Fast Determination of High and Low levels of Mineral Oils Using Temperature Programmed Injection

Jaap de Zeeuw,

Varian, Inc.

Middelburg, The Netherlands

Problems and Needs

Mineral oil analysis is a routine analysis in many environmental laboratories

Many samples to be screened

Need:

- Simple and reliable method
- Short run times

Why Mineral oil analysis ?

To Obtain certificate of “Clean” Lot/ground/Soil

For Factories that they comply within regulations

Mineral oil pollution is mainly found in:

soil

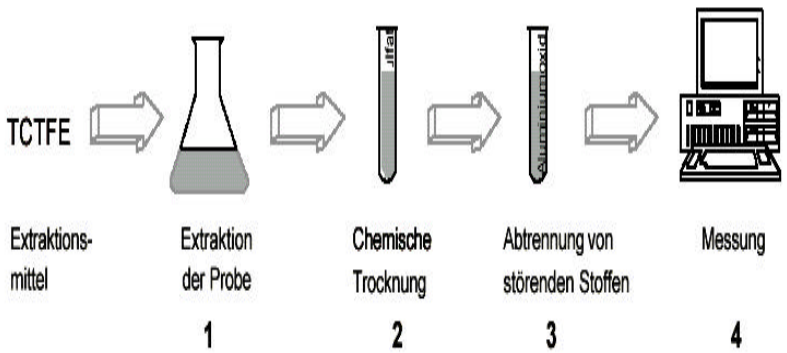
water

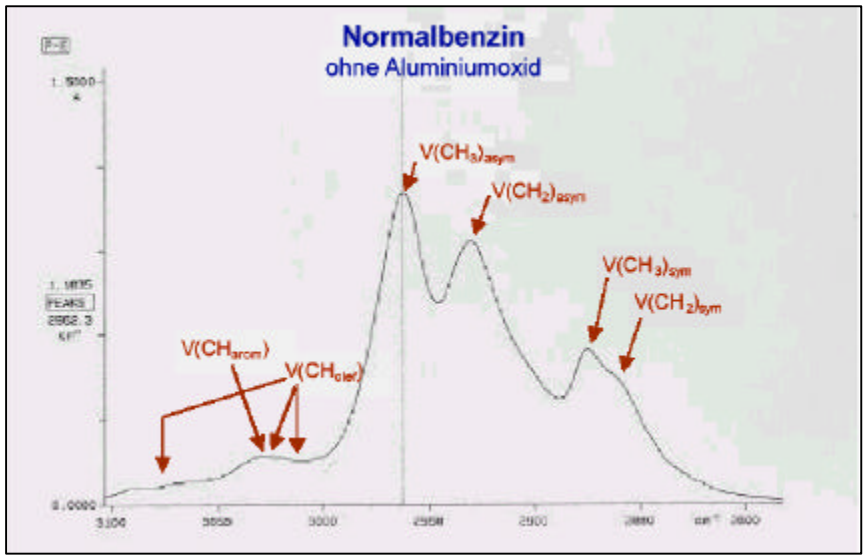
Characterization by:

- Carbon number
- Absolute amount

Mineral oil analysis via IR

The sum of Hydrocarbons can be determined under DIN 18 (This is a IR measurement, deleted per october 1st 2002).

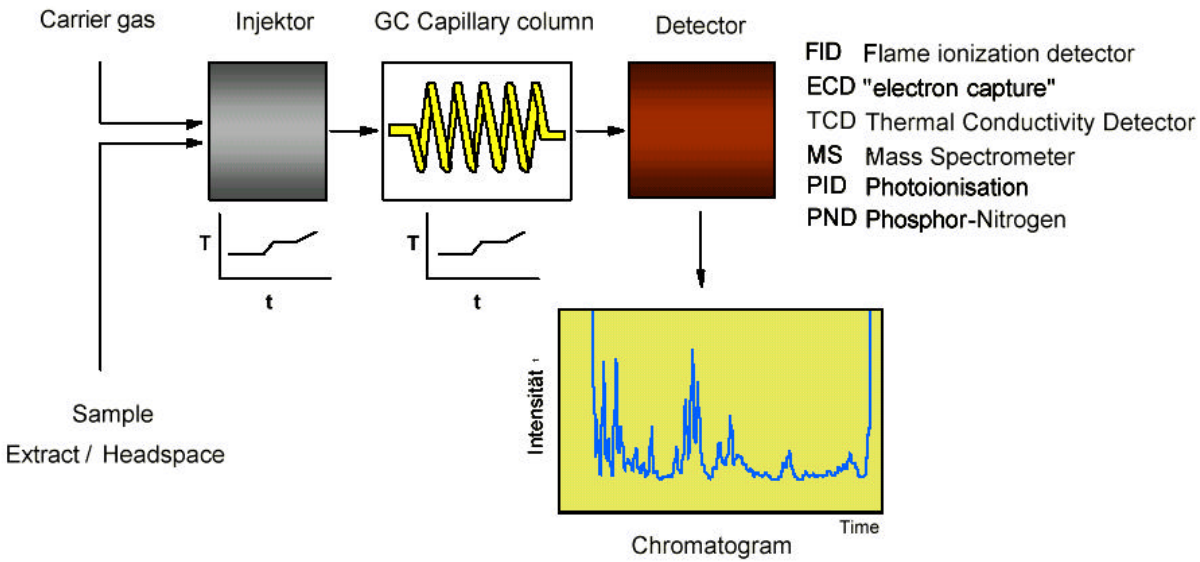




The disadvantage of this summation of Hydrocarbon determination is that it cannot distinguish between the biological parts of the sample and the contamination through mineral oil products.

Mineral oil via GC

To know the source of the contamination a GC/FID method of analysis is recommended



DIN H53 GC-Method, Range C9 - C40

ISO-9377-2 GC-Method, Range C10 - C40

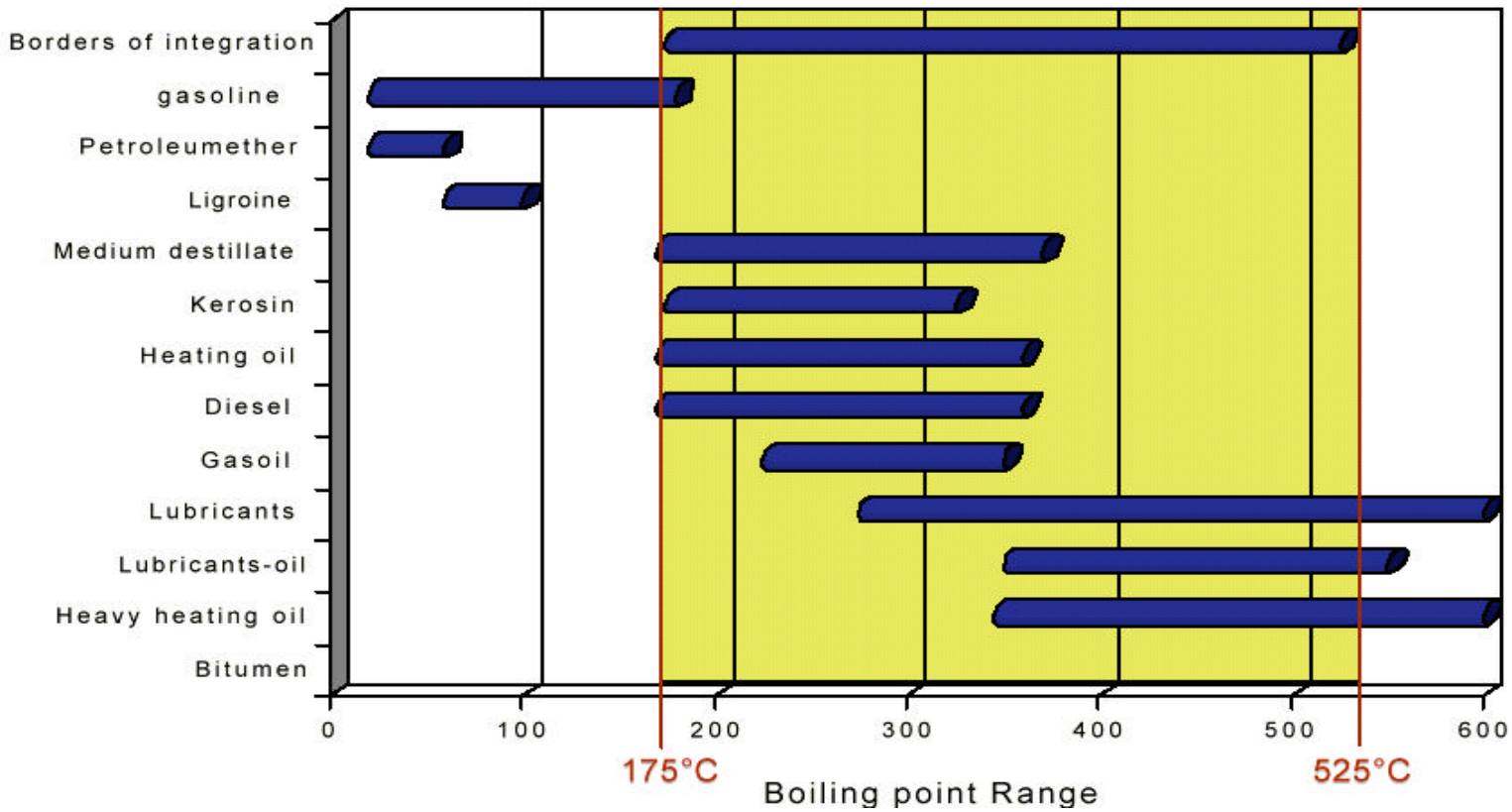
Ref: Innolab GMBH, Harburg

Why GC ?

Driving factor for Enviromental labs = COST per analysis

- Proven technology
- Fast analysis & result
- Low cost per analysis (operator & goods)
- Can be automated
- Easy periodic & preventive maintenance

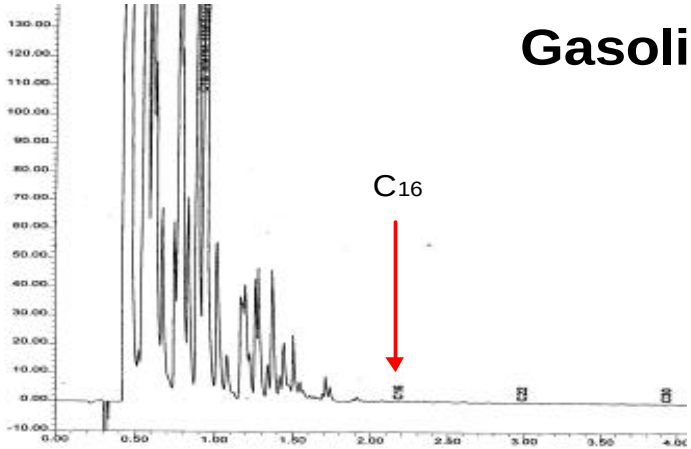
Coverage of the H53 method



Ref: Innolab GMBH, Harburg

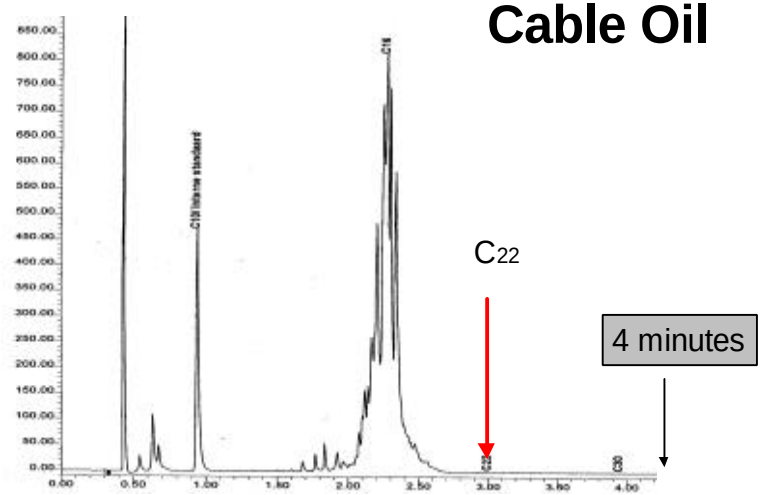
Examples of oil distribution

Gasoline



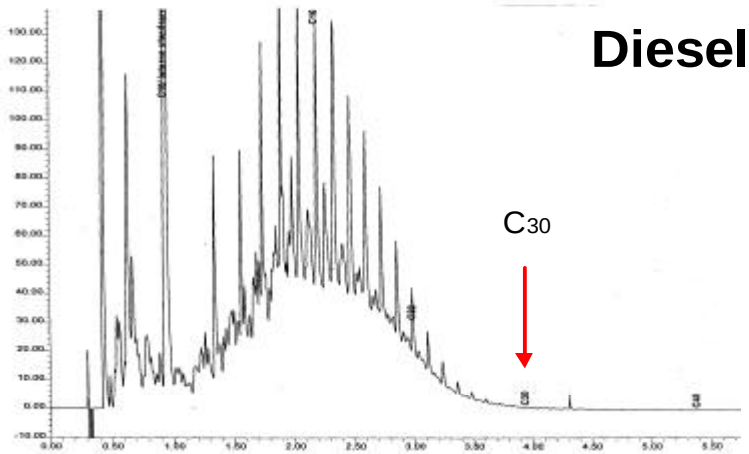
4 minutes

Cable Oil



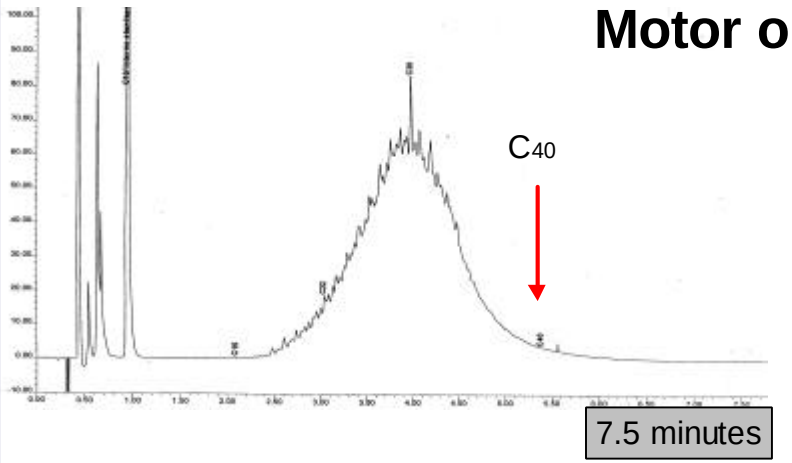
4 minutes

Diesel



6 minutes

Motor oil



7.5 minutes

Typical procedure

Extraction

" adding Acid pH 2 and magnesium sulfate (emulsions)
" extraction with solvent + n-decane / n-tetracontane
" stirring / shaking
" add water and transfer extracting-agent layer
" (in case of emulsions centrifugation)

Clean-up

" column filled with 2g Florisil and 2g sodium sulfate
" run through the column folowed by 10 ml solvent

Concentration

" concentrate to 6 ml, further to 1ml using a flow of Nitrogen
" transfer an aliquot for GC-analysis

Gas chromatographic analysis

" measure the sample (area from n-decane to n-tetracontane)
" correct area for blank (baseline correction)

Fast mineral oil analysis general needs:

Short columns with temperature stable non-polar stationary phases:

10-15m, PDMS type phase

Fast temperature programming:

30-50 °C/min, small ovens, direct heating

High Flow rates:

Flow programming, 0.32 mm ID columns

Select for Mineral oil

Column developed with: — analytico®

- Dedicated column for Mineral oil with bonded temperature stable phase
- Proven performance for fast mineral oil analysis
- Temperature stable up to 400°C
- Prepared on special HT fused silica tubing

New optimized column for Mineral oil analysis

Dimensions: 15 m x 0.32 mm

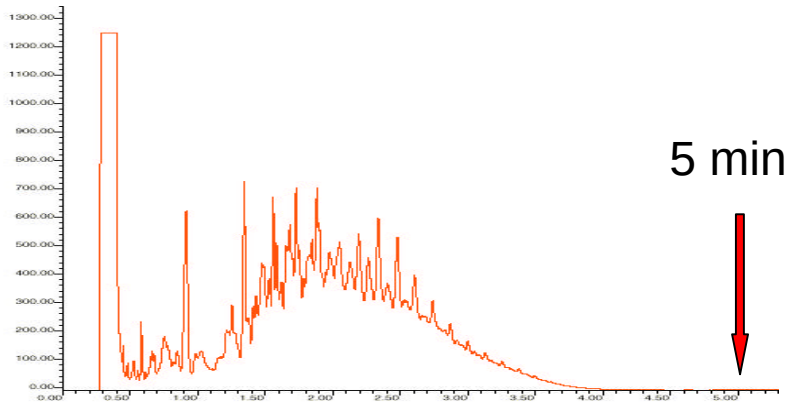
- For On column injection
- For high flow rates
- Easy to couple with pre-column

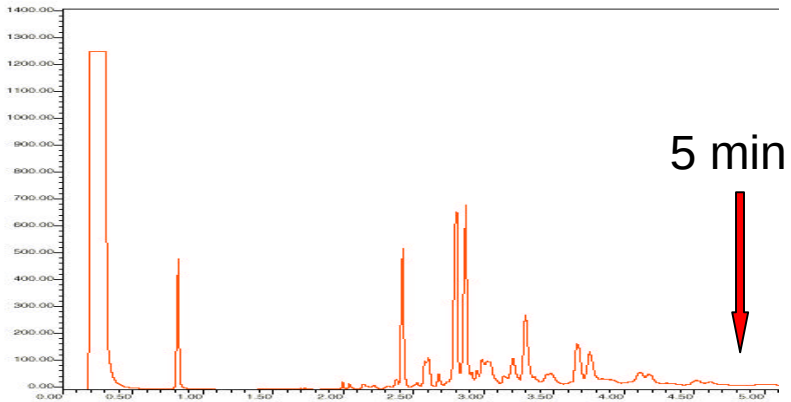
Stationary phase stable up to 400°C

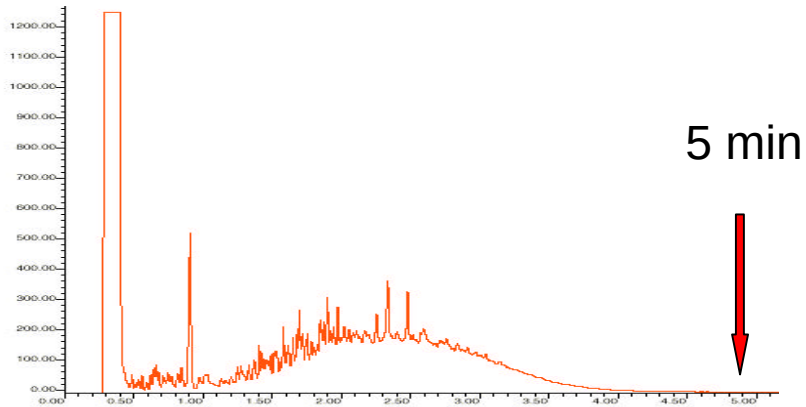
- Elution of possible “heavy” oil contaminants
- Fast bake-out of column, short analysis times
- Can withstand high injection and detection port temperatures

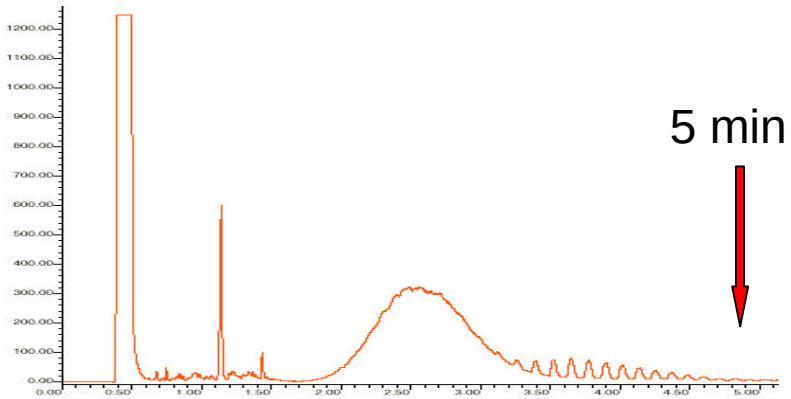
Different Samples >400 mg/l

Typical analysis times: 5-6 minutes









Ref: Jan Volkers & Jeffry de Smit, Analytico, Barneveld, The Netherlands

Injection techniques for mineral oil analysis

- On column
- PTV

These techniques can be used for:

- 1-2 µl injections
- Large Volume injection (200 - 300 µl)

Cold - On column injection

Injection volume: 1- 2 µl : concentrations > 500 ppb mineral oil

Injection volume: 100-200 µl : concentrations > 5 ppb mineral oil

Inject the sample into the column:

Need sufficient size internal diameter;

Need good on-column injection system (automation)

For a small injection band we have to:

- inject slowly
- inject a small amount..

For optimal band focusing we need to use a retention gap

Soil samples

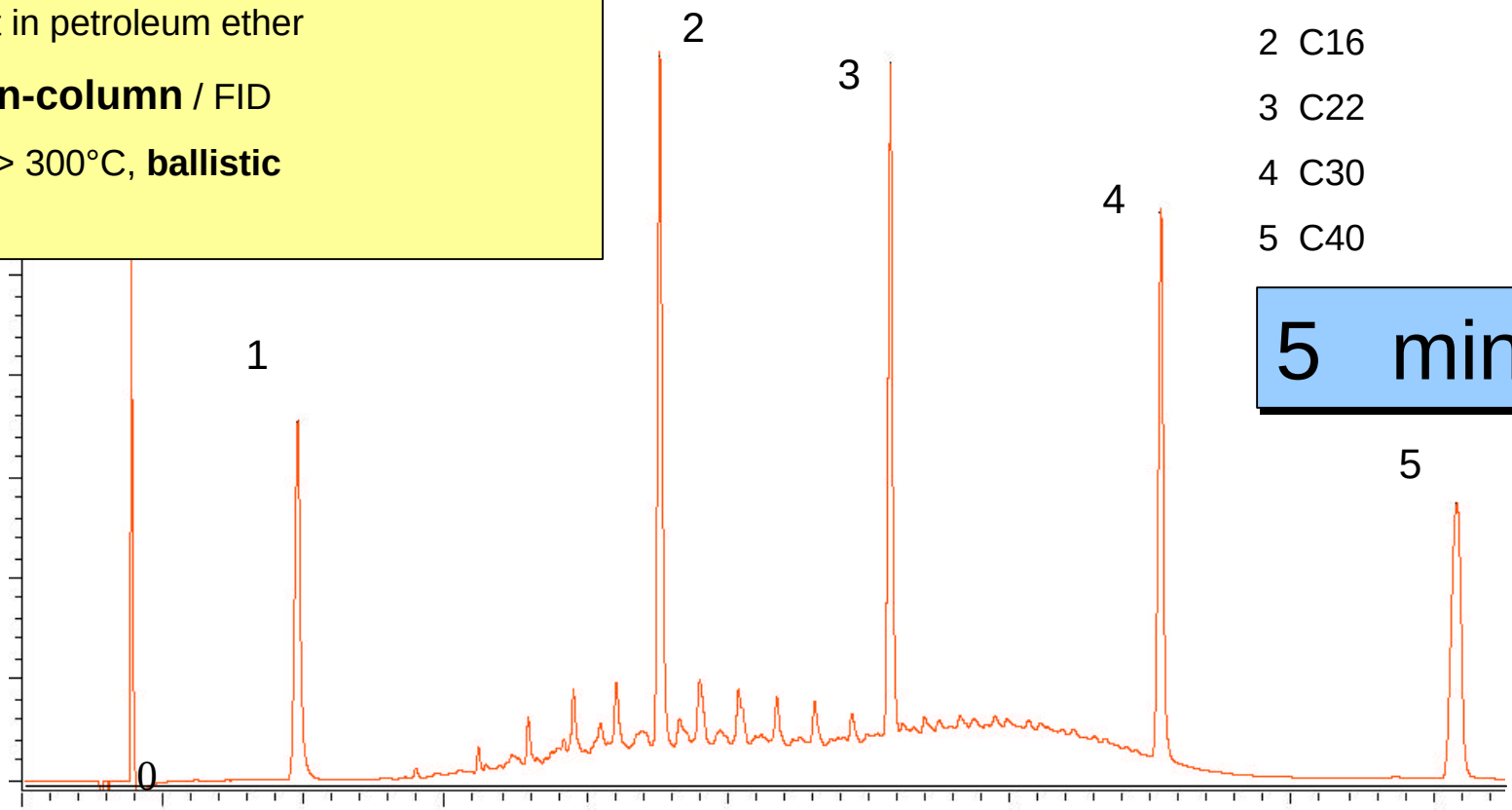
Select Mineral oil 15 m x 0.32 mm

Extract in petroleum ether

1 µl on-column / FID

55°C--> 300°C, **ballistic**

Helium



1 C10 (internal standard)

2 C16

3 C22

4 C30

5 C40

5 minutes

Short analysis time

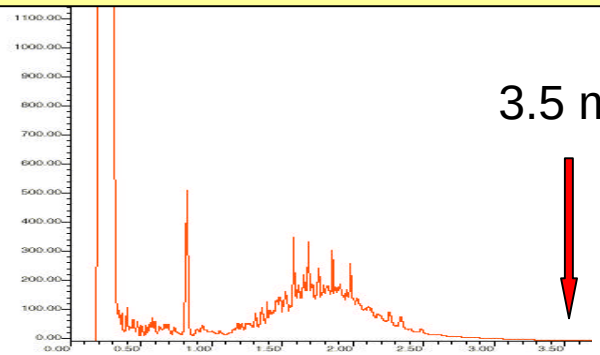
Ref: Jan Volkers, Analytico, The Netherlands

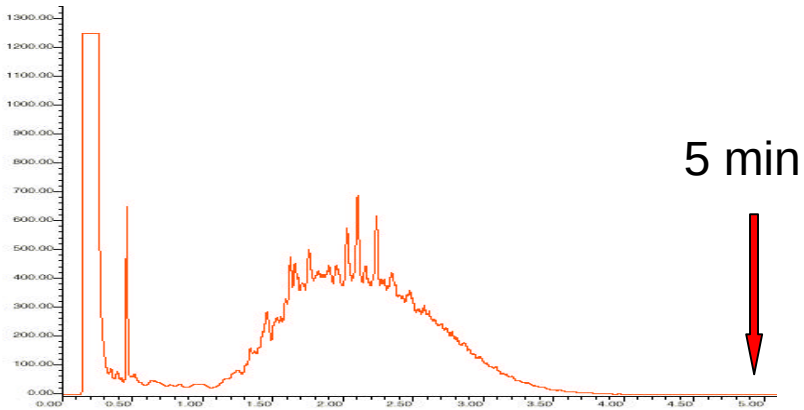
Samples > 400 mg/l

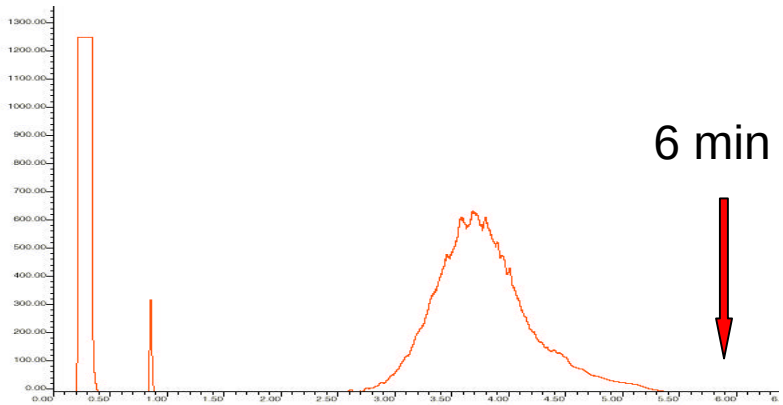
Select Mineral oil 15 m x 0.32 mm

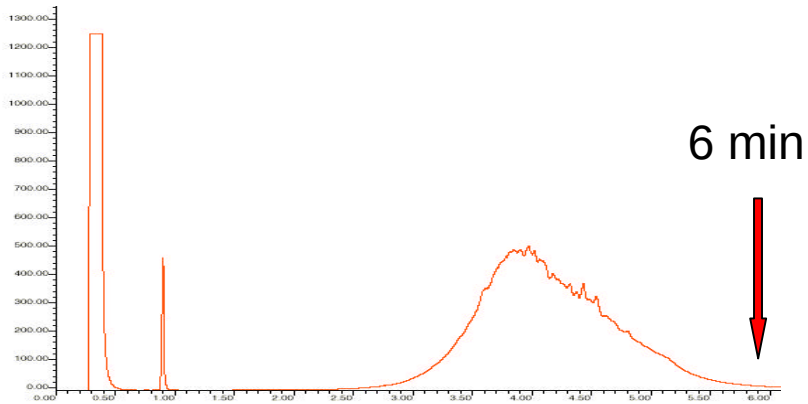
1 µl on-column / FID; 55°C--> 300°C, **ballistic**

helium



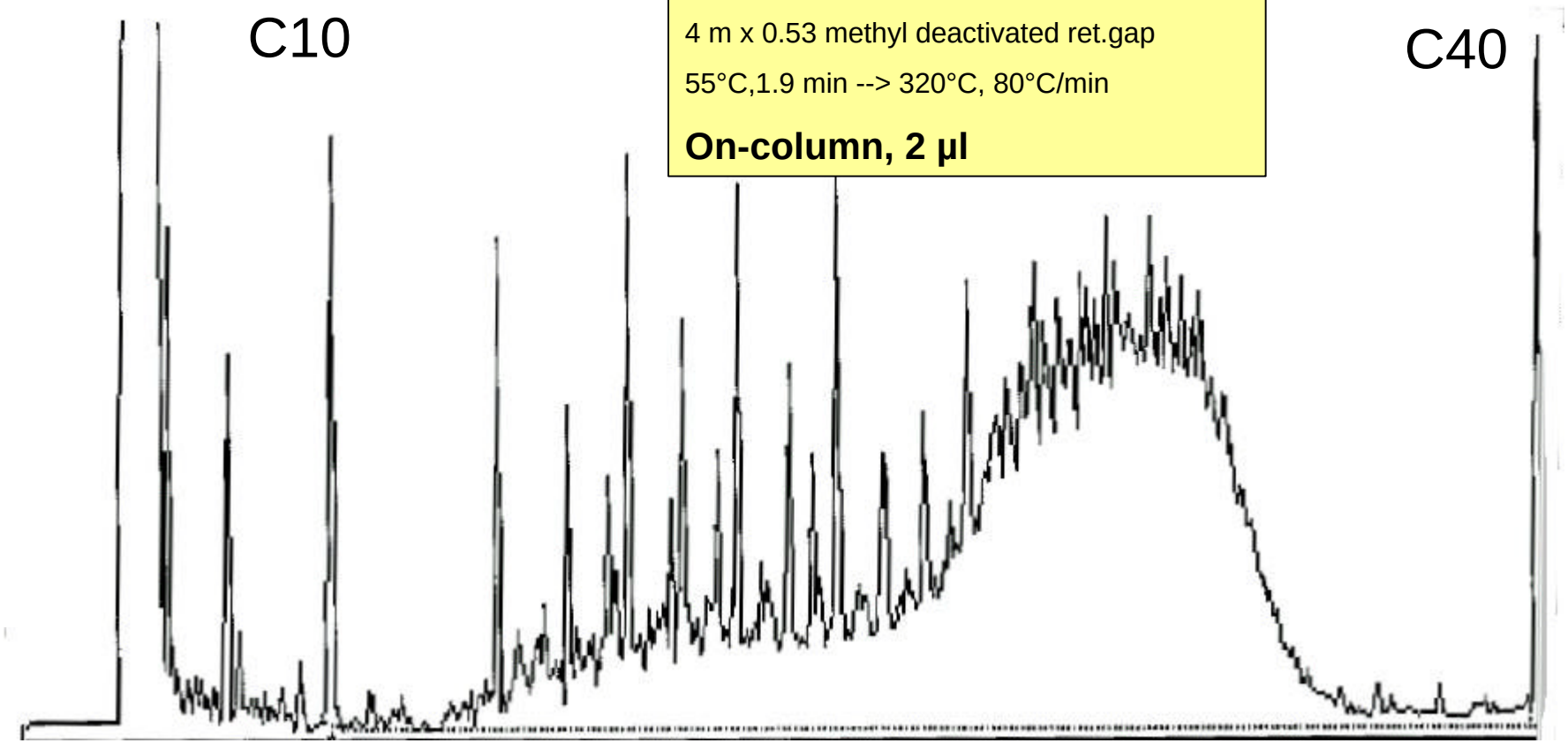






Ref: Jan Volkers & Jeffry de Smit, Analytico Barneveld, The Netherlands

Hydrocarbons acc. to DIN-EN-ISO 9377-2



Ref: Thomas Karle Chemisches labor Dr.Vogt, Karlsruhe

Hydrocarbons acc. to DIN-EN-ISO 9377-2

after 1000 injections..

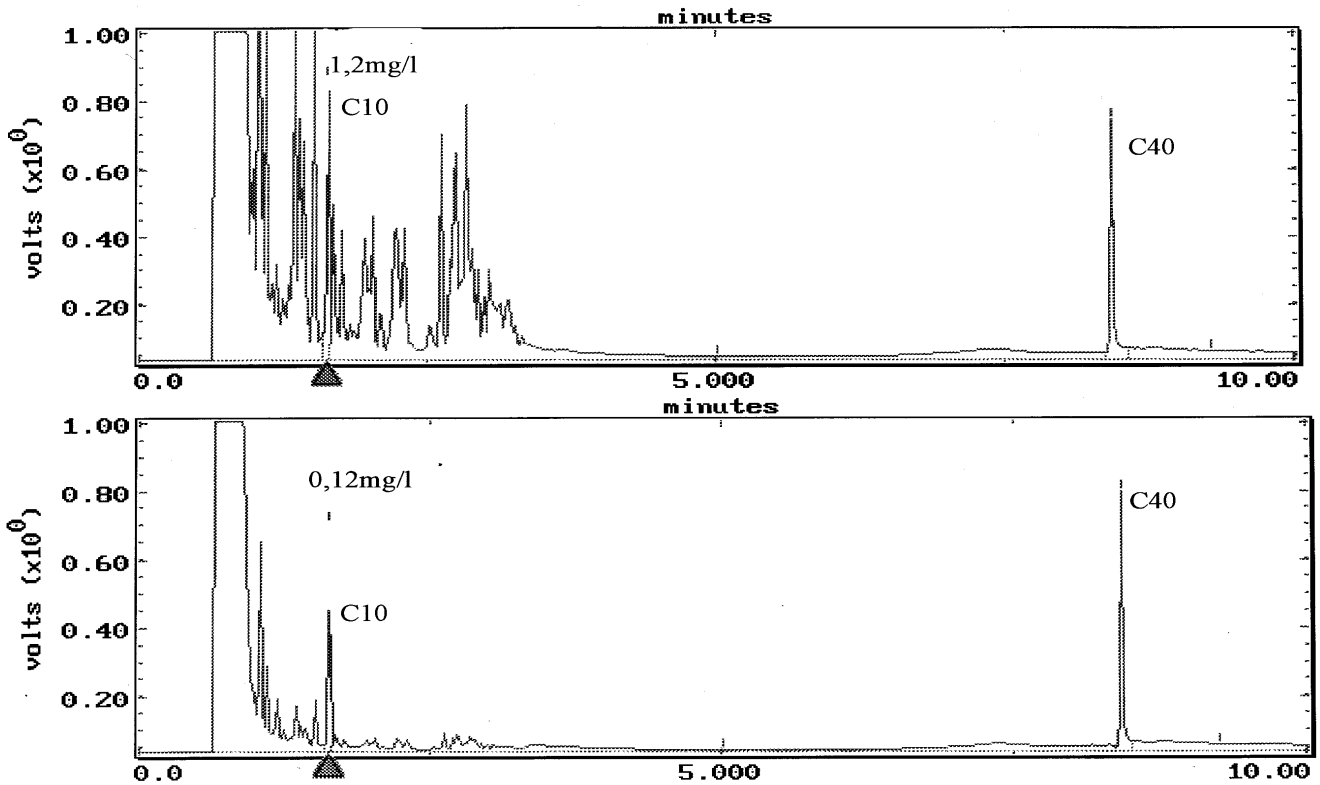
Varian Select Mineral Oil, 15 m x 0.32mm

6 m x 0.53 methyl deactivated ret.gap

55°C,1.9 min --> 320°C, 80°C/min

On-column, 2 µl

Gasoline Unleaded



Ref: Thomas Karle, Chemisches labor Dr.Vogt, Karlsruhe

Analysis of trace mineral oil

Limited by sensitivity of detectors

Solution: Inject a Large injection volume..

Using FID: need ca. 0.25 ng of component

Injection of 250 µl liquid @ concentration: 1 ppb

Technique:

Large Volume - injection

USE On-column method

USE PTV method

USE On-column method

Need to use a Large Volume Retention Gap

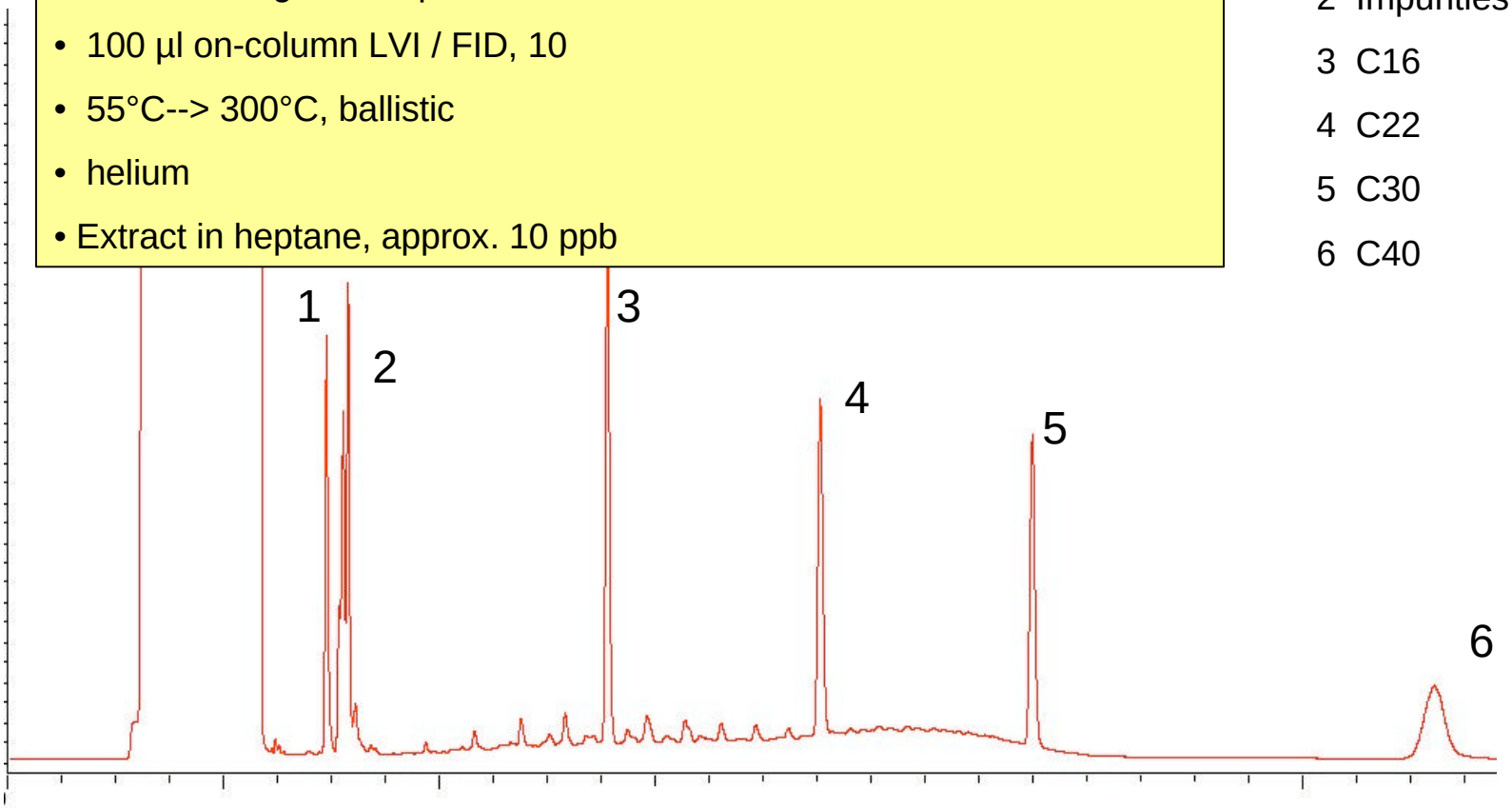
length: 5 - 15 m

Mineral oil in Water

Varian-Select Mineral oil 15 m x 0.32 mm with large Volume Guard 12 m & 3 m retaining coated pre-column

- 100 µl on-column LVI / FID, 10
- 55°C--> 300°C, ballistic
- helium
- Extract in heptane, approx. 10 ppb

1 C10 (internal standard)
2 Impurities in heptane
3 C16
4 C22
5 C30
6 C40



Shortest analysis time for 30m column at ppb levels

Ref: Jan Volkers, Analytico, The Netherlands

Advantages On-Column technique:

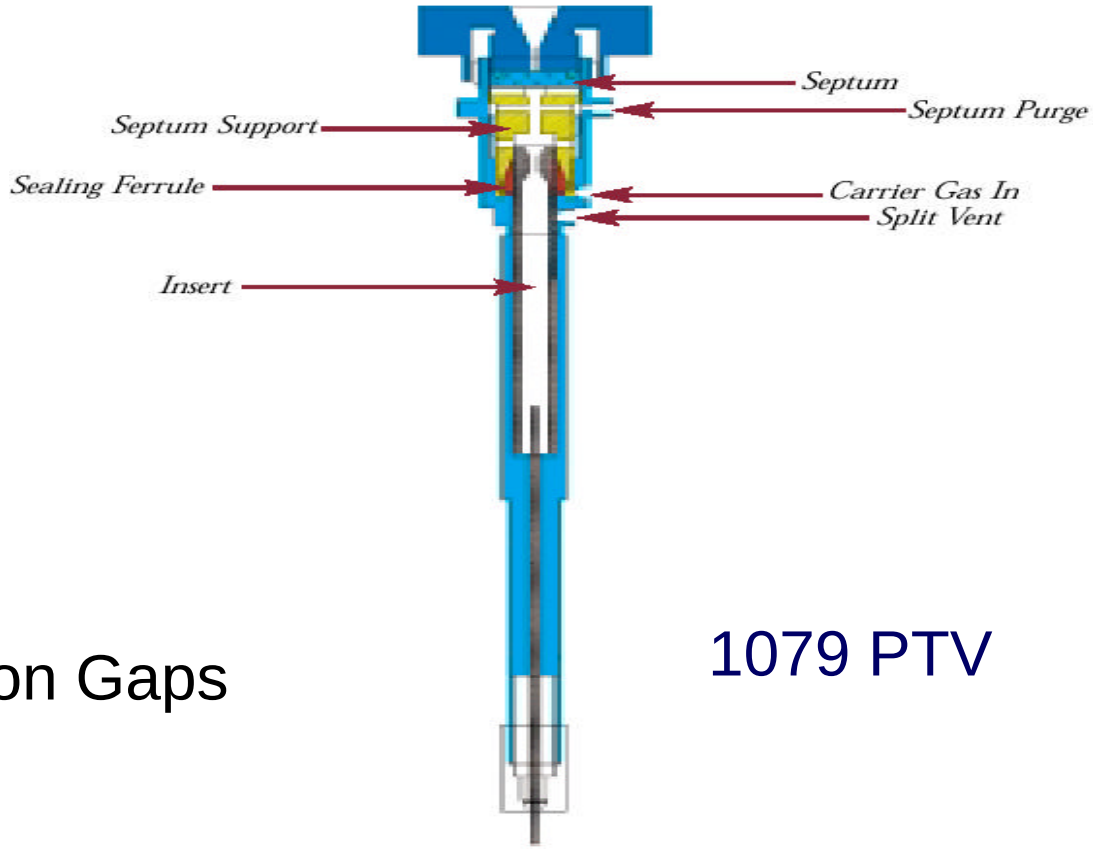
Quantitative better: No loss of volatiles

Challenges On-Column technique:

Coupling of the (long) retention gap(s) and retaining pre-columns

- Column Cutting
- Leaks
- Time consuming
- Injection system more critical
- Needs more expertise
- Have to replace retention gaps

USE PTV method



1079 PTV

No need to use a Retention Gaps

Can handle 1 up to 250 ul

Relative easy to operate

Principle:

- Injection of sample into the liner of the 1079 PTV;
- Vent off the solvent,
- Concentrate the mineral oil(s) on an adsorbent
- Program the 1079 PTV to evaporate oil(s), (Injection)
- Separate oil(s) in the capillary column

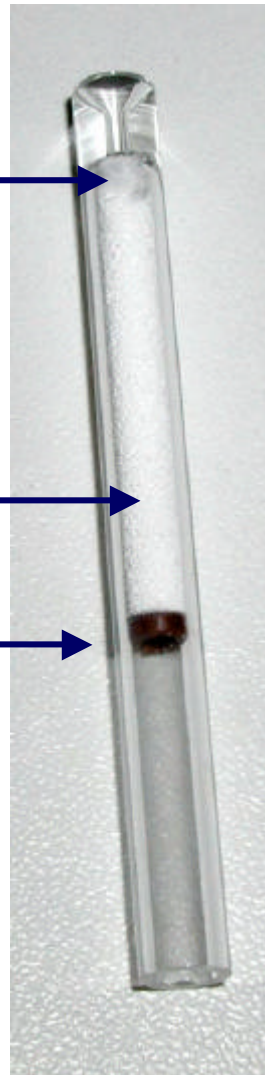
Introduction of sample in the liner

In order to trap the mineral oils, a special liner is required that traps the mineral oil:

Inert plug of glass wool

Inert trapping material, relative small mesh-size

Deactivated Seal



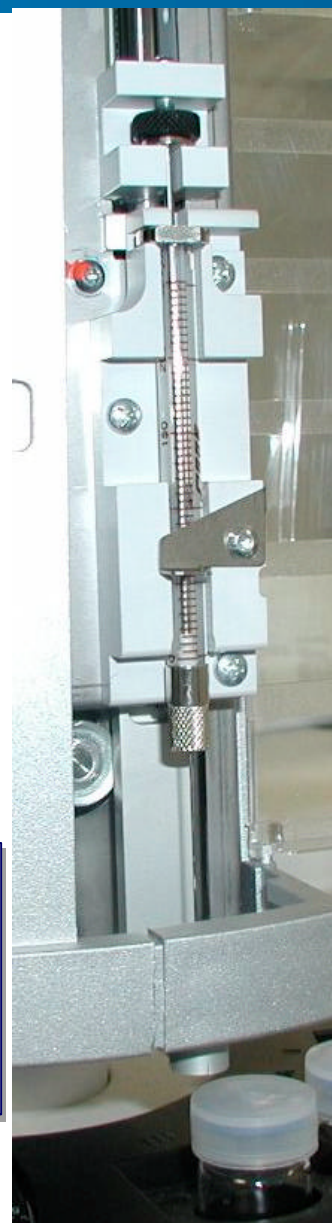
Injection

Using a 250 µl standard syringe (SGE)

Injection of 200-250 µl of sample with a speed of 15 µl/s;

(speed is software controllable);

The Split vent is in open position and solvent is vented;



Time depends on injection volume:

C10 component must be well separated from the residual solvent peak;

References: Peak areas C10:C20 and C40:C20 must be > 0.85

Timing of Solvent venting

For large volume injection the Parameters for Solvent venting must be optimized: This time depends on:

- type solvent used
- amount injected
- speed of injection
- split flow
- pressure
- injector temperature
- design and retention materials in the liner

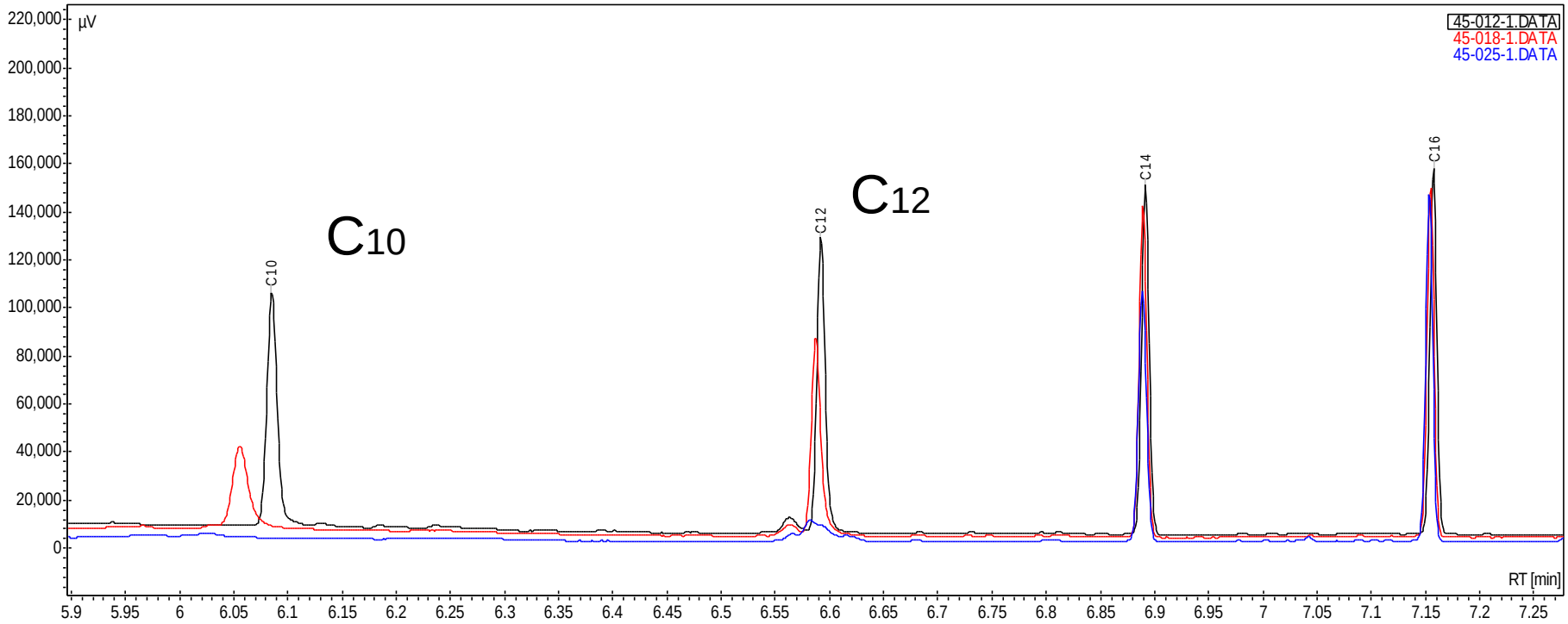
Effect of Solvent - vent timing

BLACK : 7.2 seconds

RED : 10.8 seconds

BLUE : 15.0 seconds

50 ul injections in petroleum ether



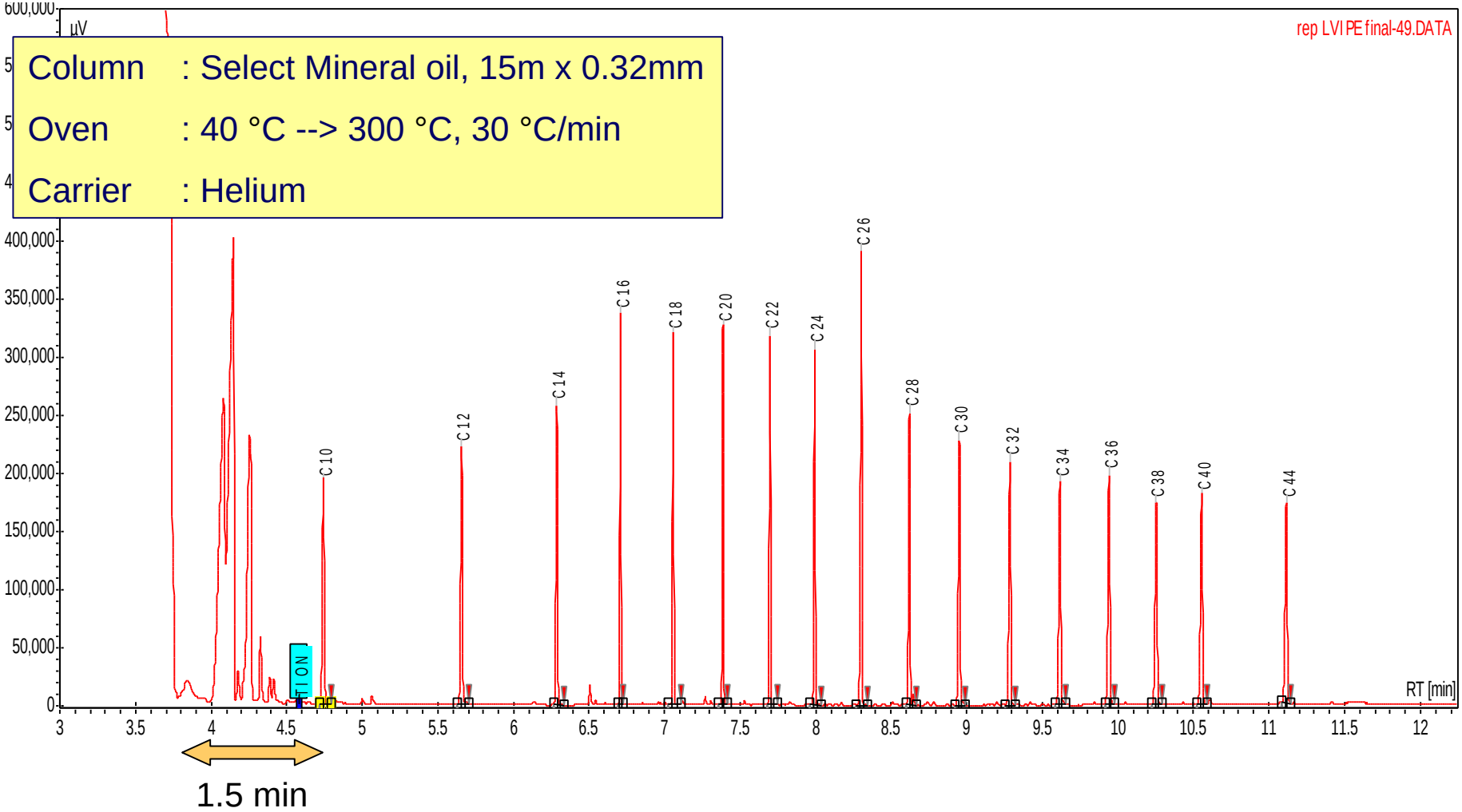
Extraction of mineral oils is done with different Solvents:

- Petroleum ether
- Hexane
- Heptane

More challenging..

Standard C10-C44 in petroleum ether

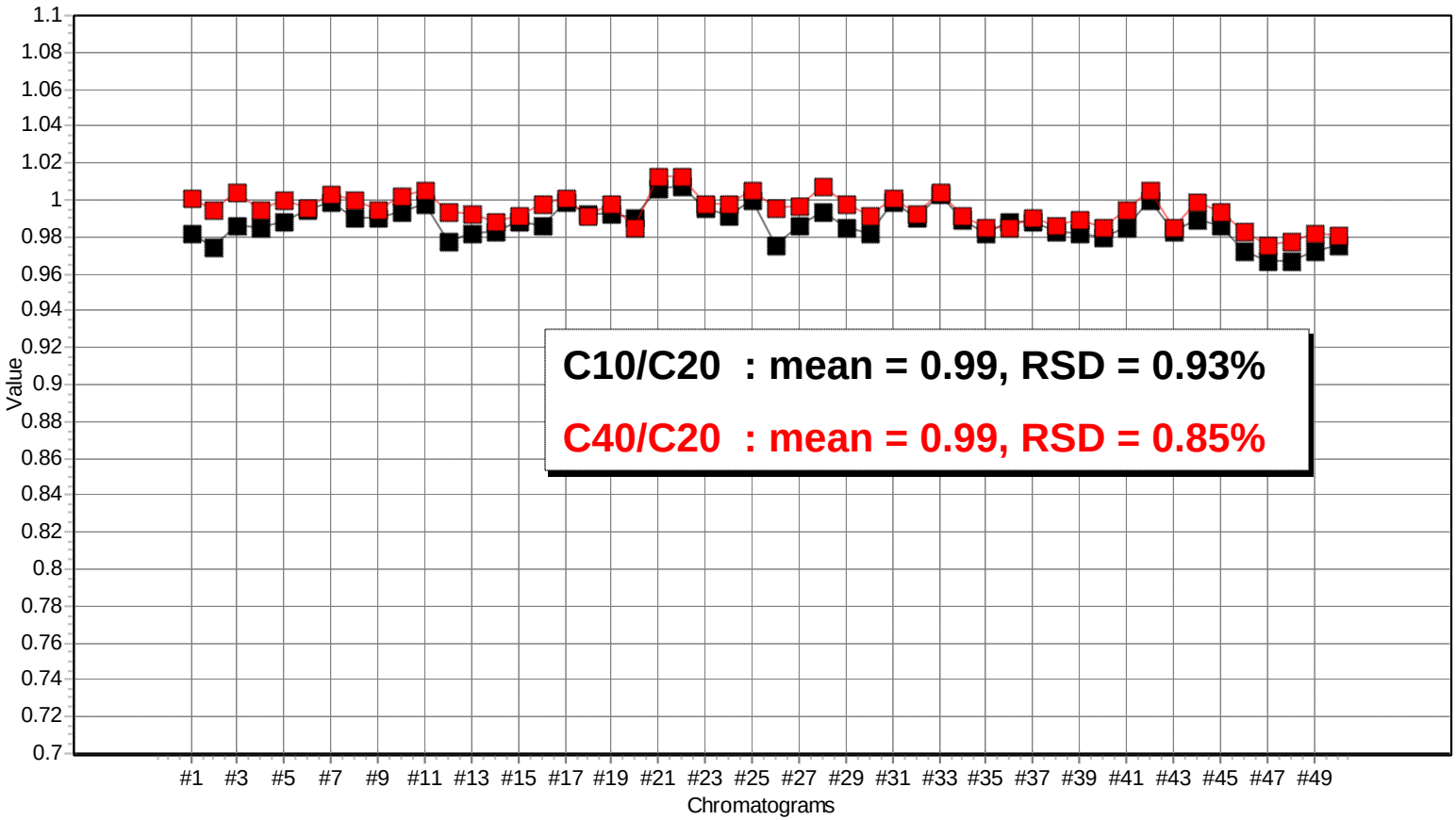
Injection volume : 150 µl with 1079 PTV



Peak ratio / discrimination

solvent: petroleum ether

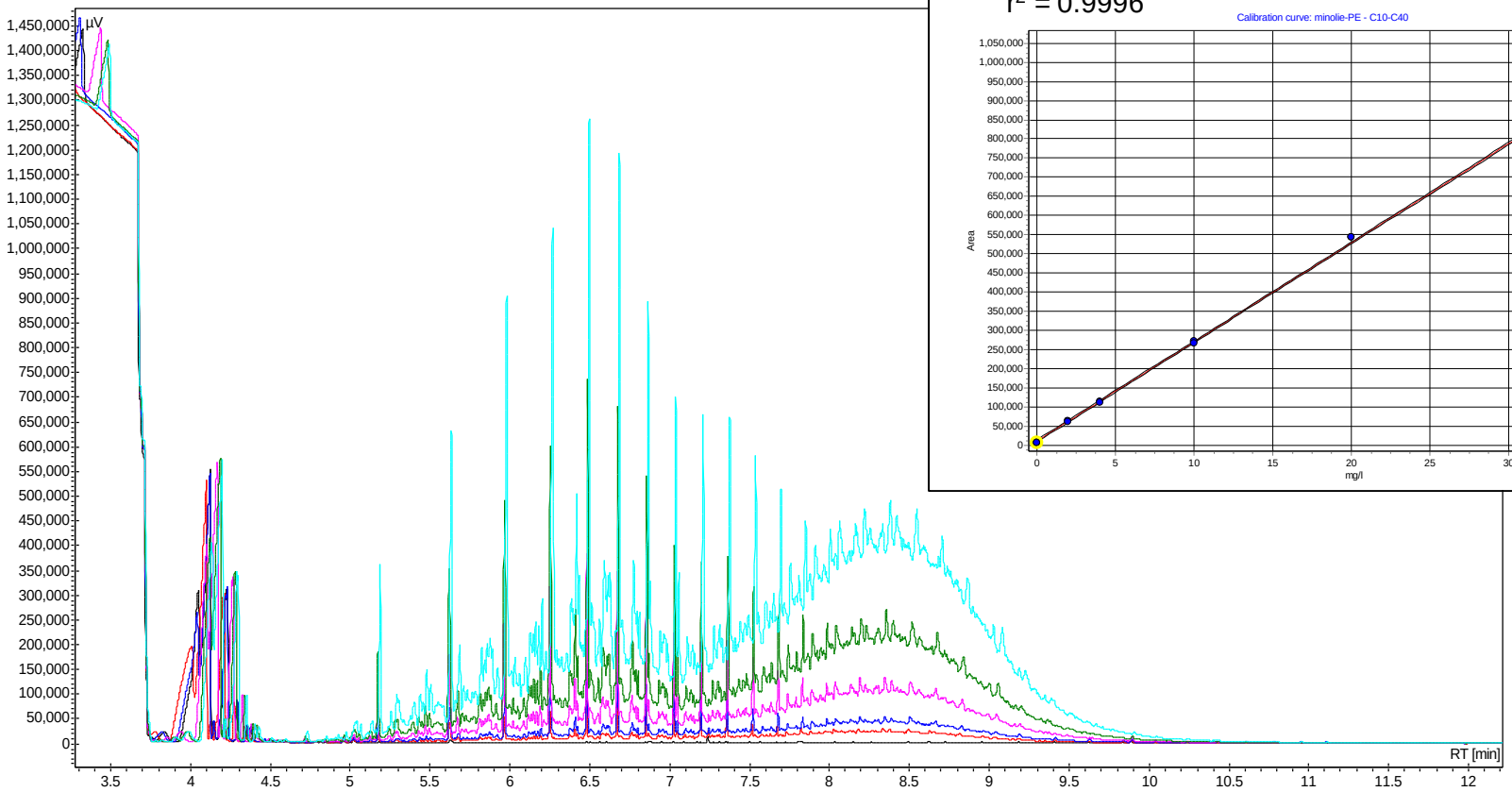
Peak area ratio of C10/C20 (black) and C40/C20 (red), 50 consequetive injections alkane standard in **petroleum ether**, injection volume: 150 uL



15m x 0.32 mm Select Mineral oil, df = 0.25 um

Calibration mineral oil in petroleum ether

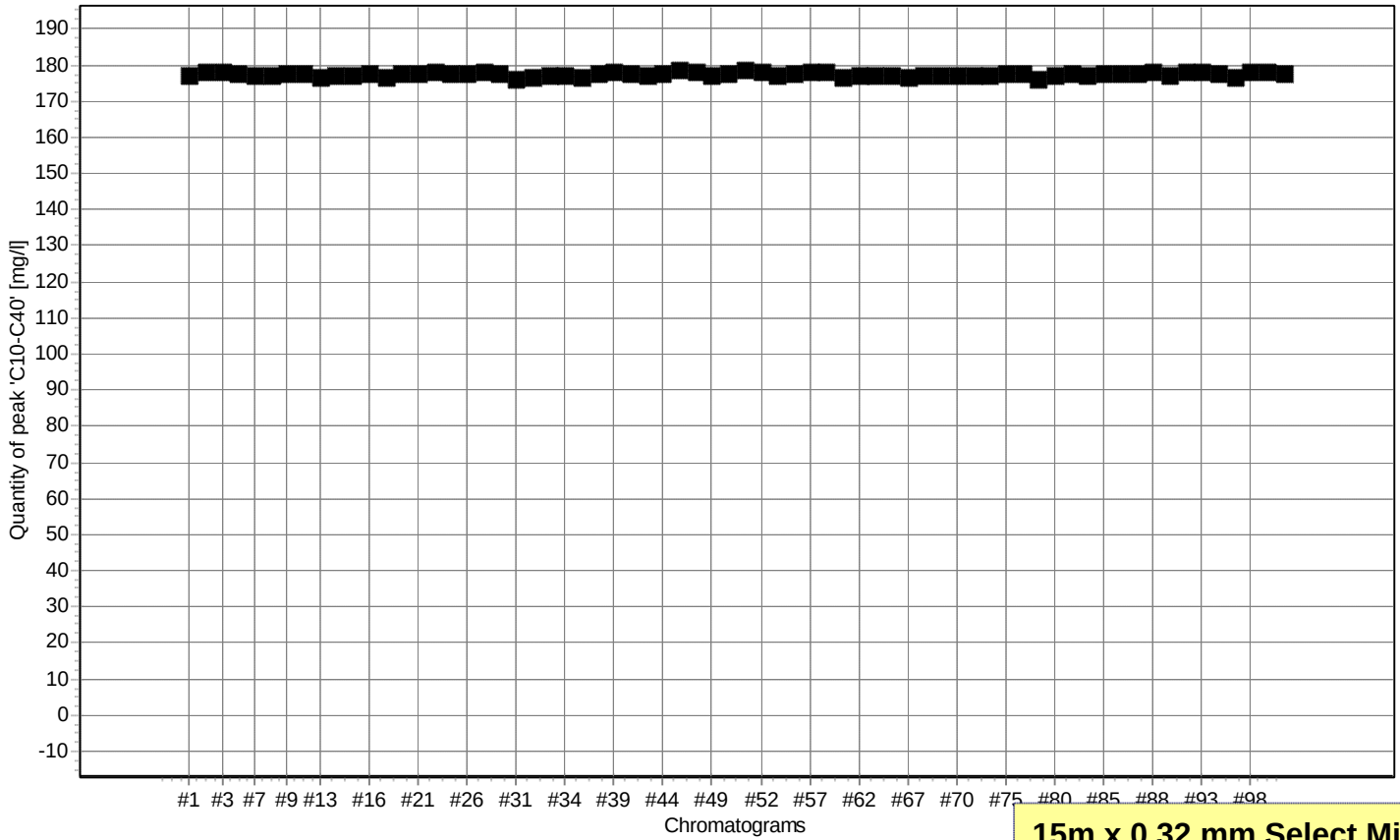
PTV Injection: 150 µl, levels: 0, 2, 4, 10, 20, 40 mg/l



Quantitative peak area measurement

Solvent: petroleum ether

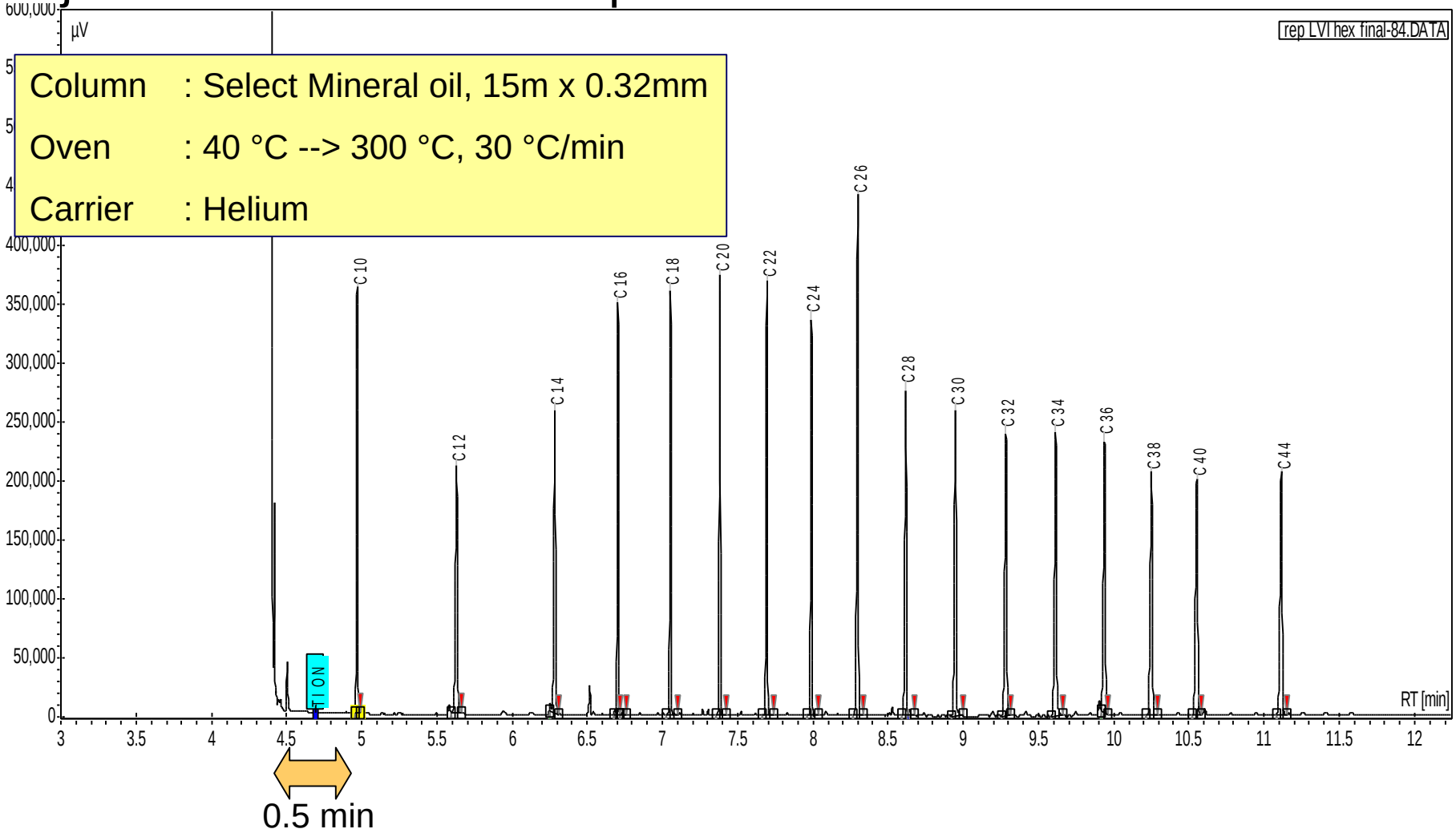
100 injections of 175 mg/l mineral oil in petroleum ether,
Injection volume: 150 uL
mean = 177.52, RSD = 0.33%



15m x 0.32 mm Select Mineral oil, df = 0.25 um

Standard C10-C44 in hexane

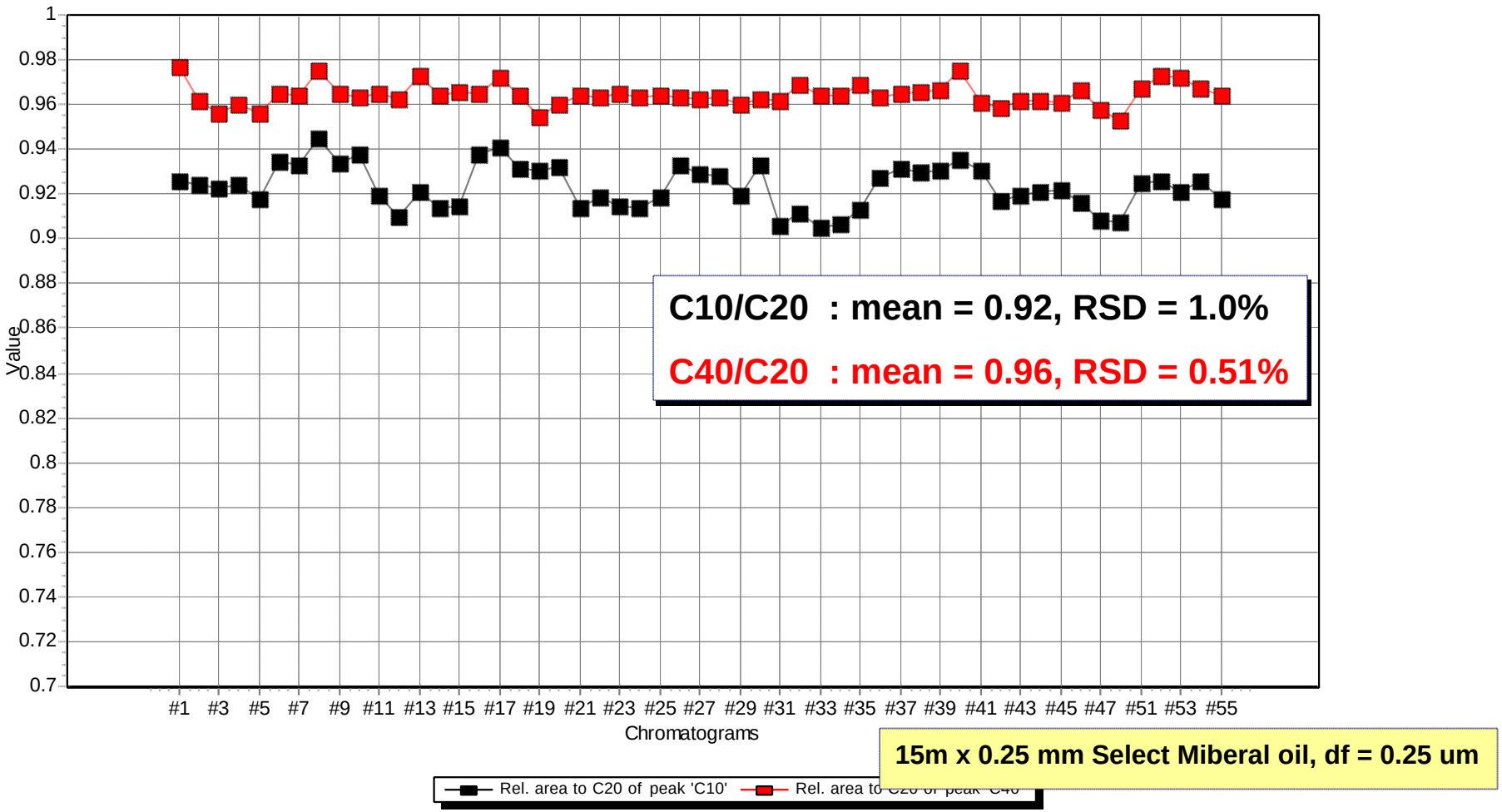
Injection volume : 150 µl with 1079 PTV



Peak ratio / discrimination

solvent: hexane

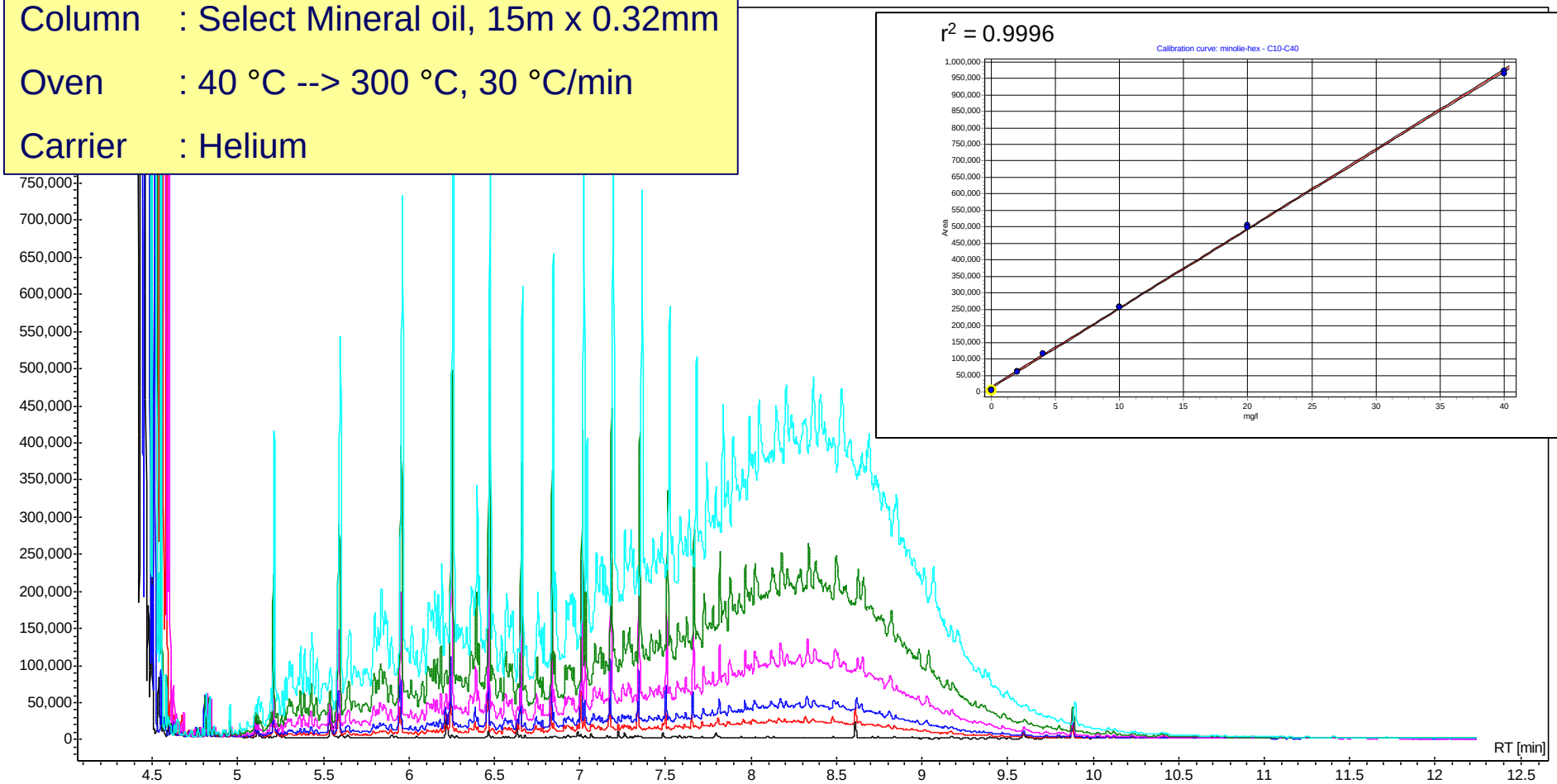
Ratio of C10/C20 (black) and C40/C20 (red), 55 injections alkane standard in **hexane,** Injectievolume: 150 uL



Calibration mineral oil in hexane

PTV Injection: 150 µl, levels: 0, 2, 4, 10, 20, 40 mg/l

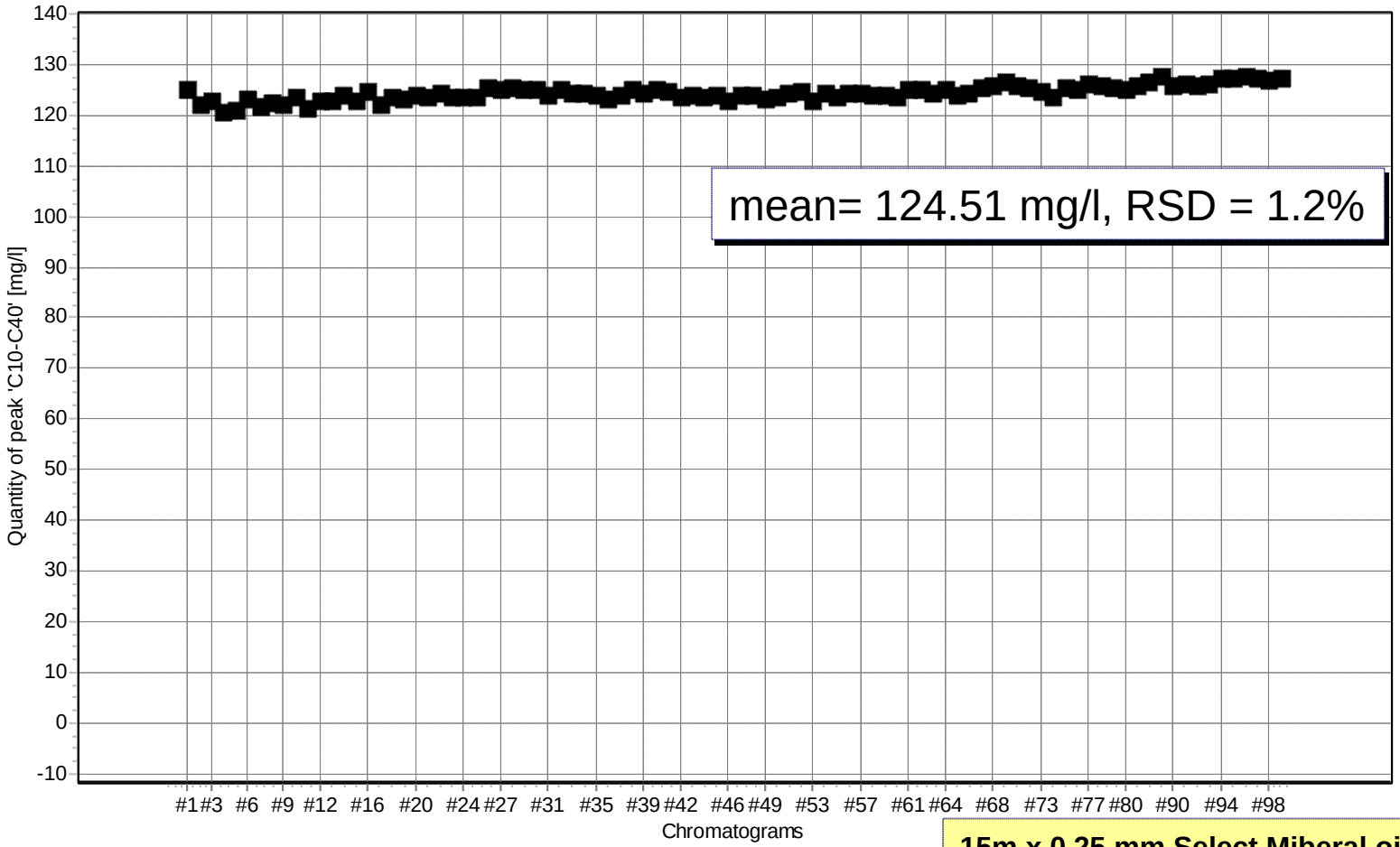
Column	: Select Mineral oil, 15m x 0.32mm
Oven	: 40 °C --> 300 °C, 30 °C/min
Carrier	: Helium



Quantitative peak area measurement

Solvent: hexane

100 injections of 125 mg/l mineral oil in **hexane**, injectionvolume 150 uL



15m x 0.25 mm Select Miberal oil, df = 0.25 um

Heptane as solvent

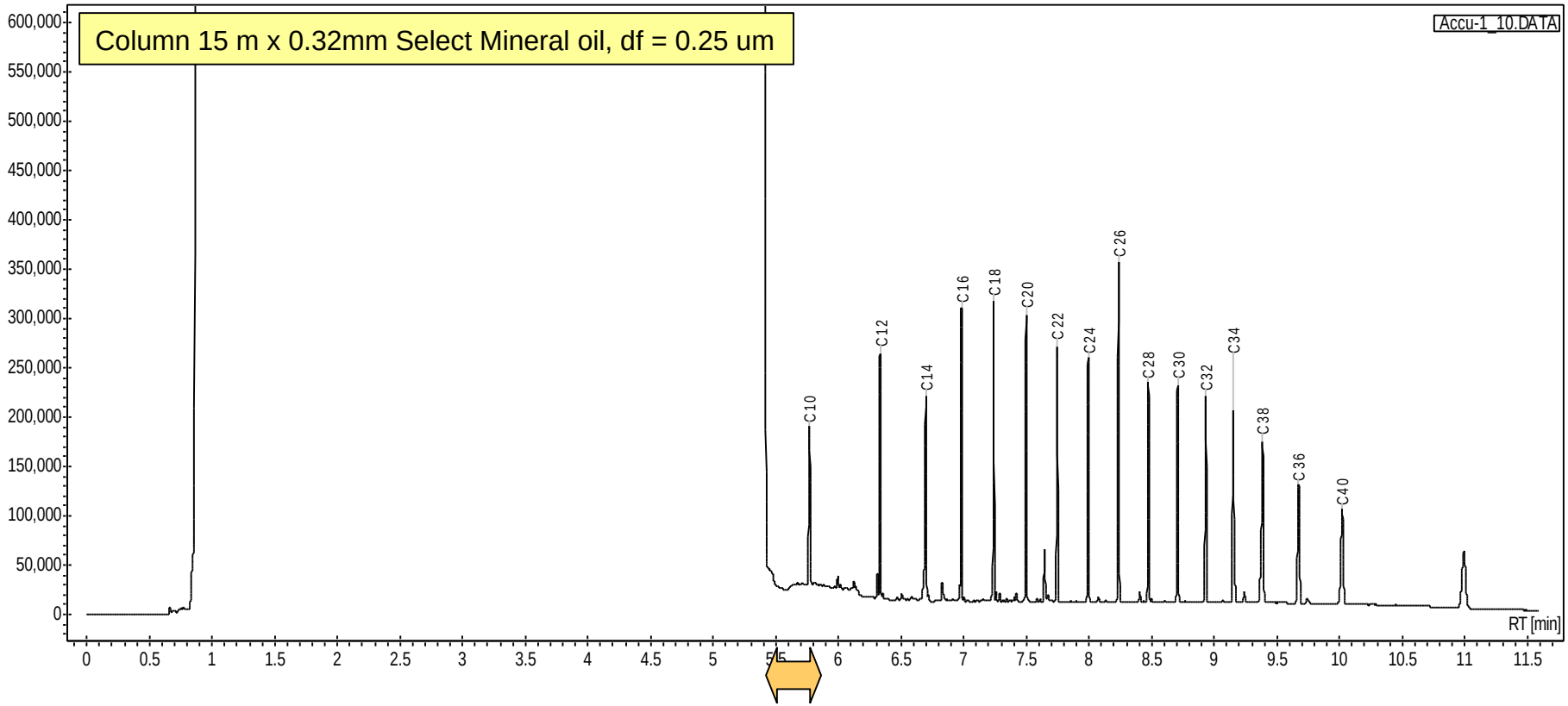
Some existing methods use heptane for the extraction

It is easier to work with (less volatile solvent)

Problem :Concentration step;

Solution :Applying large volume injection: elimination of the concentration step;

Heptane as solvent



Injection via PTV becomes more critical and solvent - vent time must be optimized:

If vent time is too short : fronting of C14 area..

If vent time is too long : loss of C10..

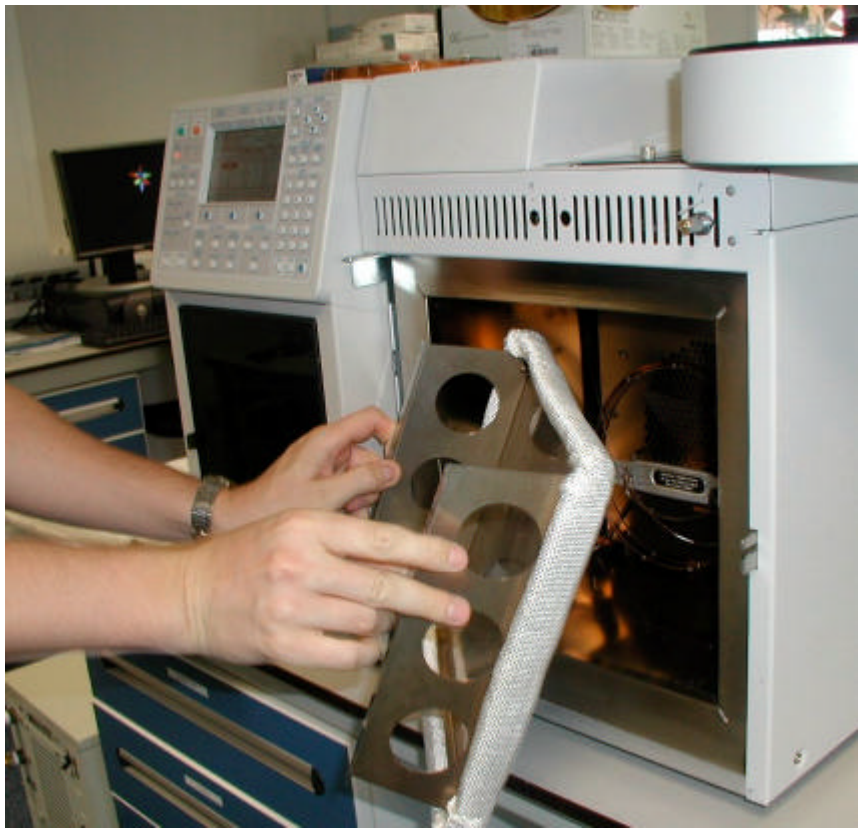
Column Temperature: The oven

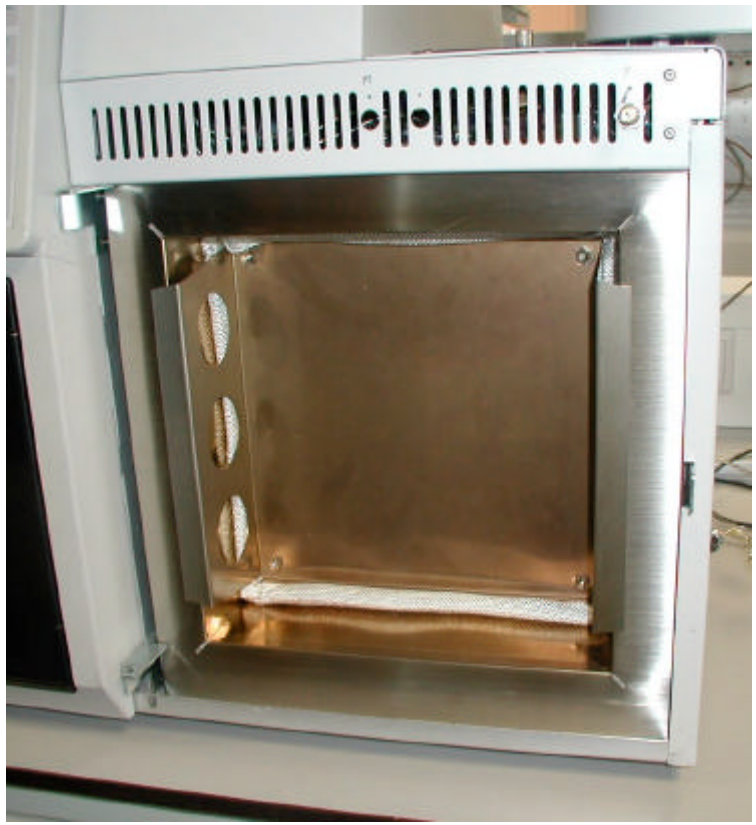
In order to get fastest analysis, the oven temperature program must be as fast as possible:

large ovens take a long time and can give temperature gradients inside the oven:

Need to reduce oven size..

Column Temperature: The oven





Reducing the size of the oven for Mineral oil application

Temperature programming possible with 100°C/min

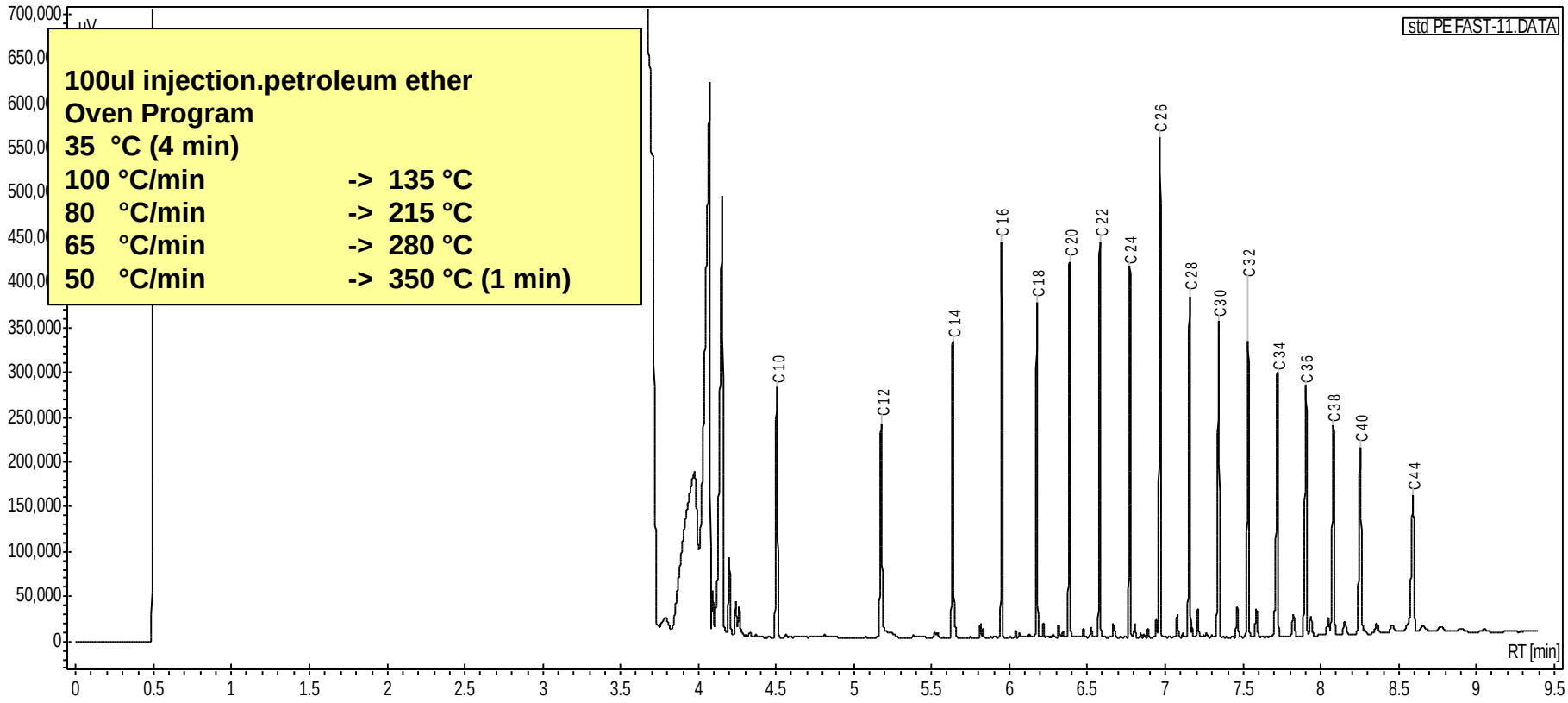
Fast ramp rates

With a smaller over, much FASTER temperature programming is possible, while we keep the flexibility of using capillary columns which we can couple and cut.

Typical temperature programs:

		35 °C (4 min)
100 °C/min	->	135 °C
80 °C/min	->	215 °C
65 °C/min	->	280 °C
50 °C/min	->	350 °C (1 min)

Application with fast ramp rate..



9 minutes !

Advantages PTV technique:

Easy to automate

No column coupling

No retention gaps required

Usable for 1 -300 µl injections

Challenges PTV technique:

Price of PTV injection

Minimize discrimination of volatile fraction (<C10)

Summary

Mineral oils can be measured accurately using GC;

Using Large volume injection, direct accurate measurement of ppm-ppb levels of mineral oils is possible without time consuming concentration steps

Using the PTV setup a simple automated method can be implemented in the routine lab for routine mineral oil measurement

Thank you for your attention

See the Varian booth for your

free sample of mineral oil..

General considerations

- Oxygen and water in a column at high temperatures means rapid stationary phase breakdown

- Depending on the type of oil and matrix, life time can be between 2 weeks and 6 months for routine analysis

- Tmax for fused silica columns= 400°C

Varian Select™ Mineral Oil

Proven performance for fast Mineral Oil analysis

- Ideal for method DIN-EN-ISO 9377-2
- Complete analysis in less than 5 minutes
- Stable up to 400 °C
- Compatible with high injection and detection port temperatures

Mineral oils are typically found in water, foods and soils. Today, mineral oil analysis from soil samples is a routine service for many environmental laboratories as industrial clients seek "clean ground" certification, and gas chromatography is the method of choice. Mineral oils are also routinely analyzed in food and water samples, where large injection volume techniques are often employed.

Optimized for fast analysis

Varian Select mineral oil columns were developed to quickly analyze mineral oils within minutes, and at temperatures up to 400 °C. The fused silica capillary columns, developed in collaboration with a leading environmental firm, are comprised of a proprietary non-polar stationary phase with a film thickness and column dimension optimized for fast analysis and excellent column longevity.

Ideal for Modern Methods

The Select Mineral Oil column delivers proven performance for methods DIN H53 and DIN-EN-ISO 9377-2. DIN-EN-ISO 9377-2 is a recently approved method, which essentially combines older European, DIN and ISO methods for GC analysis of mineral oils from C10 through C40.

Increase Throughput

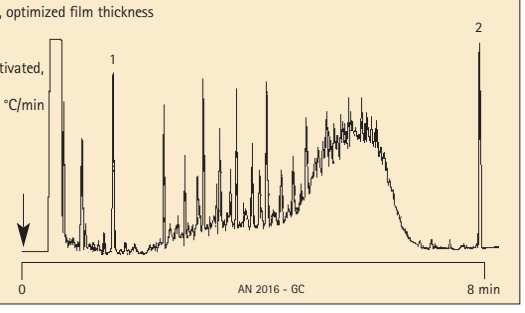
Because of the increased demand for sample analysis, shortened analysis time is essential. Select Mineral Oil columns provide complete separation of even heavy oil fractions in less than 6 minutes.

Mineral oil in water and soil acc to DIN - EN ISO 9377-2

Figure 1

Technique : GC
Column : Varian Select Mineral Oil
Fused silica 15 m x 0.32 mm, optimized film thickness
Part no. CP7491
Guard column/Retention gap
4 m x 0.53 mm, methyl deactivated,
Part no. CP8015
Temperature : 55 °C, 1.9 min → 320 °C, 80 °C/min
Carrier gas : Nitrogen, 80 kPa
Injector : On-Column
Detector : FID
Sample size : 2 µl
Concentr. range : 1 mg / ml petroleum ether

Peak identification:
1. C10
2. C40



VARIAN

In addition to fast analysis, the increased temperature stability of the columns also permits faster bake-out times.

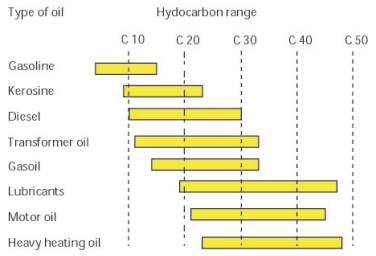
Classification

Mineral oils are generally classified by their hydrocarbon range. Mineral oil is usually in the C10 to C44 range, but may extend to C60 or even higher.

Figure 2 gives a general classification of the most common mineral oils found in environmental samples. Application of light, medium and heavy mineral oil fractions are shown in figures 3, 4, and 5.

Table of oil fractions

Figure 2



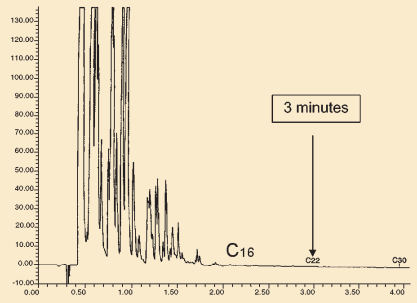
Ordering Information - Select Mineral Oil columns

Description	Part No.
Select Mineral Oil, 15 m x 0.32 mm	CP7491
3-pack	CP749103
6-pack	CP749106

Fast analysis of Gasoline (mineral oil) in Soil

Figure 3

Technique : GC
Column : Varian Select Mineral Oil Fused silica 15 m x 0.32 mm optimized filmthickness, Part No. CP7491
Temperature : 55 °C → 320 °C, ballistic temperature program
Carrier gas : Helium, 70 kPa
Injector : On-Column
Detector : FID
Sample size : 1.0 µl
Concentr. range : Gasoline contaminated soil

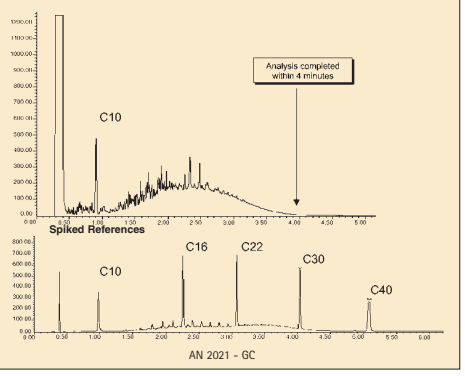


AN 2026 - GC

Fast analysis of C10-C25 mineral oil in Soil

Figure 4

Technique : GC
Column : Varian Select Mineral Oil Fused silica 15 m x 0.32 mm optimized film thickness, Part No. CP7491
Temperature : 55 °C → 320 °C, ballistic temperature program
Carrier gas : Helium, 70 kPa
Injector : On-Column
Detector : FID
Sample Size : 1.0 µl
Concentr. range : real sample, conc: >400 mg/l

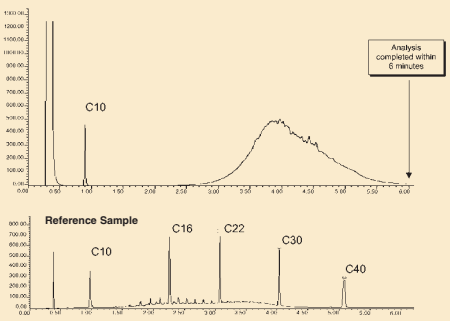


AN 2021 - GC

Fast analysis of C18-C50 mineral oil in Soil

Figure 5

Technique : GC
Column : Varian Select Mineral Oil Fused silica 15 m x 0.32 mm optimized film thickness, Part No. CP7491
Temperature : 55 °C → 320 °C, ballistic temperature program
Carrier gas : Helium, 70 kPa
Injector : On-Column
Detector : FID
Sample size : 1.0 µl
Concentr. range : real sample, conc: >400 mg/l



AN 2024 - GC

VARIAN

Varian, Inc. • www.varianinc.com
• **North America** 800.926.3000, 925.939.2400
• **Europe** The Netherlands: 31.118.67.1000
• **Asia Pacific** Australia: 613.9560.7133
• **Latin America** Brazil: 55.11.3845.0444
• **Other sales offices and dealers throughout the world**

GC • LC • MS • AAS • ICP • UV-Vis-NIR • Fluorescence • Dissolution • NMR • Consumable Products

MDL057GU0 04/03
Printed in The Netherlands