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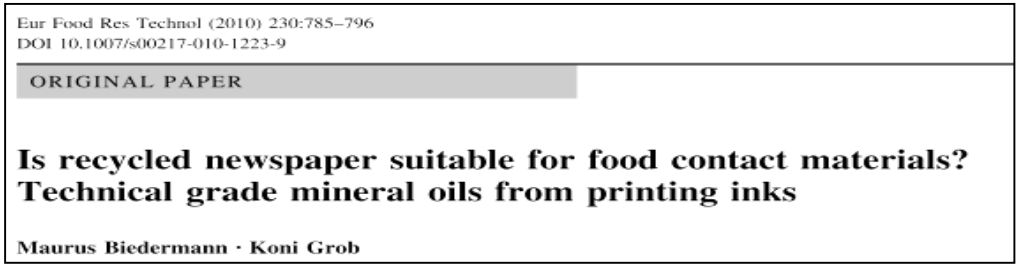
Instrument Solutions
Technology for Your Success!

MOSH/MOAH Recap and new developments

Starting point

October 2009

- Cantonal Laboratory of Zurich informed that they found mineral oil hydrocarbons (MOH) in food:
- Results up to 100 mg/kg cacao-powder (Σ MOSH +MOAH)
- Rice: 14 mg/kg MOSH (<C25)
  4,0 mg/kg MOAH (<C25)
- High results especially in food with large specific surfaces:
  cacao-powder, rice, semolina, noodles, pasta, sauce thickener
- These products are often packaged in cardboard


Eur Food Res Technol (2010) 230:785–796
DOI 10.1007/s00217-010-1223-9

ORIGINAL PAPER

Is recycled newspaper suitable for food contact materials? Technical grade mineral oils from printing inks

Maurus Biedermann · Koni Grob

BfR Opinion No. 008/2010, 09 December 2009

Bundesinstitut für Risikobewertung

Federal institute for Risk assessment

Migration of mineral oil from packaging materials to foodstuffs

- Due to the large portion of mineral oil fractions with short chain and aromatic hydrocarbons, such contaminations of foodstuffs are adverse
- Short chain hydrocarbons are more easily taken up by the body
- Frequent intake of such contaminated foodstuffs can thus lead to exceedances of the toxicological limit values
- Animal studies have shown that mineral oil mixtures with low viscosity are stored in the body and can lead to accumulations and damage in the liver, heart valves and lymph nodes

Conclusion: urgent need to minimize the migration of mineral oils to foodstuffs

Possible courses of action

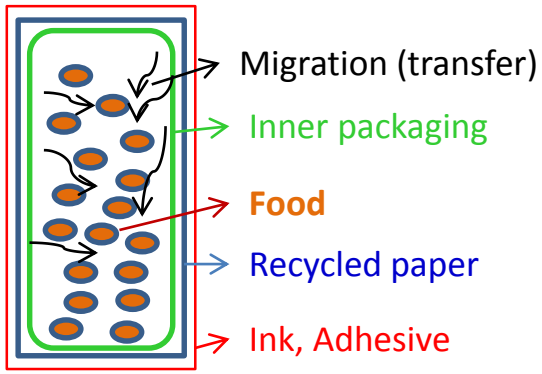
- use of inner bags in order to prevent substance migration from the cardboard box
- use of cardboard made from virgin fibres
- changing the composition of printing inks, mineral oil free systems for newspaper printing

This suggestion is further supported by the fact that the uptake of mineral oils from printing inks can also occur through skin contact

Starting point

The reasons

- The load of recycled cardboard with mineral oil components
- The printing of food-packaging with unsuitable systems



- Transfer via gas phase into the food

a. Depending on vapor pressure

b. Boiling range up to <C25

Source for the introduction of mineral oil into food

- Contamination of recycled fibres by mineral oil components
- Inks used for the offset printing which contain 20-30% mineral oil as solvent
  e.g. newspapers, leaflets, packaging material
- The recycling process cannot get all of the mineral oil out, so some of it ends up in recycled cardboard and paper
- Contamination of virgin fibres via gas phase from outer packaging
- Of special concern are dry foods having a large specific surface, containing fat and with long shelf life

If recycled fibres are used as raw material for food packagings, mineral oil can contaminate the food by transfer via gas phase

Most known Mineral Oil Sources

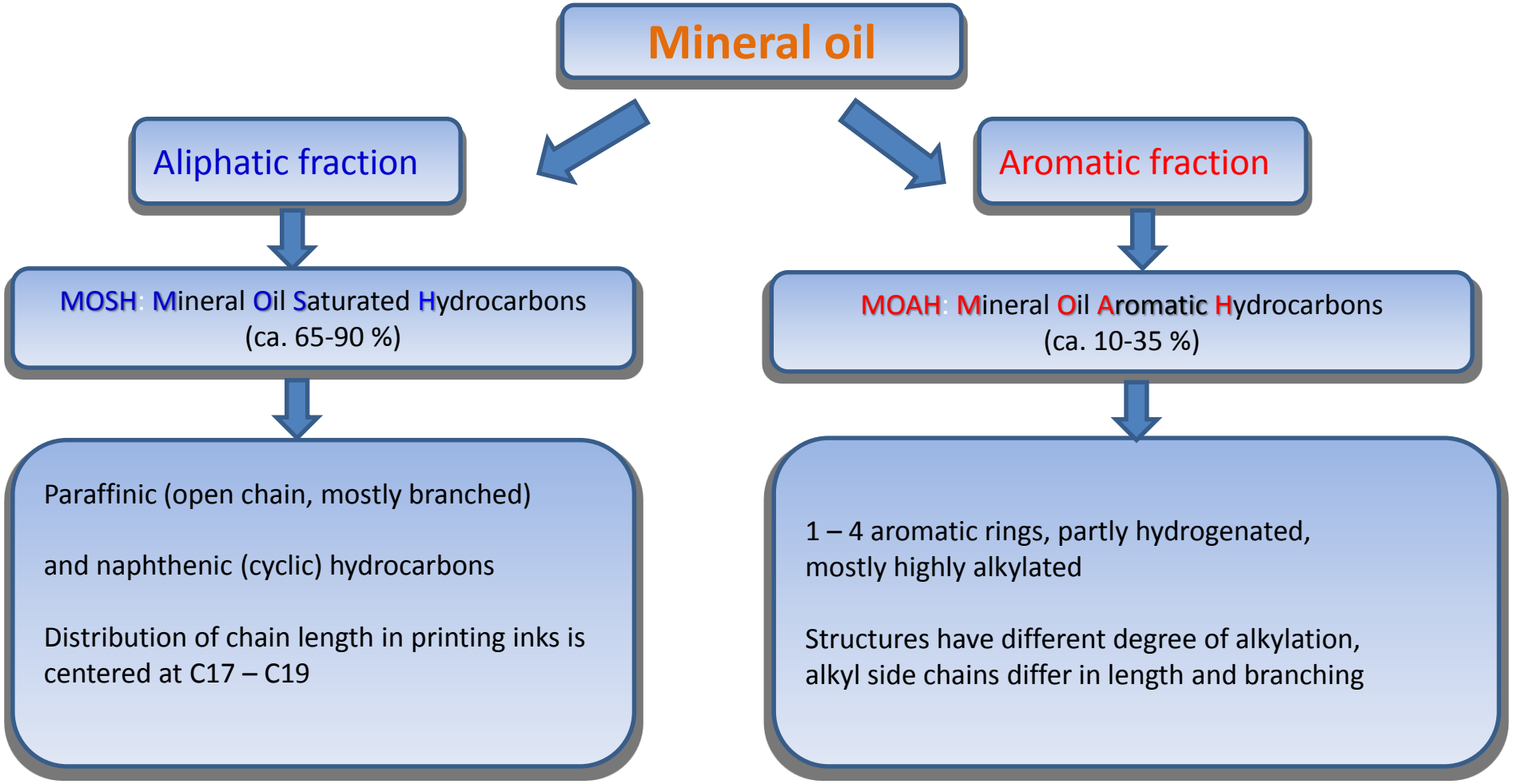
Environment

- Traffic & Industrial Pollution
- Lubricating oils (belt conveyor, agitators)
- Pesticide Formulations
- Detergent
- Cosmetics

Food

- Batching Oil for Jute- and Sisal- Bags
- Bakery & Sweets release oils
- Dust binding (rice, cereal, animal feed)
- Fruit & Dried Fruit Polishing
- Packing materials Waxes (water repellency), Inks, Polyolefins, Adhesives

What is mineral oil ?



Additonal approach

- **June 2010**
  2 days Workshop of the Federal institute for Risk assessment (BfR) and the Cantonal Laboratory of Zurich

  BfR Bundesinstitut für Risikobewertung — Mineral oil analytic — KANTONALES LABOR ZÜRICH

  - Themes : Methods for the MOSH und MOAH analytic *(GC-FID, on-line HPLC-GC-FID, GCxGC)*

    Occurrence and risk assessment

- **September 2011**
  Conference "Mineral oils in food packaging - developments and solutions", Berlin, BfR
  International discussion round with 400 participants
  Toxicology, Analytic

- **November 2011**
  Method development kit for mineral oil, BfR
  Different samples: Rapeseed oil; Mixture of Mineral oil; Mixture of n-alkanes; Extract of recycled cardboard; Mineral oil contaminated rice

  Full description of the mineral oil kit
  Standard operating procedure (SOP) of the „Manual" method Mineral oil contaminated

Decision support project (BMELV)

Recycled Paper – Appropriate for Food Packaging?

- „Ausmaß der Migration unerwünschter Stoffe aus Verpackungsmaterialien aus Altpapier in Lebensmitteln“

  BMELV (Federal Ministry of Food, Agriculture and Consumer Protection) Project 09HS012 (2010-2012)

  see: http://download.ble.de/09HS012.pdf

Confirmation of the results

- **Food from the retail 119 samples study:**

  119 dry food samples packed in recycled board were stored at room temperature and analyzed at the best before date or after 1.3 years storage at the latest

Max. amounts in food:	MOSH : 100 mg/kg	MOAH: 16 mg/kg
Main average results :	MOSH: 17 mg/kg	MOAH: 3 mg/kg

- **Migration study – storage experiments**

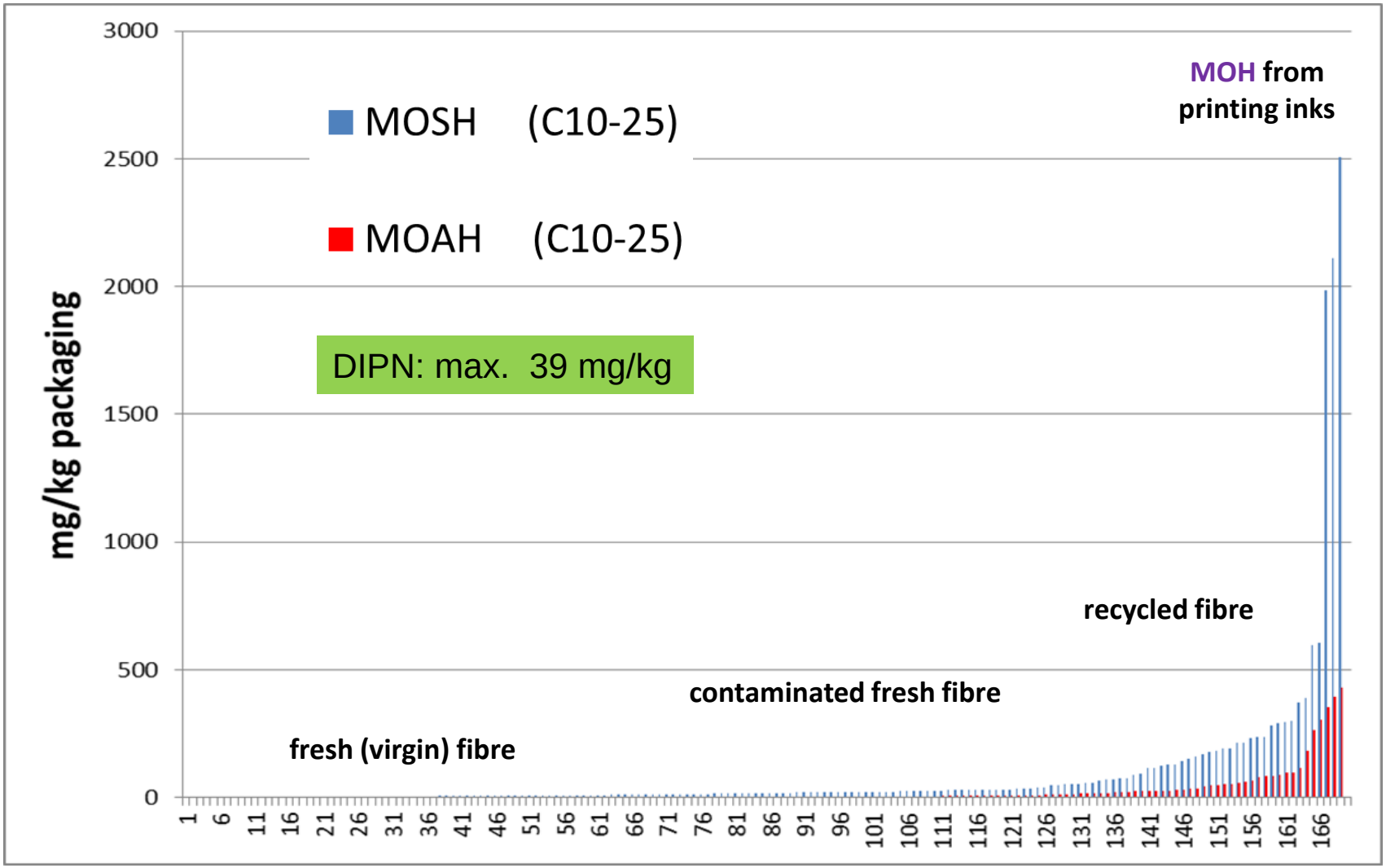
  After 2, 4 and 9 months storage at room temperature the food was analysed for migrated contaminants

  Migration in food directly packed in cardboard (% of potential):

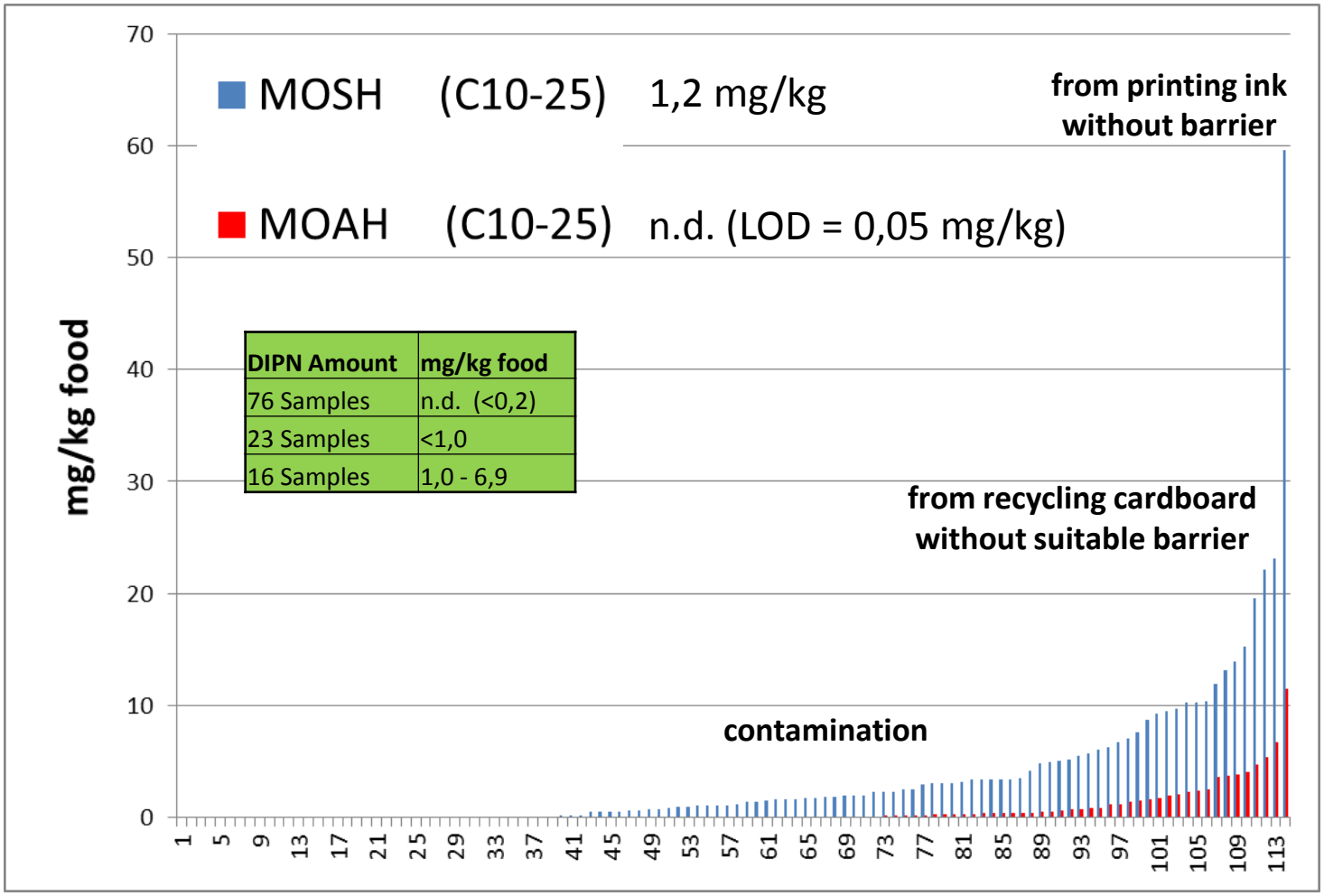
  MOSH: 35 mg/kg MOAH: 7 mg/kg (< C24: 65 to 80 %)

  Functional barriers foils in this experimental setup :
  - PE no barrier for long term storage
  - PP no barrier for long term storage
  - PP/acrylate no absolute barrier
  - PET tight barrier, with and without Al metallization

„Packaging material“



„Dry Food“



DIPN Amount	mg/kg food
76 Samples	n.d. (<0,2)
23 Samples	<1,0
16 Samples	1,0 - 6,9

Chocolate from advent calendars

November 2012

- The Goods Testing Foundation (Stiftung Warentest) has tested chocolate from advent calen and found that they contained mineral oils

24 samples	MOAH (mg/kg)
15 samples	< 0,5
6 samples	> 0,5 - 3
3 samples	> 3 (max. 7)

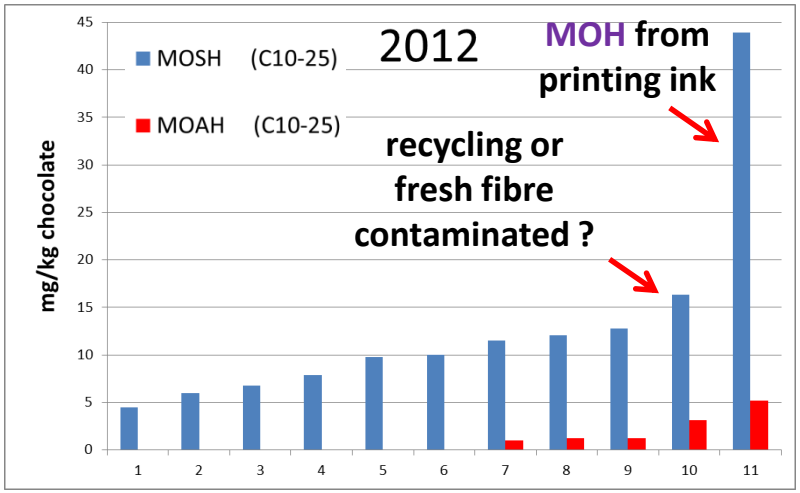
24 samples	MOSH,POSH;PAO (mg/kg)
21 samples	> 0,5 - 10
3 samples	> 10

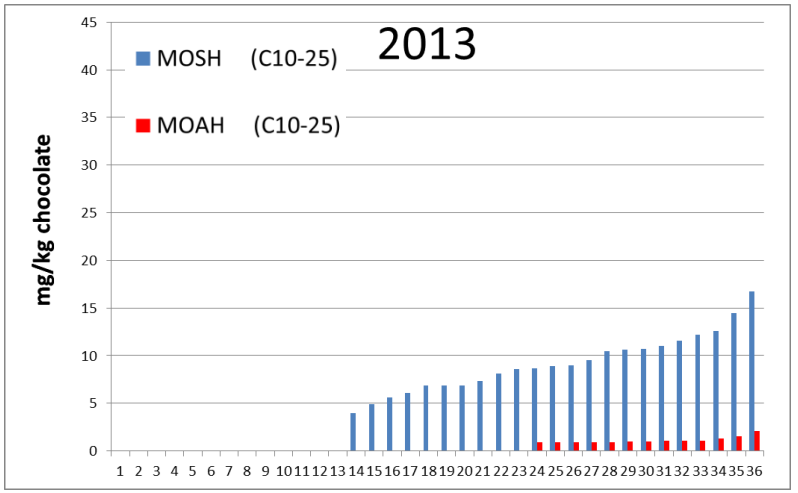
8 samples with mineral oil from other sources → lubricating oils

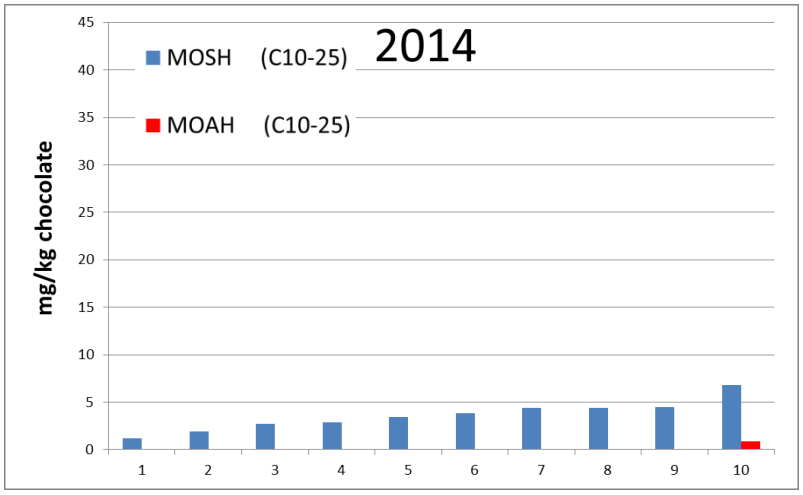
- Federal Institute for Risk Assessment (BfR) has conducted an initial evaluation to establish whether mineral oils in chocolate can pose a health risk

- It is possible to avoid such contamination, because there are calendars where none of these substances was found in the chocolates

„Advent calendars“







- no printing inks with MOH
- no recycled paper
- partially with barriers
- low basic load with MOH

Additonal approach (QM based)

Quality management

- Proficiency Test March 2013 organized from Institut Kirchhoff Berlin

  -17 laboratories

  - 4 different samples (chocolate, recycled cardboard, rice, hazelnut oil)

- German reference office for food proficiency testing and reference materials (DRRR) (commercial provider)
  a. Mineral oil in cardboard
  b. Mineral oil in food
  c. Mineral oil in fatty foods
  d. Mineral oil in Edible fats & oil
  e. Migration of mineral oil from cardboard - migration of mineral oil in the simulant: Tenax

  More info: www.drrr.de

Additonal approach (QM based)

- Collaborative trial, CEN, April 2015 organized from ITERG, France

  - Mandat M/243by European Commission to CEN (CEN/TC275/WG13)

  - „*Vegetable oils and foodstuff on basis of vegetable oils- Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line-HPLC-GC-FID analysis*

  - 12 laboratories (from 6 European countries)

  - 8 oil samples (4 sunflower-, soybean-, olive-, olive pomace-, palmoils)

  - 2 food samples (mayonnaise, margarine)

  - partly with epoxidation and ALOX-Purification

- Conclusions:

  - palm oil or olive oil need an epoxidation step for the MOAH content determination

  - Horrat values and considering as acceptable a value of 25 % for the reproducibility relative standard deviation for this specific determination

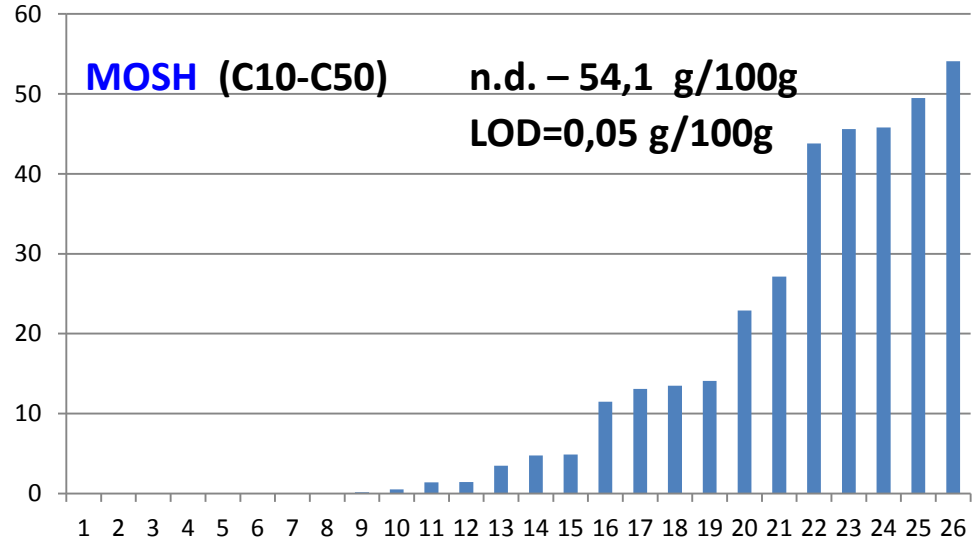
  LOQ should be fixed at 10 mg/kg for MOSH and MOAH

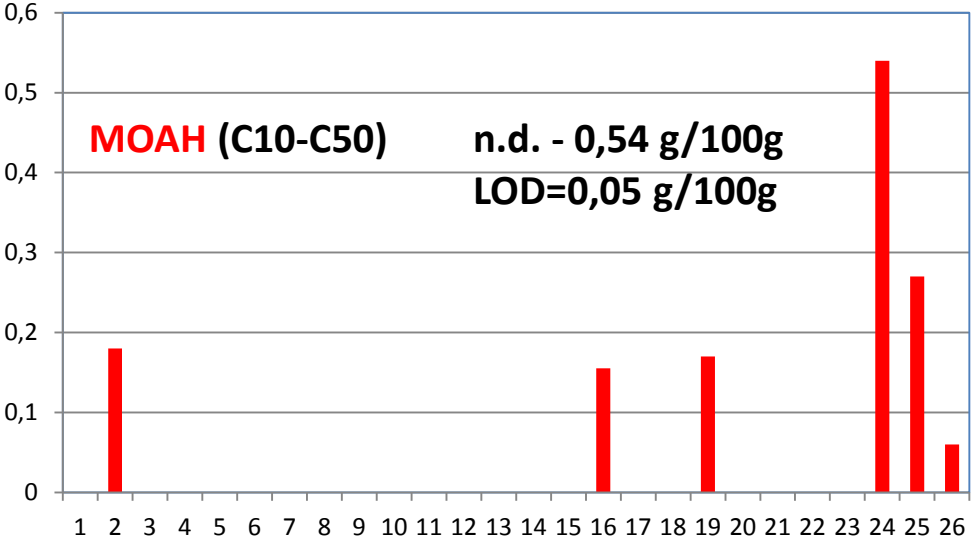
Cosmetic products

May 2015

- Goods Testing Foundation tested 25 cosmetic products (creams, baby care and lip care products, body oils, hair waxes and vaseline)
- All samples contained MOAH amount in range of 0.005 % to 9 %
- The Federal Institute for Risk Assessment (BfR) reported by up to 5 % MOAH content
- MOAH are especially problematic in products for lip care because these can be swallowed for the most part

„Cosmetics (Lip Care products)“





2016 – MOSH/MOAH Discounter

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12.3.2017 Aldi verlangt Lebensmittel ohne Mineralölverunreinigungen | foodwatch

foodwatch
die essensretter

Aldi verlangt Lebensmittel ohne Mineralölverunreinigungen

03.03.2016

Alle Lebensmittel, die als Eigenmarke von Aldi Süd verkauft werden, müssen in Zukunft frei von gefährlichen Mineralölverunreinigungen sein. Das hat der Discounter von seinen Zulieferbetrieben verlangt. In einem Rundschreiben, das foodwatch heute öffentlich machte, forderte Aldi seine Lieferanten auf, „Maßnahmen zu ergreifen, welche die Einhaltung dieser Vorgabe im Lebensmittel (…) sicherstellen.

In dem **Schreiben** vom Februar an alle Lieferanten heißt es: „Die gesundheitliche Unbedenklichkeit von Lebensmitteln ist ein zentrales Anliegen von Aldi Süd. (…) Aldi Süd hat das Ziel, dass bei den Eigenmarken des Food-Sortimentes **keine Mineralölbestandteile im Lebensmittel nachweisbar** sind. Aus diesem Grunde fordern wir Sie auf, Maßnahmen zu ergreifen, welche die Einhaltung dieser Vorgabe im Lebensmittel **bis zum Ende des MHDs, bzw. bei frischem Obst und Gemüse bis zum erwarteten Zeitpunkt des Verzehrs**, sicherstellen. (…) Aldi Süd wird die Umsetzung der Maßnahmen prüfen und bei zukünftigen Kaufentscheidungen berücksichtigen." [Hervorhebungen im Original]

Aldi Süd dreht Lebensmittelwirtschaft den Öl-Hahn zu

Die neue Vorgabe von Aldi Süd, einem der größten Handelskonzerne Deutschlands, ist ein echter Paukenschlag für die Branche. Nach jahrelangem Herumlavieren muss die Lebensmittelindustrie endlich ihre Produktionsprozesse und Verpackungen sauber machen. Krebsauslösende und erbgutschädigende Mineralölbestandteile in Lebensmitteln sind inakzeptabel – und sie sind technisch vermeidbar. foodwatch fordert daher: Es ist höchste Zeit, dass Edeka, Rewe, Lidl und Co. dem Vorbild von Aldi Süd folgen.

Zahlreiche Tests finden Mineralölverunreinigungen

Mineralöle sind die größte Verunreinigung im menschlichen Körper. Sowohl die Europäische Lebensmittelsicherheitsbehörde (EFSA) als auch das zuständige deutsche Bundesinstitut für Risikobewertung (BfR) verweisen auf das krebserregende und erbgutschädigende Potenzial aromatischer Mineralöle (MOAH). In den vergangenen Monaten waren in einer ganzen Reihe von Tests Verunreinigungen in Lebensmitteln öffentlich geworden – Öko-Test fand sie in Dr. Oetker-Produkten, das Bayerische Landesgesundheitsamt in Adventskalendern, Stiftung Warentest in Olivenölen. Im Januar hatte die Marke „Lafer. Lecker. Leben" von TV-Koch Johann Lafer wegen hoher MOAH-Werte den Verkauf einer Pfeffer-Spezialität („Malabar-Pfeffer schwarz") gestoppt.

https://www.foodwatch.org/de/informieren/aktuelle-nachrichten/aldi-verlangt-lebensmittel-ohne-mineraloelverunreinigungen/ 1/2

2017 – MOSH/MOAH

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Wie ist die entsprechende Gesetzeslage?

Da sich bei krebserregenden Substanzen keine gesundheitlich unbedenkliche Aufnahmemenge definieren lässt, bewertete die Europäische Behörde für Lebensmittelsicherheit (EFSA) die Aufnahme von MOAH durch die Nahrung generell als unerwünscht. Auch nach Einschätzung des BfR sollte kein nachweisbarer Übergang von MOAH auf Lebensmittel stattfinden und ist – soweit technisch machbar – zu minimieren. MOSH/MOAH stellen jedoch unter Zugrundelegung üblicher Verzehrgewohnheiten nach derzeitigem Kenntnisstand kein akutes Lebensmittelsicherheitsproblem dar.

Aufgrund der komplexen Fragestellungen gibt es bislang keine gesetzlichen Regelungen oder Grenzwerte für Mineralölrückstände in Lebensmitteln. Es liegen lediglich nationale und europäische Entwürfe für eine mögliche Gesetzgebung vor.

Lidl und der Umgang mit MOSH/MOAH

Auch ohne gesetzliche Vorgaben arbeiten wir seit Jahren konsequent an einer Vermeidung von MOSH/MOAH-Übergängen in Lebensmitteln, um unsere Kunden präventiv vor möglichen Spätfolgen zu schützen. Einige Lösungsansätze haben wir teilweise bereits seit geraumer Zeit umgesetzt. Bei unserer Optimierung gehen wir in zwei Schritten vor:

- Gemeinsam mit unseren Lieferanten betreiben wir intensive Ursachenforschung. So wird intensiv an der Erkennung der möglichen Eintragsquellen geforscht, um nachhaltig eine Kontamination von Lebensmitteln mit diesen Stoffen zu vermeiden.
- Gemeinsam mit unseren Lieferanten setzen wir gefundene Lösungen um, wie z.B. funktionelle Barrierelösungen, verschiedenste Beschichtungen bzw. Umstellung auf Frischfaser oder Folienstandbeutel bei Risikoartikeln wie Reis, Grieß, Cerealien.

Darüber hinaus haben wir mit unseren Lieferanten definiert, dass in unseren Lidl Eigenmarken maximal ein MOSH-Gehalt von 2 mg/kg und ein maximaler MOAH-Gehalt unterhalb der Bestimmungsgrenze vorliegen darf. Dies entspricht den aktuellen Entwürfen für die geplante Gesetzgebung in Deutschland und der EU. Die Erreichung dieser Zielvorgaben ist ein kontinuierlicher Prozess, den wir schon vor Jahren begonnen haben.

Überblick 2.3 MOSH / MOAH

Ziel	Minimierung von Mineralölrückständen in allen Lebensmitteln: **MOSH-Gehalt max. 2 mg/kg** **MOAH-Gehalt < Bestimmungsgrenze**	Schnellstmöglich
Startpunkt	Erste intensive Beschäftigung mit dem Thema Mineralölrückstände in Lebensmitteln nach Bekanntwerden der Problematik.	2009
Heute	Zahlreiche Minimierungsmaßnahmen sind bereits umgesetzt, vor allem im Bereich Verpackung.	Januar 2017

Basics of the LC-GC Technique

The method was developed from Konrad Grob and Maurus Biedermann at the Kantonales Labor Zürich.

Axel Semrau modified the method and brought it to routine labs

LC-GC coupling

Axel Semrau®

Heart-cut technique

LC as sample preparation for GC

- LC: High sample capacity→ Clean-up, separation of the matrix
- GC: High separation efficiency, selective detectors

Mostly normal phase LC or SEC for GC-compatible solvents

Why do you need HPLC-GC for MOSH-MOAH?

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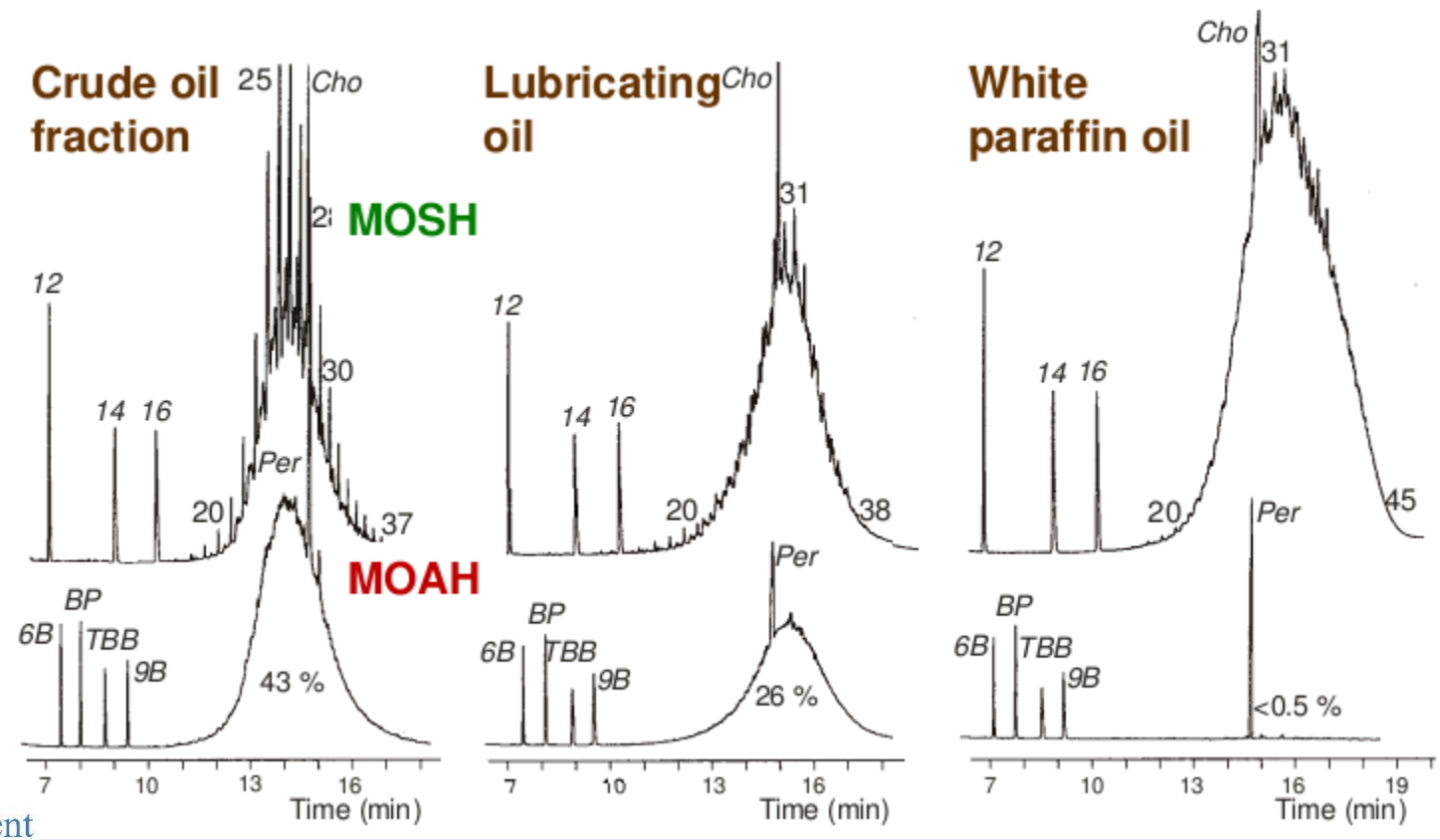
No GC separation between MOSH / MOAH on an apolar GC columns possible



(NP)LC-Conditions

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2 mm-columns

- Sufficiently high capacity for sample and matrix
- Group sizes manageable
- Flow rates: 200 - 500 µL/min → optimal GC-transfer rate
- Intermediary detector for control
- Time or signal-controlled fractionation

After transfer often back-flush used with polar solvent

- Example: direct injection of oil → example: removal of triglycerides

Requirements for the LC-GC coupling used for MOSH/MOAH analysis

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- Has to work with a FID as detector
- Must be compatible with at least 2mm colums, smaller diameter is not possible
- Solvent Hexan/Dichlormethane must be possible
- No discrimination of C10
- Up to C40, better C50+
- Heart-cut technique
- Easy to handle
- Robust
- 2 LC Fractions in one run should be possible

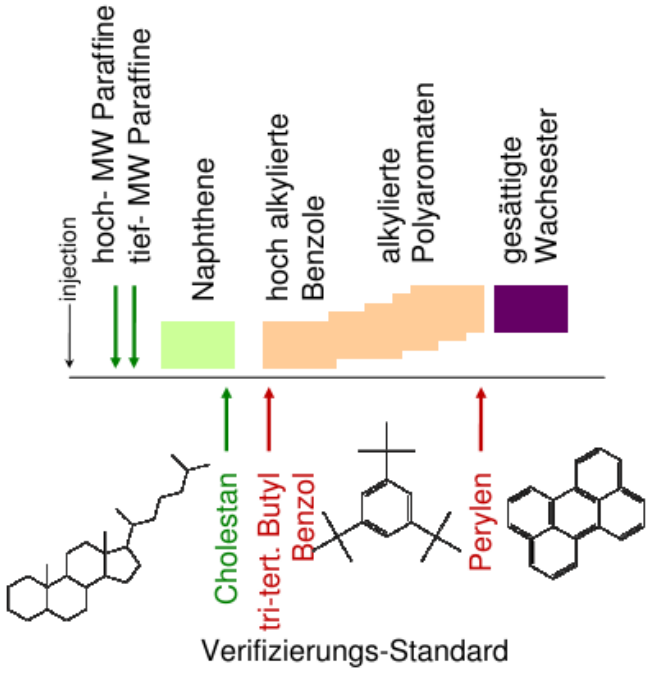
All this requirements can only be fulfilled with a LCGC solution based on retentiongap technology, Solvent split techniques based on aPTV system are not suitable.

Understanding the principle

Extraction of food / paper with hexane and hexane / ethanol

Maybe after concentration, direct injection into NPLC-GC-FID

- 2,1 mm x 250 mm Restek Allure 60 Å
- Column suitable for fatty foods
  - 20 mg Trapping capacity Triglyceride ca. 50% of the column→ Trapping function



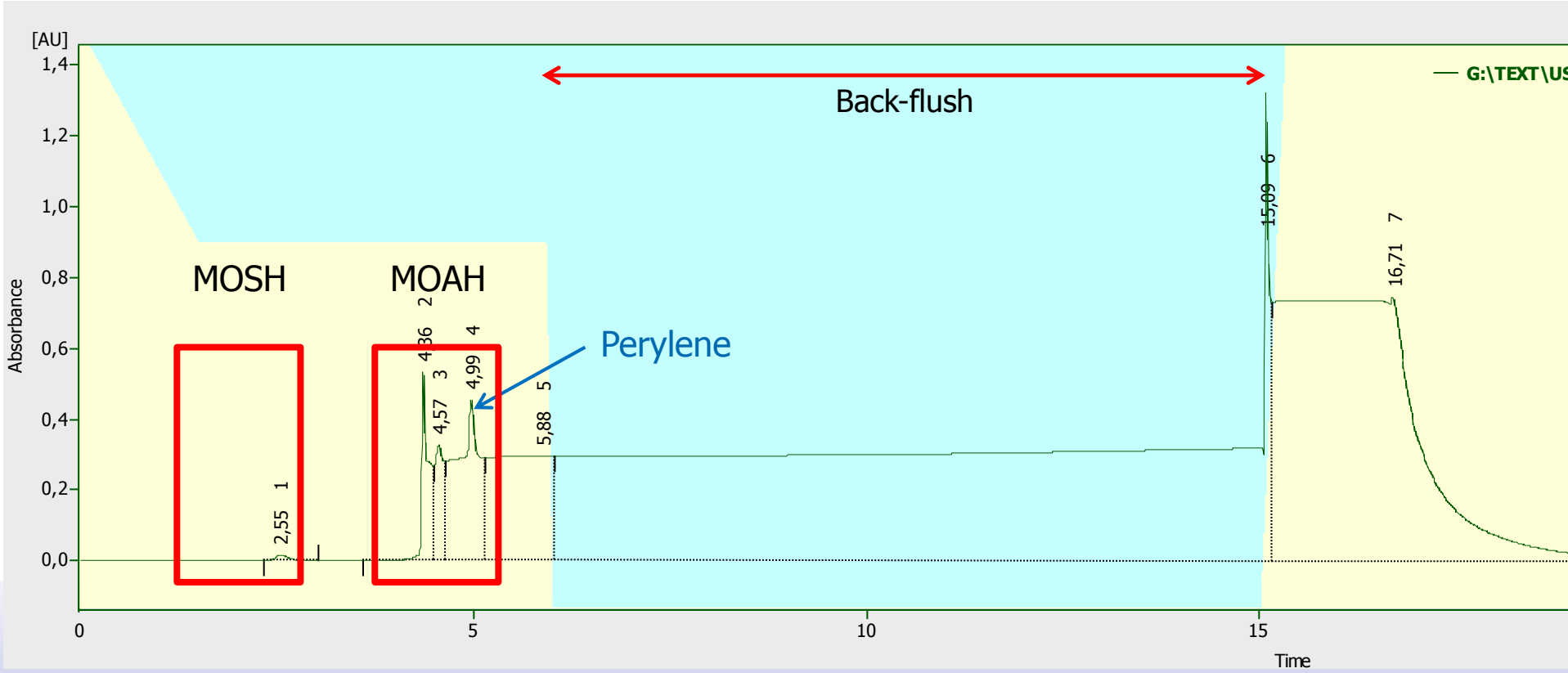
<u>Pragmatic verification standard:</u>

Cholestane → End of MOSH
TBB → beginning of MOAH
Perylene → end of MOAH

C11: Volatile component (MOSH)
Pentylbenzene: Volatile component (MOAH)

LC-gradient

- Separation of MOSH and MOAH with Hexane/CH_2Cl_2 gradients
- UV-detection (230 nm)
- Gradient tracking
- 2 fractions with each 450 µL



GC parameters

450 µL-Fractions in Hexane (MOSH) or Hexane/CH_2Cl_2 (MOAH)

- Different enrichment conditions necessary

C11 and Pentylbenzene are analyzed quantitatively

- 10 m x 0.53 mm retention gap
  - Blank, deactivated guard column,
  - most suitable: Restek MXT
  - Solvent Vapor Exit
  - Partial Concurrent Solvent Evaporation

- 15 m x 0.25 mm x 0.25 µm separation column
  - No separation of all hydrocarbons isomers possible
  - Quantification on signal hill
  - Short column, high carrier gas flow (H_2)
  - Maximum S/N-ratio
  - most suitable: Restek RXI-5Sil MS

LC-GC technique:
Partial Concurrent Solvent Evaporation

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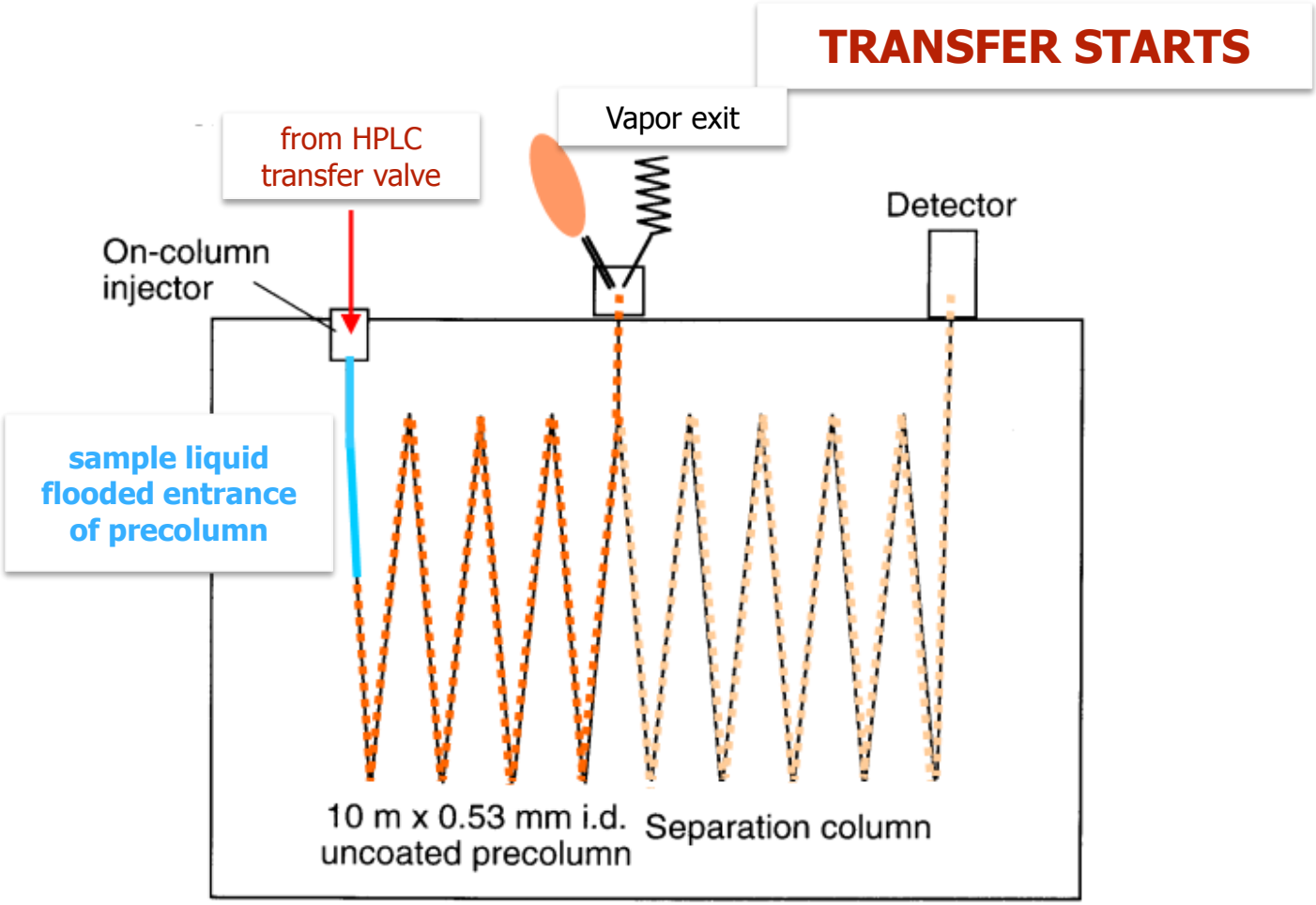

LC-GC technique:
Partial Concurrent Solvent Evaporation

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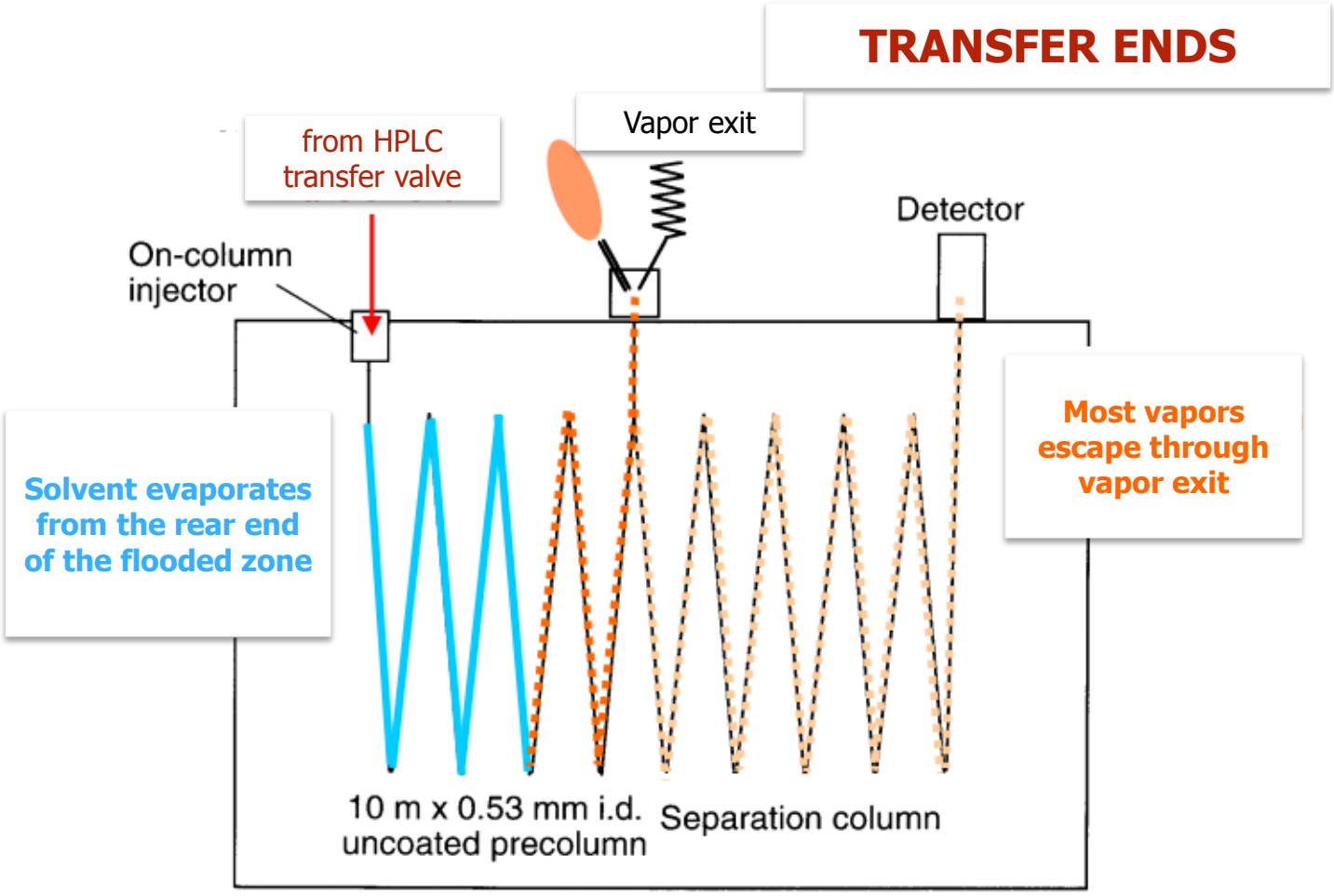

LC-GC technique:
Partial Concurrent Solvent Evaporation

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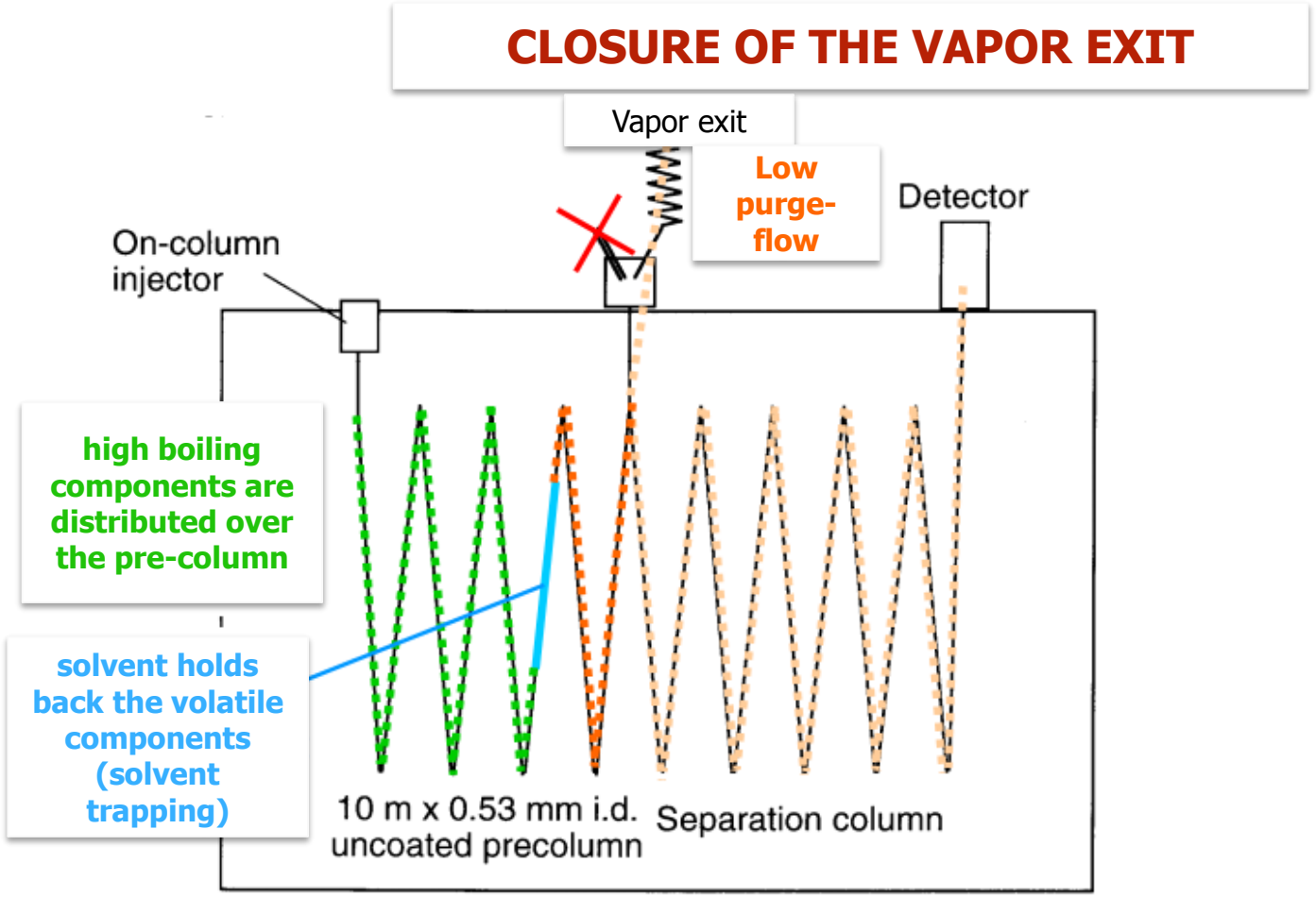

LC-GC technique:
Partial Concurrent Solvent Evaporation

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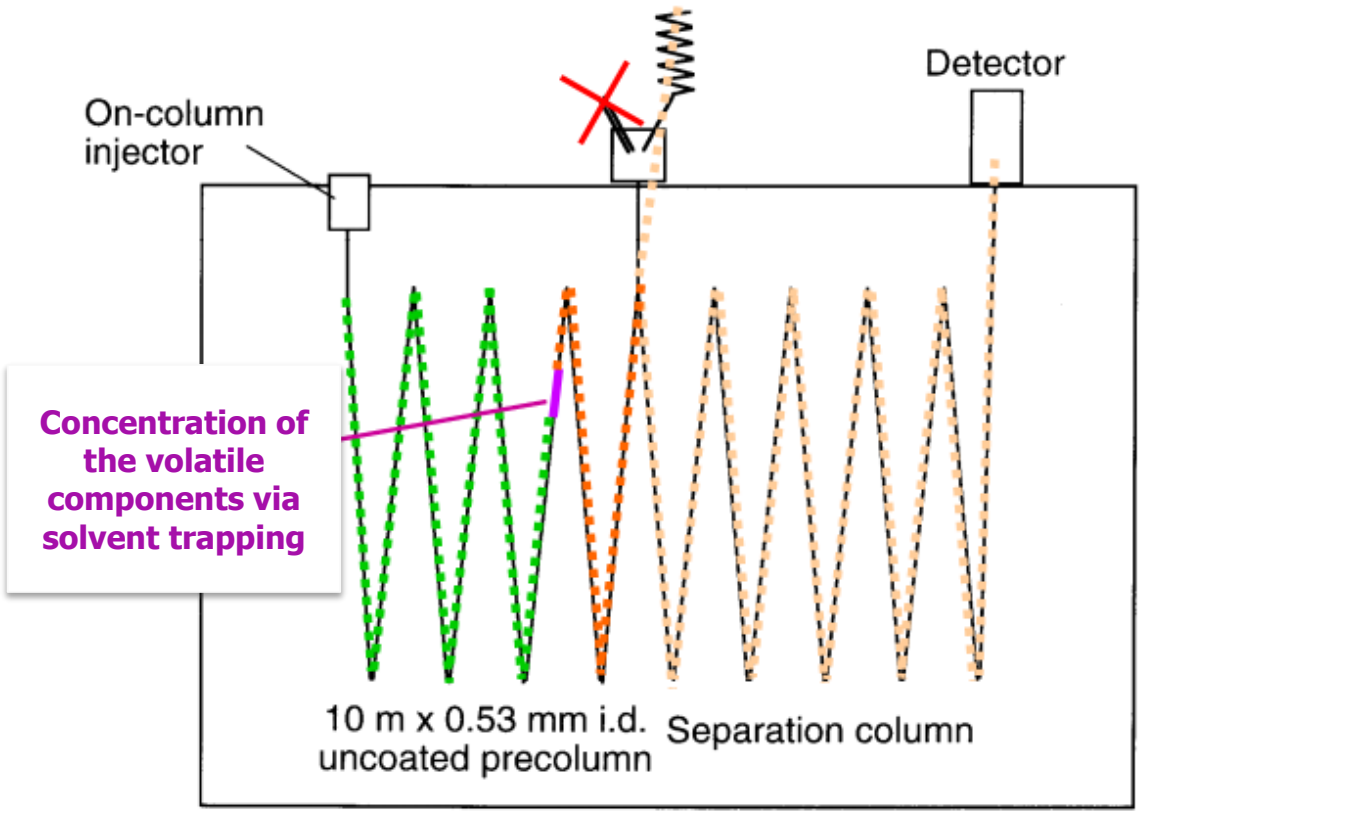
SOLVENT TRAPPING ENDS



LC-GC technique:
Partial Concurrent Solvent Evaporation

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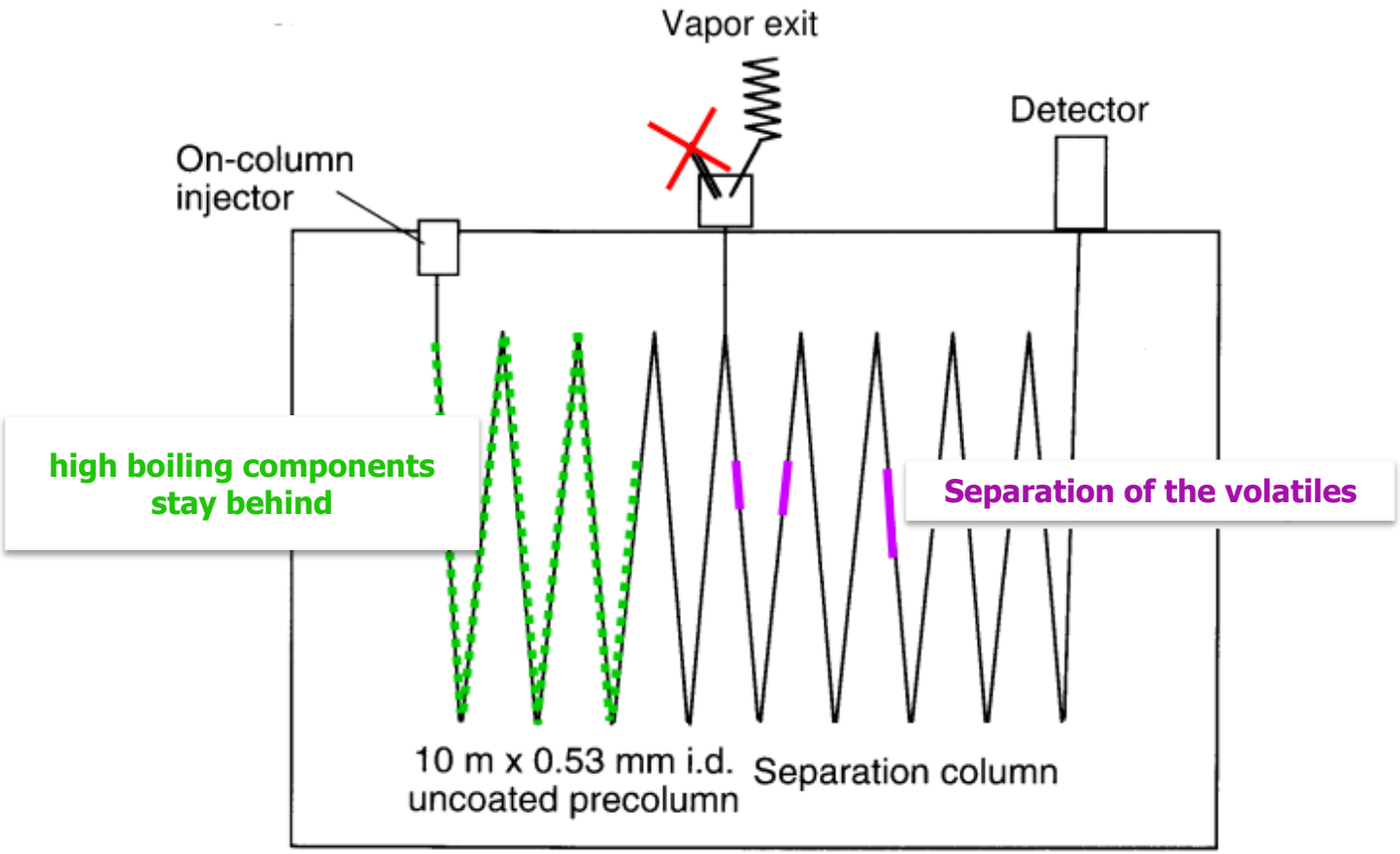
SEPARATION OF THE VOLATILES



LC-GC technique:
Partial Concurrent Solvent Evaporation

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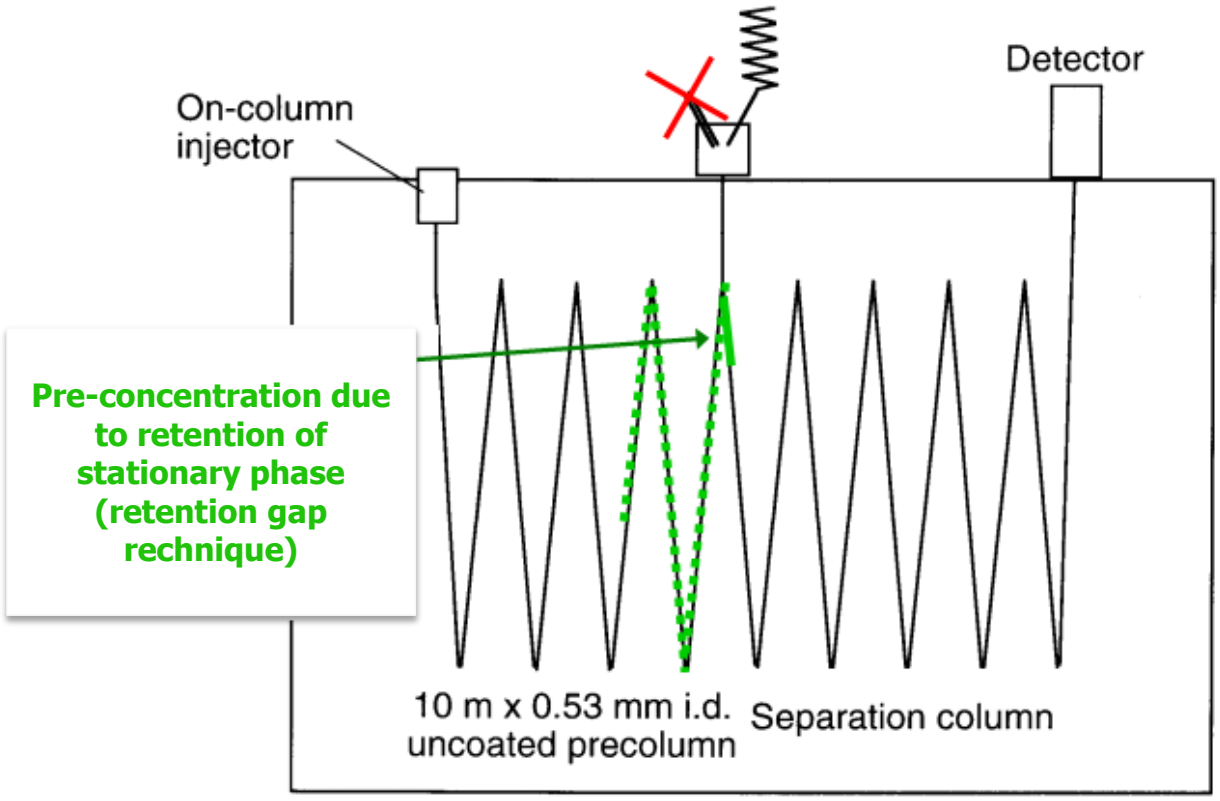
CONCENTRATION OF THE HIGH BOILERS



Pre-concentration due to retention of stationary phase (retention gap rechnique)

LC-GC technique:
Partial Concurrent Solvent Evaporation

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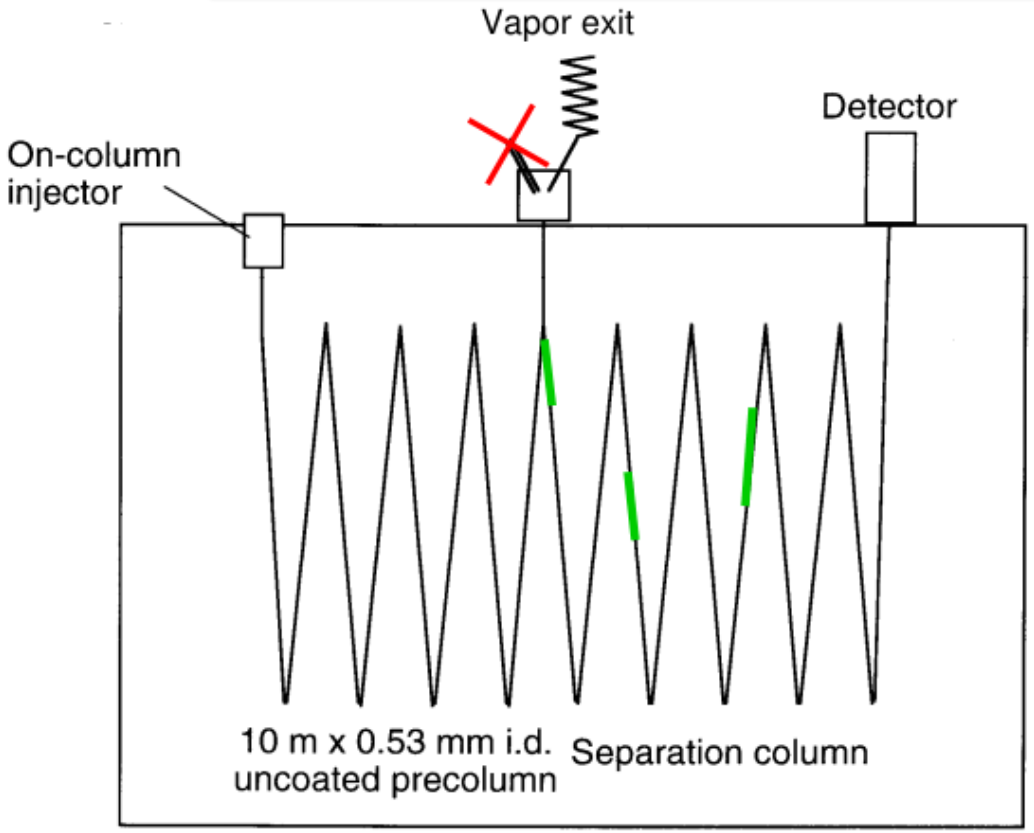
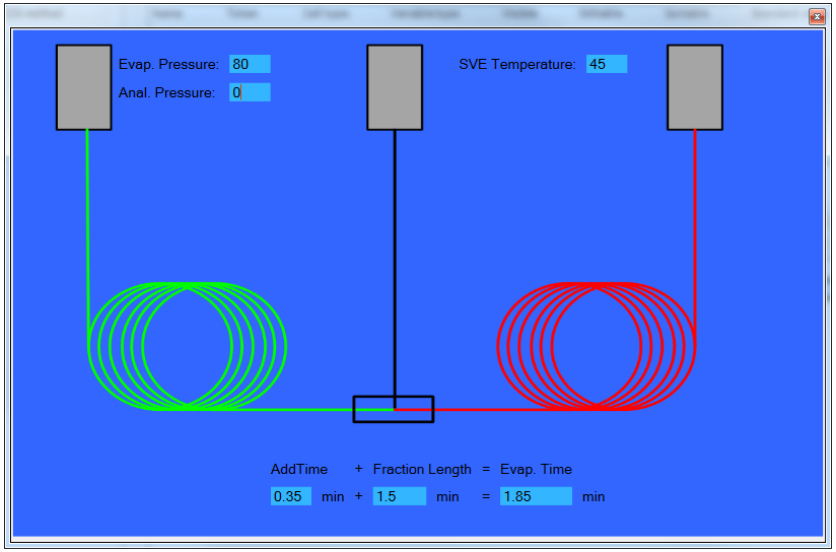
SEPARATION OF THE HIGH BOILERS



The interface – CHRONECT LC-GC

To be connected with any GC
1 or 2 channel operation

Complete CHRONOS Integration



General System Design

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Agilent 1260 with UV-det

Agilent 7890 GC with FID

CTC PAL

Clarity

Chronos

Samplelist using Chronos

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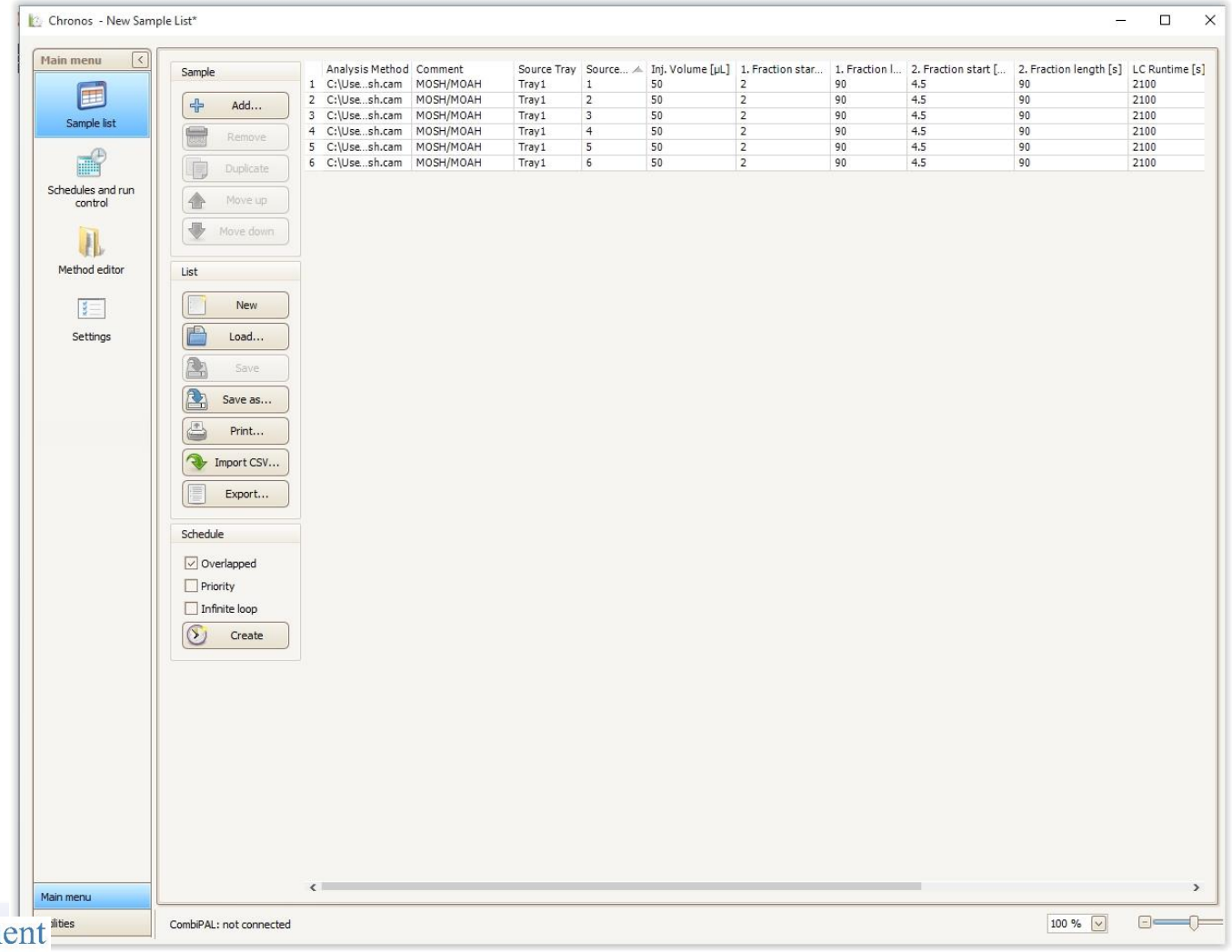
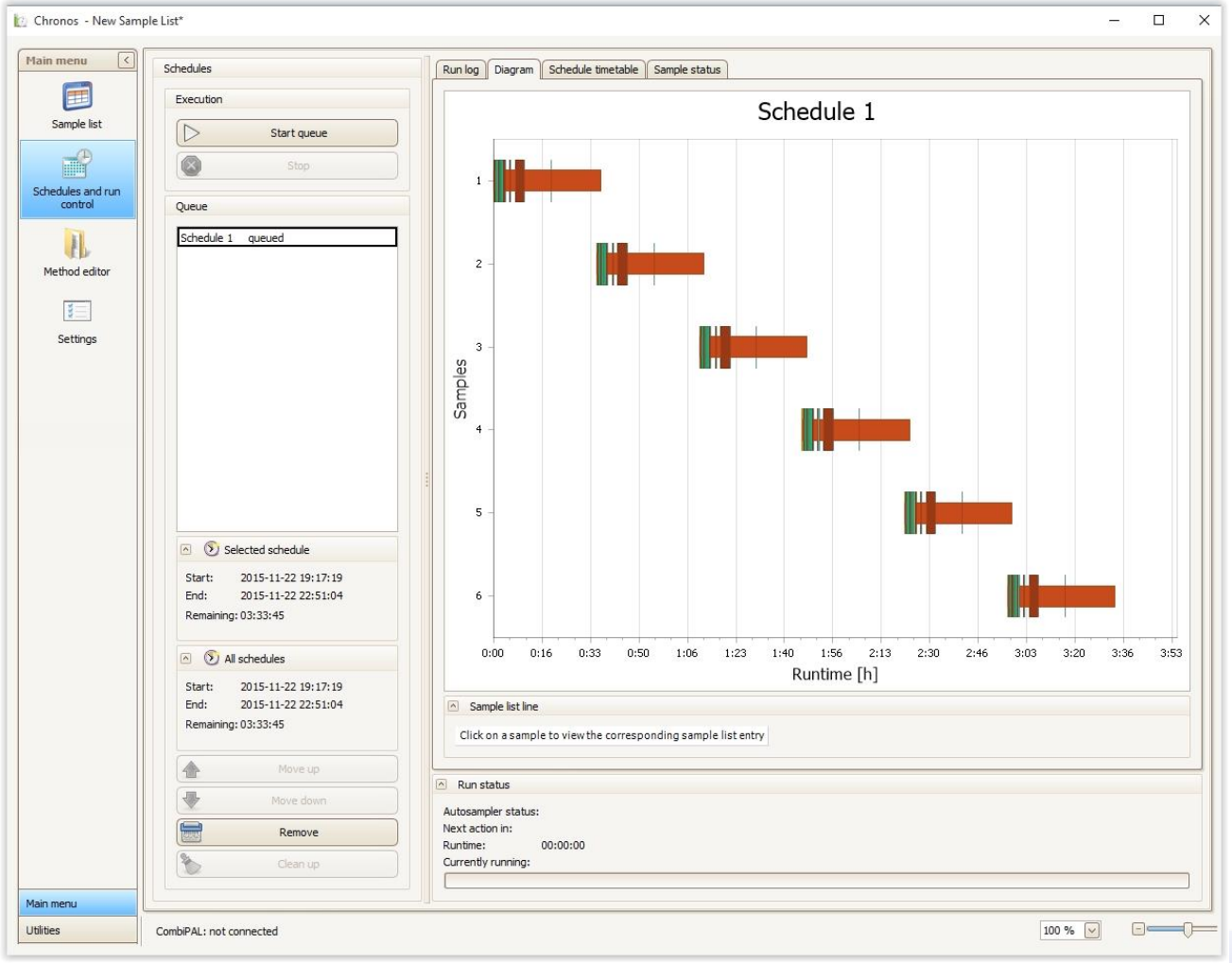


Schedule for samples



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Technology for Your Success!

Method in Chronos

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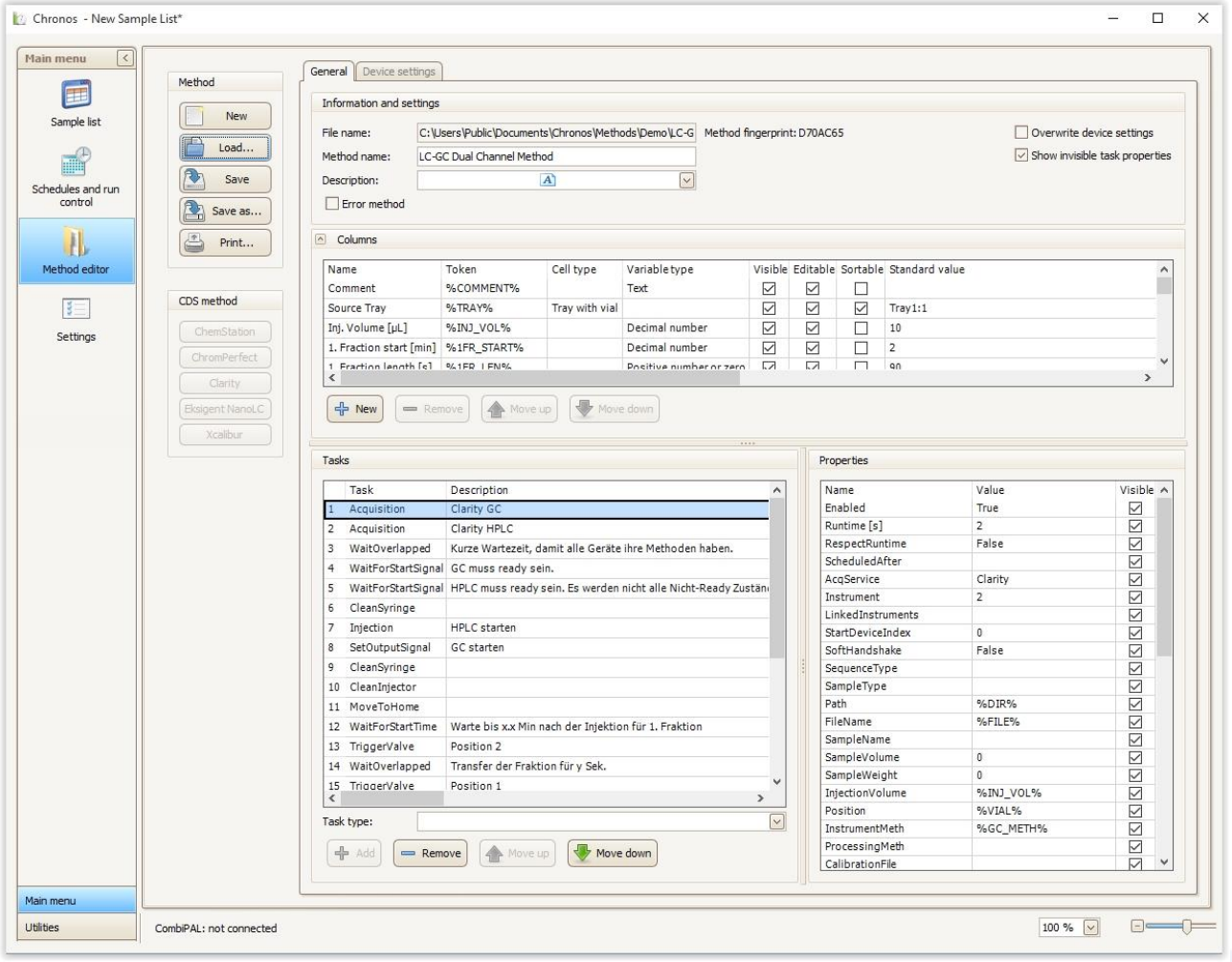

Instrument Solutions
Technology for Your Success!

The system in reality

Axel Semrau®

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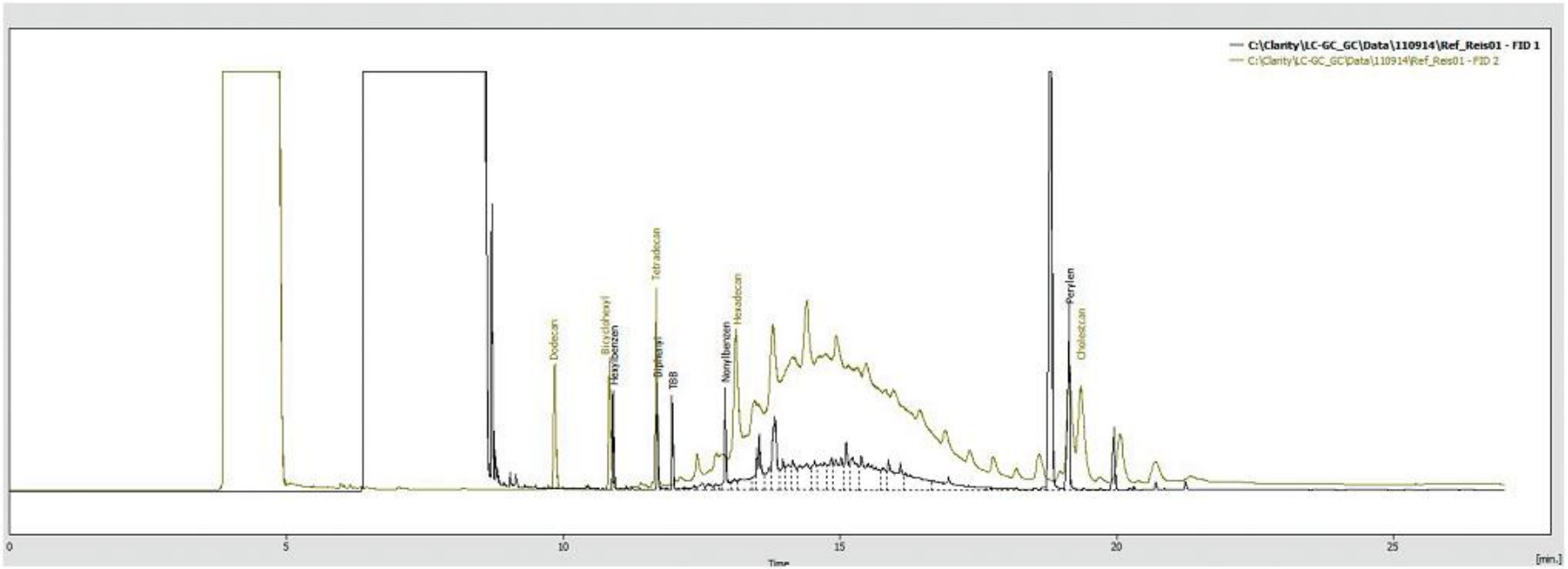
Axel Semrau

Chronect LC-GC System
für die MOSH/MOAH Analytik

CHRONECT® Robotic

How the chromatograms look like :

- **MOSH + MOAH in the same GC-run**



Status instrumentation 2017

- **50 systems installed in routine labs in Germany, Austria, Benelux, France**
- **Service and support by Axel Semrau; SIM GmbH; Instrument Solution; Sugelabor**
- **Development of FAT and SAT procedure by Axel Semrau**
- **Further automation options and improvement of the methodology**
- **First european regulation**

DIN EN 16995:2016-05 Draft :

Foodstuffs - Vegetable oils and foodstuff on basis of vegetable oils - Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis; German and English version prEN 16995:2016

will be finished in 2017

New Developments for MOSH/MOAH

- **Fract and Collect option for further identification of MOAH fraction toexample by GCxGCMS**
- **Automated expoxidation**

Fract and Collect Option

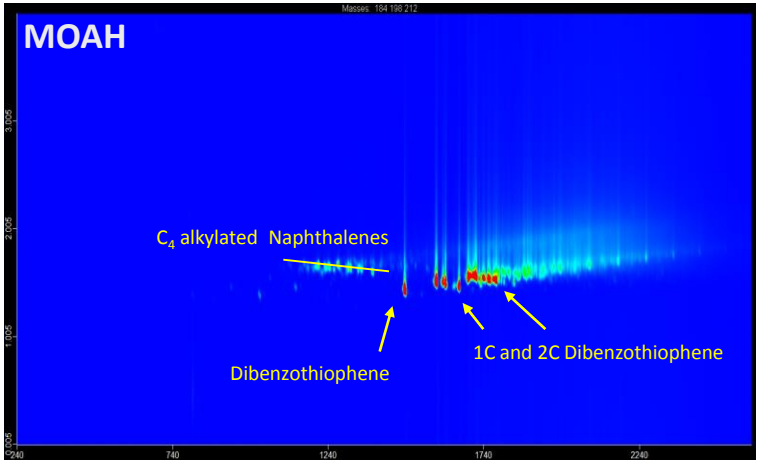
- Requires additional valve on the system
- Requires PAL RTC
- Complete integration in samplelist
- Collects a complete Fraction (MOSH or MOAH; selectable by user)
- Fraction can be used for further identification of compounds using other techniques like GCxGC TOFMS or NMR

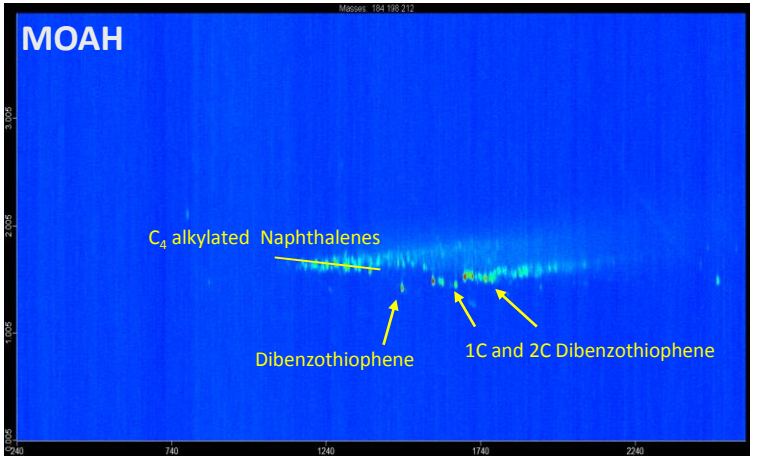
Coffee + Jutebag

GCxGC/TOFMS

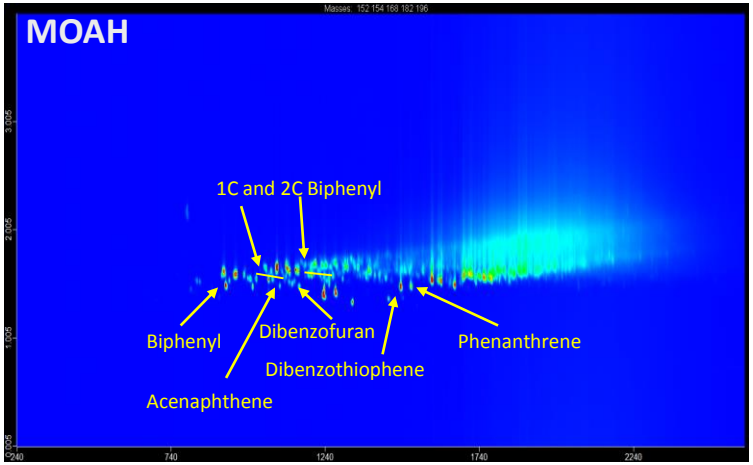
jutebag

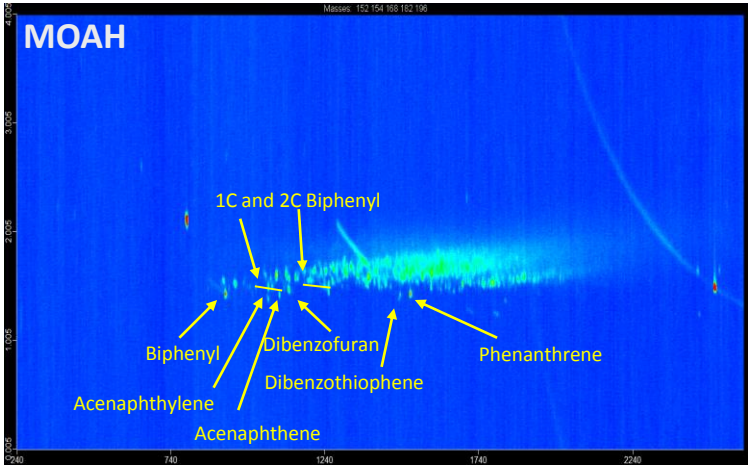
coffee





m/z 184 198 212 – Dibenzothiophene, 1-2C alkylated Dibenzothiophenes, 4C alkylated Naphthalenes





m/z 152 154 168 182 196 Biphenyl, 1-2C Biphenyl, Acenaphtylene, Acenaphtene, Dibenzofuran, Dibenzothiophene, Phenanthrene

Automated Epoxidation

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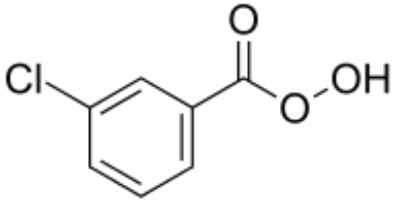
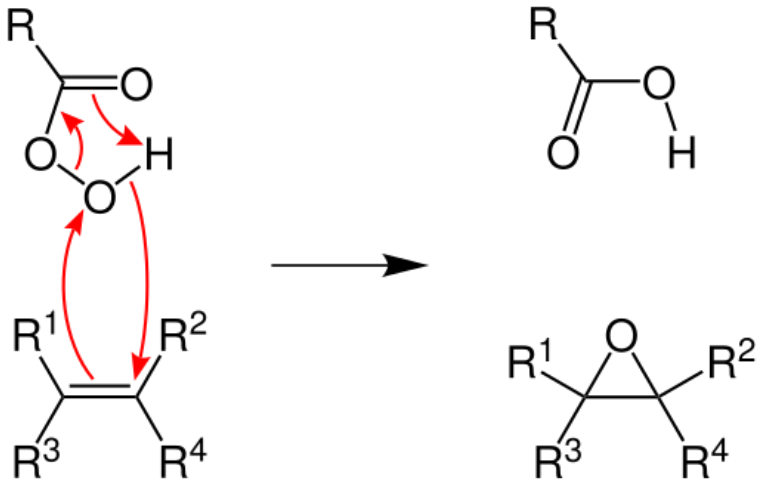
- Requires additional modules like centrifuge; solvent reservoir; tools
- Requires PAL RTC
- Modification of manual method for better automation

Why Epoxidation ?

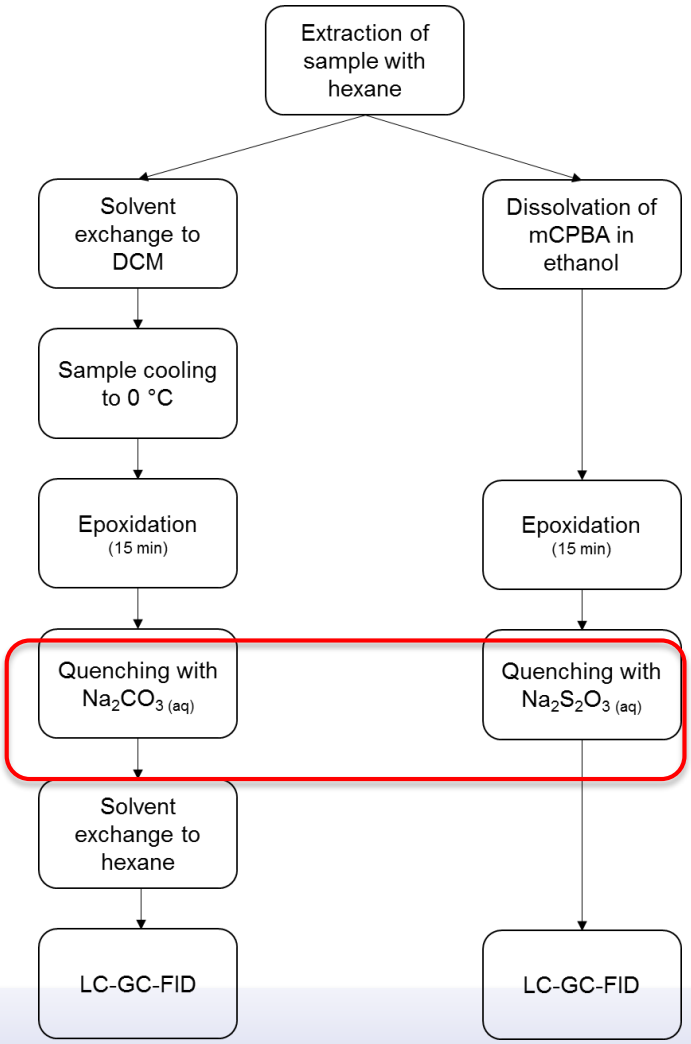
Selective derivatisation of matrix compounds

- Olefine are derivatisied to be removed during LC
- Epoxidation using mCPBA





Automated Epoxidation

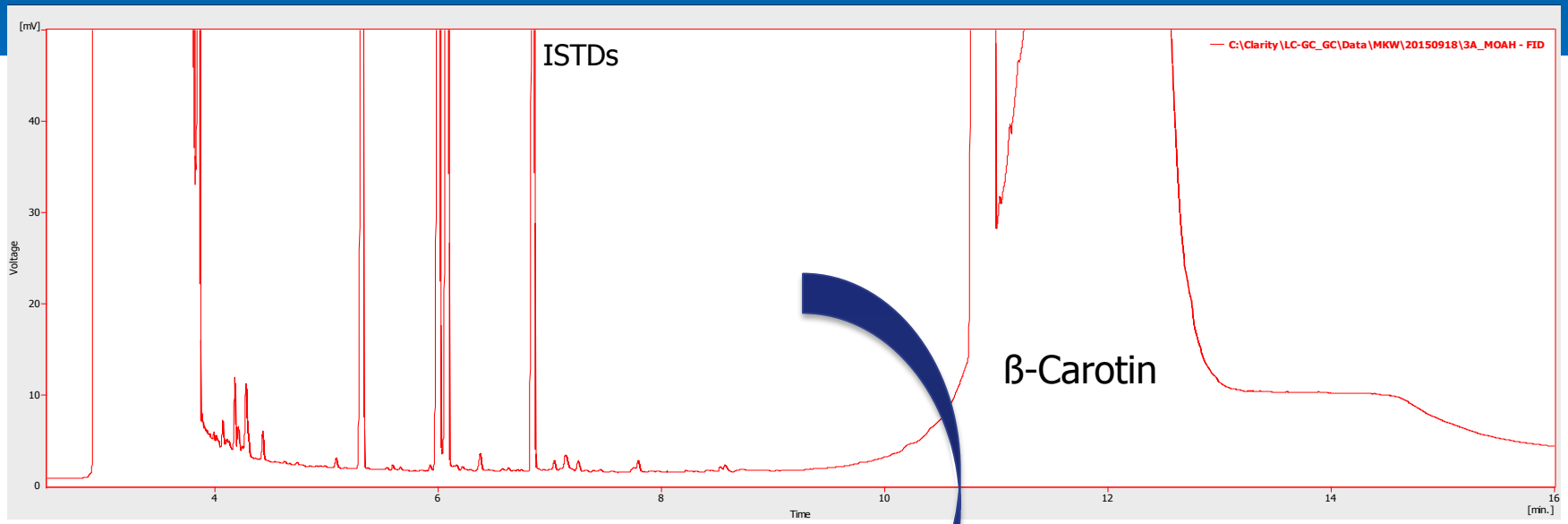


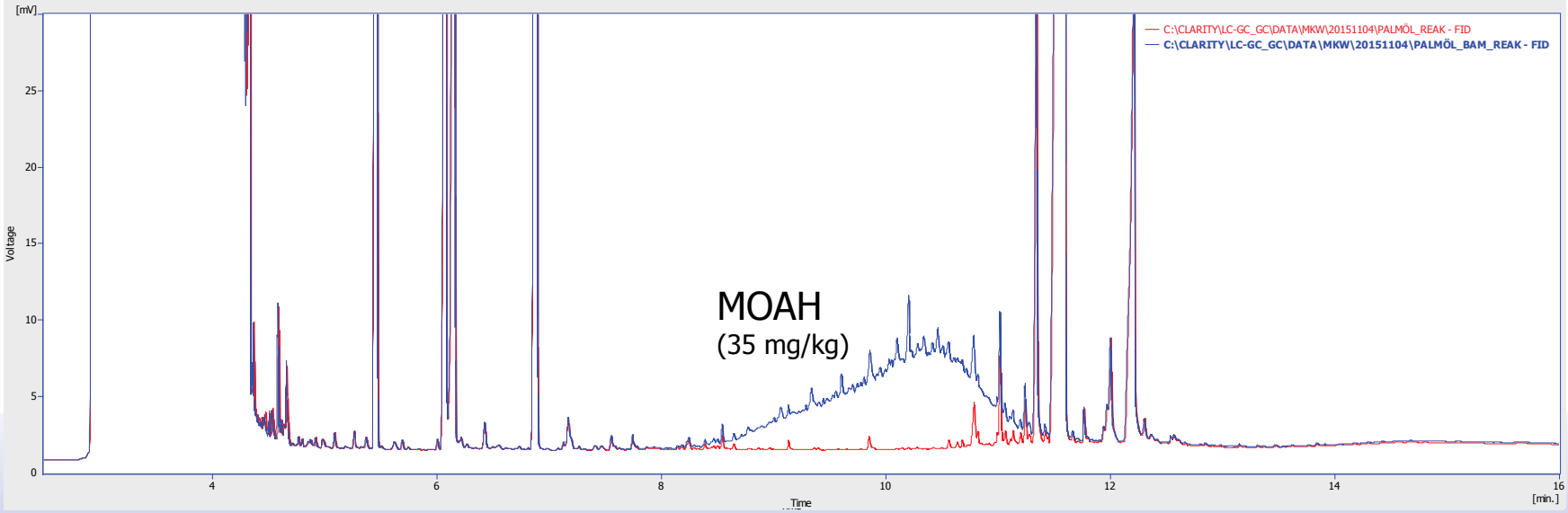
- No solvent exchange necessary
- Epoxidation direct in Hexane instead of DCM
- Ethanol as solvent for mCPBA

→ Complete automation is possible!

→ Quenching using $Na_2S_2O_3$

Example Palmoil





Summary

- LCGC-FID is a routine method for the analysis of MOSH/MOAH
- Runs in a lot of routine labs 24/7
- Further automation steps were developed to reduce manual interaction
- Service and support infrastructure is available by a strong network of different partners

Thank you for your attention!