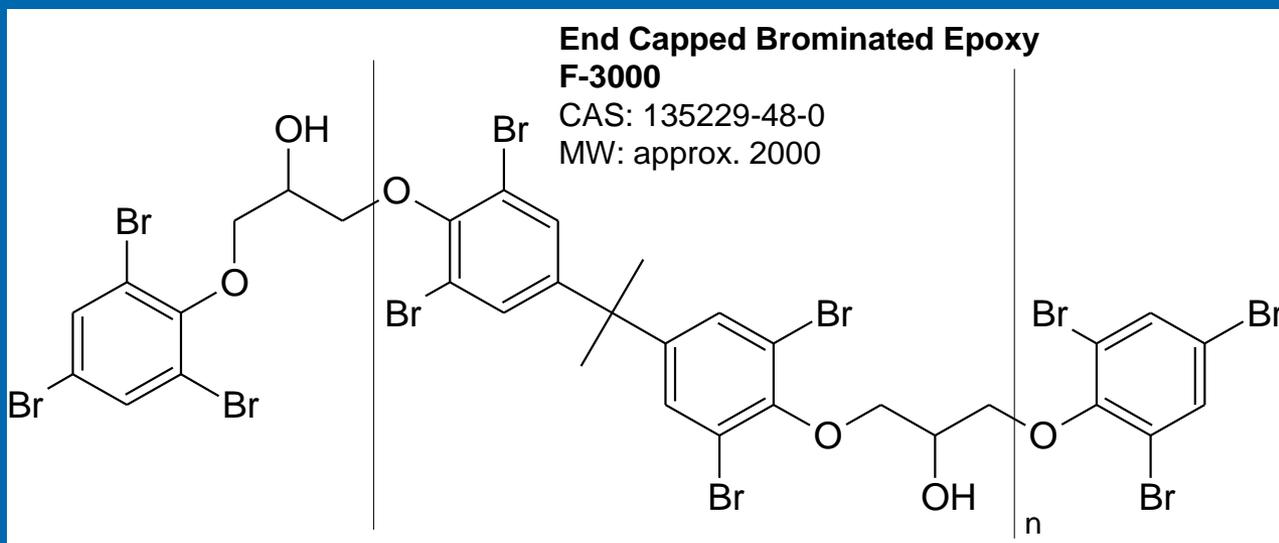


Can we find glyceroltrimethylether with reactive pyrolysis?



Brominated polymeric additives

- BFRs in toluene extracts from PBT – reactive pyrolysis



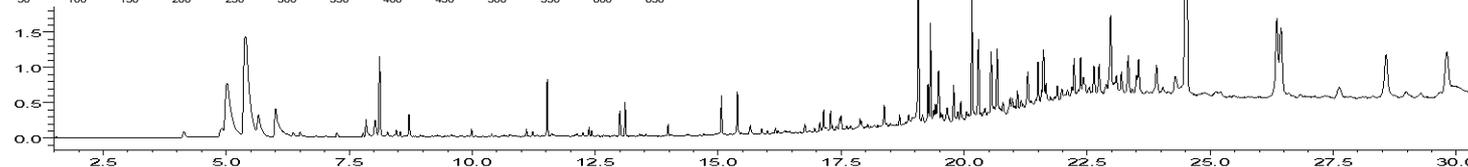
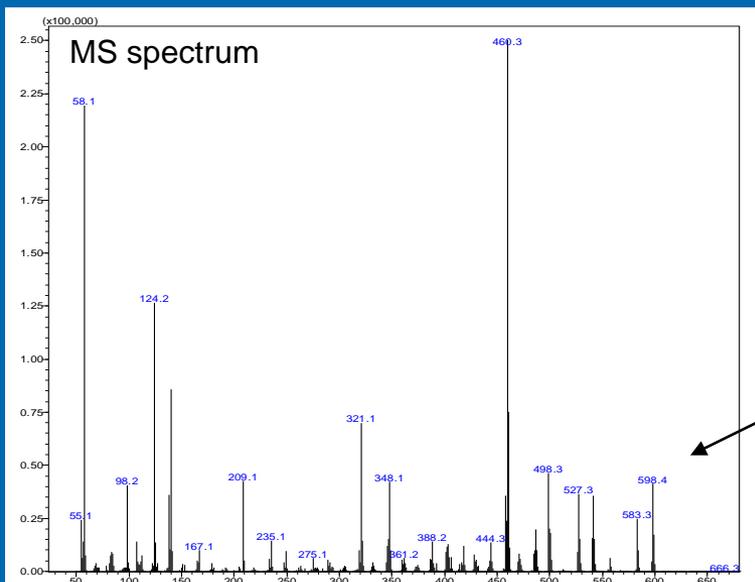
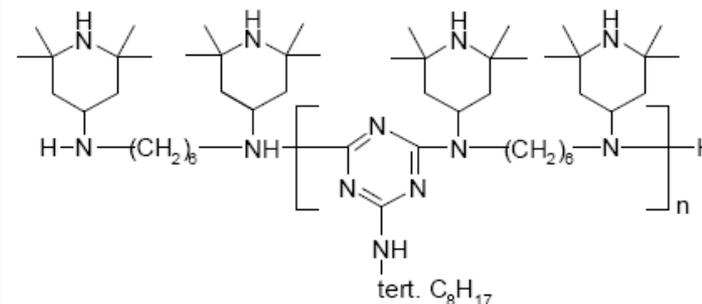
[Mass spectrometric analysis of polymeric additives in polymer extracts by pyrolysis-GC-MS](#)

Puype F., Samsoněk J. (4/2011) Chemické listy, ISSN 0009-2770

Polymeric hindered amine light stabilizers (p-HALS) – stabilizer 944

- Mn = 2000-3100
- Polyolefins/PVC/PA
- Cyclic depolymerization

CHIMASSORB 944



Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Direct liquid injection-GC

Headspace-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

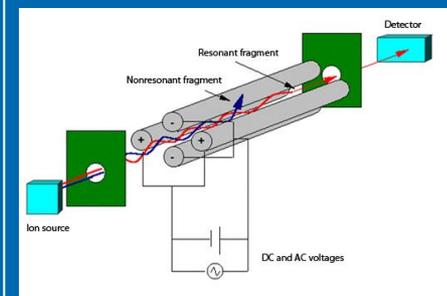
Pyrolysis-GC

Direct Inlet

EI (70eV)

NCI

PCI

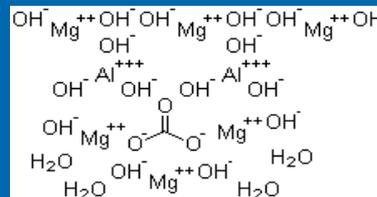


MS

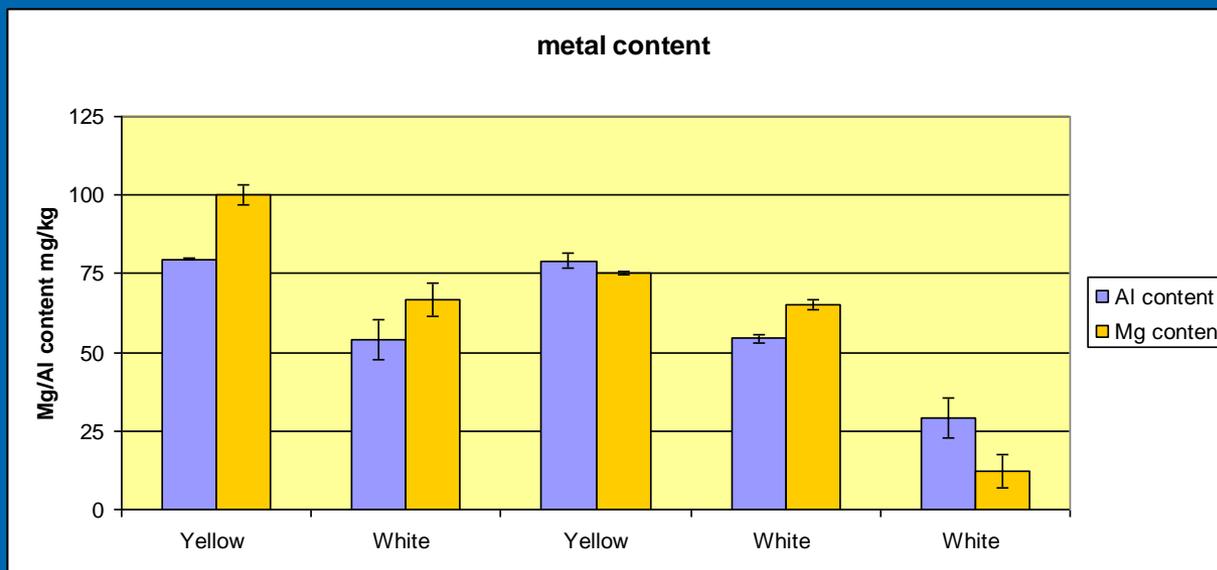
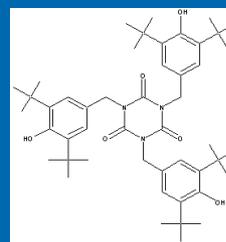


Hydrotalcites in polymers, sources for yellowing?

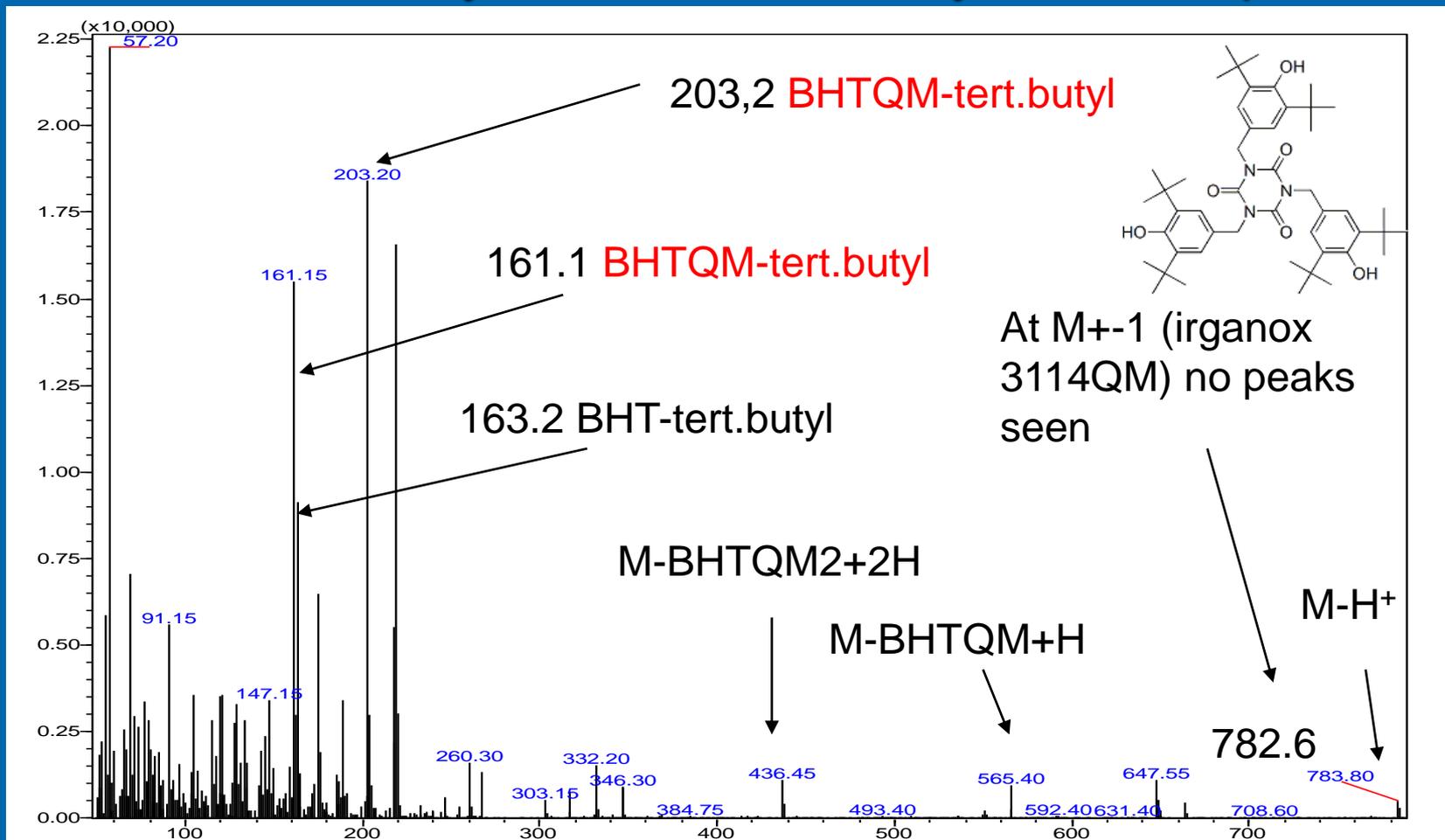
Hydrotalcites - $Mg_6Al_2CO_3(OH)_{16} \cdot 4(H_2O)$ –
 can catalyze the releasing of
 BHT and BHT derivates from
 phenolic antioxidants



Irganox 3114 is a big molecule
 cannot be separated by classical GC
 (MW 784 Da)



Direct inlet analysis: extracts from yellow samples



Defect analysis for automotive industry – from the analytical point of view

Puype F., Samsonok J. (4/2011) Chemické listy, ISSN 0009-2770

Quadrupole - mass filter

Solid Phase Micro Extraction (SPME)-GC

Direct liquid injection-GC

Headspace-GC

Direct Thermal Desorption-GC

Refocussation Thermal Desorption-GC

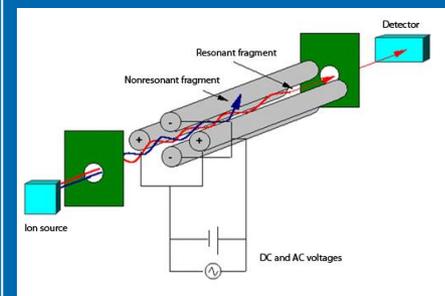
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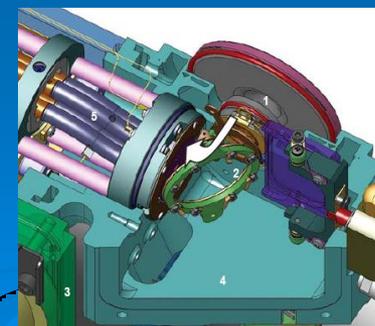
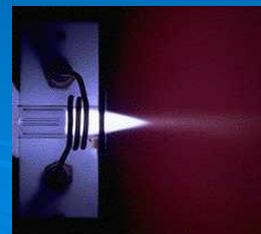
NCI

PCI



qMS

ICP (hot and cool)



qMS

Inductively coupled plasma-MS

Sample preparation

Migration test
Dilution
Internal standard
External calibration

Sample introduction

Pumping
Nebulization
Atomization
Ionization

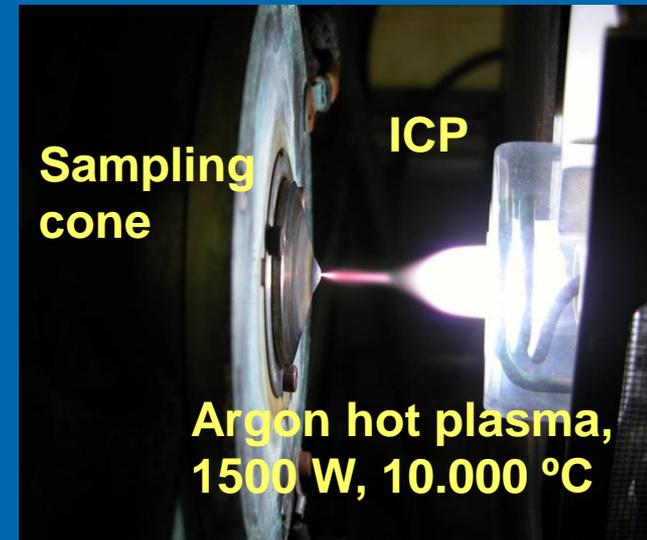
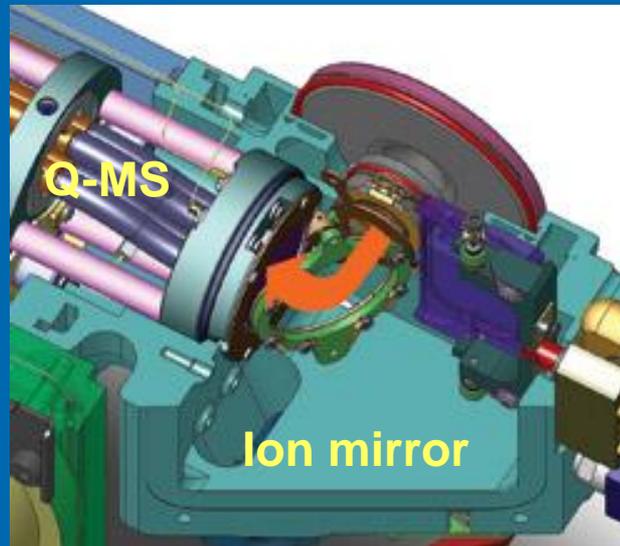
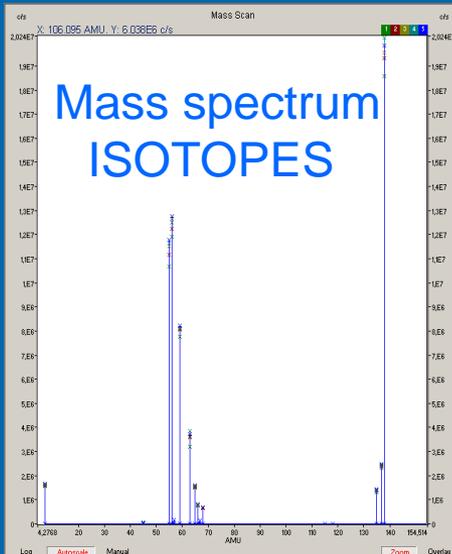
Detection

Background corr.
Resolution
Spectral interference
Mass spectrometry
Polyatoms

Results
RSD (< 5 %)

Recovery
Duplicates
LOD (ppt)

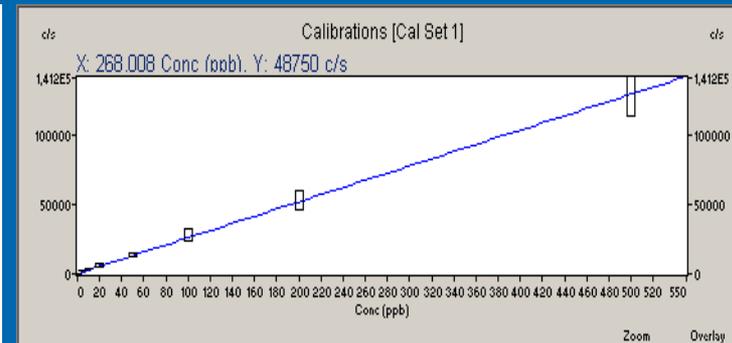
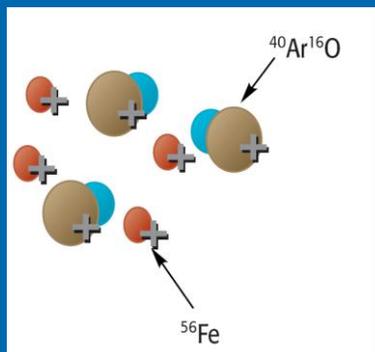
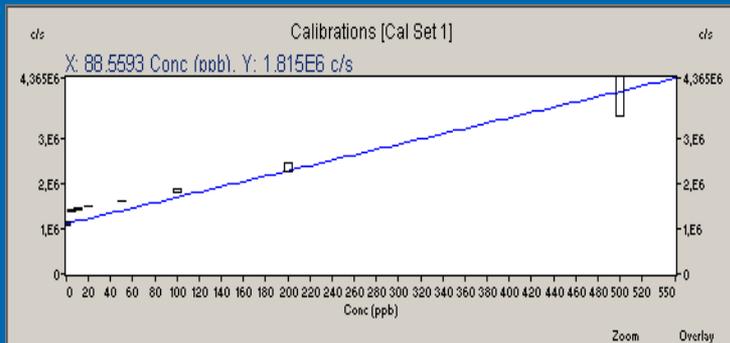
Test report





Spectral interferences (isobaric overlap) for ^{56}Fe ...Polyatoms!

- ^{54}Fe : $^{40}\text{Ar}^{14}\text{N}$, $^{53}\text{Cr}^1\text{H}$, $^{108}\text{Cd}^{++}$, $^{108}\text{Pd}^{++}$,
- ^{56}Fe : $^{40}\text{Ca}^{16}\text{O}$, $^{40}\text{Ar}^{16}\text{O}$, $^{55}\text{Mn}^1\text{H}$, $^{112}\text{Cd}^{++}$, $^{112}\text{Sn}^{++}$
- ^{57}Fe : $\text{Ar}^{16}\text{O}^1\text{H}$, $^{40}\text{Ca}^{16}\text{O}^1\text{H}$, $^{56}\text{Fe}^1\text{H}$, $^{114}\text{Cd}^{++}$, $^{114}\text{Sn}^{++}$
- ^{58}Fe : Ar^{18}O , $^{40}\text{Ca}^{18}\text{O}$, $^{42}\text{Ca}^{16}\text{O}$, $^{57}\text{Fe}^1\text{H}$, $^{116}\text{Cd}^{++}$, $^{116}\text{Sn}^{++}$, ^{58}Ni



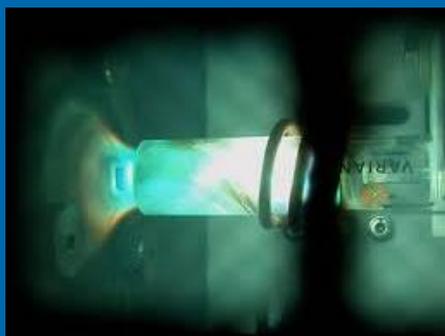


se	Iron 26 Fe 55.85	Cobalt 27 Co 58.93
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- Trace analysis in food contact materials
- Elemental speciation analysis
- Impurities
- Defect analysis
- Difficult matrixes (e.g. low power explosives, tetrahedral white phosphorus, LiBr from heat pumps, etc...)
- Supporting research and development
- Toy testing



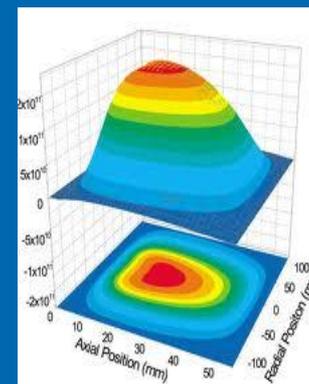
Varian ICP-qMS



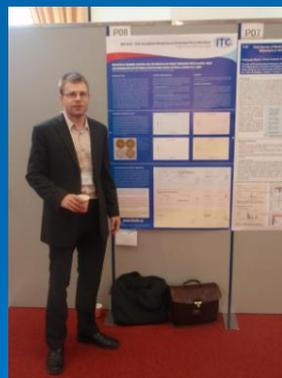
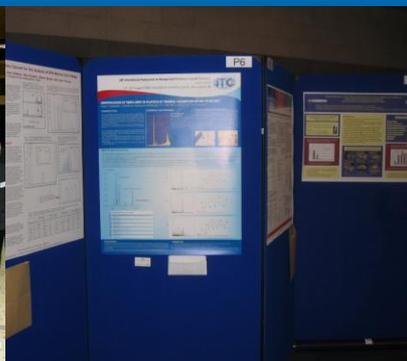
And, and, and,...

**- Analytical laboratory:
analytical plasma spectrometry
and
atomic emission spectrometry**

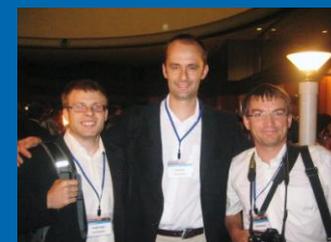
**- Analytical laboratory:
analytical mass spectrometry
and
separation science**



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Many thanks
for your
attention !



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Analytical laboratory