FEDERAL INSTITUTE FOR RISK ASSESSMENT

BfR
Bundesinstitut für Risikobewertung

UPDATE

Research project:

„Migration from elastomers for food contact“

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Samples and substances:

Different kinds of elastomers

- Natural rubber (NR)
- Synthetic rubbers (PUR, EPDM, NBR, CR, FKM/FPM, etc.)
- Thermoplastic elastomers (TPE-S, TPE-O, TPE-V, etc.).

Applications for food contact

- Teats, gaskets, plugs, tubes, pressure hoses for food processing, milking plants, conveyor belts, moulds, sealing rings, caps etc.

Different kinds of additives used for elastomer production

Antioxidants,
UV-stabilisers,
Vulkanising agents,
Anti-aging agents,
Slip agents,
Flame retardants,
Cross-linking agents

Fillers,
Plasticisers,
Vulkanisation accelerators,
Processing aids,
Mould release agents,
Pigments

Aims of the project:

Samples

- Representative samples (semi-finished products from wholesalers and consumer goods from retail stores)

Polymer-characterisation

- FT-IR; pyrolysis-GC/MS

Screening for substances

- Inventory of potentially migrating substances (GC/MS; LC/MSMS; LC/DAD; ICP/MS)
- Quantification or estimation of the content via semi-quantitative methods

Migration experiments

- Measurement of migration into food or food simulants for the identified substances

Risk Assessment

- Risk assessment of released substances for possible actions concerning risk management
- Is there need for action concerning the revision of BfR recommendation XXI?

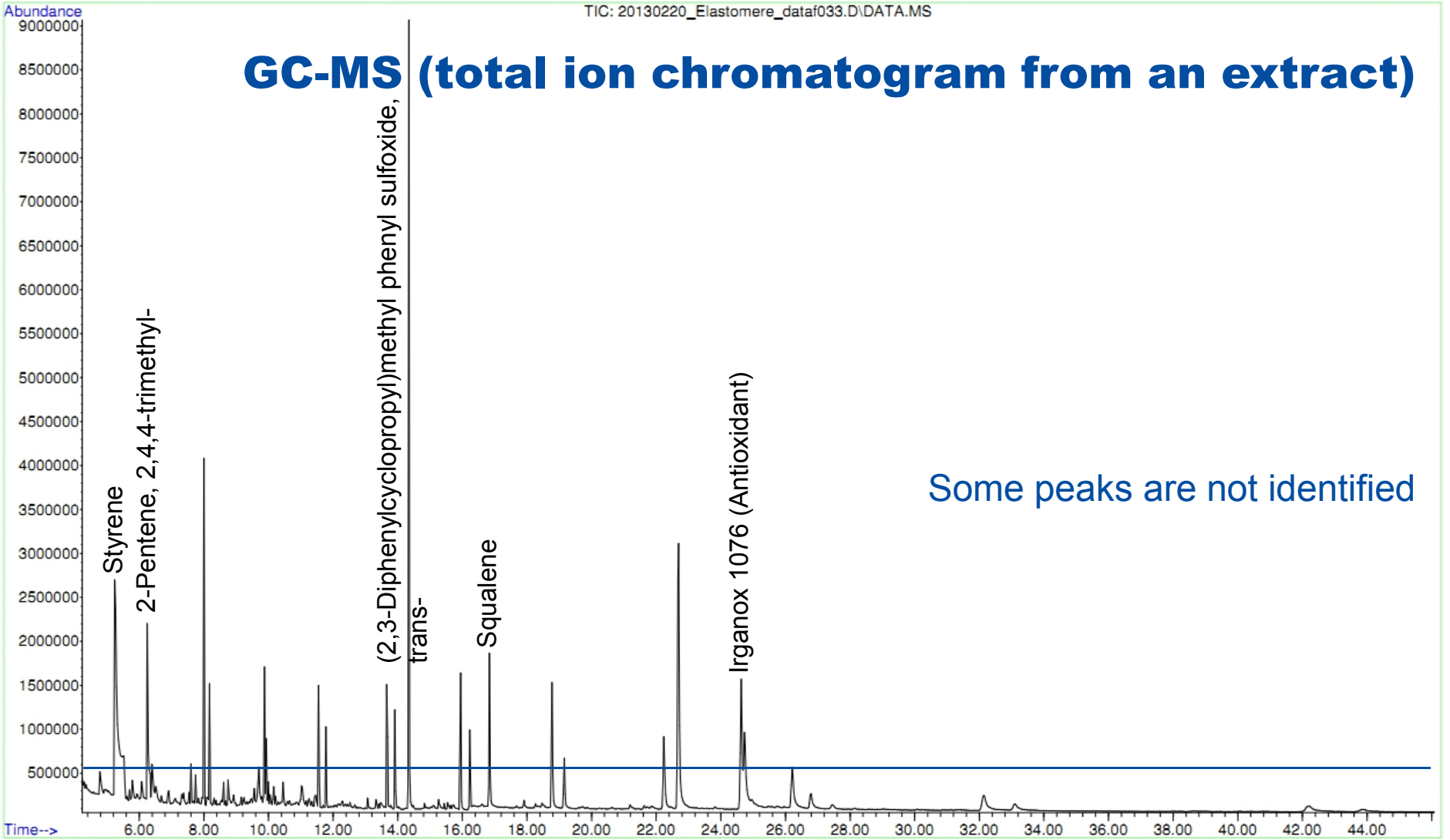
Results of screening:

- **Samples:**

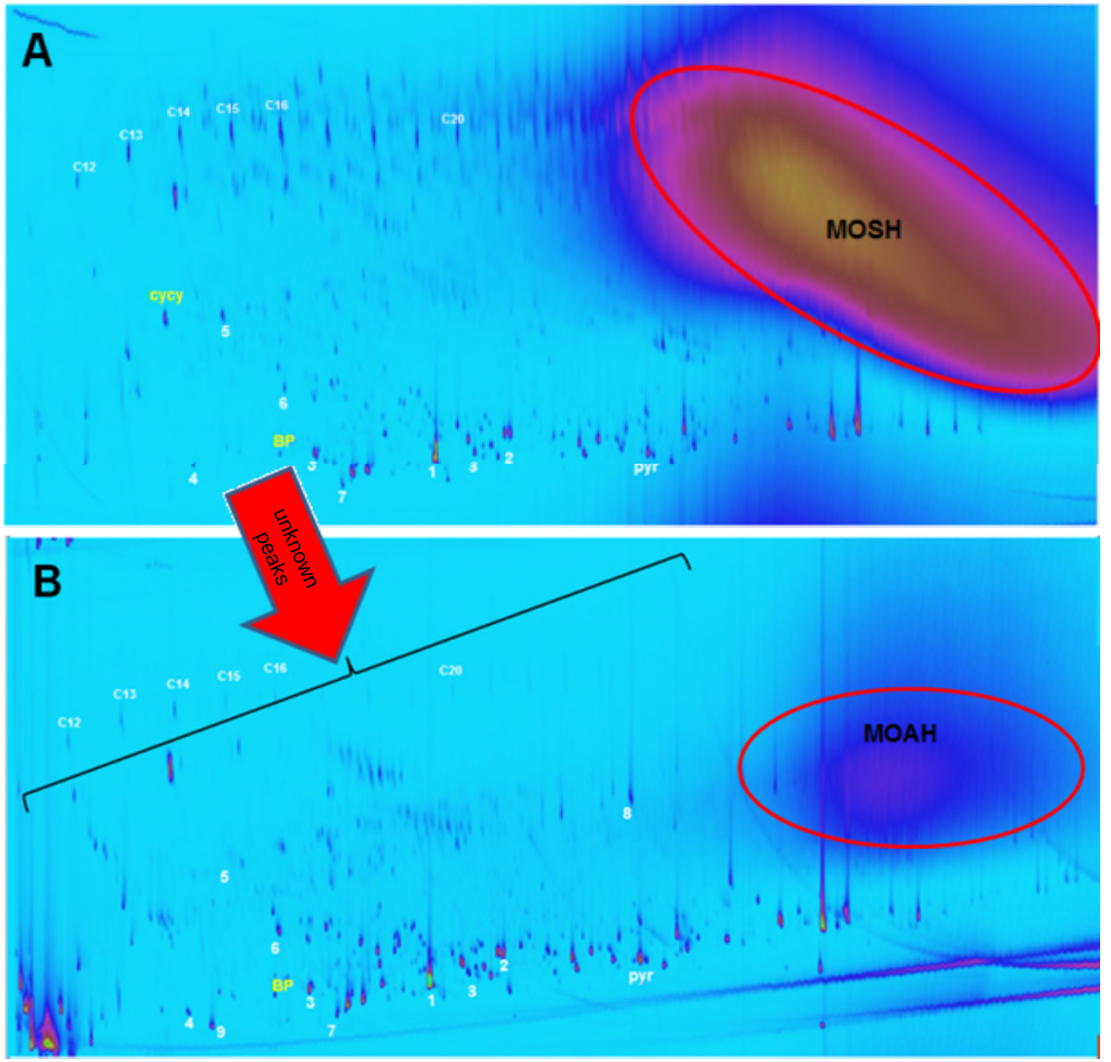
  50 elastomer samples; semi-finished products, hoses, caps, seals etc.

- **Identified volatile substances (GC/MS)**
  - Plasticisers (e.g. DEHP, DEHS)
  - Vulcanisation accelerators (e.g. Ziram)
  - Anti-aging agents (e.g. Irganox 2246, Tinuvin 326)
  - Vulcanisation retarders (e.g. stearic acid)
  - Processing aids (e.g. palmitic acid, DEHA)
  - Antioxidants (e.g. Irganox 1076)
  - Emulsifying/dispersing agents (e.g. abietic acid)
  - PAHs (e.g. pyrene, fluoranthen, BaP)
  - MOSH
- **Not-identified substances**
  - GC/MS
  - GCxGC/ToF

Non-target analysis: thermoplastic elastomer (TPE) sealing gasket

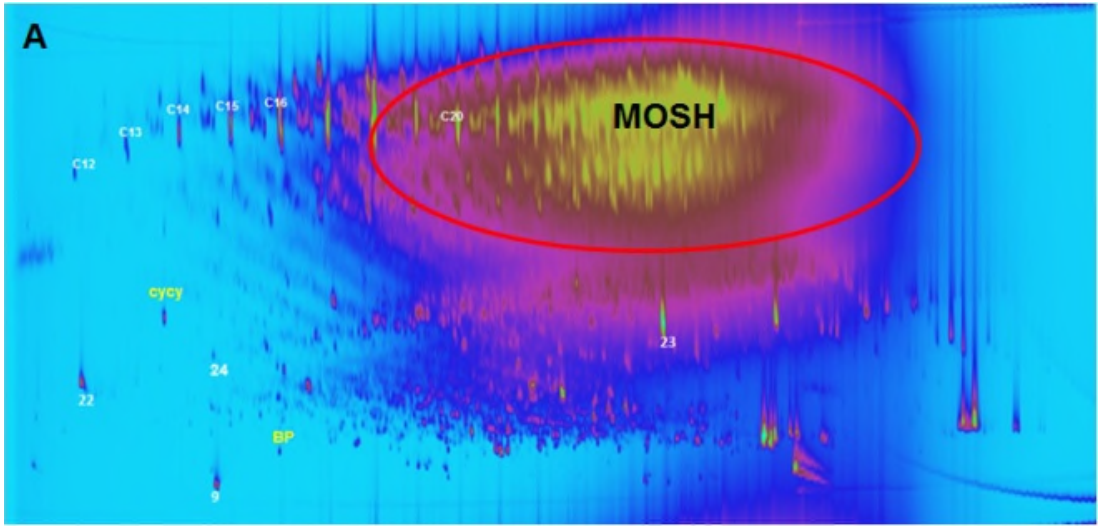


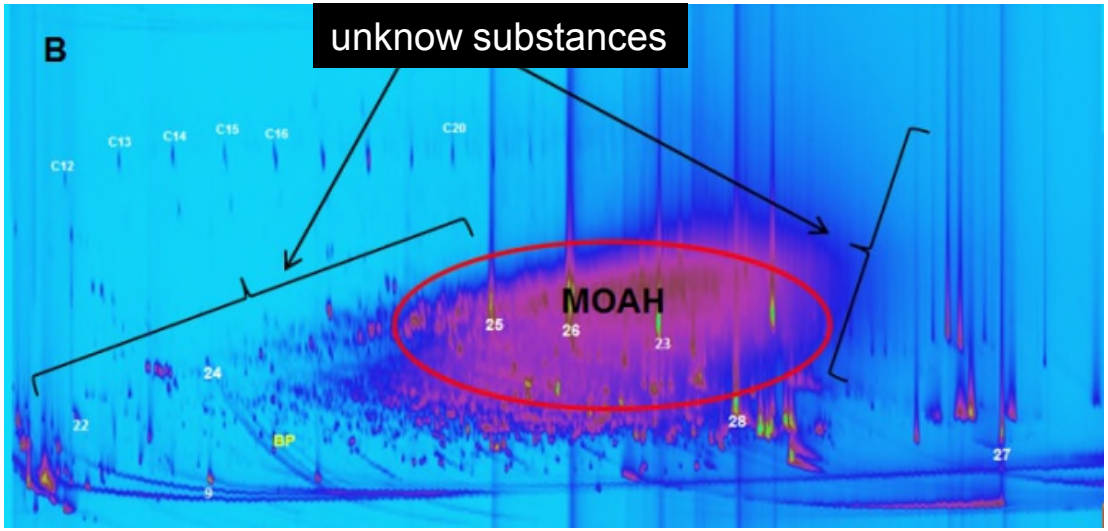
Non-target analysis: ethylene propylene diene monomer (EPDM) rubber



GCxGC/ToF: EPDM-extract (A); after removal of MOSH (B)

Non-target analysis: natural rubber

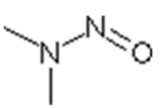


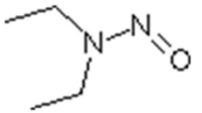


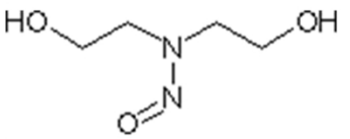
GCxGC/ToF-MS: Extract (50% ethanol) from natural rubber gasket (A) MOSH- and (B) MOAH-fraction

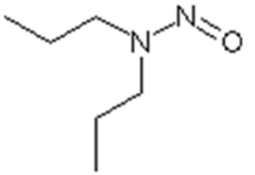
Validation: N-Nitrosamines HPLC-APCI-MS/MS method

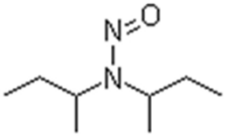
Structures

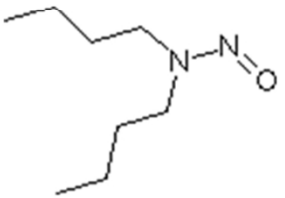

Nitrosodimethylamin (NDMA)

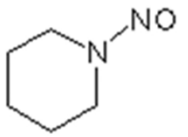

Nitrosodiethylamin (NDEA)

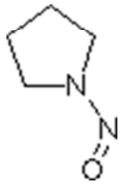

Nitrosodiethanolamin (NDELA)

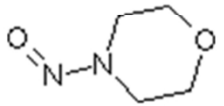

Nitrosodipropylamin (NDPA)

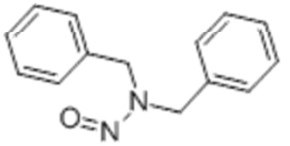

Nitrosodiisobutylamin (NDiBA)

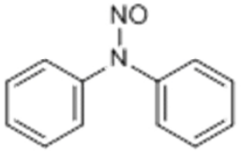

Nitrosodibutylamin (NDBA)

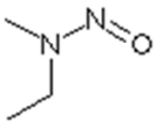

Nitrosopiperidin (NPIP)

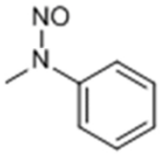

Nitrosopyrrolidin (NPYR)

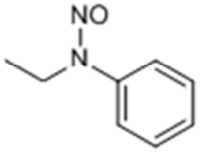

Nitrosomorpholin (NMOR)


Nitrosodibenzylamin (NDBzA)

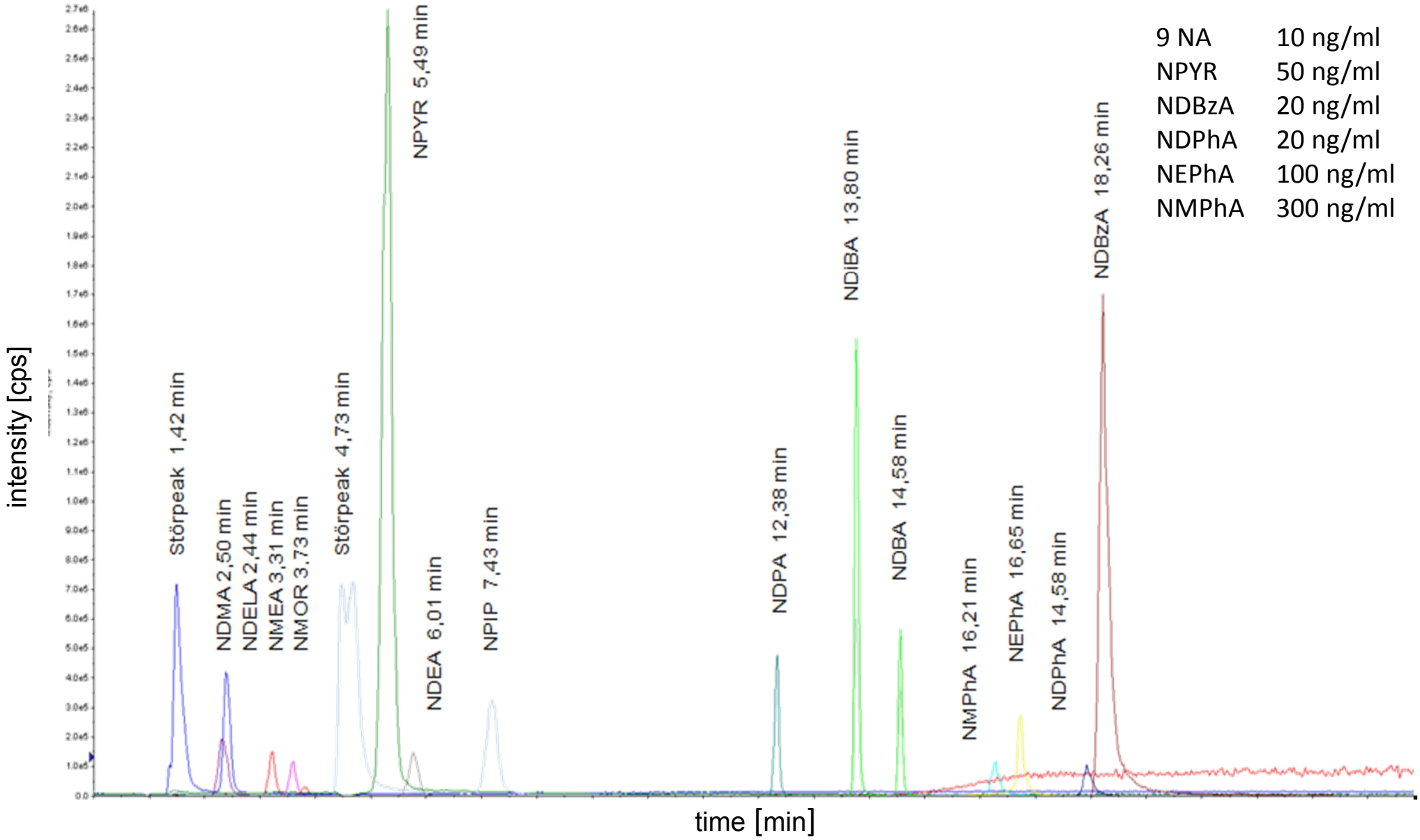

Nitrosodiphenylamin (NDPhA)


Nitrosomethylethylamin (NMEA)


Nitrosomethylphenylamin (NMPhA)


Nitrosoethylphenylamin (N E PhA)

MRM chromatogram in 3% acetic acid



Validation

	in 3% acetic acid	in 50% ethanol
Limit of detection	☑	☑
Limit of quantification		
Working range		
Stability		
Selectivity		
Recovery		
Repeatability		
Reproducibility		
Linearity		

substance	4°C	-18°C
NDMA	not stabil*	not stabil*
NDPA	stable	stable
NDBA	stable	stable
NDiBA	stable	stable
NDELA	stable	stable
NMOR	stable	stable
NPYR	stable	stable
NPIP	stable	stable
NDBzA	stable	stable
NDPhA	not stabil*	not stabil*
NDEA	stable	stable
NMPhA	stable	stable
NEPhA	stable	stable
NMEA	stable	stable

*stable for 14 days, not stable for 28 days

Summary and future plannings:

Summary

- Selective identification of elastomers by pyrolysis-GC/MS
- GC-MS screening is finished
- Primary aromatic amines and N-nitrosamines were detected
- Along with not identified substances, for 81% of the identified substances no risk assessment is available
- The suitability for food contact is questionable.

In progress…

- HPLC-screening of polar substances is continued (e.g. LC-Q-ToF)
- Migration experiments
  - According to requirements in BfR Recommendation XXI and Regulation (EC) No 10/2011
  - Dynamic migration testing should be established (elastomer-tubing)
- Validation of multi-analyte-methods
  - Polar substances (GPC in combination with LC-MS/MS)
  - Unpolar, volatile substances
- Assessment of results, consideration in BfR Recommendation XXI

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Thank you for your attention

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