

A Closer Look at Mineral Oil Fractions

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■ Introduction

A currently heavy discussed theme in the field of packed food concerns mineral oil residues of different sources. The mineral oils fractions can be described by their chemical properties, so a MOSH and a MOAH fraction can be found (MOAH – mineral oil saturated hydrocarbons and MOAH – mineral oil aromatic hydrocarbons). MOSH consist of linear and branched alkanes, and alkyl substituted cycloalkanes, whilst MOAH include mainly alkyl-substituted polyaromatic hydrocarbons up to four aromatic rings. The main focus is thereby on the aromatic fraction, covering about 15-30% of the whole aromatic fraction, which is suspected to include potential carcinogenic and mutagenic constituents. Nevertheless the methods which are normally used lacking specific information of the composition of the mineral oils constituents.

A common method uses the combination of HPLC and GC (either on-line or off-line) with non specific FID detection which quantifies only the total concentration of MOSH and MOAH. FID is used due its universal detection principle which eliminates structural influence of different molecules. In addition the methods uses a large volume injection with quite a steep temperature ramp resulting in broad unresolved humps as shown in FIG. 1.

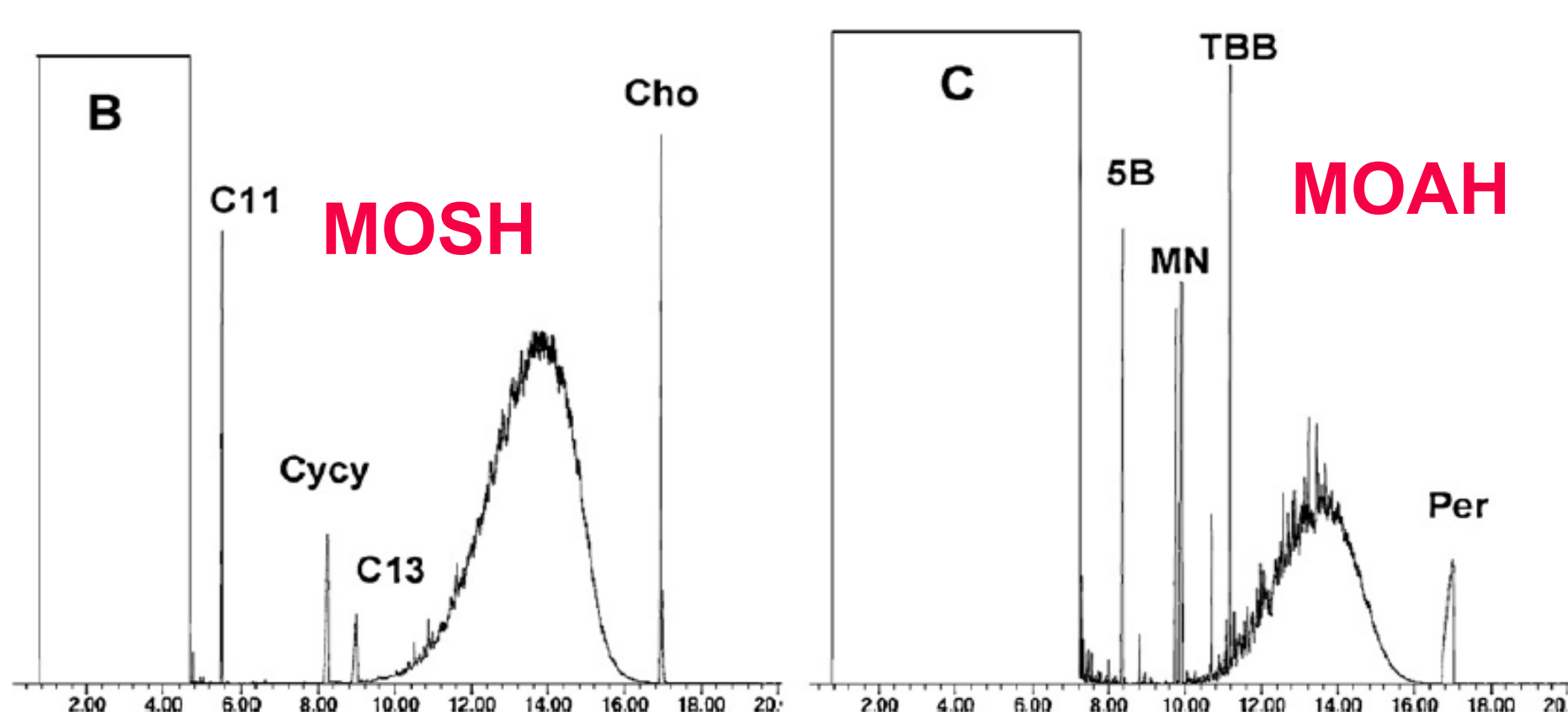


FIG. 1: GC-FID chromatogram of MOSH and MOAH [1]

■ Multidimensional methods

For the identification of individual substances in the MOSH and MOAH fraction multidimensional chromatography can be powerful tools. GCxGC based methods have the advantage to increase chromatographic resolution AND sensitivity.

■ Research strategy

Different types of paper products (fresh fiber, recycled and newspapers) were analyzed for the identification of individual substances and substance-classes of the MOAH. Thereby the focus was on newspapers, as they seem to be one of the sources of mineral oil in recycling products.

For analysis paper were extracted and fractionated according to the protocol given by the Kantonal Labor Zürich and BfR [2]. Extracts were fractionated by HPLC into MOSH and MOAH and the MOAH fraction was analyzed by GCxGC-MS. For identification purposes a large set of individual substances which might be possibly identified in the MOAH fraction (alkylated aromatic compounds, PAH's, internal standards of the MOSH/MOAH separation) were mixed and diluted to concentration close to the expected values in real samples and analyzed by GCxGC.

■ Method Parameters

Analysis were performed on a Shimadzu GC-MS QP 2010 ultra with a Zoex cryogenic modulator.

Column 1st dimension:

Zebron HT 1 (30 m x 0.25 mm i.d. x 0.25 µm df)

Column 2nd dimension:

SGE BPX 50 (2.5 m x 0.15 mm i.d. x 0.15 µm df)

TAB. 1: Analysis parameter GCxGC-MS analysis

Analysis Parameter GCxGC-MS	
temperature program	
50 °C (1min) – 10 °C/min – 120 °C – 2 °C/min – 280 °C (5 min)	
injection	1 µl splitless, 270 °C
carrier gas	He 155 kPa, constant flow
modulation	5 s, 280 °C hot jet pulse 350 ms
ion source	200 °C
interface	270 °C
data acquisition	Scan, 50-340 amu, 50 scans/s
Solvent cut	7 min

■ Phenylalkanes – dominant substance group

Performing a multidimensional GCxGC-MS analysis, linear phenylalkanes and their branched analoga could be identified as one of the main substance classes of the MOAH, present in all analysed samples. An unequivocal identification of the phenylalkanes was carried out using a standard mix that contained linear phenylalkanes with carbon chain length from C5 to C18 (FIG. 2).

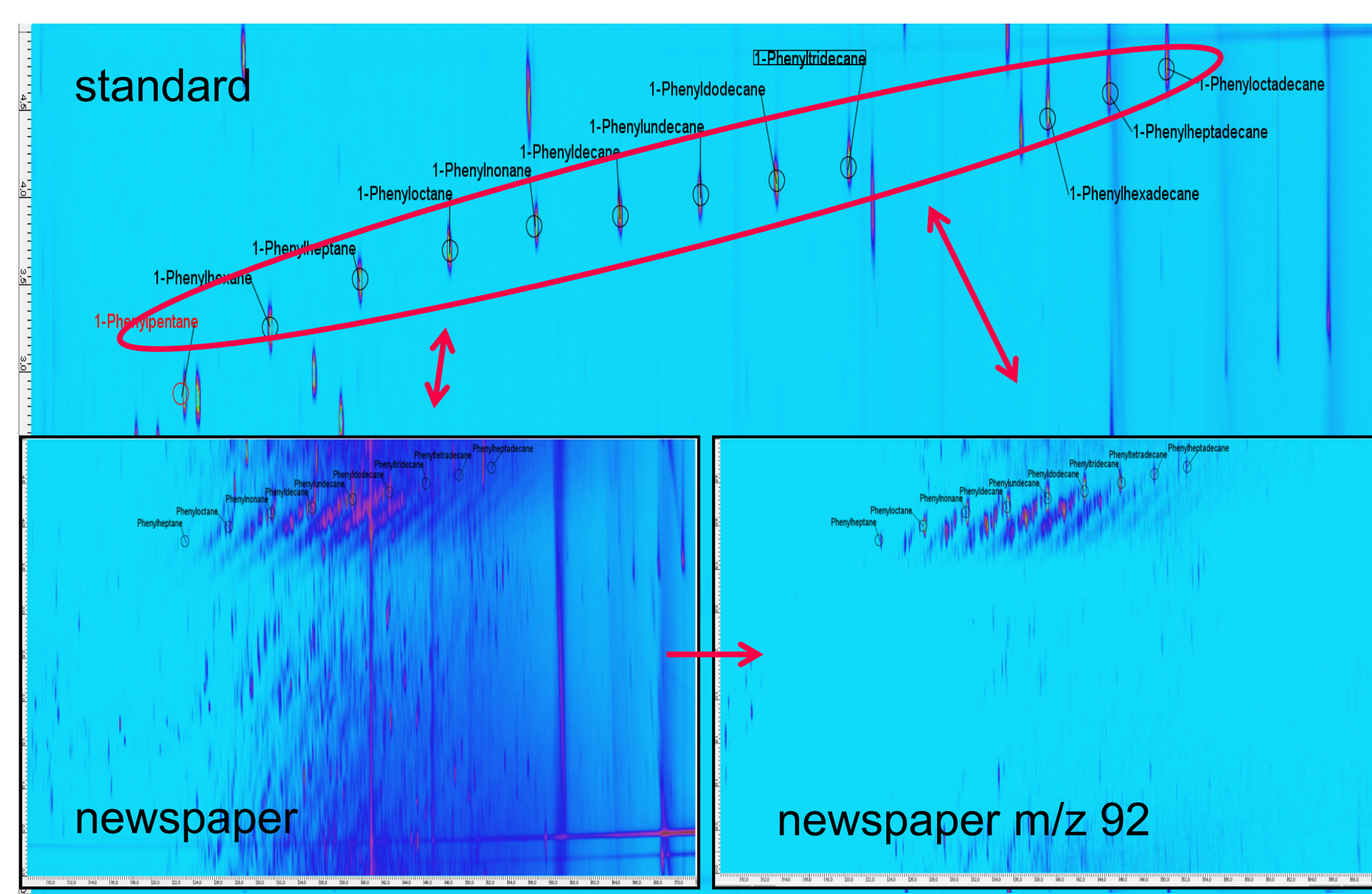


FIG. 2: Phenylalkanes (TIC and m/z 92) in standard und sample

Through extraction of the mass fragment m/z 92, characteristic for the phenylalkanes, not only linear phenylalkanes could be identified, but also diagonal lines of unknown compounds become apparent. These compounds are characterized by the same molecular mass fragment as the corresponding linear phenylalkanes, which points towards differently substituted and branched analogs This is illustrated for phenyldodecane (FIG. 3).

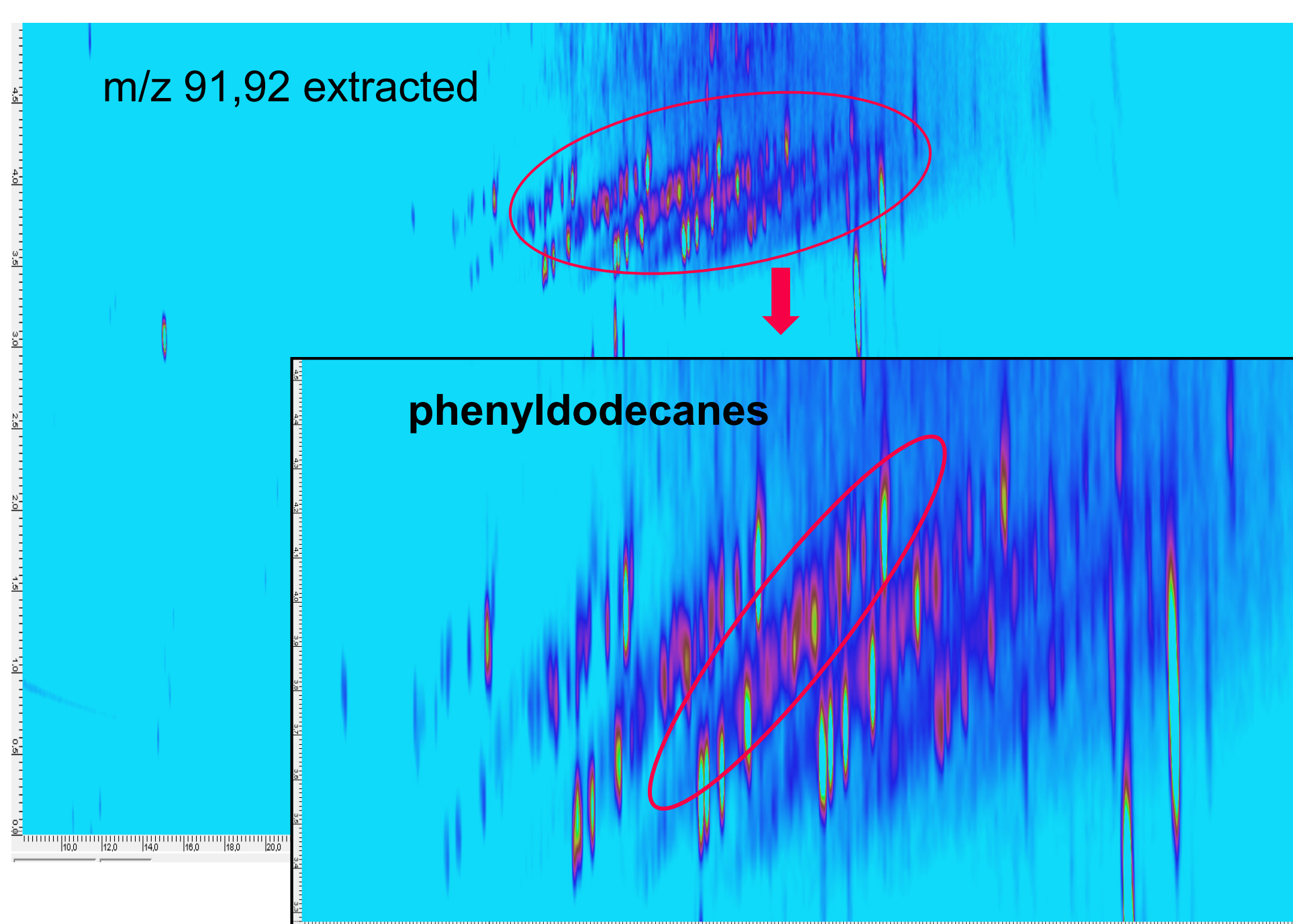


FIG. 3: Phenylalkanes (m/z 92) and their branched analoga

This could be shown by verification of the compounds 1-phenylpentane, isopentylbenzene and (1-methylbutyl)benzene contained in the standard mix (FIG.4). Extraction of the characteristic molecular mass fragments m/z 148 revealed that these three compounds are on a straight line (see dotted line).

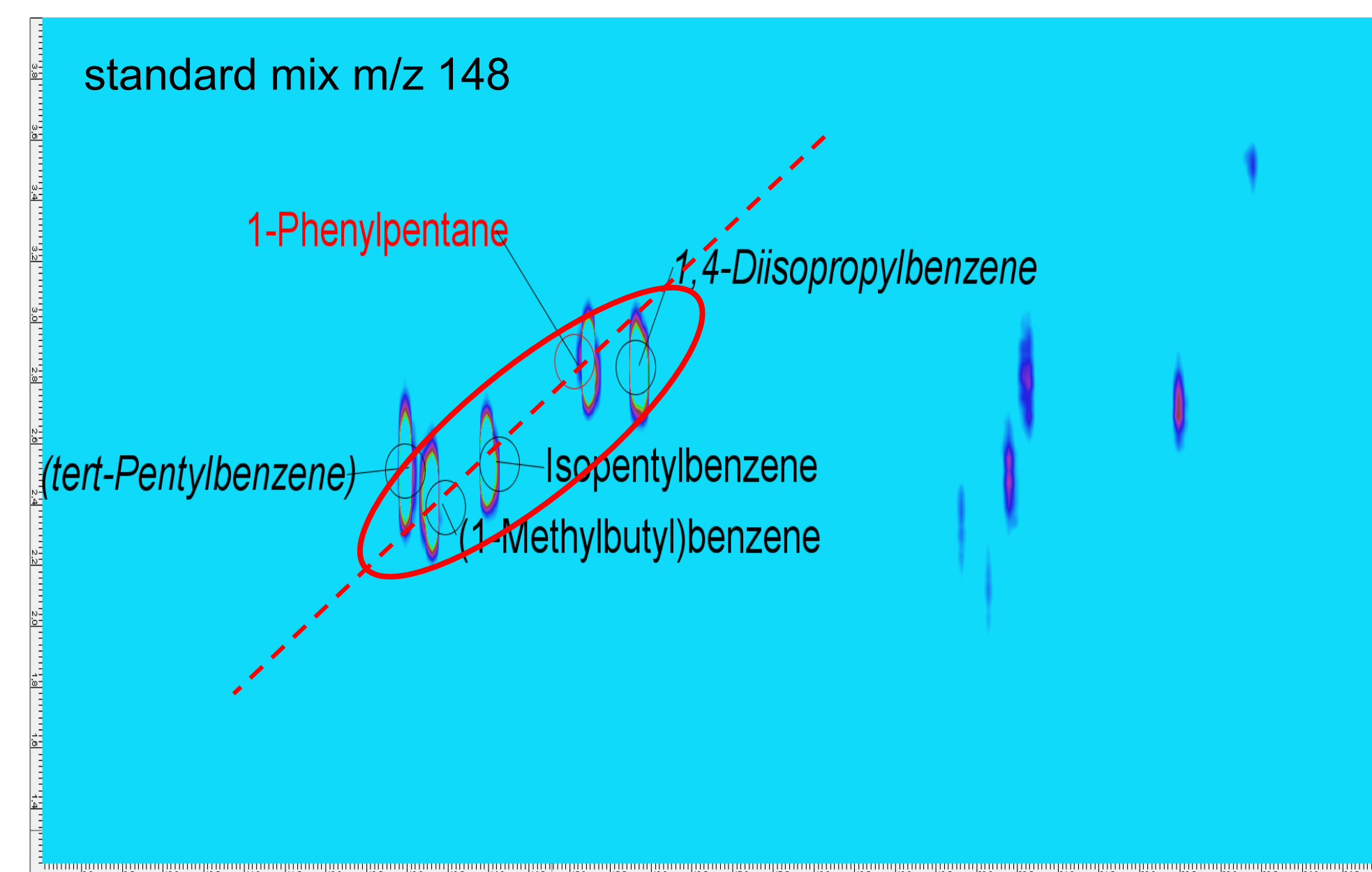


FIG. 4: Different branchings and substitutions exemplified by 1-phenylpentane

The next step was the identification of the analogs by their fragmentation pattern. Fragmentation of phenylalkanes follows established fragmentation rules, stipulating that the largest alkyl group is preferentially lost as neutral fragment. Following this rules analogs with an α-methyl, α-dimethyl, α-ethyl, α-propyl, α-butyl, α-pentyl and α-methyl-β-methyl structure could be identified (FIG. 5).

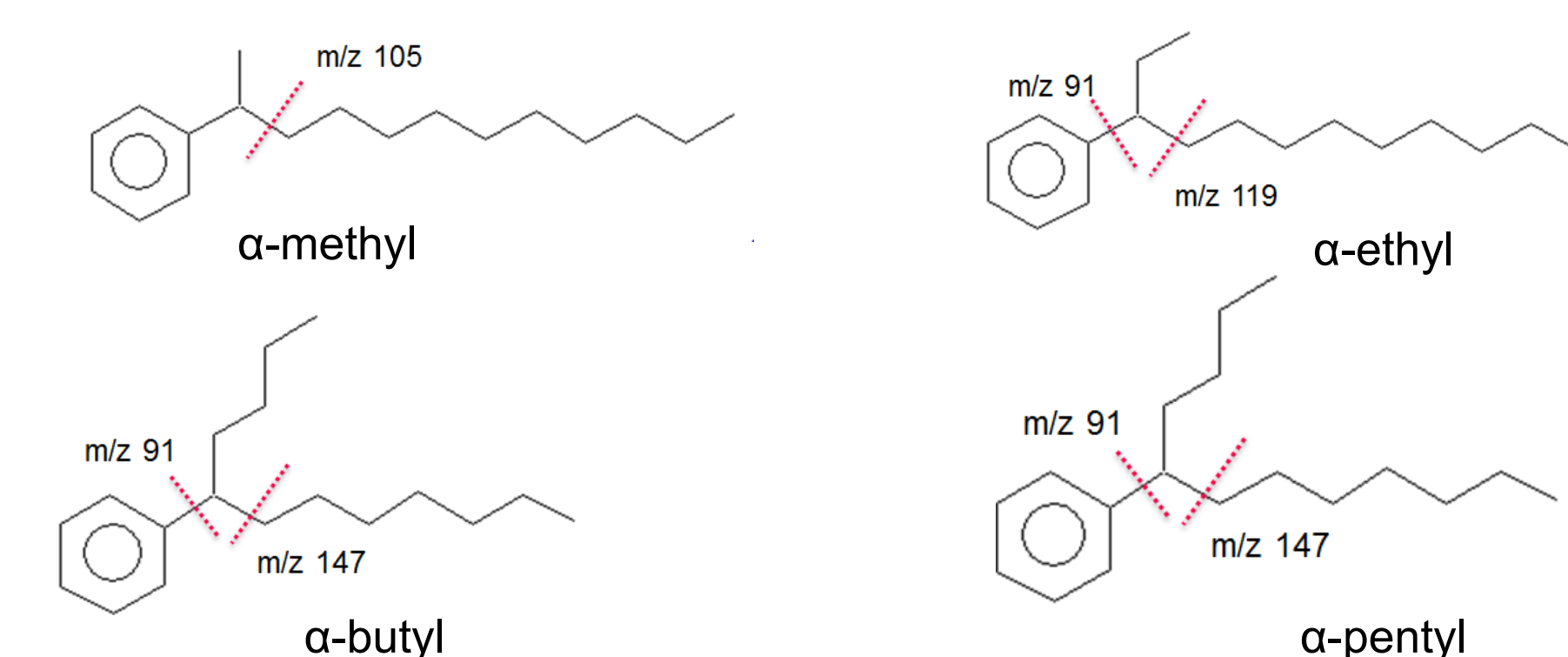


FIG. 5: Structures of identified analogues by their fragmentation

However, up to now only an structural identification of the unknown analogs is possible. An unequivocal identification of all unknown analogues, especially with larger carbon chains is currently not possible because of a lack of standards available (FIG.6).

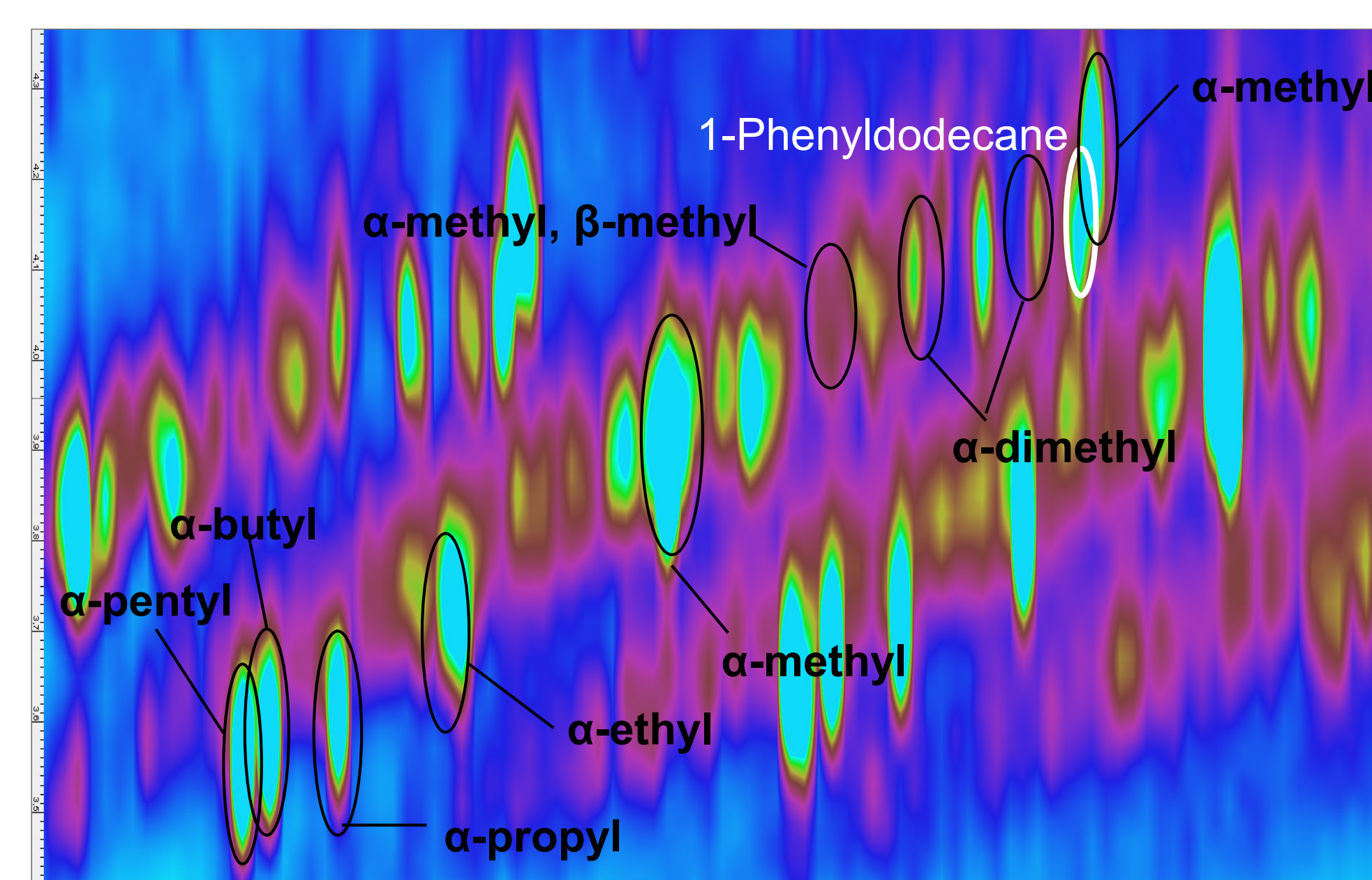


FIG. 6: Identified structural elements of phenylalkane analogues in a newspaper sample

■ Summary

GCxGC is a valuable tool which is able to deliver a more detailed information about the composition of mineral oil fractions. Nevertheless, more progress still needs to be made in the elucidation of the composition, which could eventually enable correct risk assessment.

■ Literature

- [1] K. Fislier, F. Grundböck, K. Schön, O. Kappenstein, K. Pfaff, C. Hutzler, A. Luch, K. Grob, J. Chromatogr. A 1271 (2013) 192-200
- [2] BfR-Bundesinstitut für Risikobewertung; Messung von Mineralöl – Kohlenwasserstoffen in Lebensmitteln und Verpackungsmaterialien