Polymer Analysis – GC/MS

A Review of Applications and Why Small Molecules are Important

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DOW

"See what I mean? Nobody gives a damn anymore!"

Purpose/Outline

- NOT - review of "GC/MS of polymers"
- Maybe - nudge to get people thinking about:
  - Methods
  - Applications
  - Problem-solving

using a familiar conventional tool

Soft/Selective Ionization & Detection

- EI/CI/K+IDS/etc. – well characterized response
- EC, nitrogen, FPD, AED, etc. GC detectors
- MS/MS
- AMDIS
- High resolution/exact mass

Polymers & GC/MS – Why bother?

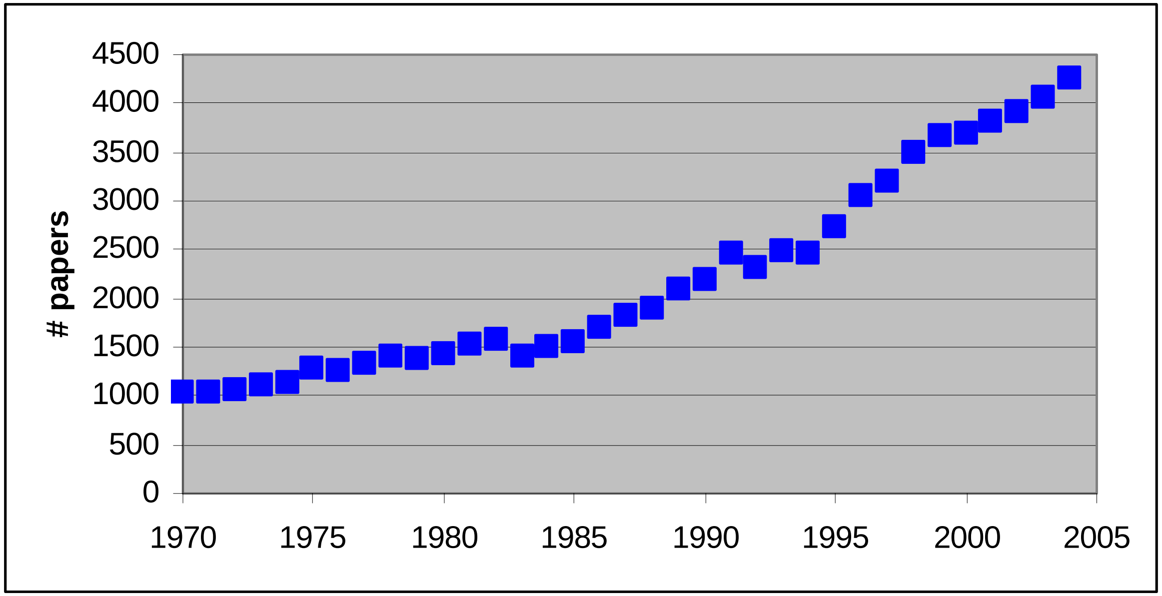
- Tradition – inexpensive, readily available, simple
- High dynamic range of concentrations
- *Very* high separation power
- Small molecules are important!

  Odor, taste, leachates, catalyst poisons

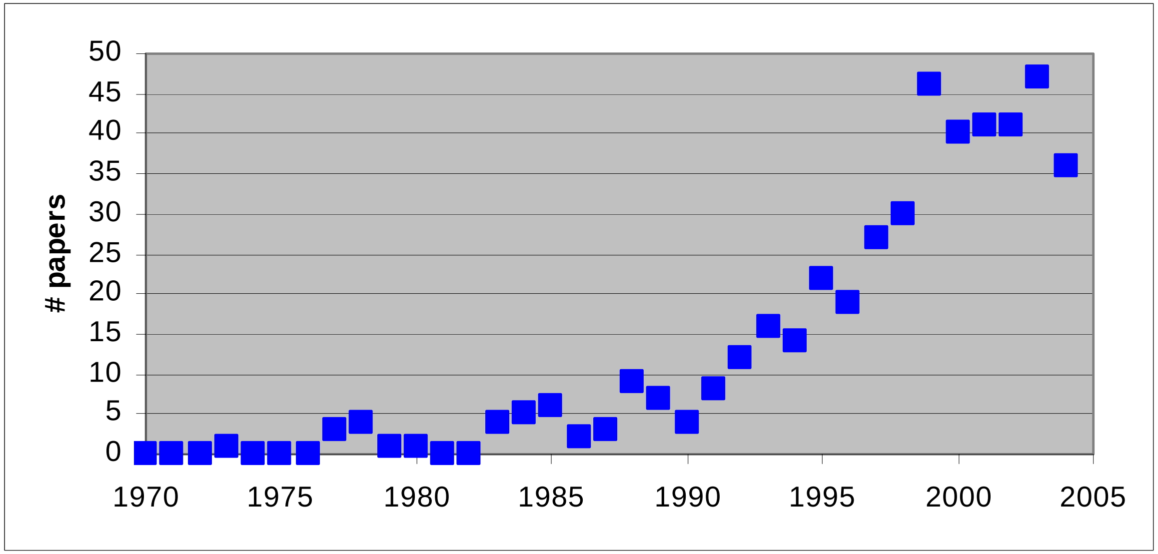
- **Thermal behavior of polymer**
- **Structural details via pyrolysis**
- **Additives & degradation products**

Publications? – not so much; the “good stuff” is ™, ®, ©, ⊗, ☠

polymer analysis



polymer analysis via GC/MS



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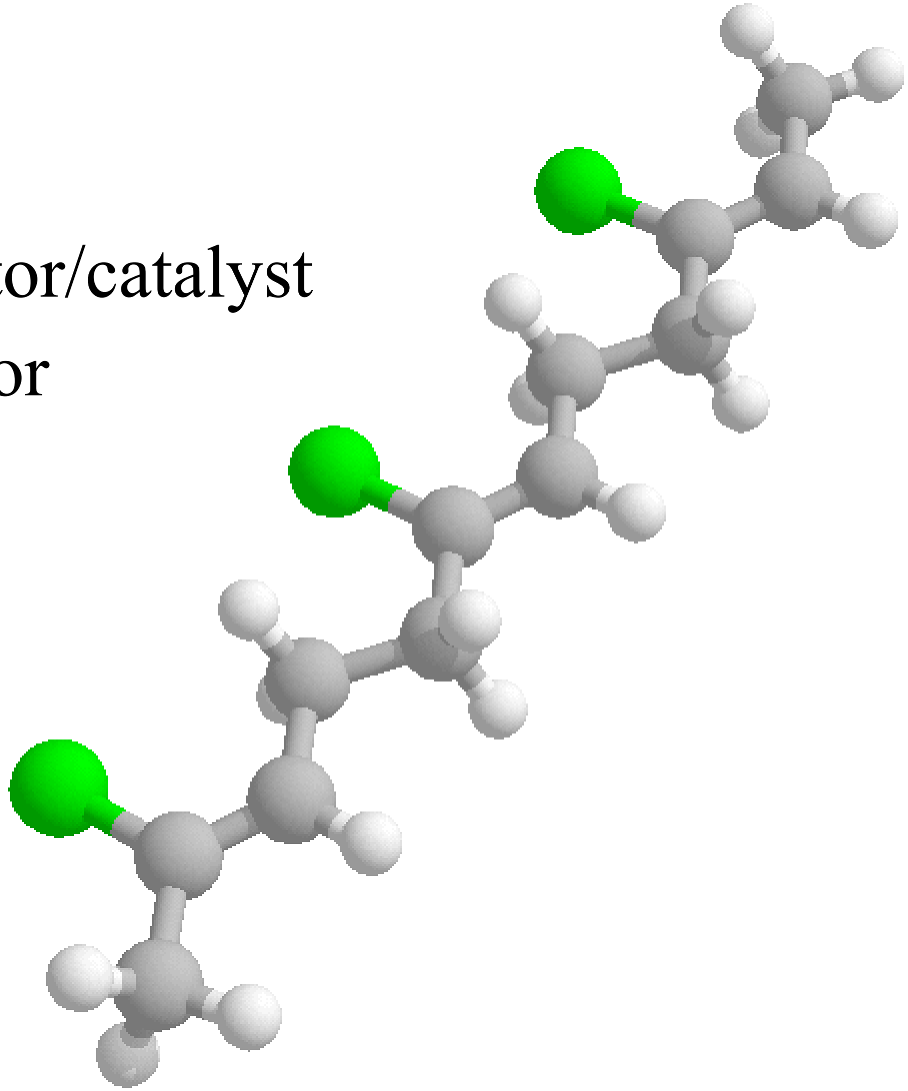
Neoprene Additives

- Acid acceptor
- Vulcanizing agent
- Vulcanizing accelerator/catalyst
- Vulcanizing terminator
- Antioxidant
- Antiozonant
- Filler
- Plasticizer
- Lubricant
- Rheology adjuster



Potential Small–Molecule Additives

- adhesion promoter
- anti-biologics (fungi, bacteria, virus, algae)
- anti-foam/foaming agent
- anti-fog agent
- anti-oxidant
- anti-static, anti-dust agent
- biodegradation enhancer/facilitator
- blowing agent (inert gas, reactive decomposition agent)
- coupling/cross linking
- dye, mordant, dye facilitator, anti-migration
- fabrication (spin/mold/inject) aid
- flame-retardant
- free-radical scavenger, quenchant
- heat stabilizer
- nucleating agent
- odorants, flavors
- optical brighteners
- packaging/barrier scavenging agents (H_2O, O_2, C_2H_4)
- plasticizer
- surfactants, compatibilizers
- time-release agents (anti-oxidants, drugs, etc.)
- UV absorber/inhibitor
- viscosity/rheology adjusters

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Emerg -ing -ed Technologies

- GC/GC/MS
- Exact mass GC/MS (ionizing and non-ionizing radiation by-products)
- Newer column technologies: PLOT; T_{max}>400º
  - light reactive gases (HCN, HCl, CH_2O_2, NH_3, COCl)
  - heavy components (Irganox 330, 1076, 1035 – MWs 500-700)
- New adsorbents, dynamic headspace, SPME, supercritical fluid extraction
- Advanced sample introduction – PTV, TCT, Cold-on-column, TGA/MS
- py-GC/MS for polymer architecture coupled with modeling, 2D-GC, exact mass identifications

Small Molecules Matter

Japanese automakers putting nix on new-car smell

By Hans Greimel
The Associated Press

TOKYO — Anyone who's pulled away from the dealer's lot in a shiny, new sedan knows the seductive scent of fresh plastic, paint and upholstery that evokes a rush of pride and consumer satisfaction.

But that unmistakable new-car smell may soon be heading the way of the rumble seat: Recent research linking it to a toxic cocktail of harmful chemicals is spurring efforts by Japanese automakers to tone down the fumes.

Japanese manufacturers, including Toyota Motor Corp., have become the first to set an industry-wide goal of reducing cabin concentrations to within government guidelines. The push could spur similar action by U.S. and European rivals, making interior air quality an emerging auto safety issue.

"The industry in Japan as a whole has recognized the need for this and is coordinating efforts," Toyota spokesman Paul Nolasco said. "Cutting down on the things that lead to these smells is only something that can be better for you."

The new-car smell emanates largely from chemicals known as volatile organic compounds, or VOCs, that leach from glues, paints, vinyls and plastics in the passenger compartment. The fumes can trigger headaches, sore throats, nausea and drowsiness. Prolonged exposure to some of the chemicals can lead to cancer, though there's no evidence linking that to concentrations in cars.

Critics liken the problem to so-called sick-building syndrome, which traces some illnesses to similar agents seeping from the walls, carpets and fixtures of new buildings.

Just sitting in a new car can subject riders to toxic emissions several times the limits deemed safe for homes or offices by some health authorities, though the problem tends to dissipate after about six months, according to a 2001 study by Australia's Commonwealth Scientific and Industrial Research Organization.

"We find new car interiors have much higher VOC levels than any building we've researched," research leader Steve Brown said. "Ultimately, what we need are cars with interior materials that produce lower emissions."

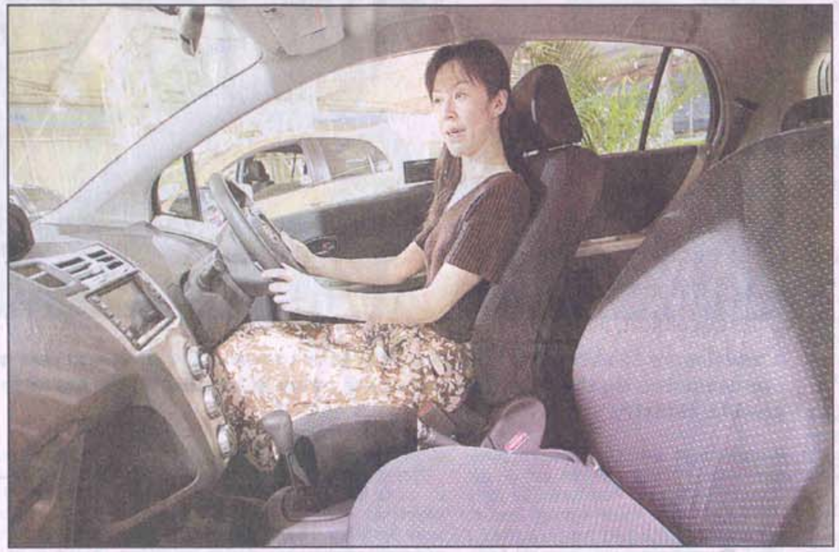
Japanese automakers are now trying to do just that.

Earlier this year, they agreed to cut cabin levels of 13 VOCs, including possible cancer-causing agents styrene and formaldehyde, by 2007 to match Japanese Health Ministry guidelines for air quality in homes.

The Japan Automobile Manufacturers Association initiated the drive after tests found some models made by three of the nation's top carmakers failed to meet government recommendations.

The industry group refused to identify which companies or models were evaluated.

Automakers worldwide have been trying to reduce volatile organic compounds for years. But the Japanese effort marks



Toyota Motor Corp. employee Reiko Ito sits in the driver's seat of a new vehicle produced with less of that unmistakable new-car smell. The fumes have been linked to harmful chemicals.

AP photo

the first time the industry has adopted government guidelines, JAMA's Tatsuya Ota said.

Most of Japan's top five makers — Toyota, Nissan, Honda, Mitsubishi and Mazda — are already rolling out cars in compliance and touting the lower VOC levels as a key selling point, a move that is likely to catch on globally.

"There is good potential for the Japanese to take the lead in this field," said Koji Endo, an auto analyst with Credit Suisse First Boston in Tokyo. "People are starting to feel that VOCs are an issue, and the new efforts are one advantage that they [Japanese manufacturers] can claim."

Brown doesn't know of any government with VOC guidelines for car interiors, but says matching building levels is a good start. Japan's recommendations were adopted in 2002 to combat sick-building syndrome.

The U.S. Environmental Protection Agency sets no guidelines for VOCs in nonindustrial settings, though formaldehyde is regulated as a carcinogen by the Occupational Safety and Health Administration.

The Washington-based Alliance of Automobile Manufacturers, which represents nine carmakers, including General Motors Corp., Ford Motor Co. and DaimlerChrysler AG, says it doesn't follow the issue of VOCs. DaimlerChrysler said it has no initiatives on the VOC-induced new car fumes, while Ford said it's actively trying to reduce them and General Motors said it's monitoring the issue globally; neither automaker would elaborate.

Toyota, Japan's largest automaker, has six models on the road that meet the new standards, while Nissan has four. Honda's new Civic, unveiled this month, is that company's first, while Mitsubishi will begir its lineup with the "i" next year

All say they are on track tc have all new models pass muster from 2007.

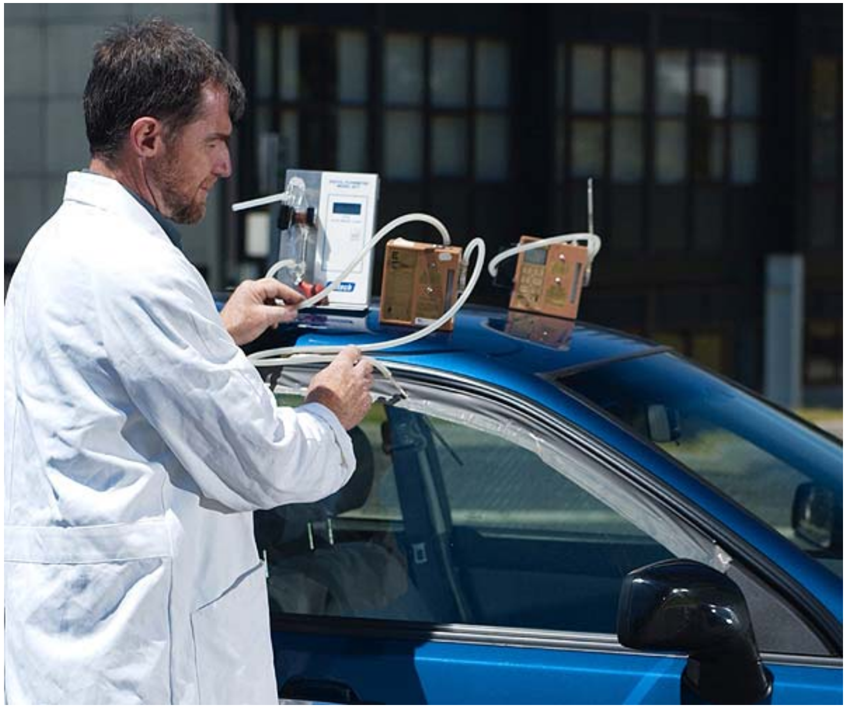
The changes affect cars built ir Japan for the domestic marke and export, but concrete plans tc lower VOCs in vehicles built over seas are largely up in the air.

Cutting levels will initially cos more because the changes are being introduced with new mod els one at a time and therefore lack economies of scale.

There are also additional re search costs for finding alterna tive materials.

Polymer VOC Sampling

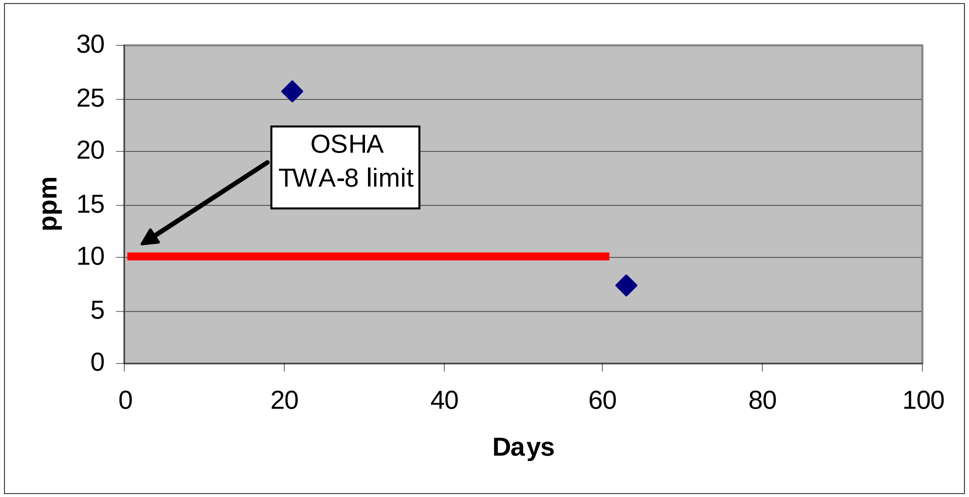
Benzene - known human carcinogen
Acetone - a mucosal irritant
Cyclohexanone - possible human carcinogen
Ethylbenzene - systemic toxic agent
MIBK - systemic toxic agent
n-Hexane - CNS agent
Styrene - probable human carcinogen
Toluene - CNS agent
Xylenes - fetal development toxic agent



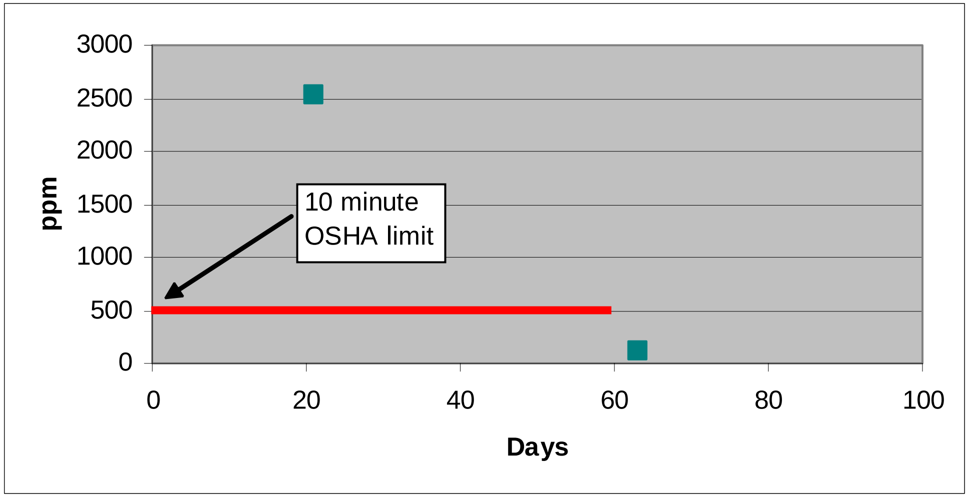
Stephen Brown (CSIRO) monitoring VOC emissions.

New Automobile VOCs

Benzene levels exceed standard for 2 months. After 2 years, 5.5 ppm is > 50% of the TWA_8.



Toluene levels exceed the 10-minute exposure standard for about 2 months.



Headspace

- Techniques:
  - static & dynamic
  - large volume injection, “TCT”
- Applications:
  - residual monomer
  - odor defects
  - blowing agents
  - outgasing

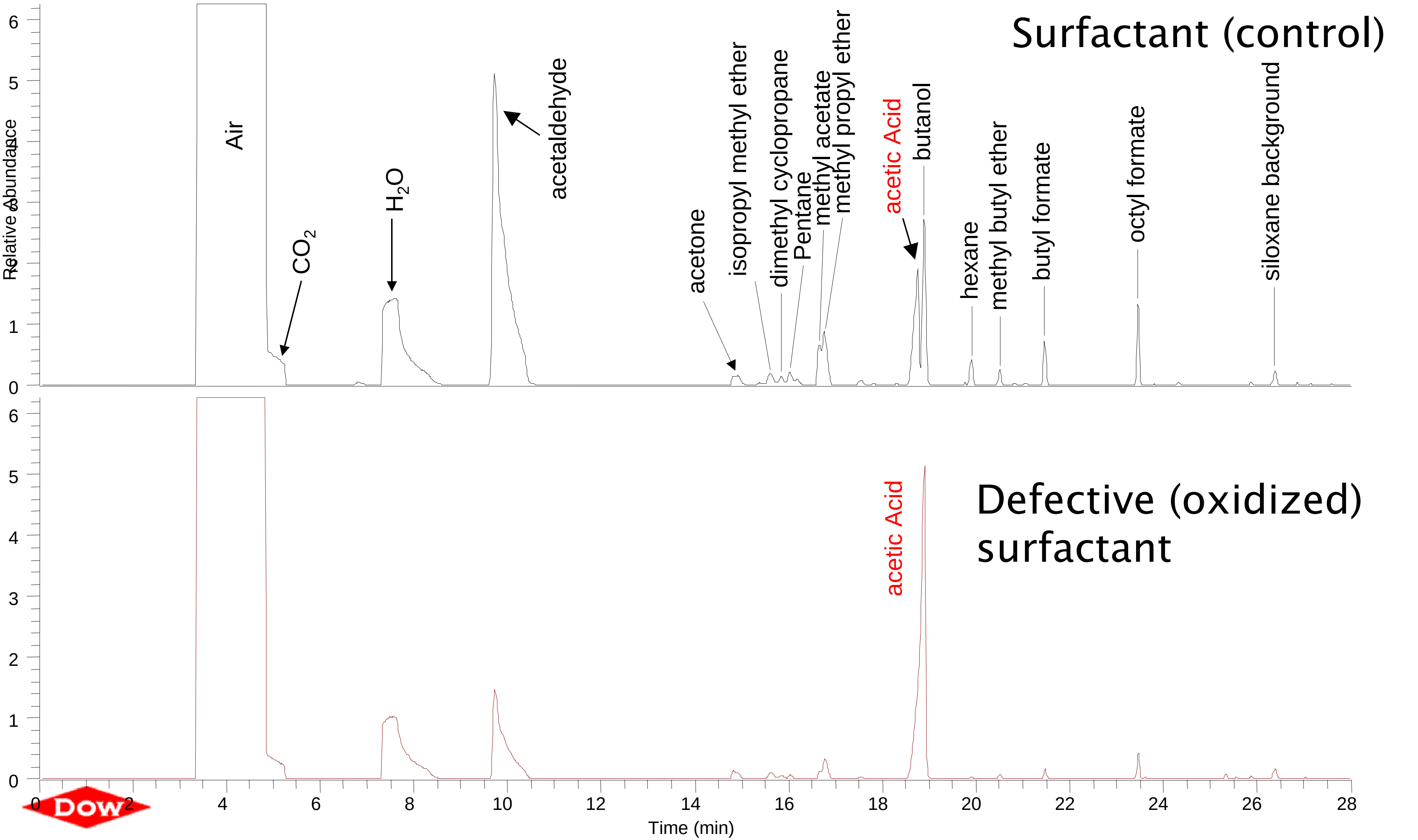
Headspace – polymer genealogy

Components trapped within a polymer – fingerprint for synthesis, additives, processing:

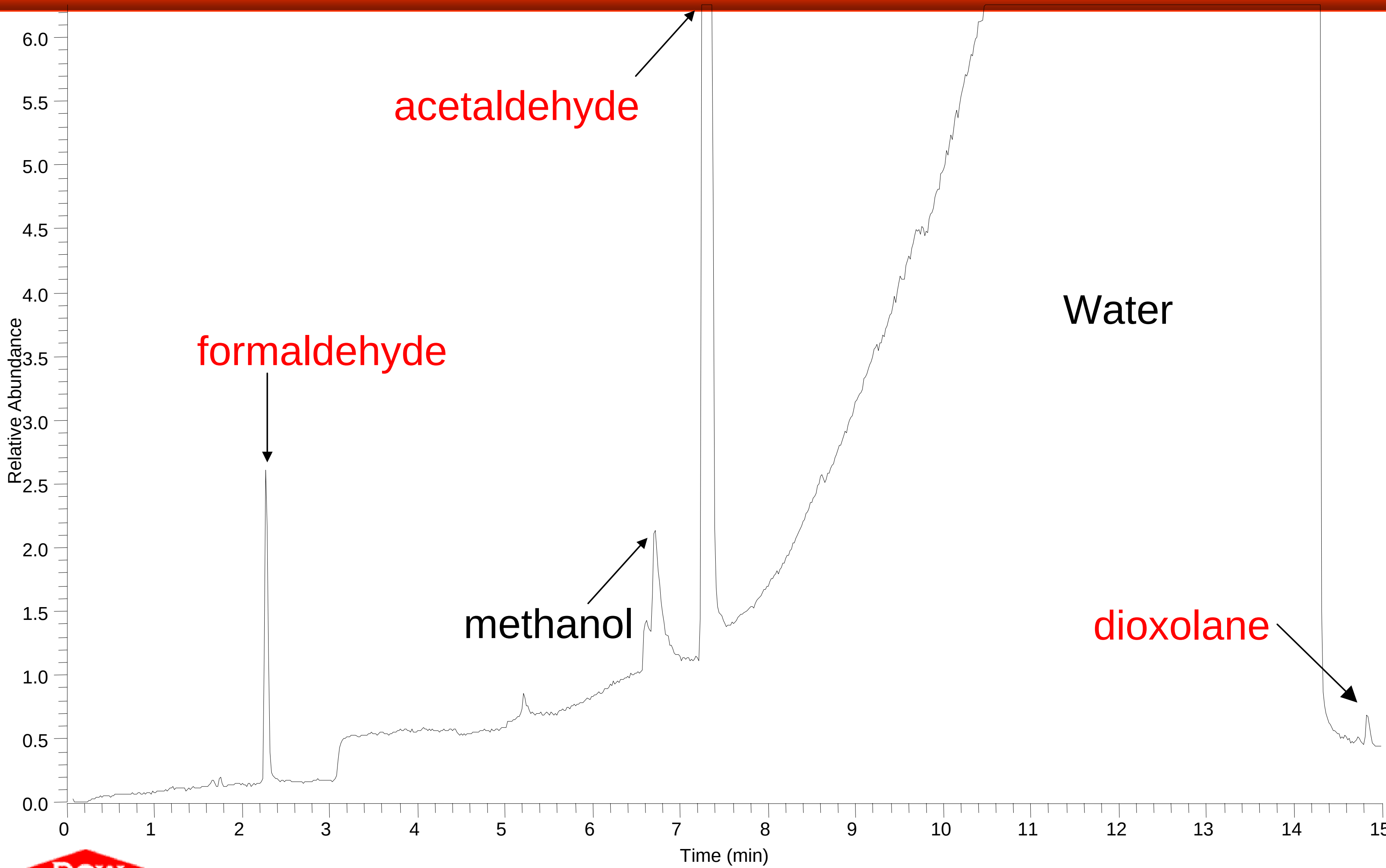
Polyolefin	alkanes:olefins
HDPE	49:51
LLDPE	83:27
LDPE	62:38

Work with BP, Willoughby, et al. Polymer Testing 22 (2003) 553-570.

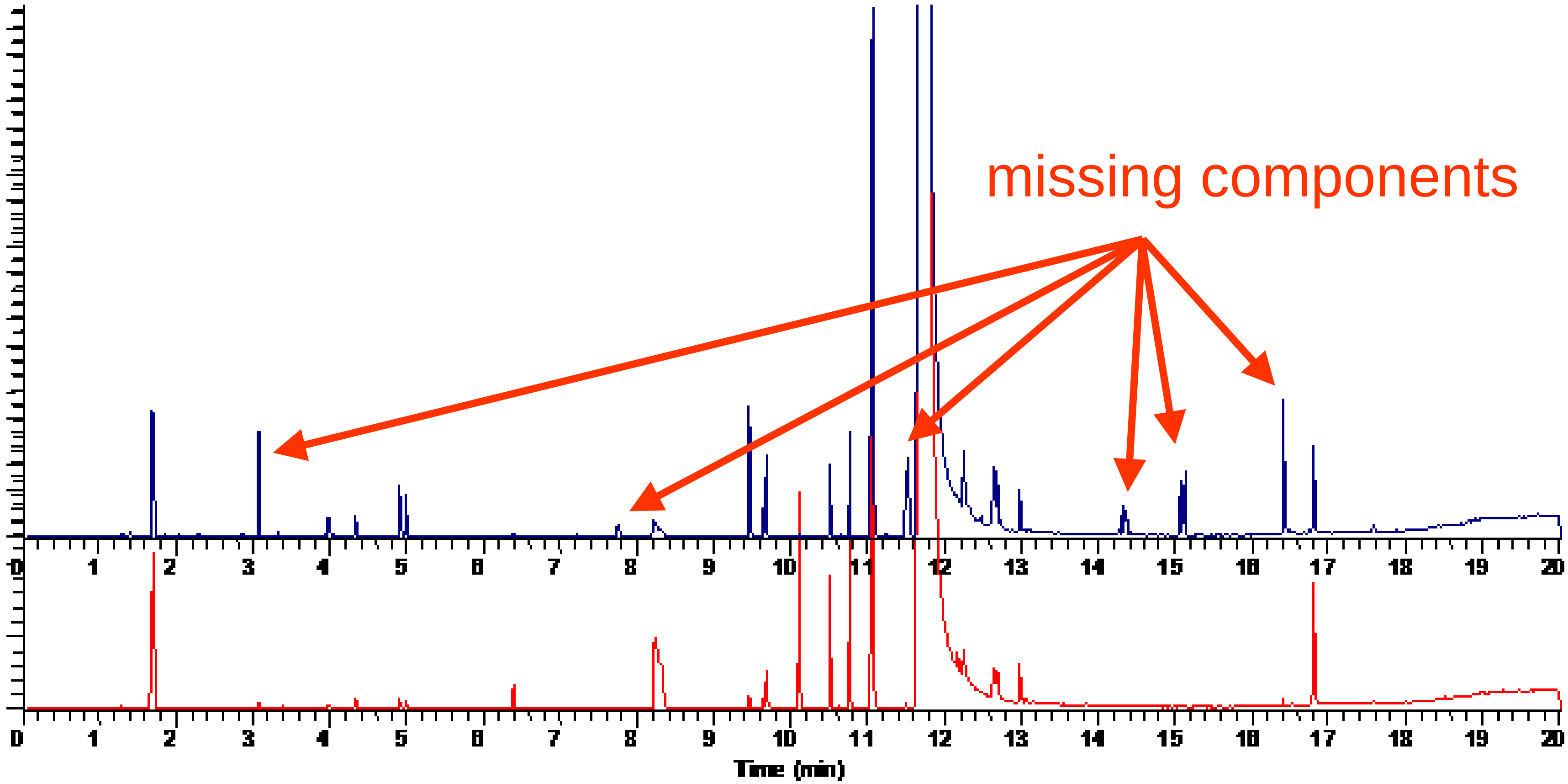
Headspace – defective surfactant



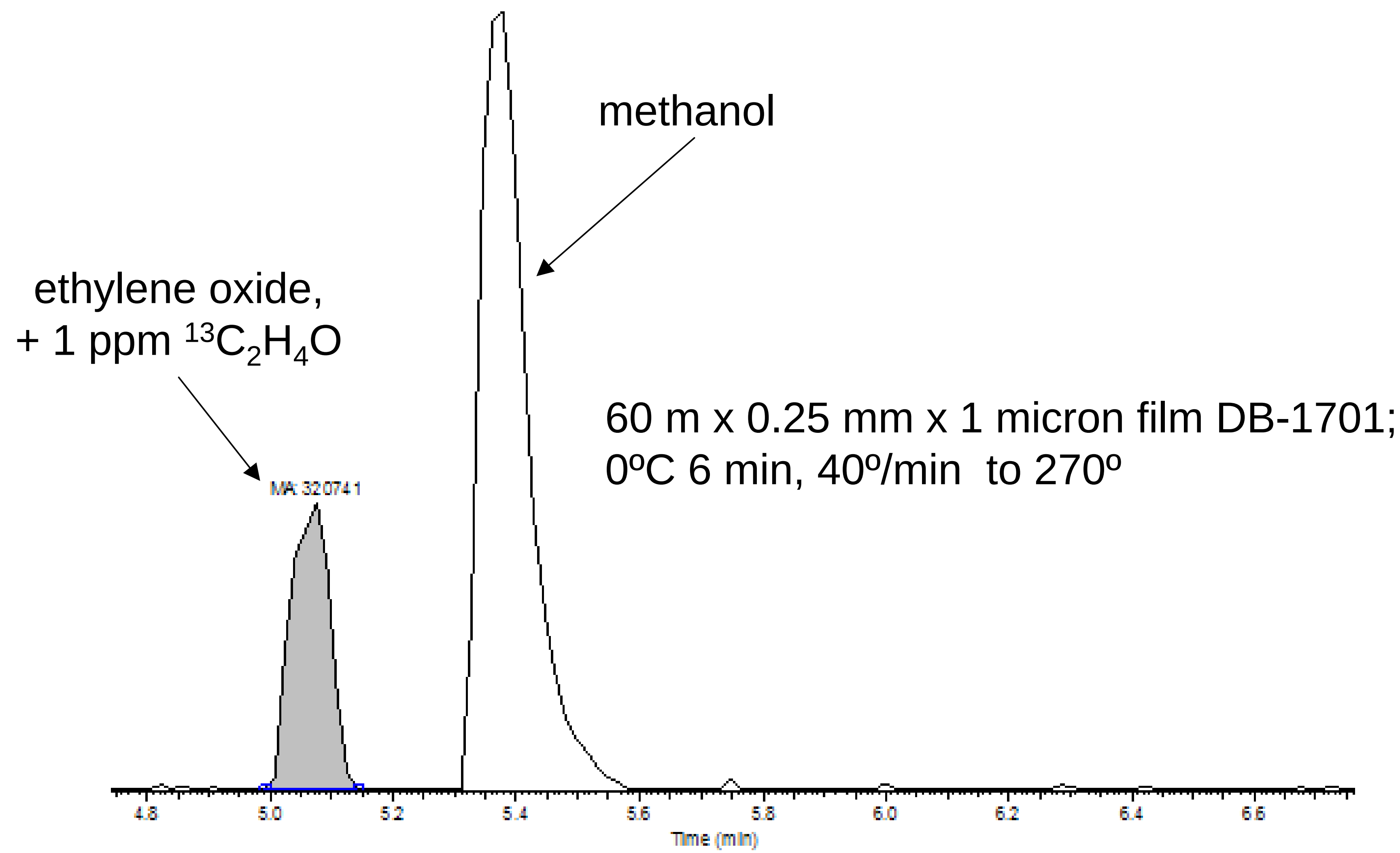
Headspace – dynamic + cryo-trap



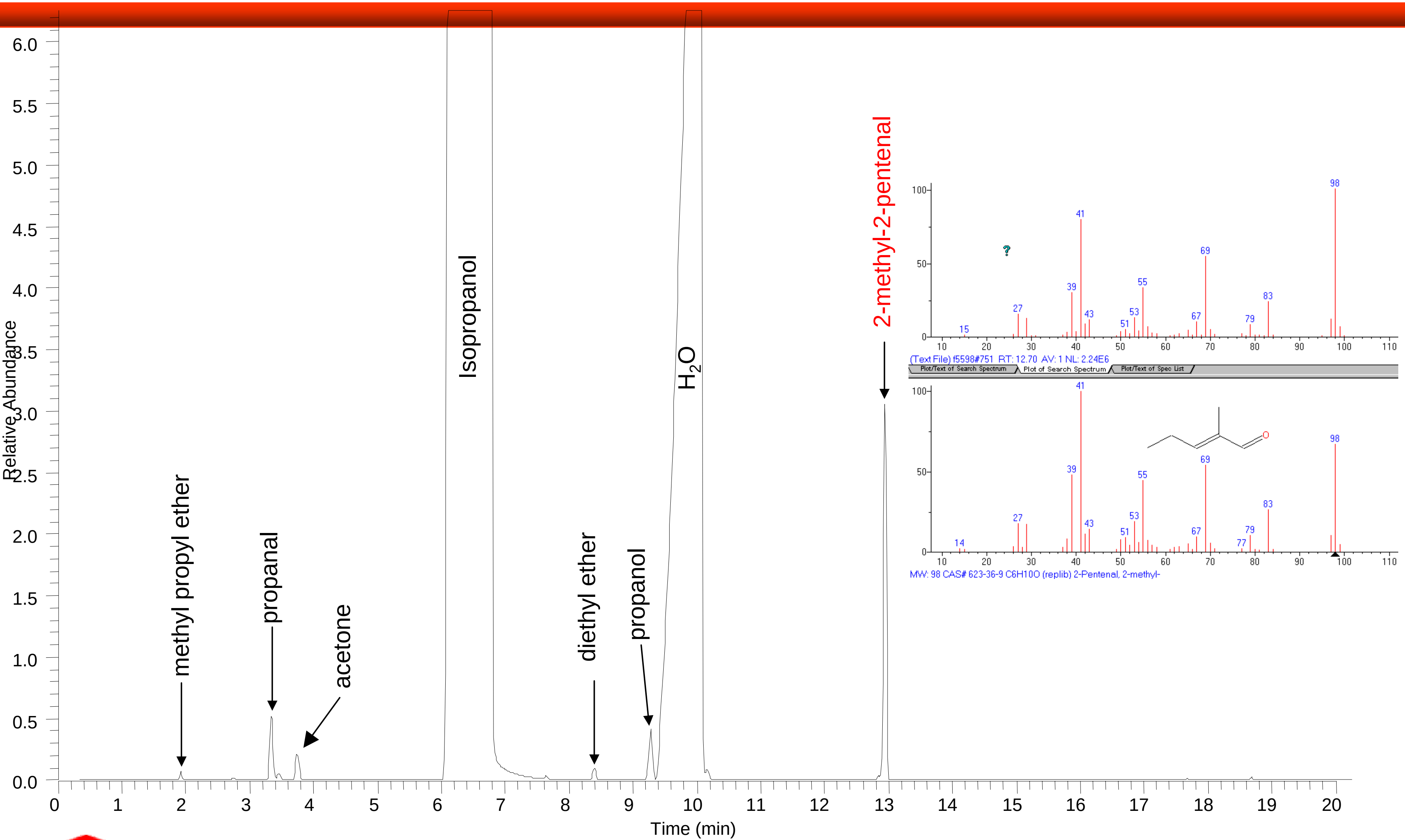
Headspace – additive package problem



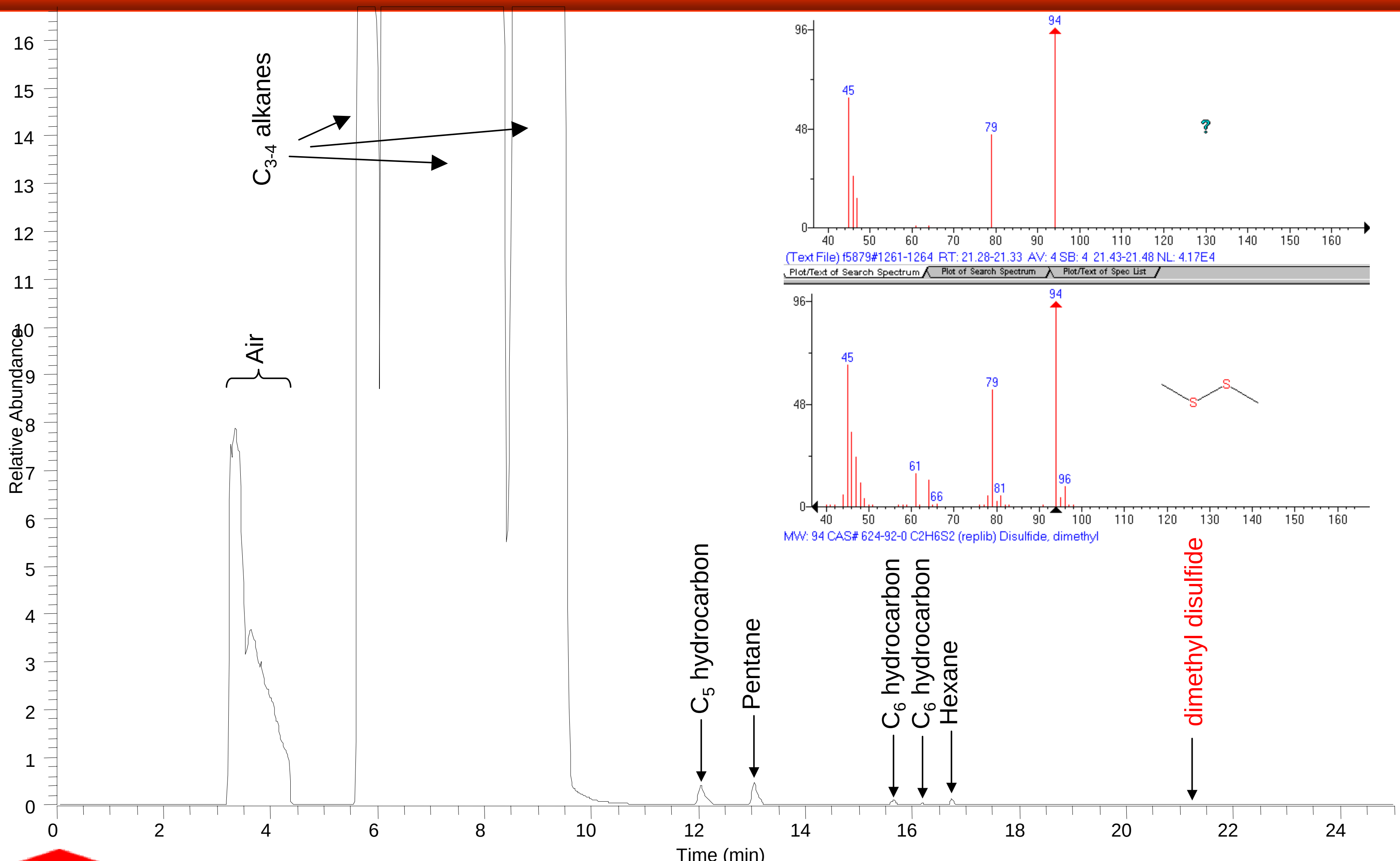
Headspace – EO monomer



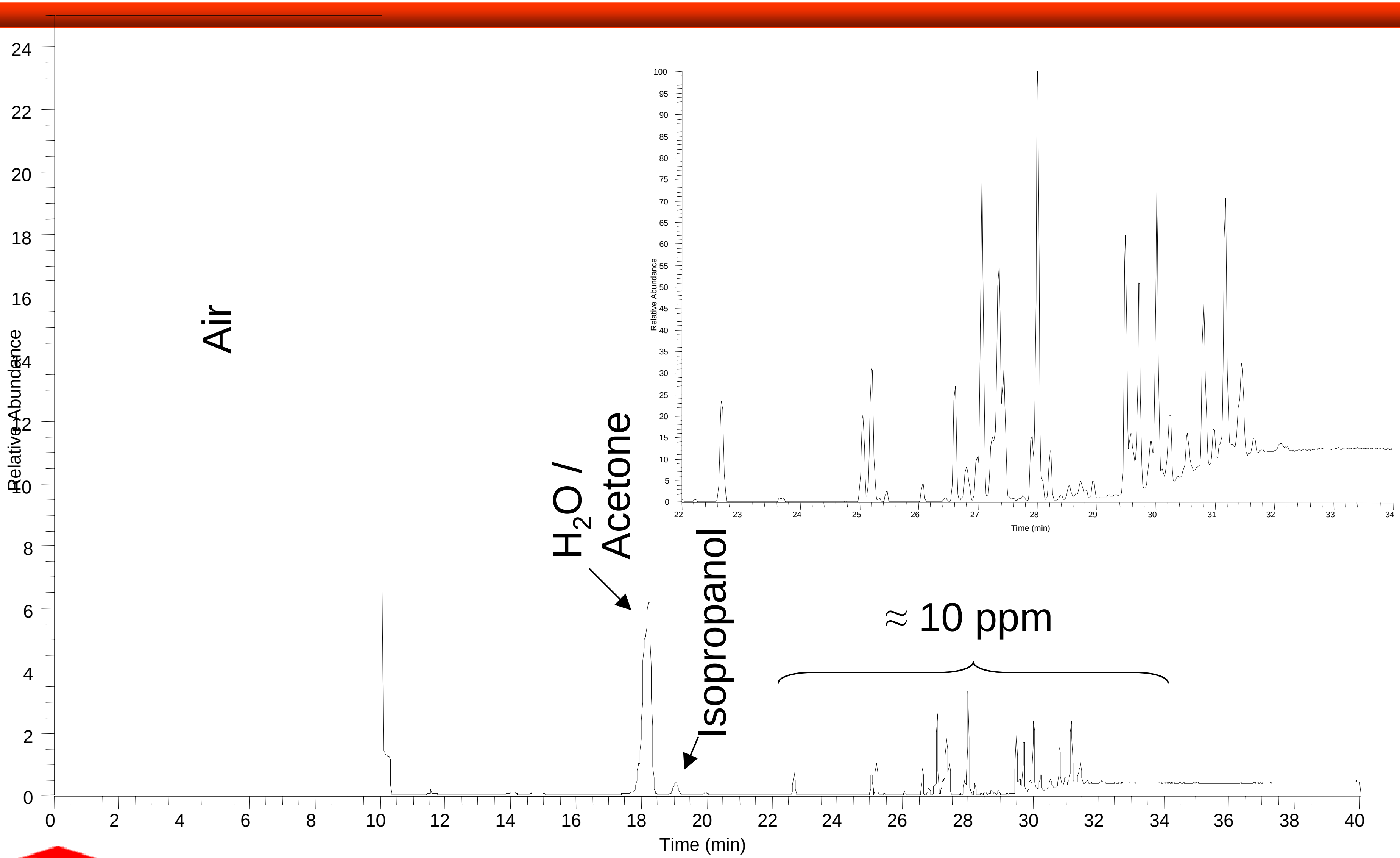
Headspace – Odor in plastic



Headspace – odor in blowing agent



Headspace – co-monomer oligomers

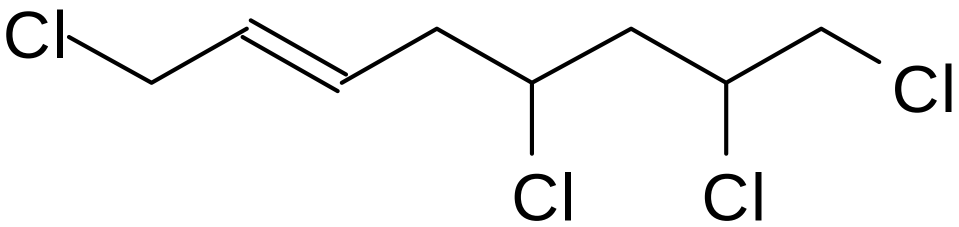


Extraction

- Techniques:
  - "conventional"
  - cryo/grinding
  - hot solvent/melt state
  - supercritical fluid
  - SPME

- Applications:
  - Flame retardants, additives
  - light oligomers (hexane, ethanol, acetic acid, etc. extractables tests)
  - polymer & additive decomposition products

Beyond VCM - PVC tetramer



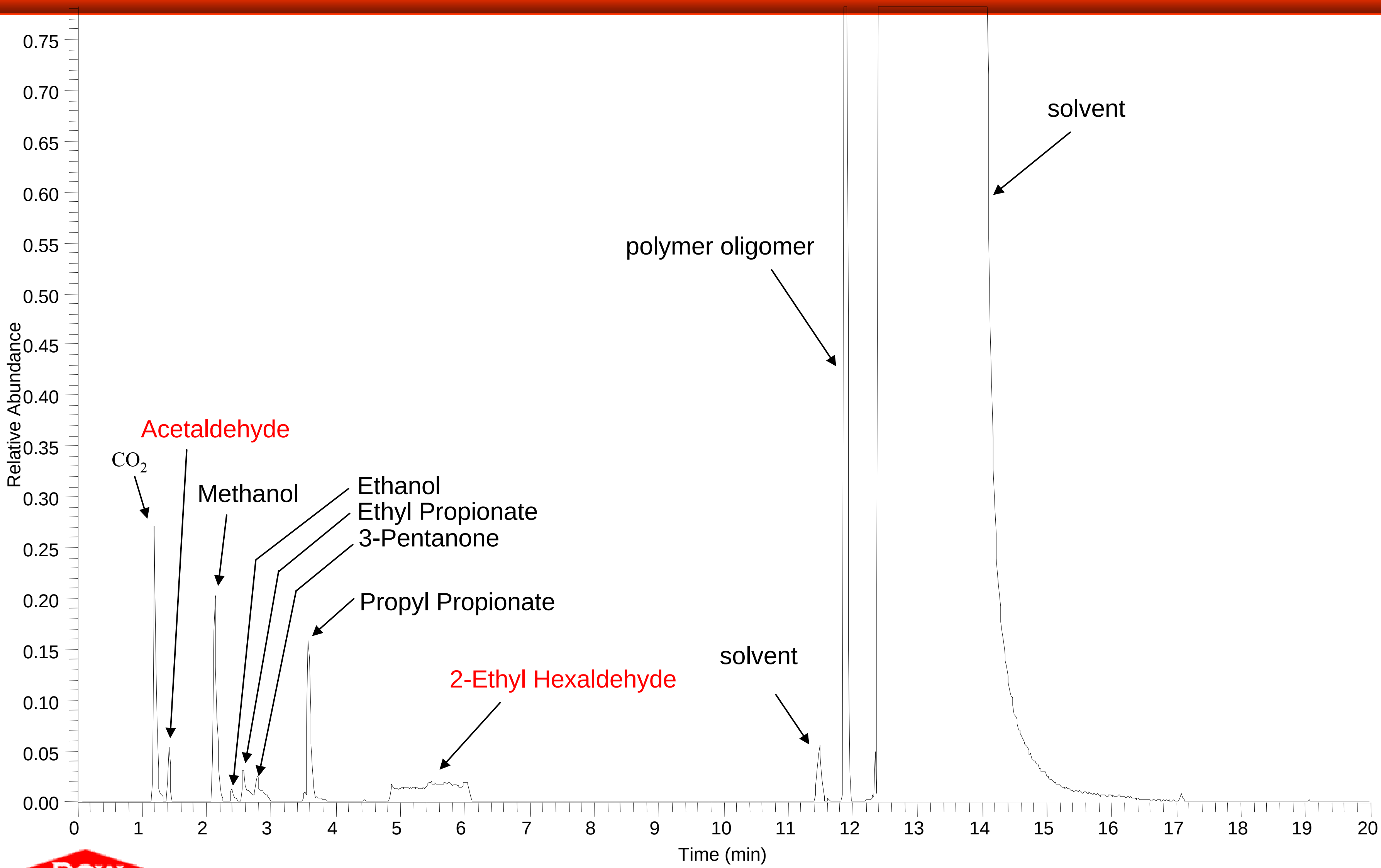
1960s – workers at the Tech. Hochs. in Muenchen noted after 42 days, “beer from plastic bottles was similar in flavor to beer from glass bottles”.

1990s - PVC tetramer, typically 10-20 ppm in bottle resin

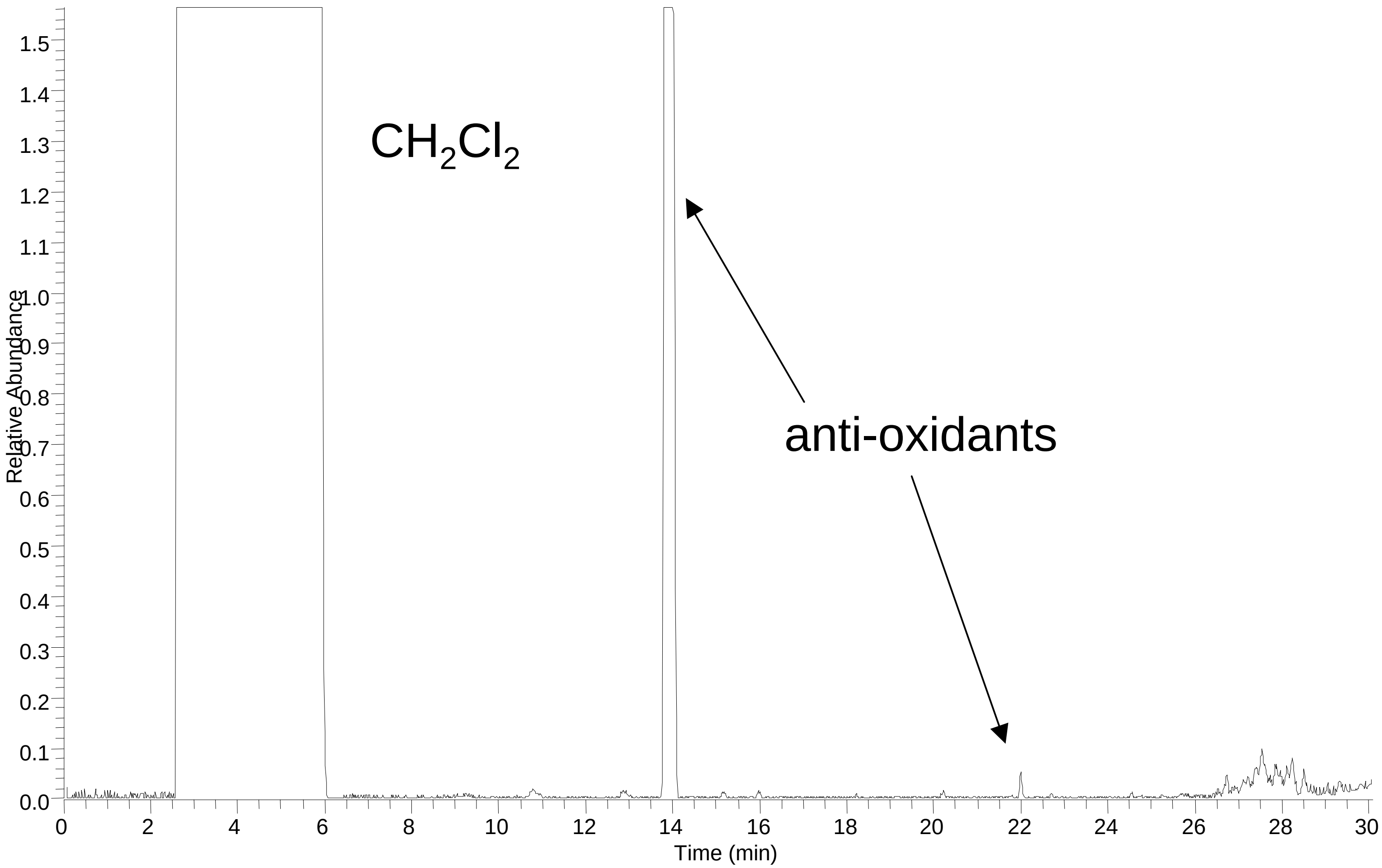
1980s – VCM limited to < 1 ppm

now – medical devices & sterile packaging may require < 100 ppb

polymer odor problem extract



plastic – CH_2Cl_2 extract



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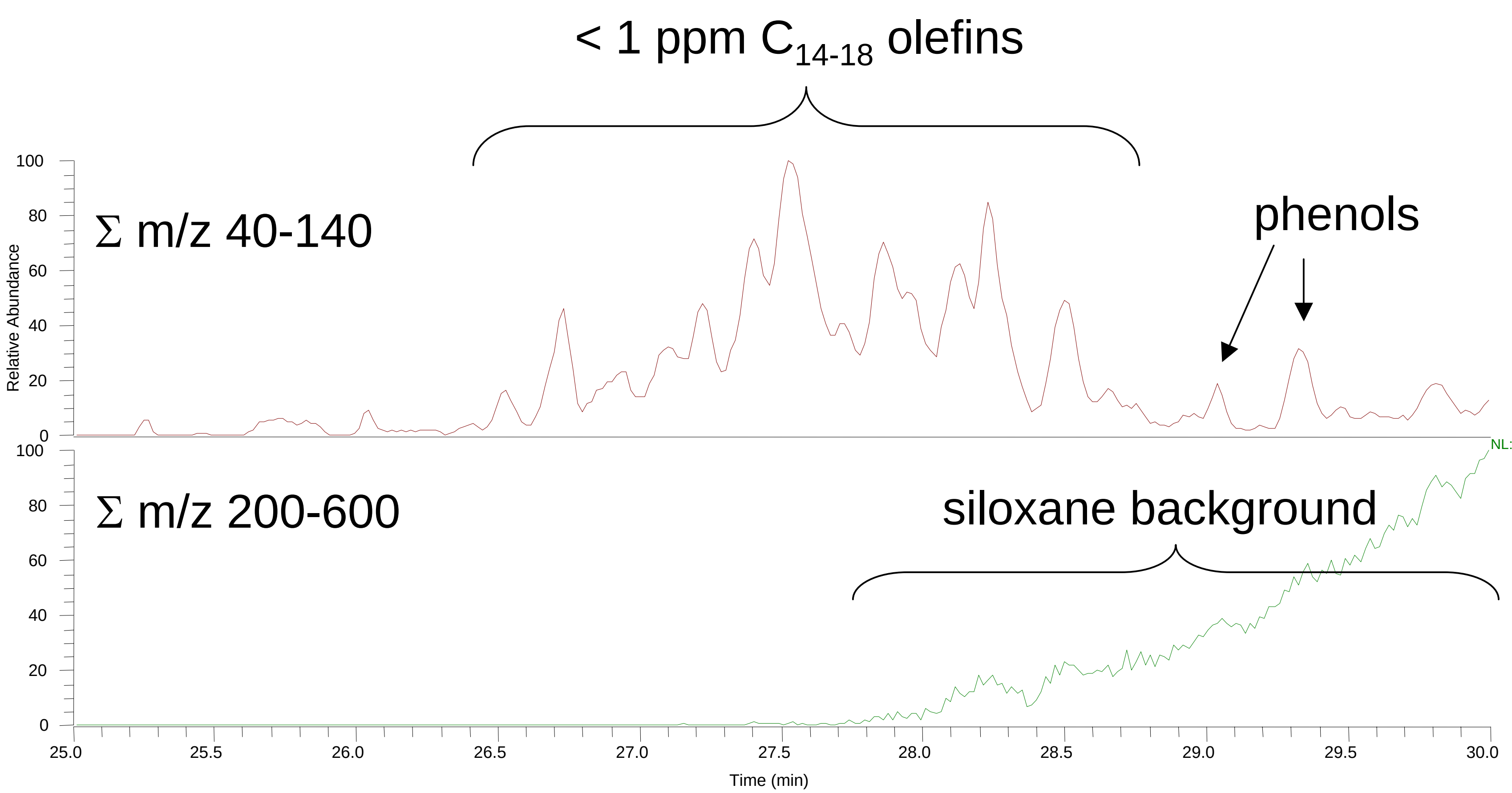

Pyrolysis GC/MS

Began in 1954, Dunlop Research Center, Birmingham, UK; W. H. T. Davison; vulcanized and unvulcanized rubber

- Applications:
  - Monomers
  - End groups
  - Branch points
  - number average sequence length (based on dimers & trimers)
  - mole % composition
  - Blockiness
  - Flame retardant studies (mechanisms, active agents, degradation products)

- Example systems examined:
  - vinyl chloride/vinylidene chloride
  - chlorinated polyethylene
  - styrene/butadiene
  - styrene/butyl acrylate
  - styrene/methylmethacrylate
  - styrene maleic anhydride
  - PMMA tacticity
  - vegetable oils

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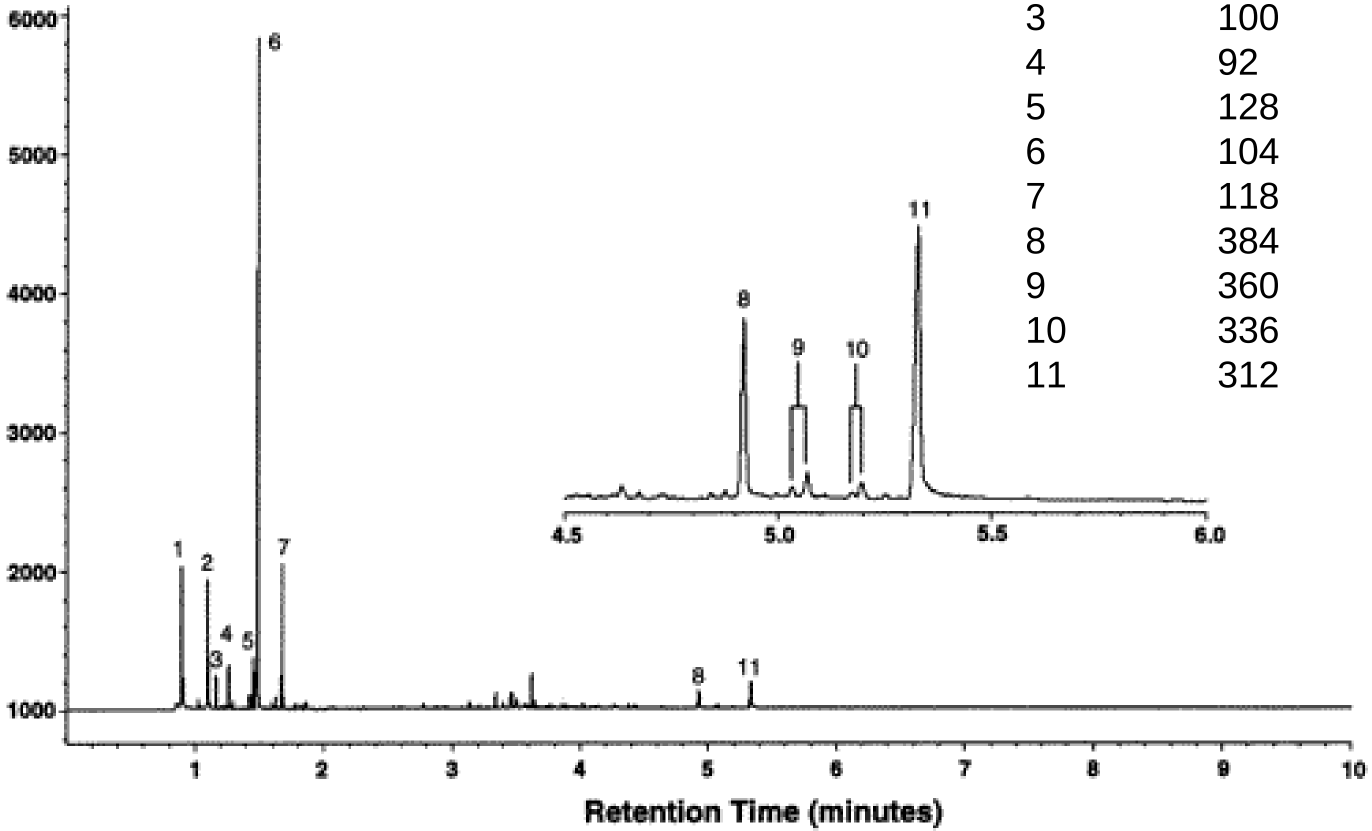
py-GC/MS Derivatization

- Hydrolysis & methylation of acids to esters (tetramethylammonium hydroxide; trimethylsulfonium hydroxide)
  - methacrylic acid polymers, simplifies & directs pyrolysis
  - polycarbonates, methyl esters facilitate CNL MS/MS scans
  - Hindered Amine Light Stabilizers, quantitation from 0.1-5%
- Hydrogenation of mixed alkane/olefin products – simplified branch point identification
- Steam hydrolysis/cleavage - polyurethanes, epoxies, aging
- Silylation with BSTFA or hexamethyldisilazine – polar, oxygenated resins

Pyrolysis – Copolymer Latex



peak #	MW	structure
1	56	butene
2	74	butanol
3	100	methyl methacrylate
4	92	toluene
5	128	butyl acrylate
6	104	styrene
7	118	methylstyrene
8	384	butyl acrylate trimer
9	360	(styrene)(butyl acrylate)$_2$
10	336	(styrene)$_2$(butyl acrylate)
11	312	styrene trimer

latex methanol extract reacted with tetrabutylammonium hydroxide (40% in water). see Frank Cheng-Yu Wang, Analytical Chemistry, 1999

GC/GC/MS

- Driven by:
  - improved switching/modulator technology
  - improved columns
  - increased (MS vs. FID) sensitivity
  - improved software (> 1Gig/sample!)
- Typical polymer-related applications:
  - Feedstocks: trace components
  - Pyrolysis: high complexity
  - Extracts: matrix removal

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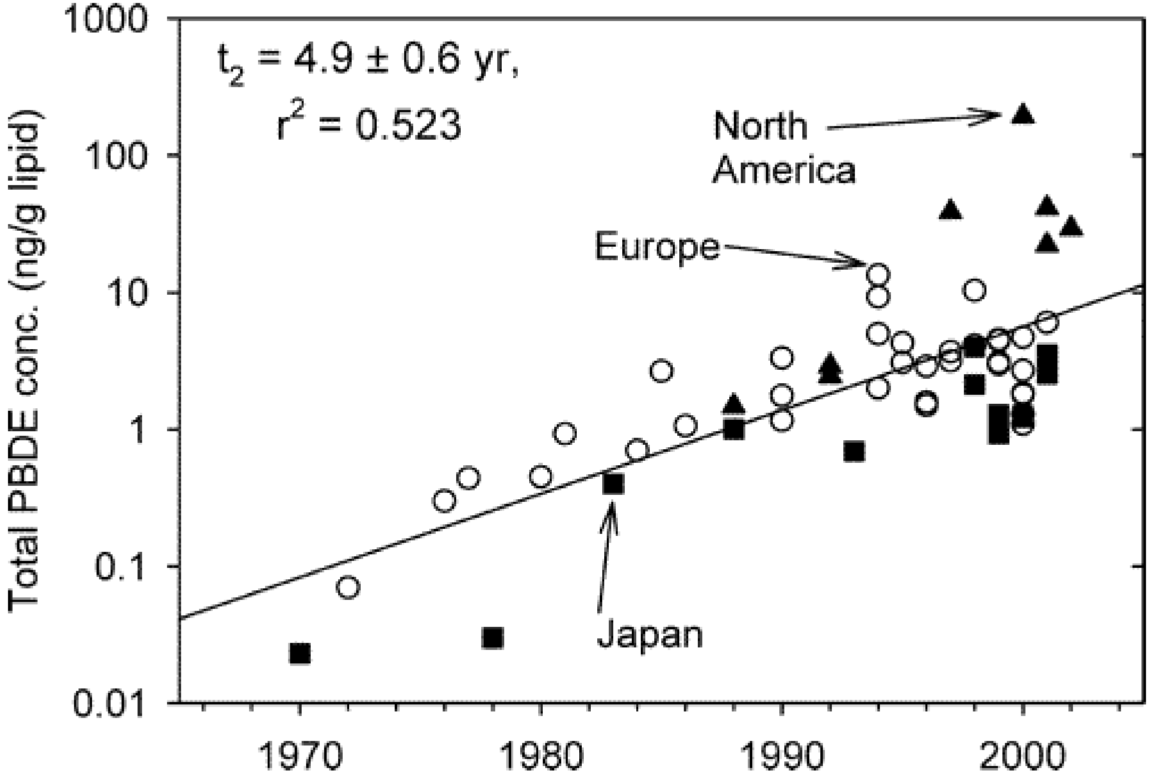
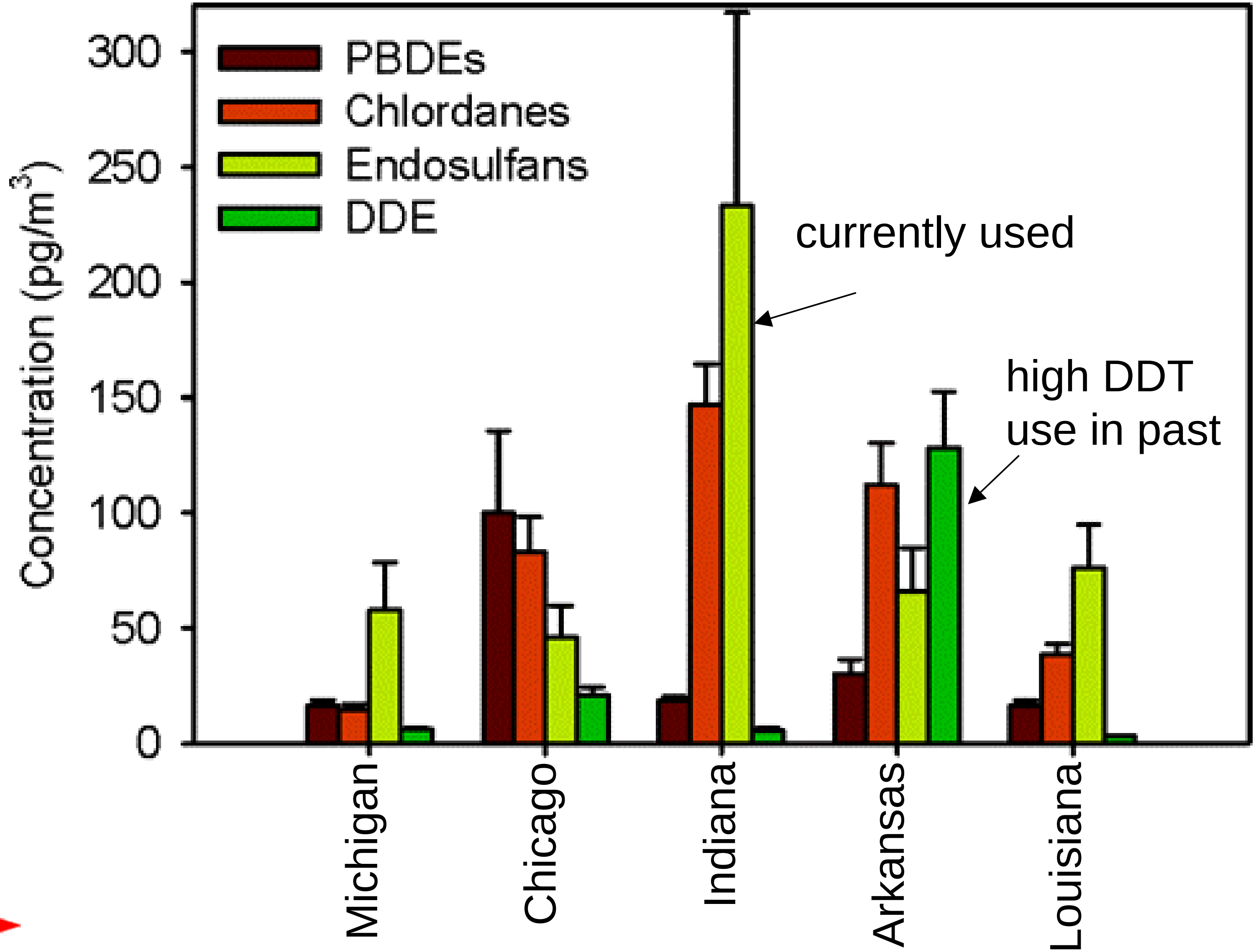
Flame Retardants - background

EU directive 2003/11/EC, effective 8/15/2004, prohibits sale of materials with > 1,000 ppm each of pentabromodiphenylethers and octabromodiphenylethers

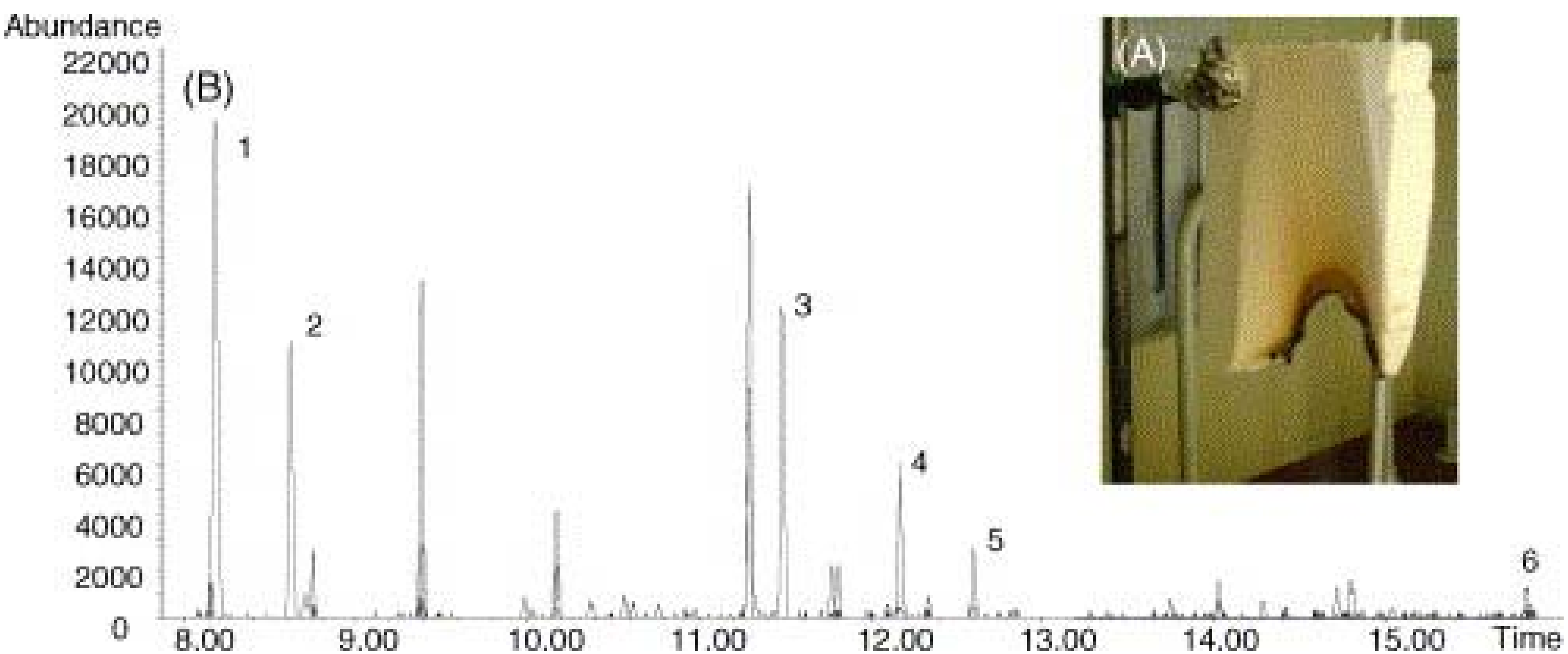


"Brominated Flame Retardants in the Atmosphere of the East-Central United States". Eunha Hoh and Ronald A. Hites. *Environ. Sci. Technol.*, **39** (20), 7794 -7802, 2005

PDBEs – urban source?



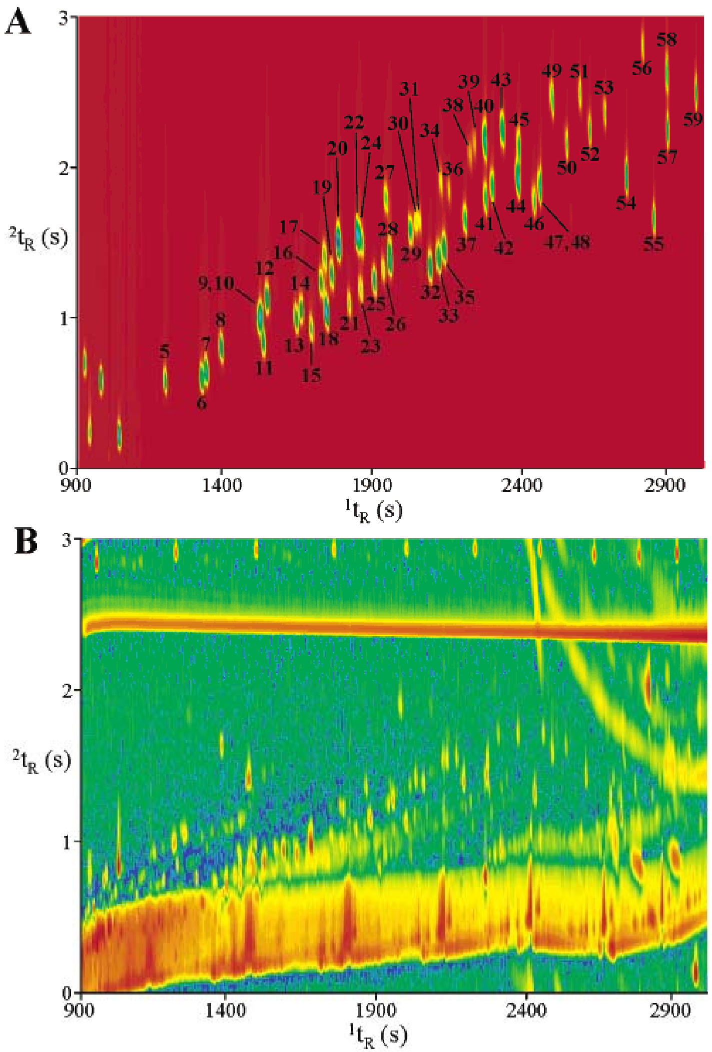
Flame Retardants – active sampling



Combustion products from PS, indicating brominated species formed: 2-bromophenol (1), benzylbromide (2), 1-allyl-2-bromobenzene (3), 2,4-dibromophenol (4), 2,6-dibromophenol (5), 2,4,6-tribromophenol (6).

Koen Desmet, Marc Schelfaut and Pat Sandra. Journal of Chromatography A ; Volume 1071, Issues 1-2 , 15 April 2005, Pages 125-129

Flame Retardants – GC/GC/MS

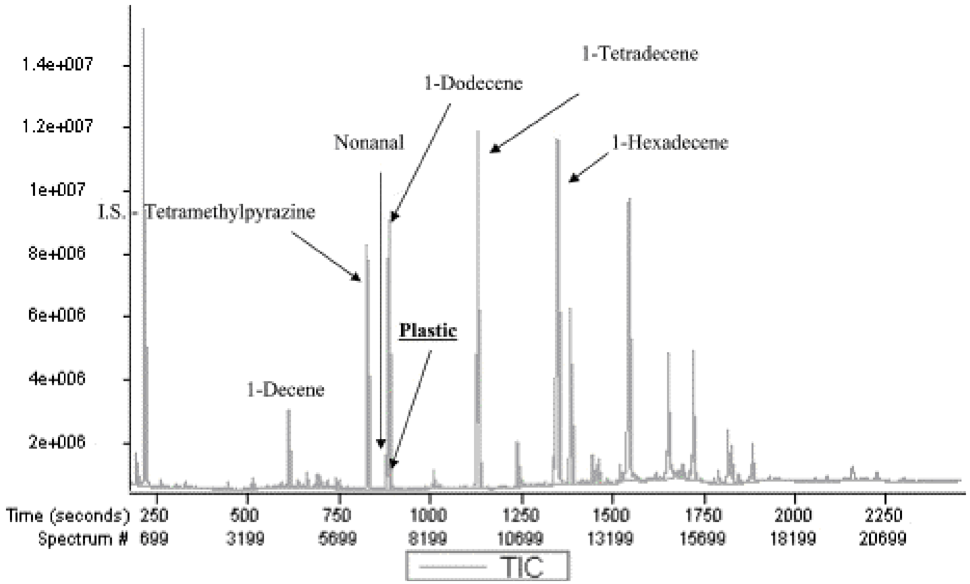


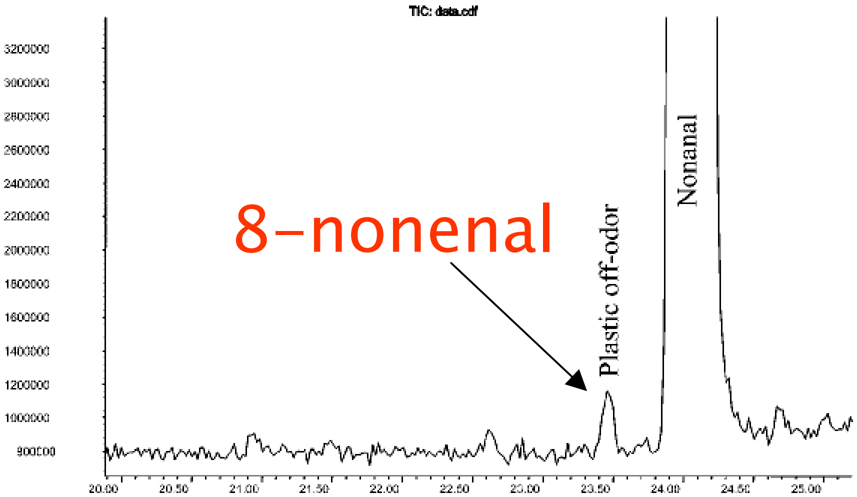
external standard calibration

human serum sample

“Measurement of Selected Polybrominated Diphenyl Ethers, Polybrominated and Polychlorinated Biphenyls, and Organochlorine Pesticides in Human Serum and Milk Using Comprehensive Two-Dimensional Gas Chromatography Isotope Dilution Time-of-Flight Mass Spectrometry”. Jean-François Focant,* Andreas Sjödin, Wayman E. Turner, and Donald G. Patterson, Jr. *Anal. Chem.*, **76** (21), 6313 -6320, 2004

“Plastic” taste from HDPE Packaging





2D GC by Bob Sanders @ Procter & Gamble
aldehyde in resin: 4 ppb max, anti-oxidants reduce to < 1ppb

need for forensic analyses

Body armor firm faces criminal probe

Research chief pleaded with company's president to replace vests, memos show

By John Solomon
The Associated Press

WASHINGTON — The Justice Department is investigating whether a company sold defective bulletproof vests for President Bush, federal agents and local police and then waited nearly two years to alert customers that the body armor could be unsafe.

A former research chief for Second Chance Body Armor Inc. is cooperating with the criminal investigation and testified this month that the Secret Service tested and bought some of the defective vests for the president and first lady Laura Bush. The Pentagon obtained the same armor for elite troops who guard generals, according to transcripts obtained by The Associated Press.

Many sales occurred well after Michigan-based Second Chance had been alerted that the Japanese-made Zylon synthetic material in the vests was degrading faster than expected from heat, light and moisture exposure, allowing bullets to potentially penetrate the armor, according to the former employee's testimony and other company documents.

AP file photo

Pennsylvania Attorney General Jerry Pappert holds a Second Chance bulletproof vest while announcing a lawsuit against the company in 2004.

and the security detail that protects him and other VIPs, federal procurement records show.

Legal professionals and government officials familiar with the inquiry confirmed Westrick's account about the Secret Service and Bush. They said the criminal investigation is in addition to a Justice Department lawsuit filed last summer that accuses Second Chance and Toyobo of fraud. The officials spoke only on condition of anonymity, citing grand jury secrecy.

Robert H. Skilton, Second Chance's lawyer, did not return calls to his office last week. Some of the company's non-Zylon assets have been sold and others are in bankruptcy.

Westrick's lawyer, Stephen M. Kohn, said Sunday that his client was cooperating with the criminal investigation.

"Greed prevailed over the safety of police, soldiers and even the president of the United States," Kohn said. "The officials who personally profited from selling the defective vests to law enforcement must be held accountable to the fullest extent of the criminal code."

Throughout 2001 and 2002, agencies from the Pentagon to local police bought vests from Sec-

or greedy and uncaring for knowing and not doing anything about it," the memo said.

The second option recommended the company publish an ad "denouncing" the vests and "decline to make them" unless customers know of the problem and still want them.

While it waited until fall 2003 to alert buyers, Second Chance arranged in the interim for Toyobo to begin paying it refunds in 2002 for the Zylon problems, promising to use the money to fix vests already sold in the United States, according to documents in Second Chance's bankruptcy case.

Toyobo told the bankruptcy court that Second Chance took the money but "failed to implement the corrective actions."

"It is apparent that Toyobo was duped by Second Chance," Kent Jarrell, a U.S. spokesman for Toyobo, said Sunday. "We were shocked by the level of Second Chance's deception when their behavior was finally uncovered because of documents that surfaced in litigation and through investigation."

The Justice Department's lawsuit this summer accused both Second Chance and Toyobo of allowing vests to be sold to lo-

"Solution 1: We continue to operate as though nothing is wrong until one of our customers is killed or wounded or Germany, Japan, DuPont or some other entity exposes the Zylon problem."

From memo prepared by Second Chance Body Armor executives on options, a year before customers were alerted to problems when a police officer was killed

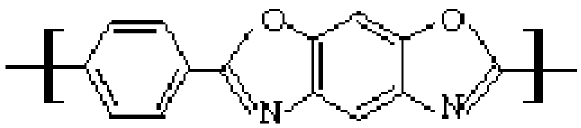
Service testing, he warned his company that Zylon would soon degrade and allow bullets to pierce the armor. "I said it would be a problem," he testified.

Secret Service officials declined to say whether Bush ever wore the vest, saying they don't discuss presidential protective measures.

Westrick was told Bush wore Zylon protection during the 2001 inauguration and during a 2002 event with police that Westrick's

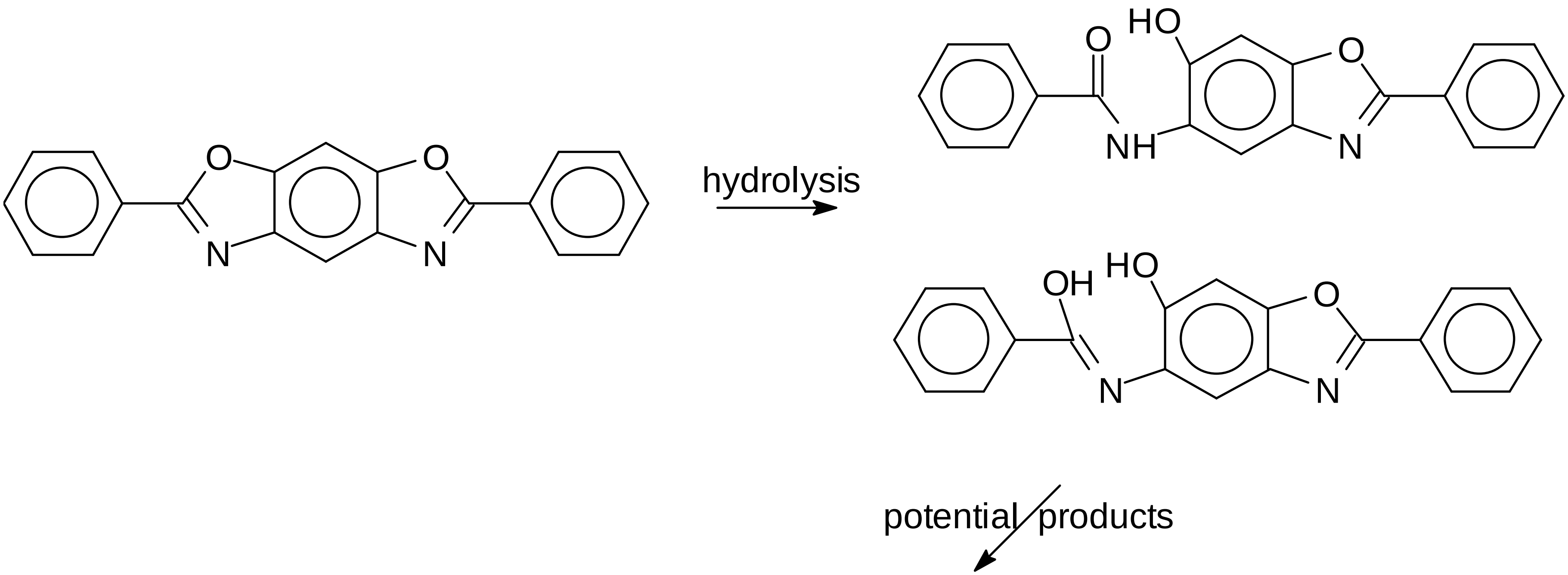
PBO Fibers

- New fiber type on the market
- Currently marketed by Toyobo (Japan)
- Very high ballistic resistance at light weight
- Tradename “Zylon”



Poly(p-phenylene-2,6-benzobisoxazole), or PBO structure
[http://www.toyobo.co.jp/e/seihin/kc/pbo]

PBO Decomposition Possibilities



phenols, anilines, benzonitriles, HCN, CO_2

Analysis of ***chemistry*** behind failures requires GC/MS

On-line & At-line Analysis

- High speed analyses, process MS &/or GC backed by GC/MS:
  - manufacturing/fabrication support
  - Symix, catalyst studies, formulations development
- Now driven by:
  - “inexpensive” process MS & GC instruments
  - popularity of High Throughput and Combi-chem approaches
  - improved software & control systems

Polymer Barrier Film Transport

- gas phase: oxygen, water
- liquid phase: osmosis, water purification
- “active/intelligent” packaging - ***emerging area***
  - dessicants
  - odor scavengers (acetaldehyde)
  - ethylene absorbers
  - anti-microbials (ClO_2, ethanol)

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Conclusions

- ***All*** polymers contain residual small molecules (synthesis, processing, history)
- ***Most*** polymers contain complex mixtures of additives
- ***Most*** polymers can be reproducibly degraded/derivatized to useful "bites"
- GC/MS approaches "re-energized" by new technology
  - extraction/concentration: SPME, supercritical fluids
  - GC: 2D-GC, injectors, columns
  - MS: inexpensive MS/MS, exact mass