

Chemical Detection of Fire Accelerants in Car Fires by Methods of the Gas- Chromatography Coupled to a Mass Detector

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Abstract

Fire tests have been carried out with different fuels and in different scales, such the lab- scale, the third- scale and the full scale. By that samples of soot, condensate, flammable liquids and partial fire debris as well have been collected. The focus was set on the qualitative analysis of soot and condensate in respect to the content of hydrocarbons which might be typical for a combined combustion of flammable liquids and plastics. All samples have been analysed by methods of the gas chromatography coupled to a mass detector. Different flammable liquids and plastics have been used as fuels. The plastics are common for automotive construction. The liquids are often used as accelerators in arson fires. The solid- phase- micro- extraction (SPME) has been applied for transferring the samples onto the analytical apparatus.

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List of Abbreviation

LKA	Landeskriminalamt (corresponding to the Swedish Länskriminalen)
SKL	Svenska Kriminalteknisk Laboratoriet
GC / MS	Gas Chromatography coupled to a Mass Spectrometer
SRV	Statens Räddningsverket
SPME	Solid- Phase Micro- Extraction
StGB	German Penal Code
TMTM	Tetramethylthiurame Monosulfide (a pesticide)
CNBA	4-chloro-3-nitrobenzoic acid (a pesticide)
FID	Flame Ionisation Detector
GC / HWD / FID	Gas Chromatograph coupled to a Hot Wire Detector and Flame Ionisation Detector
FTIR	Fourier- Transformation- Infrared Spectroscopy
XAD-2	Adsorption Material based on a Polystyrene
NDIR	Non- Dispersive Infrared Spectroscopy
OPGV	Optimal Practical Gas Velocity
SCN- Mode	Mode of Operation of the Mass Spectrometer, a continuous scan of the whole mass range adjusted will be performed
TDI	Toluen- Di- Isocyanate
BBQ- Lighter	Barbecue Lighter
SBSE	Stir Bar Sorptive Extraction

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1 Introduction

The investigation of combustion products is important for reasons of the clarification of fire causes as well as health, safety and environmental aspects and the further improvement of the preventive fire protection. The use of the results can be defined according to the temporary relation to a fire.:

1. Prior to the fire

All measures derived in respect of the preventive and defensive fire protection and risk assessment, e.g. provided by insurances, and the inclusion of planned new buildings into municipal development planning belong to this aspect.

2. During the fire

The received results can be consulted for the evaluation of effects on humans and environment and as decision making aid for measures to be introduced by the rescue services and other authorities in charge.

3. After the fire

The formation of specific combustion products as a function of the fuel is of an immense importance for the investigation of fire causes and fire courses. Combustion products of so called fire accelerators used in arson fires are of particular interest. (according to [52])

This reports deals with the third relation.

2 Theoretical Background

2.1 Combustion of Plastics

Prior to the selection of the plastics applied in the tests some specific information of the combustion of foamed polypropylene and polyurethane foam are given below.

It can be stated in general that organic fuels initially combust under homolytical separation of hydrogen and further on under aggregation of oxygen or the condensation to non-saturated substances respectively (according to [50]). As products of an incomplete combustion, as supposed to be the regular case in the sense of this report, condensed systems e.g. single- and multiple-core aromates may occur. The formation of aromates is favoured by the radicalic mechanism of the reaction. The ratio of carbon to hydrogen increases in the course of the combustion, which leads to an increased formation of soot.

Troitzsch [30] describes the combustion of plastics based on their affiliation to a certain group of substances.

Polyolefines, to which polypropylene belongs to will combust hesitant at the beginning with a small, light blue flame and later on with a light yellow flame which consists burning even after removal of the ignition source. The fire gases have a waxy smell (according to [30]). These descriptions have been found to be true when compared with the observations done during the tests.

According to [31] the main decomposition products of polypropylene at a temperature of 400°C are pentane, 2-methyl-1-penten and 2,4-dimethyl heptane. An important role of these decomposition products under the course of the combustion is to be expected. Little research work is done on the thermal decomposition and the affiliate kinetic parameters (according to [31]).

The decomposition of the polyolefines includes statistical fragmentation of chains leading to a mixture of short, medium and long (chain) fragments, consisting mainly of olefins, paraffines and cyclic hydrocarbons (according to [30])

Soft polyurethane foams depolycondensate during the combustion to their monomers, the iso cyanates and alcohols. The flames are coloured bright light yellow and the combustion itself is quite intensive (according to [30]).

2.2 Arson

2.2.1 General

Arson is mentioned in literature as fire cause when human activities like intention or carelessness are the actuating events (according to [33]).

Arson probably goes along with the community already since fire is in active use by human beings. There has been hardly a war where arson wasn't of importance. Arson frequently is connected to more or less large damages to health, matter, ideals or policy. Many big fires caused by arson can be found in history, e.g. the burning of Rome. A widespread software used for burning CD's and DVD's got its name originating from this event.

Further historical examples for arson are:

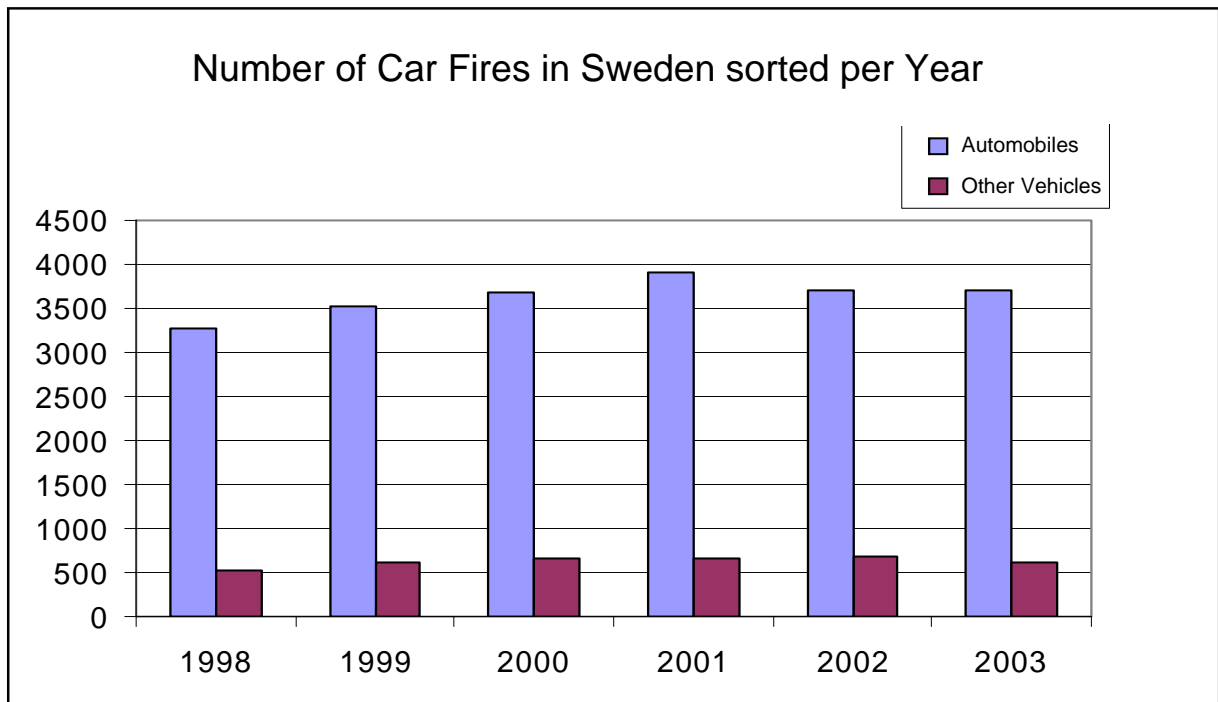
- Fire of the synagogues in the „Night of Broken Glass“ in Germany in 1938 (intention)
- Fire of a stadiums tribune in Bradford, UK in 1985 (carelessness)
- Fire of the Düsseldorf airport, Germany in 1996 (carelessness)
- Fire of a discotheque in Gothenburg, Sweden in 1998 (intention)

Arson is treated different in the different nation's criminal laws. In Germany the ignition of cars by human beings is no arson, since arson is coupled to compartments. At court these fires are treated as wilful damage to property or insurance fraud. (according to [33]). However, for reasons of simplicity and the different treatment mentioned above within this report the term arson to cars shall be allowed.

2.2.2 Arson to Cars

No uniform fire statistics exist in Germany. Even the associations of insurances where unable to provide details on frequencies and degrees of damages caused by arson. According to [40] about 30% of all fires in Sweden are caused by arson. According to [33] approximately 30% of all car fires, 6% of all fires in buses and lorries and 65% of fires on motorcycles are caused by arson.

The following statistics arises from Sweden:



Picture 2.2.2-1: Fire statistics from car fires (adopted from: Statens Räddningsverket [41])

It is obvious that after a continuing raise from 1998 to 2001 the number of car fires remains stable at approximately 3700 per year. In order to get a rough estimations of the damage extent some assumptions are done:

1. The fraction of proved arson in cars is approximately 30% (similar to the information given in [33] and [40]).
2. 75% of all car fires cause a total economical loss of the car. According to experts the duration until flashover in car fires is in between 10 and 20 minutes. The duration for the fire detection, alarming of the rescue services, their access to the scene and the time until their fire fighting measures take effect is of the same size. Even in case the fire is knocked down in time can extinguishing media cause additional damages. For clarification see picture 6.2-1 on page 43.
3. The averaged value of a car lost in an arson fire is estimated to be 10.000€.

From the information above an annual damage of SEK 83.000.000 can be calculated.

This value represents the fraction of total losses only. Including partial damages and assuming that from the unknown fire causes further fires originate from arson a total value of SEK 100.000.000 seems to be suitable.

2.2.3 The Arsonists

Kästle [34] defines four sectors of arson:

- Arson committed by children
- Arson driven by self advantage
- Arson driven by wish to do damage to somebody else as a single crime
- Serial arson

The sectors can be categorised according to table 2.2.3-1, but very often a sharp division is impossible.

Table 2.2.3-1: Sectors of arson, motivation and personalities of the arsonist (collected with help of [34])

Type of Arson	Motivation	Personality of the Arsonist
Committed by children	Curiosity, excitement for experiments	Irrational handling
Driven by self advantage	Selfishness, intention for self-enrichment connected to insurance fraud,	Rational handling
Driven by wish to do damage to somebody else as a single crime	Vandalism, arson on request, covering of other crimes like house-breaking, murder or economical crimes	Manifold but inconspicuous, most times less educated
Serial arson	Fun for fires as substitutional act and compensation of personal deficiency, terroristical or political background, covering of other crimes, arson on request	Teenagers and people up to the age of 30

The behaviour of all types of arson can be combined or dominated with more or less strong psychological disorders or diseases. Kästle [34] explicit figures out, that a classification of the arsonists often is almost impossible due to their different motivations and personal structures. The table given above is to be considered for that reason as an example only.

2.2.4 Sampling in real Fires

The proof of arson is very difficult sometimes, especially when most of the traces have been destroyed due to the intensity of the fire. For that reason fire investigators eliminate other fire causes easier to detect. Whenever no other fire case is likely or

no other explicit indications are obviously in advance investigations will turn towards the possibility of arson.

Sometimes traces of the application of an accelerator (e.g. flammable liquid) can be found after the fire. Even residues of a flammable liquid can resist unchanged a fire within porous materials, e.g. floors of wooden materials, or thick carpets made of textile. Unusual signs of burn up compared to the surrounding in the area of the suspected location of the initial fire or the smell of volatile components of an accelerator can point out arson. Another possibility of the detection of volatile components is the given by the use of special trained animals, especially canines [44] or apparative methods, like a **Photo- Ionozation- Detector (PID)** [45]. All methods mentioned before can't deliver sure information about the type of the liquid applicated. However, this information is important most often when it comes to court. The classic application of the chemical- analytical proof of fire accelerators is for that reason the trace analysis of materials which have been in direct touch with the fire accelerator.

Normally a sample of the material is taken from the suspected place of application, packed gastight, and transferred under cooling to a laboratory. Most often a second sample suspected not have been i touch with the accelerator is taken for reasons of comparison.

At this point the different approach of this work to the usual practice becomes obvious.

2.3 Results of the Literature Research

A total of about 100 sources of literature have been reviewed. A lot of fire tests with plastics and other fuels can be found, even some publications about the prove of accelerants from fire residues are available. All the research work dealt to a large extend with one of the following topics:

- a) Characterisation of the fire behaviour of the fuel, e.g. to classify the fire load or to test the effects of flame and smoke retarders

- b) Characterisation of the toxicity of fire gases and the smoke potential, very often connected to optical measurements of the smoke density and concentrations of pre- defined substances
- c) Description of the analytical process for the detection of non- combusted fractions of accelerants

Reports similar to the work to be done, which means without predefining of the substances to be analysed and detection of species specific for the combustion with accelerants were not found. Especially no literature about the analysis of soot and condensate towards the application of accelerants is available. This appears to be comprehensible due to the necessary secrecy of forensic methods in chemical analysis.

Some research work is listed in respect to the equipment in table 2.3-1.

Table 2.3-1: Research on Analysis of Combustion Products

Author and Literature	Fuels	Equipment / Annotations
B. Andersson et.al., TOXFIRE, [11]	Heptane, Chlorobenzene, Nylon- 6,6 and three pesticides: TMTM, CNBA, Dimethoat in Third Scale	GC/MS, FID, Analysators for CO, CO ₂ , O ₂ , NO _x ,
O. Höyland, [8]	Polystyrene (PS), Polyurethane (PU), PVC, Spruce and Pine	GC/HWD/FID, Titration, Dräger Tubes
P. Blomqvist et.al., TOXFIRE, [7], [12]	Polypropylene, Nylon- 6,6, TMTM, Chlorobenzene, PS, PS fireretarded, CNBA,	GC/FID, GC/MS, FTIR, Teenax- TA, Carbotrap/ Carbosieve, Aktiv Carbon, XAD-2
T.J. Ohlemiller et. al. [10]	Pine and Red Oak	NDIR, FID, GC/MS, GC/HWD, GC/FID
P. Basmer et. al. [1]	Three Pesticides	GC/MS, Teenax- TA, Aktiv Carbon, Graphitized Carbon,
J. Koskelainen [13]	Fire protective Colors	GC/HWD, GC/FID
R. M. Aseeva et. al. [31]	Different Polymers	General description of the combustion of polymers
J. Troitzsch [30]		General description of the combustion of polymers
W. Bertsch et. al. [32]		General description of analytical methods at the state of the publication
Anthony D. Cafe [43]	Fire residue	GC/FID

The third scale used by Andersson et. al. is derived from ISO 9705 ab. This standard defines a corner fire test in a standard compartment. The third scale compartment is approximately one third of the standard compartment in volume. It is 0,8m in width, 1,1m long and 0,8m in height. Since the block-shaped plastics used as fuel in the tests and the fragments of the car seat to be combusted fit very well to these measures the term „third scale test“ has been adopted. The results of the literature research and their application in the development of the single steps of the test setup and sampling will be reviewed in detail in the further course of this report.

2.4 Solid- Phase- Micro- Extraction

2.4.1 General

The process of the **Solid- Phase- Micro- Extraction** (SPME) is based on the adsorption of the analyte to a special polymer stationary phase at the sampling and the thermal desorption in the gas chromatograph. The SPME- method has been significantly developed in the nineties by Pawliszyn (see [35]). SPME is appropriate for headspace- analysis as well as direct sampling from liquids and is patented by. (see [14]).

A suitable SPME- fibre and a fibre holder is needed to conduct a SPME- analysis. Different polymers and thicknesses are available as fibre coatings, e.g. polydimethylsiloxane or acrylate. Thicknesses diversify between 5 and 100µm. It is obviously that adsorption materials similar to the stationary phases used in capillary gas chromatography are offered. The selection of the coating material is done for that reason according to the polarity of the analytes expected. The coatings ensure a very good reproduction of the mixture of substances in a sample as well as an excellent reproducibility of the results of the analyses. Meanwhile the sample introduction to the gas chromatograph can be done automatically by an autosampler.

The fibres are reusable up to onehundred times whereas thermal desorption and conditioning is sufficient. The long term temperature limit of the coatings differs by their type and is up to 290°C [14].

The SPME has important advantages when compared to other methods of sample preparation and sample introduction to a gas chromatograph:

- No solvent is needed. This means that effects from matrices and contaminations caused by solvent can be avoided and waste from solvents doesn't appear at all.
- The time need for sample preparation is reduced significantly if compared to a liquid extraction.

- The effort in apparatuses for sample preparation can be reduced since if suitable sampling containers are available extraction can be done directly out of them. Linked with the reusability of the fibre costs can be reduced significantly here.

2.4.2 SPME and its Use in Detection of Fire Accelerants

SPME in Germany is in use since the second half of the nineties for the detection of fire accelerators. It became a standard process for sample introduction into the gas chromatograph due to its simple handling. The German Federal Bureau of Criminal Investigation temporarily initiated interlaboratory tests where several Bureaus of Criminal Investigation of several federal states analysed the same sample. A statement about the quality of the applied analytical process can be done based on the results. [36], [37].

Even abroad SPME is in use for the detection of fire accelerators.

Headspace sampling as well as direct liquid phase sampling is applied. [23] [24] [45] [46] [47] [48].

3 Experimental Part

3.1 Object of Investigation

Samples of condensate and soot have been analysed.

Two different plastics usually applied in automotive construction have been used as fuels in the lab scale tests. Different liquids often used in arson fires and easy to obtain has been applied to simulate the fire accelerator. A further discussion on the selection is done in chapter 3.3 .

The tests carried out are given in table 6.2-1 on page 52.

Masses of 100g up to 2kg at the plastics and volumes of 10 ml up to 0,5 l at the liquids have been used. More details are given in chapters 3.5 and 3.6 .

Combustion products may occur, just like potential fuels in a gaseous, liquid or solid state. The combustion products being gaseous at ambient temperature however were of minor interest since in a real fire they will have been disappeared before any fire investigation has started.

It was envisaged that the combustion was well ventilated in every test. However for further research it is necessary to meet pre- defined parameters in order to simulate real underventilated fires. Ventilation conditions are suspected to dominate the formation of certain species.

The material composition and homogeneity of the fuel is an additional criterion since in a real fire almost never only one pure chemical is involved. A consideration of the components of the fuel applied is important therefore when reviewing the results. This might be relatively easy for the tests in lab- and third- scale, apart from the liquids. The vehicles of the large scale tests however represent a complex mixture of fuels. For that reason transferability of the results of the lab- and third- scale experiments is a question.

3.2 Description of the applied Methods of Investigation

3.2.1 Gas Chromatography- Mass Spectroscopy (GC/MS)

The applied GC/MS consists of a gas chromatograph FISIONS 8065 with heatable sample inlet and a quadrupol mass detector MD 800. The inletliner in the gas chromatograph allows for the split application.

Two different capillary columns have been available. More details are shown in table 3.2.1-1.

Table 3.2.1-1: Available capillary columns (details from [19])

Manufacturer	Type	Length	Inner Diameter	Stationary Phase	Temperature Range	Film-thickness
J&W Scientific	DB-5ms	60 m	0,32 mm	Equivalent to (5%-Phenyl)- methyl-polysiloxane	-60°C to 350°C	0,25 µm
J&W Scientific	DB-5	30 m	0,25 mm	Equivalent to (5%-Phenyl)- methyl-polysiloxane	-60°C to 350°C	0,25 µm

Both stationary phases are classified as non- polar by the manufacturer. For that reason they are very good capable for the expected substances (aliphates, aromates with few hetero- atoms, see chapter 2.1.3). The difference in both stationary phases is, that DB-5ms has been optimised for MS application and has an extremely low column bleeding.

The separation of the components of a mixture at non- polar phases takes place within one group of substances according to the boiling points of the single components. This can be seen in picture 6.2-14 on page 55.

The goal was to end up at a short running time for an analysis with a sufficient separation performance. The running time is dominated by the elution time of the analytes on the capillary column. For that reason a column length as short as possible is desired when comparing the same stationary phase. The number of the theoretical plates of a capillary column is directly proportional to its length, by doubling the length the number of theoretical plates will be doubled as well. The resolution how-

ever isn't directly proportional to the length but directly proportional to the square root of the length. This means quadruplicating the length will result in doubling the resolution.

The number of theoretical plates is inversely proportional to the column's inner diameter, which means that columns with a smaller inner diameter but the same stationary phase tend to give a better resolution. The loss of resolution by the selection of a shorter column in this case has been partially compensated by the smaller inner diameter. The smaller carrier gas flow additionally supports the selection of the smaller diameter column. For reasons of construction the whole carrier gas flow enters the mass selective detector, but the detector reaches its best performance at low pressure. Therefore systems with low carrier gas flows are to be preferred. Low carrier gas flows occur at small inner diameters. [20]

Based on these considerations the shorter column has been used.

Similar stationary phases are given in table 6.2-4 on page 54.

For sample introduction of liquid samples an autosampler FISIONS/ CTC A200S, equipped with a tray capacity of 200 vials and 0,7ml volume each has been used.

The controlling of the analytical system was done by a PC and the software package Masslab 1.4.

3.2.2 Sampling Procedure

A new strategy for sampling had to be developed meeting the goal of especially sampling the heavier hydrocarbons.

Ohlemiller describes sampling of condensate by the help of a cooling trap. [10] Blomqvist collected soot samples on a glass filter. [12] B. Andersson et. al. Used Teflon filters for the same task followed by an extraction in an ultrasonic bath. [11]

The goal with the sampling of soot and condensates was to simulate the deposit of these products in real fires on surfaces, e.g. seat belt locks and window panes. Different alternatives, for instance a cooled condensate plate has been reviewed but dismissed, since the combustion products would have to be transferred to a sample

container prior to make up them for headspace SPME. At the end silanised glass wool has been selected for different advantages within the analytical process. These advantages are:

- The reactive centres are deactivated by the silanisation process, so no reaction with organic compounds are to be feared.
- The glass wool can simply be fixed with a wire right above the combustion zone.
- Glass wool is even suitable for sampling in full scale tests as it acts as an abrasivum, e.g. for wiping from window panes.
- Glass wool is able to resist higher temperatures unchanged due to the inorganic character. Contamination can be excluded for that reason.
- It can be transferred easily and quickly into a suitable container when the test is finished or after sampling respectively

For these reasons different fittings for the glass wool and the different test scales have been developed. The fittings are shown in picture 6.2-2 on page 44.

3.2.3 Sample Preparation

The glass wool has been removed from the fitting after the sampling was finished with tweezers. It was transferred into screw-top jars with 220ml in volume. Additionally these jars have been tightened with Parafilm M and stored until their further processing in a lab fridge at 4°C.

The sample jars applied have been purchased as new ones. They are usually in use in the food industry for packaging purposes. The avoidance of contamination is of extraordinary importance in the food industry sector since otherwise changes in taste and smell could be consequences very easy. That's why the gaskets cover only the area where the top is directly in touch with the jar and don't cover the whole top area. These circumstances ease the desire for avoidance of contamination. However, blind samples of non-used glass wool have been extracted and analysed under the same conditions for safety reasons.

One of the screw tops got an aperture, where a GC- septum was attached to with glue. The SPME- fibre was introduced into the sample jar through this septum with help of a fibre holder. The sample jar was heated up to 80°C in a water bath.

Subsequently it turned out the concentration of the analytes being to low. Therefore another aperture was drilled into the top and a connector for a vacuum hose of a water jet pump was attached to it. A safety washing bottle in order to prevent a backflow of water into the sample jar was introduced in line to the water jet pump (see picture 6.2-3, page 45). The vapour pressure of liquids can be raised by pressure dropping and heating and thereby the directly proportional the concentration in the headspace above the sample. No significant accumulation took place by all these measures. Therefore a fitting made of glass was created allowing to directly introduce the fibre into the flow line to the water jet pump. (picture 6.2-4, page 46) The old septum was sealed with tape. According to the manufacturer the water jet pump realises a pressure of 100 to 200 mbar. Water, which entered the safety washing bottle, was boiling at room temperature. Thus these pressure values have been confirmed. A Teflon filter at the connector to the vacuum line, mesh size 0,45 µm, disabled the entrainment of soot particles (see picture 6.2-5, page 46). Soot particles potentially would have covered the stationary phase in the capillary column of the GC. Thus the column wouldn't have been usable any longer. The optimum duration for extraction was fixed to 20 minutes since it was found out in pre- tests that a prolonged duration didn't end in a further accumulation.

In order to get an even larger accumulation of analyte on the glass wool different long term combustion tests up to almost 90 minutes have been carried out. In addition the sooty fire gases have been actively sucked. Therefore glass wool was fixed in an upside down hopper. Sucking was provided by a water jet pump through the hopper.

All these measures didn't provide an acceptable raise of concentration. That's why extractions with diethyl- ether, tetra- hydrofurane, methanol and n- heptane in an ultrasonic bath have been done in order to get a comparison with another extractive method. The glass wool was transferred for this method into test tubes and covered with the solvent. The duration of the extraction in the ultrasonic bath was set to five minutes.

After that a filtration through a 0,45 μ m filter was done by transferring the extract with a pipette into a gas tight syringe with the filter on its tip. The filtrate was collected in autosampler vials which were immediately closed with a septum.

The volume of the volatile extraction agent was to be kept quite well since a considerable fraction evaporated during the subsequent extraction in the ultrasonic bath. It was found out that of 1,2ml from the beginning 0,5ml was left after the extraction. However a too low concentration of the analytes was to be feared when differing to much from the upper limit.

The gas tight syringe was swept with diethyl ether and methanol subsequently.

In parallel a blind sample of glass wool was extracted every time. A different result to the SPME- method was recognisable only at the extraction with n- heptane where one additional peak was found in the gas chromatogram.

3.2.4 Analytics with the GC/MS

Optimising the GC - Parameters

The GC was to operate in an anisothermal manner in order to improve the separation efficiency by temperature control, since the distribution equilibrium in the capillary column is dependent on temperature.

Helium was used as carrier gas. A very important parameter for the separation performance of a capillary column is the carrier gas velocity. The van Deemter- equations for different carrier gases give a relation of the linear carrier gas velocity and the height of a theoretical plate. [15] As the height of a theoretical plate is minimised, the number of theoretical plates is at the maximum, which means that the separation performance is optimised.

The minimal theoretical plate height corresponds to the optimal linear carrier gas velocity. However, for different reasons a higher velocity (1,25 up to 2 times) is best practice. This velocity is the so called optimal practical gas velocity (OPGV). The main reason is that already a small increasing leads to a considerable reduction in time demand for an analysis run. Another reason is due to the non- isothermal oper-

ating gas chromatograph since the viscosity of gases increases with temperature. [20] This leads to higher pressure drops and as the pressure drops the velocity decreases as well.

The van- Deemter Curves for helium raise slower in the area of higher carrier gas velocities as they do in the area of lower carrier gas velocities, both around the minimum of the plate height. For that reason a not to strong increasing of the velocity gives an advantage. Values of the OPGV are given in tables related to column lengths, diameters and film thicknesses of the stationary phase. The recommended OPGV- range for the column used in this work is 40- 70cm/s [20].

The carrier gas velocity was to adjust now. This was done by adjusting the pressure at the column head and the measurement of the retention time of the so called "non-retained peak". A non retained peak represents a substance with no interaction with the stationary phase of the column. For that reason the velocity of this substance through the column is the same as the carrier gas velocity. The manufacturer of the column proposes different analytes to measure this retention time. For reasons of simplicity air was selected in this case and the measuring range of the mass detector was switched to the typical components of air.

The carrier gas velocity was selected to be 60cm/s which corresponds to a retention time of the non- retained peak of about 50s when using a 30m column. The pressure at the column head in the gas chromatograph was adjusted after different measurements to 65 kPa.

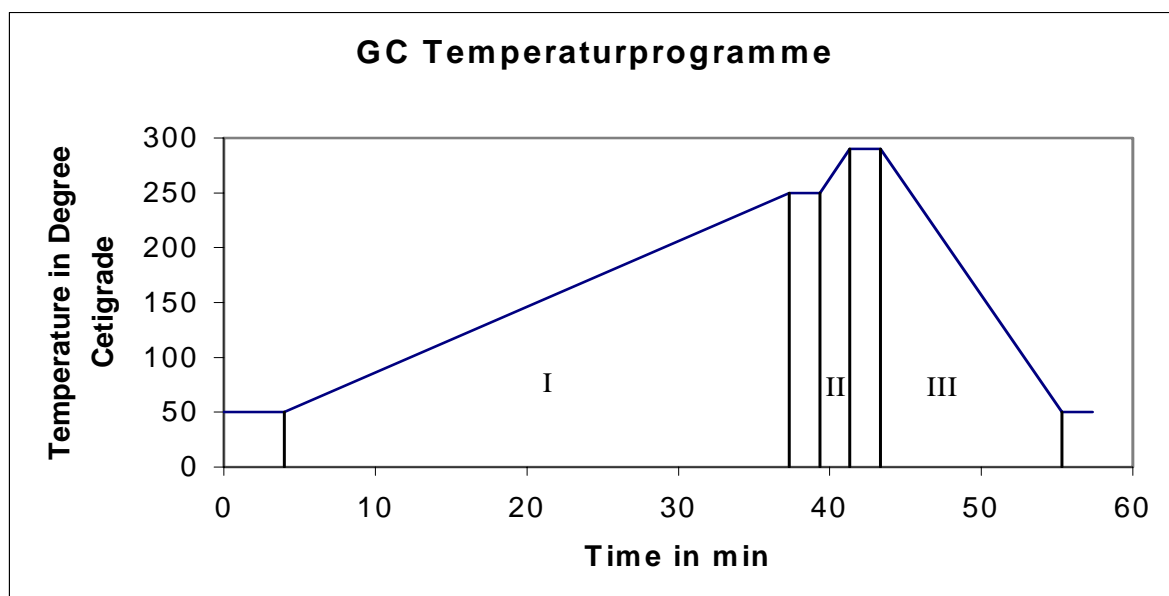
The isothermal start- up phase is used to separate the lightly volatiles. It should be twice as long as the retention time of the non- retained peak. The subsequent temperature controlled phase must have a low heating rate in order to get a sufficient separation. However as the heating rate is too low the time demand for an analysis increases to much. In pre- tests diesel has been selected as representing a very complex mixture in order to optimise the heating rate and the separation performance. In the end of the temperature programme a quick heating up to 290 °C followed to remove eventually present residues from the column.

A blind run which means an analysis run without sample introduction was done every morning to check for contamination freedom of the system.

The temperature programme applied of the gas chromatograph is shown in table 3.2.4-1 and picture 3.2.4-1

Table 3.2.4-1: Temperature programme applied

Temperature in °C	Hold up time in min	Heating rate/ Annotation
50	4	
		6°C/min to 250°C (I)
250	2	
		20°C/min to 290°C (II)
290	2	
		Cool down to 50°C
50	2	Stabilisation of the System



Picture 3.2.4-1: Temperature programme applied

A special inlet liner had to be used, applicable for the SPME. Supelco, as the manufacturer of the SPME fibres recommends an optimum inner diameter of the liner of 0,75mm in order to receive a proper peak shape in the chromatograms. Such a liner has been used in this work.

Due to the concentration range applicable for a mass detector which is in most cases much lower than the sample volume that can be introduced to the gas chromatograph usually only a subset of the sample introduced is forwarded to the detector by using the so called split ratio.

The split ratio is defined as the ratio of volumetric flow entering the column of the gas chromatograph to the volumetric flow leaving the inlet system of the gas chromatograph via the split valve. The total of both flows is the flow passing the inlet liner (see picture 6.2-6, page 47 [20]). This flow shouldn't be below 20 ml/min since otherwise backflashes resulting in too broad peak bases in the chromatogram are to be feared.

Recommendations are available even for the split ration related to the columns diameter. [20]. Based on the selected OPGV of 60 cm/s a flow through the column of 1,7 cm³/min is received due to the columns diameter. In order to meet the 20 ml/min-criterion the split valve was adjusted 25 ml/ min, corresponding to a split ratio of approximately 1:15. This ratio is on the upper limit of the recommended range and has been confirmed by Supelco even for SPME- applications [21].

Smaller split ratios allow for larger sample volumes, larger split ratios however are interesting for trace analytics. After performing a couple of analyses it became obviously that the concentration of the analytes was too low. For that reason the split ratio was reduced to 0,5cm³/min.

As a further measure a rinse flow for the septum is to be adjusted. This flow is necessary for to reasons. Firstly it is used to decontaminate the septum from possible sample material and secondly to minimise the effects of a backflash. A backflash is a backward flow due to a flash evaporation of a liquid sample in the inletliner connected in a expansion of the volume. This happens every time when introducing a liquid sample. However the rinse flow can reduce the effect within certain limits. The effects of a larger backflash are broad and tailing peaks similar to them when the flow through the liner is too low. The rinse flow was adjusted according to the recommendations of the GC manufacturer to 15 ml/min [22].

The pressure at the column head was checked every time something in the system was changed and readjusted as needed in order to keep the carrier gas velocity constant.

The temperature of the sample inlet was set constant at 250°C. The sample volume for liquid samples was fixed at 0,1µl.

Optimisation of the MS- Parameters

Both temperature of the interface and ion source have been constant at 250°C and 200°C respectively. For reasons of reproducibility not the exact value is important of these two temperatures but the lowest possible fluctuation.

The scan range of 40 to 350 atomic mass units (amu) turned out in pre- tests to be suitable. This range excludes the mass fragments of air to a large extend, only argon and carbon dioxide give a signal. The upper limit of the scan range has been fixed after pre- tests. In general the scan range should be as small as possible to allow for more precise data acquisition when the scan time is kept constant. The scan time is the duration of one scan over the whole adjusted mass range (310 amu in this case). It has been fixed in pre- tests as well to 0,9 s with an interscan delay of 0,1s.

Analyses

All analyses have been processed in the SCN- mode of the mass detector which means that the whole adjusted scan range was scanned within the adjusted scan time.

Two parameters can be used for the qualitative analysis in SCN- mode, the retention time of the substance peak in the gas chromatogram and the fit of the recorded mass spectrum with the internal library. The boiling point to retention time correlation was introduced as an additional parameter as used by Basmer et. al. [1] This correlation will be discussed more detailed in chapter 4.2 .

First of all a background chromatogram was recorded as shown in picture 6.2-15 on page 56 in order to detect peaks arising from column bleeding and residues.

3.3 Pre- Tests and Selection of the Fuels

It was acknowledged to test such plastics which are most common in automotive construction.

Polyurethane soft foam (made out of an polyether alcohol and a mixture of 80% 2,4- and 20% 2,6- toluene diisocyanate, trading name Lupranat T80) and foamed poly-

propylene (trading name Neopolen) manufactured by BASF Schwarzheide GmbH, Germany in accordance with SKL [49] were selected as plastics. According to the manufacturer both of these plastics are used in automotive construction to a large extend. The flame retarded polyurethane foam is used for upholstery for example and the Neopolen for door lining. The polyurethane soft foam is flexible due to an open cell structure whereas Neopolen is more rigid due to a closed cell structure. (according to [51]).

Even a couple of often used fire accelerators had to be selected.

The accelerant had to match a few criteria:

1. suitable fire behaviour under the given conditions
2. no certain permits for access and possessing necessary
3. simple to obtain
4. easy to ignite, the ignition energy of a match or cigarette lighter should be sufficient

The number of possible accelerants was considerably reduced due to the given pre-conditions. It was to ensured as well that the soot formation even in the 10 ml range was sufficient for analysis.

In pre- tests samples of the fuels have been ignited in a metal bowl. Even the continuum of the combustion and the flame height has been studied in order to get information about a suitable sampling position. It was envisaged to take a soot sample approximately 10cm above the flame zone since to a large extend stable products have been expected there. Even Höyland used this height. [8]

As accelerants have been selected:

- for the lab scale tests barbecue lighter and kerosene
- for the third scale tests heptane and Lacknafta.

Lacknafta is produced in Sweden by Färghandelskompaniet. It is a mixture of hydrocarbons containing 17 till up to 22% aromates. The boiling range is between 100 and 300 °C (according to [52]). Lacknafta is a medium distillate.

Even kerosene is a medium distillate however the boiling range is between 170 till 280°C. It contains hydrocarbons of the boiling range mentioned before from the crude oil distillation. [32]

The barbecue lighter is a mixture of hydrocarbons typically containing certain fractions from the catalytic cracked light kerosene fraction. [32]

3.4 Test Setup

All considerations were based on the conditions to be fulfilled which means e.g. avoidance of contamination came first. It should be an easy to create, fast to decontaminate and quickly to rearrange for the next test setup. Therefore a special oven wasn't suitable. Even the ventilation conditions had to be measured in that case where it would have been a little compartment instead of a free combustion.

In the end it was decided to carry out the lab scale and third scale tests under a hood.

Different alternatives of fuel containers have been considered. They should fulfil some preconditions

1. No decomposition products visible in the gas chromatogram
2. No contamination with combustion products from prior tests
3. Easy to clean or cheap to obtain to have a new container for each test

Ceramic bowls as well as mouldings from aluminium foils have been considered, the latter were found to be suitable.

These mouldings are 2cm in height and an upper diameter of 7cm conical decreasing till the bottom to 4,5cm.

The plastics have been stored in the third scale tests during combustion on a special table. At the combined combustion with accelerants and at the single combustion of the accelerants bowls made of stainless steel have been used protected with aluminium foil from too much radiant heat.

Overview pictures of the test setups are given in picture 6.2-2 on page 44.

3.5 Processing the Lab Scale Tests

All tests have been carried out under ambient conditions under a hood. No controlling of ventilation, temperature nor pressure took place and no extinguishing media has been used. In all tests the sampling procedure was finished when the flames went out.

All samples have been transferred directly after the test was finished into sample jars which were closed gas tight.

In picture 6.2-2 on page 44 a fire test is shown
Table 3.5-1 gives the fuel portion for each test.

Table 3.5-1: Fuel portions

Fuel	Mass or Volume	
	Starting Mass /- Volume	Total Mass /- Volume
Kerosene	10ml	30ml
BBQ Lighter	10ml	30ml
Kerosene	10ml	30ml
Lacknafta	10ml	30ml
BBQ Lighter (Long Term Combustion)	10ml	250ml
Neopolen	20g	100g
Polyurethane Foam	20g	100g
Polyurethane Foam (Long Term Combustion)	20g	800g

In order to keep fluctuations in flame height and heat radiation as low as possible a smaller portion was ignited at the beginning (starting mass) and subsequently depending on the burning rate fuel was added continuously until the total mass was reached.

3.5.1 Single Combustion

The tests with barbecue lighter and kerosene were carried out with 30ml of fuel each. The aluminium foil mouldings mentioned earlier were used as fuel containers. After the ignition was provided by a propane gas burner the sampling apparatus was turned towards the flame zone. In the long term combustion tests this was the point where the water jet pump was turned on.

With both fuels the burning intensity was increasing after a short startup phase until the liquid phase was boiling. Just shortly before all of the fuel was burnt up the visual intensity of the fire decreased.

In parallel tests with Lacknafta and diesel fuel were carried out for reasons of comparison.

The fire behaviour of the polymers was something different. At the beginning there was a longer period until they burnt spontaneously which could come from the flame retarder. Neopolen lost very rapidly stability and became a viscous liquid. This process took something longer in the case of polyurethane foam but was with the same result in the end. The intensity of the fire increased more and more until all of the plastic was liquefied. Subsequently Neopolen burnt up with a nearly constant intensity. In the case of the polyurethane foam a floating cover of charcoal was formed expanding over the whole liquid in the end. By that the combustion handicapped itself since the transfer of fuel into the gaseous phase was decreased until the flames went out from their own.

Fuel was added continuously until the total mass was reached during the test.

3.5.2 Combined Combustion

The plastics were put in the moulding and subsequently sucked with the accelerant. Ignition was provided by a propane gas burner.

Sampling started after the material burnt from its own. The plastics sucked with accelerant were added continuously until the total mass was reached.

For comparative reasons tests with Lacknafta, Neopolen and polyurethane rigid foam have been carried out in parallel.

3.6 Third Scale Tests

All tests have been carried out under ambient conditions under a hood. No controlling of ventilation, temperature nor pressure took place and no extinguishing media has been used. In all tests the sampling procedure was finished when the flames went out.

All samples have been transferred directly after the test was finished into sample jars which were closed gas tight.

Picture 6.2-7 on page 48 shows different tests.

Table 3.6-1 gives the fuel portions for each test.

Table 3.6-1: Fuel portions

Fuel	Mass or Volume
Heptane	0,5 l
Lacknafta	0,5 l
Neopolen	2 kg
Polyurethane Foam	2 kg
Volvo 245 Seat	2 kg
Volvo 245 Seat	2 kg

3.6.1 Single Combustion

Single combustions have been carried out with the plastics polyurethane foam and Neopolen only whereby the whole fuel portion was ignited at once. After ignition was provided by a propane gas burner the sampling apparatus was turned towards the flame zone.

The burning intensity increased after a short startup phase enormously at both fuels. Just shortly before the whole fuel was consumed the visual intensity decreased.

3.6.2 Combined Combustion

Even here the whole fuel portion was ignited at once. The accelerants were placed in a pit which was cut in the block shaped plastics.

Sampling started after the fuels burnt from their own.

3.7 Large Scale Tests

The sampling apparatus was placed inside the car at a head supporter prior to ignition. The cars were ignited by different methods (see. Table 6.2-3 on page 53) and have been extinguished with water directly after reaching the flashover stadium inside the passenger cell. No further extinguishing media were applied and it was ensured that no water came in direct contact with the sampling unit. Wiping samples were taken from window panes still intact after the fire with tweezers and glas woll. For comparative reasons samples from the plastics inside the car were taken after the fire. All samples have been transferred directly after the test was finished into sample jars which were closed gas tight.

Pictures 6.2-8 till 6.2-13 on pages 49 till 51 show the tests.

4 Review and Discussion of the Results

4.1 General

First of all should be a definition of terms. Whenever a peak should occur in a chromatogram it will be mentioned as „substance is detected“.

The review was done according to the four topics as following:

1. Changes in the detected substances when detecting single and combined combustion
2. Changes in the detected substances when the test scale was changed
3. Changes in the detected substances when the plastic was combusted with different accelerators
4. Comparison of the results from the 1/1- scale tests

According to the four topics mentioned above the chromatograms have been reviewed as shown in table 4.1-1.

Table 4.1-1: Comparison of the chromatograms

	GC / MS- Files	Picture / Page
To 1.	42, 45, 47	6.2-16 / 57
	43, 45, 49	6.2-17 / 58
	42, 44, 46	6.2-18 / 59
	43, 44, 48	6.2-19 / 60
	78, 79, 80	6.2-20 / 61
	68, 69	6.2-21 / 62
	68, 81	6.2-22 / 63
	82, 85	6.2-23 / 64
	83, 85	6.2-24 / 65
To 2.	44, 68	6.2-25 / 66
	45, 85	6.2-26 / 67
	68, 89	6.2-27 / 68
	68, 90	6.2-28 / 69
To 3.	47, 49, 82, 83	6.2-29 / 70
	46, 48, 69, 79, 81	6.2-30 / 71
To 4.	64, 65, 66, 86, 87, 88, 91	6.2-31 / 72; 6.2-32 / 73

To identify a substance it was envisaged to use the support of a correlation of boiling points and retention time (see chapter 4.2) in addition to the review of the mass spectra. However it became obvious that due to the very low concentrations the suggestions of the library search of the PC were connected with a quite large uncertainty. The identification suggestions made by the PC are to be considered as advices only. A further evaluation is necessary. Attempts of the identification of the detected substances would be of a speculative matter.

For these reasons just one mass spectrum is reviewed here as an example. The spectrum comes from a sample of diesel fuel and is shown in picture Bild 6.2-33 on page 75. The retention time of the peak is 24,158 min from the chromatogram in pictures 6.2-34 and 6.2-35 on pages 76 and 77.

Obviously there are regular and strong signals up to a m/z - ratio of 183, differing in most cases by 14 units from each other. Mainly in the lower m/z - range double signals occur with the characteristic difference of 14 as well. The intensities of the peaks at $m/z = 71$ (base peak) and $m/z = 57$ are strongest and characteristic for fragments of hydro carbons. In the range above $m/z = 183$ only weak signals occur, but a 14-units difference can be recognised up to $m/z = 214$. The highest signal recorded is at $m/z = 268$. This signal could represent the molecule ion. All other peaks can be associated based on that mass by the help of fragmentation tables. (by help of [25] [26] [27] [28] [29])

The difference of 14 arises from the mass of a CH_2 - radical and the difference of 15 occasionally occurring comes from a methyl radical.

Hetero- atoms are very unlikely to occur, since there are usually no such in diesel fuel except from perhaps sulphur or nitrogen.

The suggestion of the PC did contain just one substance with a relative molecular mass of 268. It was named as 2,6,10,14- tetramethyl- pentadecane. The synonym is pristane. It is known from the literature, that pristane occurs in diesel fuel and that it eluates next to the C_{17} - n- alkane (see chapter 4.2). [32] [37] Even this condition was fulfilled and so the suggestion was accepted.

4.2 The Correlation between Boiling and Retention Time

Due to the non- polarity of the column used the separation of a mixture of one group of substances takes place according to the boiling points of the single components.

Basically the signals in the gas chromatogram of the combustion products are substantially weaker than they would be from the non- combusted accelerator. For the same reason the fit of the identification suggestions decreases. This effect was tried to minimise as described in chapter 3.2.3 by increasing the vapour pressure and optimising the volume of the extraction agent in the comparative analysis.

The correlation of boiling points and retention time was intended to have a closer look on in order to minimise uncertainties. To do so in pre- tests a mixture n- alkanes

was introduced and the retention times have been saved. It is known from the diesel fuel that it contains a wide range of homologues of n- alkanes, approximately from octane (C_8H_{18}) up to hexacosane ($C_{26}H_{54}$). Their concentration is that big that the corresponding peaks mainly in the range of the heavier n- alkanes become obvious. The peaks of C_{17} and C_{18} are doubled since there following to the n- alkanes pristane respectively phytane (2,6,10,14- tetramethyl- hexadecane) eluate. [32] [37]

The separation sharpness of the latter peaks can be considered as a measure for the separation performance. At the same time both peaks allow for a safe orientation within the chromatogram. The retention times of the n- alkanes from the pre- tests match very good with them out of the diesel fuel. Based on the homologous n- alkanes now a curve of the boiling points against the correlating retention times has been created. This curve is given in picture 6.2-14 on page 55.

The correlation of boiling points and retention times can be approximated linear with sufficient correctness. Two online databases have been used to get the boiling points of the desired substances. [17], [18]

An additional tool for the identification is the advantage from this correlation. The fit of the calculated to the actual boiling point can be used as a criterion beside the review of the mass spectra. Substances of similar polarity will have similar retention times in the gas chromatogram and therefore similar boiling points as well. This principle however is right exactly within one group of substances only e.g. for the n- alkanes in this case. For other groups of substances a similar correlation would have to be created.

But there is still another advantage by the notification of the retention times of the n- alkanes. By that the transmission of the retention times of all substances detected onto another gas chromatographic system becomes possible when applying the Kovats- indexes. Chromatograms created with different gas chromatographic parameters can be compared with this tool which was impossible when only applying the retention times. [32]

In table 6.2-6 on page 55 all retention times of the n- alkanes acquired under the conditions of these analyses are given.

4.3 Changes in the Substances detected when comparing single and combined Combustion

It is obviously that the chromatograms acquired from single and combined combustion differ quite much in partial. This fact supports the supposition that in a combined combustion even other products are formed compared to them being formed in the single combustion. At least a couple of these substance could therefore be an advice to guiding substances for the detection of an accelerator. It is noted hereby that these results have been observed only in the comparison of the chromatograms from the lab- scale and third scale tests.

4.4 Changes in the Substances detected when changing the Test Scale

The relevant chromatograms have to be reviewed towards similarities in the peak sequence for this viewpoint. Table 4.4-1 gives the results of the comparison.

Table 4.4-1: Results of the comparison between the chromatograms

GC / MS- Files	Picture / Page	Similarities?
44, 68	6.2-25 / 77	no
45, 85	6.2-26 / 78	no
68, 89	6.2-27 / 79	no
68, 90	6.2-28 / 80	no

No similarities at all can be found in the peak sequence. Subsequently a comparison of the tests in different scales is impossible.

4.5 Changes in the Substances detected when the Plastics are combusted with different Accelerators

When reviewing these chromatograms changes in the peak sequence are interesting. Table 4.5-1 gives the results of the comparison.

Table 4.5-1: Results of the comparison between the chromatograms

GC / MS- Files	Picture / Page	Changes in the peak sequence?
47, 49, 82, 83	6.2-29 / 81	yes
46, 48, 69, 79, 81	6.2-30 / 82	yes

Based on the changed peak sequence it can be stated that with the same plastic but different accelerator other combustion products are formed.

Comparison of the large Scale Tests

Table 4.6-1 gives the results of the comparison.

Table 4.6-1: Results of the comparison between the chromatograms

GC / MS- Files	Picture / Page	Characteristics detected?
64, 65, 66, 86, 87, 88, 91	6.2-31 / 83; 6.2-32 / 84	Yes, accumulation of peaks in the range of retention time from 27 min to 28,5 min, similar peak sequence

The similarity in the peak sequence indicates the same substances in the sampling material. By that the supposition is allowed that at least the large scale tests are allowed for direct comparison. Even the reproducibility seems to be very good. This is a surprising result when keeping the different car models, manufacturers and their year of production in mind. Otherwise it can be supposed, that the formation of combustion products is dominated to a large extend by the most applied plastic in each case.

4.7 Ability to proof Fire Accelerators in a combined Combustion

The chromatograms of the combustion products of all the applied plastics together with one applied accelerator have been considered at once prepare the proof of accelerators. Peaks had to be found occurring in the chromatograms arising from the samples from the combined combustion but not in them from the plastics. Additionally a sufficient range without peaks due to the fluctuation in retention time had to be

found in the chromatograms of the plastics. Therefore the number of suitable peaks reduced considerably. A listing of the elected peaks is given in table 6.2-5 on page 54.

The applied method of the combined combustion of an accelerator and another fuel is seldom when it comes to practice. Usually the accelerator has a more or less large pre- burning phase until the intended effect of ignition of another fuel takes place. Additionally very often the ventilation conditions are not as good as in the lab tests which leads to a more incomplete combustion. By that more products significant for an accelerator can be expected. These facts should simplicate the proof of fire accelerators based on the analysis of soot.

5 Conclusive Considerations

5.1 General

The report shows that the research area of combustion gas and soot analysis has a big potential and is possibly hardly explored. It has been found out that the applied fuels under the test conditions will form to a large extend identical combustion products when repeating the tests. The transmission of the results from the lab scale to the large scale tests however is insufficient and uncertain.

The proof of fire accelerators in cases of arson is of special interest as becoming obvious in a presentation of the research results on a meeting of the reference group to this work. Information acquired from the analysis of soot and condensate would be very helpful and would support the state of the art trace analysis.

The SPME had found out to be suitable for the detection of substances suspicious to come from flammable liquids however, their low concentration doesn't allow for identification. Therefore the transmission of the results into practice is impossible yet at this moment.

For that reason this work only can represent a beginning. In order to use the results in a practical application the investigations are to be extended and the techniques applied are to be further optimised.

Some proposals are given in the following chapter.

5.2 Proposals for further Work

The most important goal is the increasing of the concentration of the analytes. Two different methods seem to be suitable:

1. The use of another process for sampling, sample preparation and sample introduction into the GC. The application of a cartridge filter resistive up 300°C has

been discussed within the reference group. [39] [40] By the collection of the glass wool loaded with soot and condensate at the fire scene a further increase of temperature under vacuum conditions with a direct line of the cartridge to the GC becomes possible. The maximum allowed temperature mustn't be higher than the temperature of the inlet system of the GC. Otherwise the prevention of uncontrolled decomposition processes can't be ensured. The sampling without glass wool directly into the filter cartridge can be considered as an alternative depending on the state of the sampling material.

2. The application of the Stir Bar Sorptive Extraction (SBSE) could as well cause an increased concentration. The method is similar to the SPME however the sensitivity of this method is up to 1000 times improved. (according to [38] [53]) This effect is based on the improved phase ratio in the extraction due to a thicker coating of the stationary phase.

The possibility of a headspace analysis with SBSE is still uncertain since the method is quite new and Merkator [53] only did extraction from the liquid phase. At this point it has to be assessed whether or not the disadvantages of using a solvent can justify the advantages expected.

The impact of changed ventilation conditions related to the qualitative composition of fire gases and soot has to be clarified.

Further fuels and changed fuel compositions have to be considered in order to get results useful for practical work.

Suitable parameters to simulate real fires have to be defined and tests under these conditions must be carried out. These parameters could be acquired from CFD/ calculations and would further increase the reliability. [52]

A calibration with external standards would be very intensive in time and costs since the mixtures are quite complex as turned out in the tests. Standards for each component would have to be used. A simplification which requires much less effort without too much mistake is proposed by P. Basmer et. al.. They describe the concept of the molar response. A wide range of analytes can be covered with a few external standards by setting equal the ionisation cross section of chemical similar substances.

Basmer et.al. used a calibration with benzol for all occurring aromatic components for example. [1]

6 Appendix

6.1 List of Literature

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6.2 Charts and Pictures



Schüler bleiben unverletzt

Reisebus ausgebrannt

Bad Dür rheim (lsw). Ein Reisebus mit 45 Schülern und Betreuern aus dem Raum Leonberg ist am Samstag auf der A 81 in Richtung Singen vollständig ausgebrannt. Verletzt wurde bei dem Feuer, das kurz hinter dem Autobahnkreuz Bad Dür rheim ausgebrochen war, nach Polizeiangaben niemand. Eine Schülerin wurde wegen Herzkreislaufproblemen im Krankenhaus ambulant behandelt. Rund zwei Stunden lang war die Autobahn wegen Lösch- und Bergungsarbeiten gesperrt. Die Schüler der Klassen 10 bis 12 waren auf dem Weg zum Skifahren in die Schweiz, als der Motor des Reisebusses vermutlich wegen eines technischen Defekts in Brand geriet. Der Sachschaden wird auf etwa 50 000 Euro geschätzt.

Picture 6.2-1: Coach fire, Relation of damage extend and time until emergency response measures take effect at the scene
(Source: www.zoomies-place.de)



Picture 6.2-2: Sampling devices; top left in lab scale, top right in full scale, bottom in third scale tests



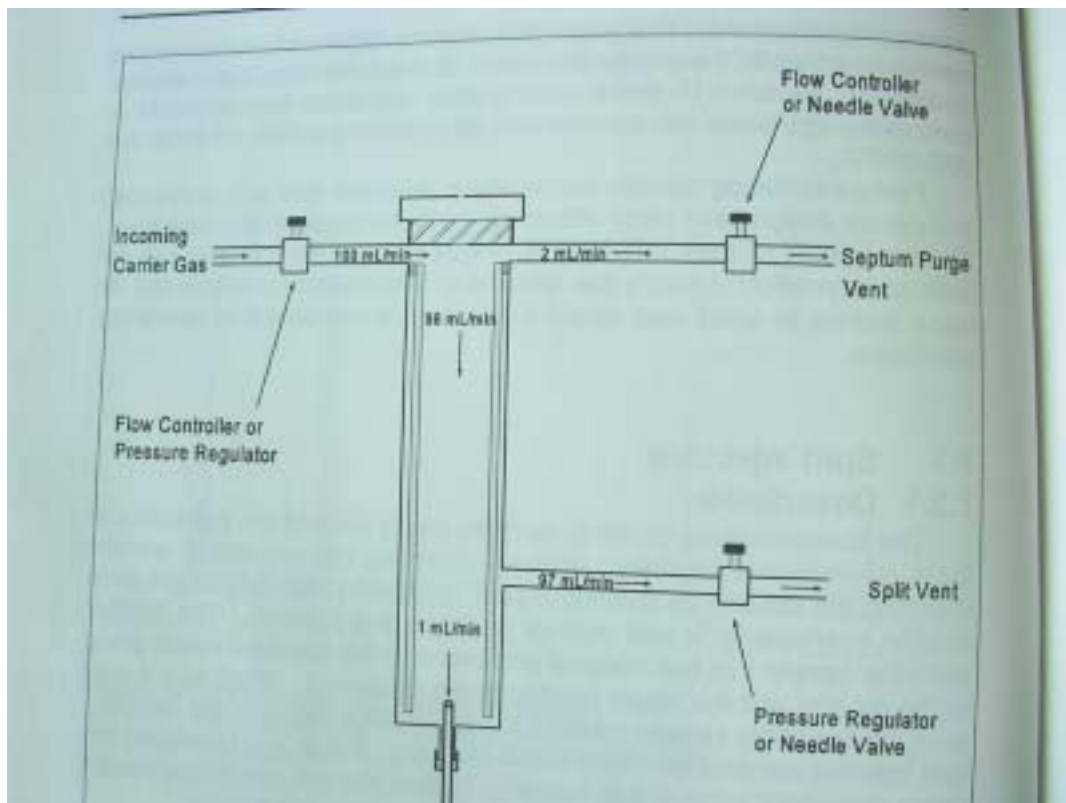
Picture 6.2-3: Overview of the extraction unit with water jet pump and safety washing bottle



Picture 6.2-4: Introduction of the SPME- fibre into the vacuum system



Picture 6.2-5: Vacuum connector with filter



Picture 6.2-6: Carrier gas system of the gas chromatograph at the inlet unit (from [26])



Picture 6.2-7: Fire tests in the third scale; top left: Neopolen; top right: polyurethane foam and heptane; bottom: Volvo 245 model car seat



Picture 6.2-8: Full scale fire test, Volvo XC 90, Model 2003



Picture 6.2-9: Full scale fire test, Volvo XC 90, Model 2003



Picture 6.2-10: Full scale fire test, Volvo V70, Model 2004



Picture 6.2-11: Full scale fire test, Opel Kadett, Model 1975



Picture 6.2-12: Full scale fire test, Opel Kadett, Model 1975



Picture 6.2-13: Full scale fire test, Saab 900 GLi, Model 1984

Table 6.2-1: Tests carried out in lab scale

Lab scale tests			
No.	Fuel	Ignition source	GC/MS-file
1	Diesel, single combustion	Propane gas burner	36, 39
2	Lacknafta, single combustion	Propane gas burner	41
3	Kerosene, single combustion	Propane gas burner	42
4	BBQ- lighter, single combustion	Propane gas burner	43
5	Polyurethane foam, single combustion	Propane gas burner	44
6	Neopolen, single combustion	Propane gas burner	45
7	Polyurethane foam + Kerosene	Propane gas burner	46
8	Neopolen+ Kerosene	Propane gas burner	47
9	Polyurethane foam + BBQ- lighter	Propane gas burner	48
10	Neopolen+ BBQ- lighter	Propane gas burner	49
11	Long term combustion Polyurethane foam, single combustion	Propane gas burner	78
12	Long term combustion Polyurethane foam + BBQ- lighter	Propane gas burner	79
13	Long term combustion BBQ- lighter, single combustion	Propane gas burner	80
14	Neopolen resins, Polyurethane foam, Lacknafta	Propane gas burner	84

Table 6.2-2: Tests carried out in third scale

Third scale tests			
No.	Fuel	Ignition source	GC/MS-file
15	Volvo 245 seat, Model 1985	Heptane	89
16	Volvo 245 seat, Modell 1985	Lacknafta	90
17	Polyurethane foam, single combustion	Propane gas burner	68
18	Neopolen, single combustion	Propane gas burner	85
19	Polyurethane foam + Lacknafta	Propane gas burner	69
20	Polyurethane foam + Heptan	Propane gas burner	81
21	Neopolen + Lacknafta	Propane gas burner	82
22	Neopolen + Heptan	Propane gas burner	83

Table 6.2-3: Tests carried out in full scale

Full scale tests			
No.	Fuel	Ignition source	GC/MS-file
23	Volvo XC 90, Model 2003,	Burning candle and cellulose in the glove compartment	87
24	Volvo V70 Kombi, Model 2004	Petrol and burning candle in the car boot	91, 66, 65
25	Saab 900 GLi, Model 1984	Burning textiles in the motor compartment	86, 64
26	Opel Kadett, Model 1975	Manipulation at ignition sticks and petrol line	88

Table 6.2-4: Capillary columns similar to the one used

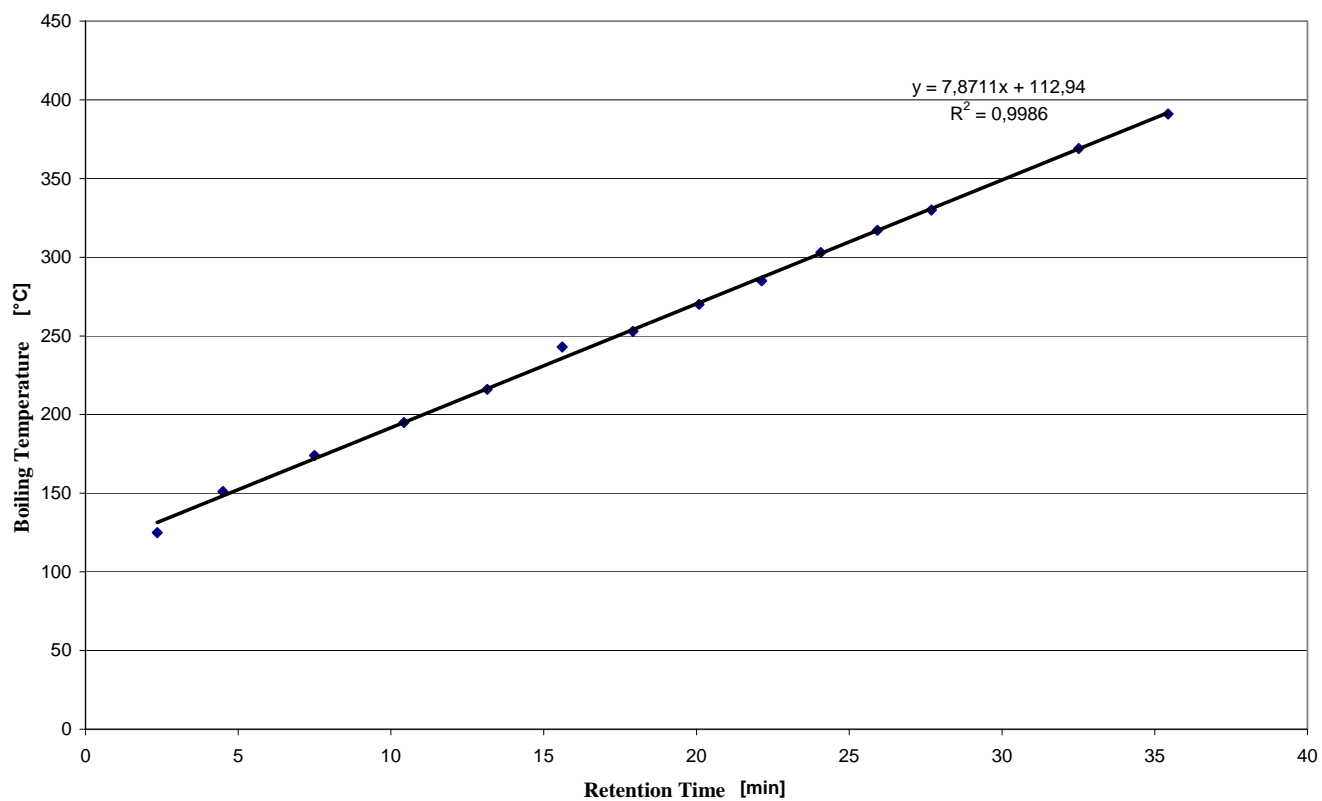
Manufacturer	Stationary phase
J&W Scientific	DB-5ms, DB-5.625
Hewlett- Packard	Ultra-2, HP-5,HP5-TA, HP-5MS
Supelco	SPB-5, BPX5
Resteck	Rtx-5MS
Chrompack	CP-Sil8P

Table 6.2-5: Peaks suspected being special for accelerants in combined combustion

GC / MS-Files	Picture / Page	Retention times of the suspected peaks (min)				
42, 45, 47	6.2-16 / 57	1,831	6,692	16,858	21,212	24,791
		30,602	39,138			
43, 45, 49	6.2-17 / 58	8,798	10,223	13,042	20,341	20,801
		24,601	26,913	32,012	38,013	41,56
42, 44, 46	6.2-18 / 59	5,853	10,476	11,078	19,613	20,801
		23,049	34,26	36,905	40,278	
43, 44, 48	6.2-19 / 60	3,952	7,943	13,944	15,67	17,317
		21,371	30,523	30,603	31,632	37,238
		38,425				
78, 79, 80	6.2-20 / 61	6,343	8,228	26,565	28,702	32,043
		34,957				
68, 69	6.2-21 / 62	8,307	8,576	10,271	10,54	11,11
		15,749	19,993	31,774	32,55	
68, 81	6.2-22 / 63	6,343	16,573	23,192	25,393	25,472
		25,979	27,151	27,388	27,752	28,053
		28,132	29,811	30,381	34,26	36,367
82, 85	6.2-23 / 64	3,414	4,174	5,251	7,943	8,148
		12,741	16,794	28,243	31,885	
83, 85	6.2-24 / 65	8,845	10,524	18,156	29,447	34,973

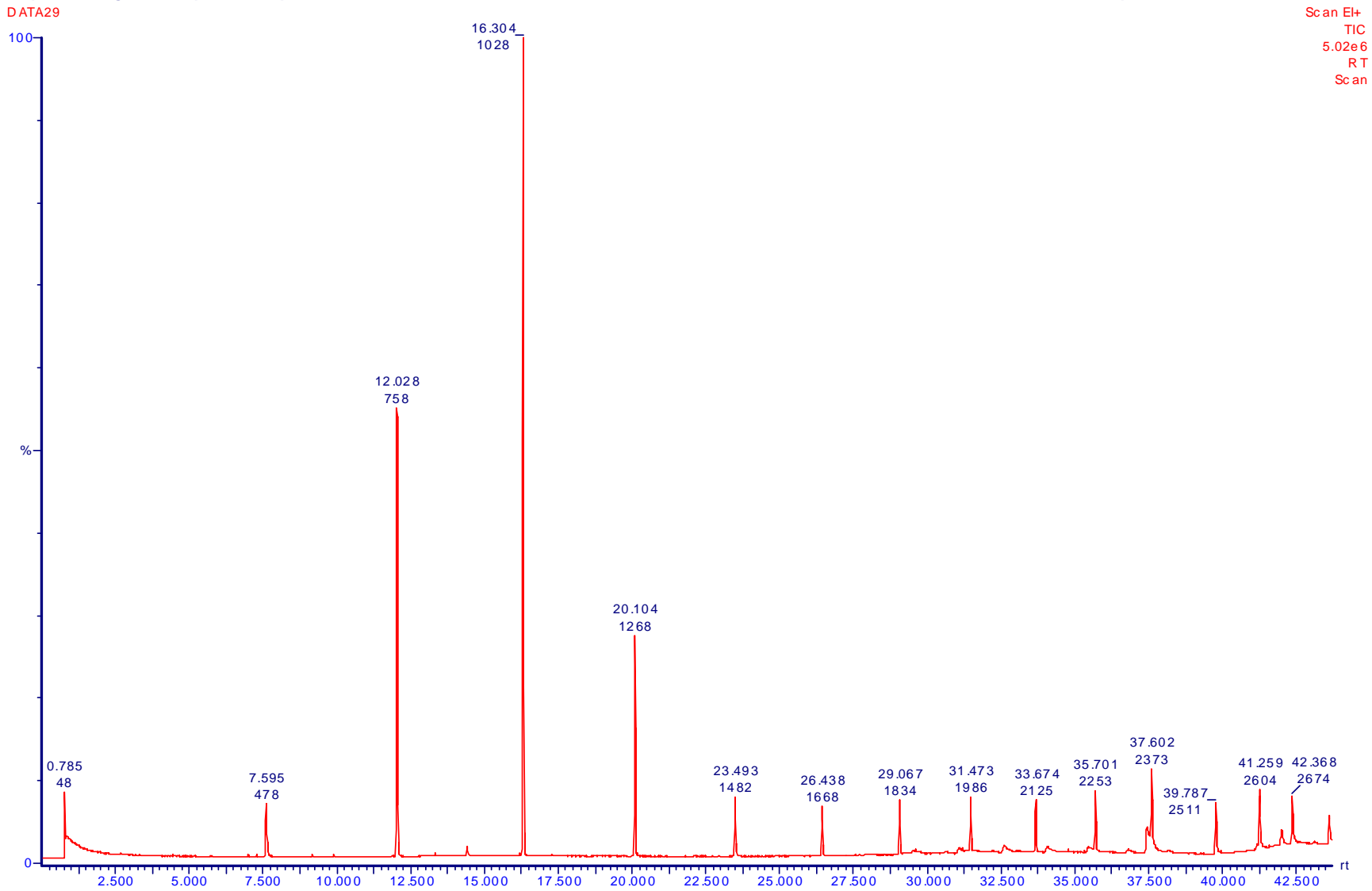
Table 6.2-6: Retention times and boiling points of n- alkanes on the GC- system used

	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄	C ₂₅	C ₂₆
RT (min)	2,351	4,503	7,492	10,421	13,145	15,607	17,919	20,088	22,131	24,071	25,923	27,689	29,368	30,999	32,511	33,991	35,433	36,81	38,22
Kp (°C)	125	151	174	195	216	243	253	270	285	303	317	330	n.s.	n.s.	369	n.s.	391	n.s.	n.s.



Sample ID: Background Sample Glass, Tape, Glasswool,
DATA29

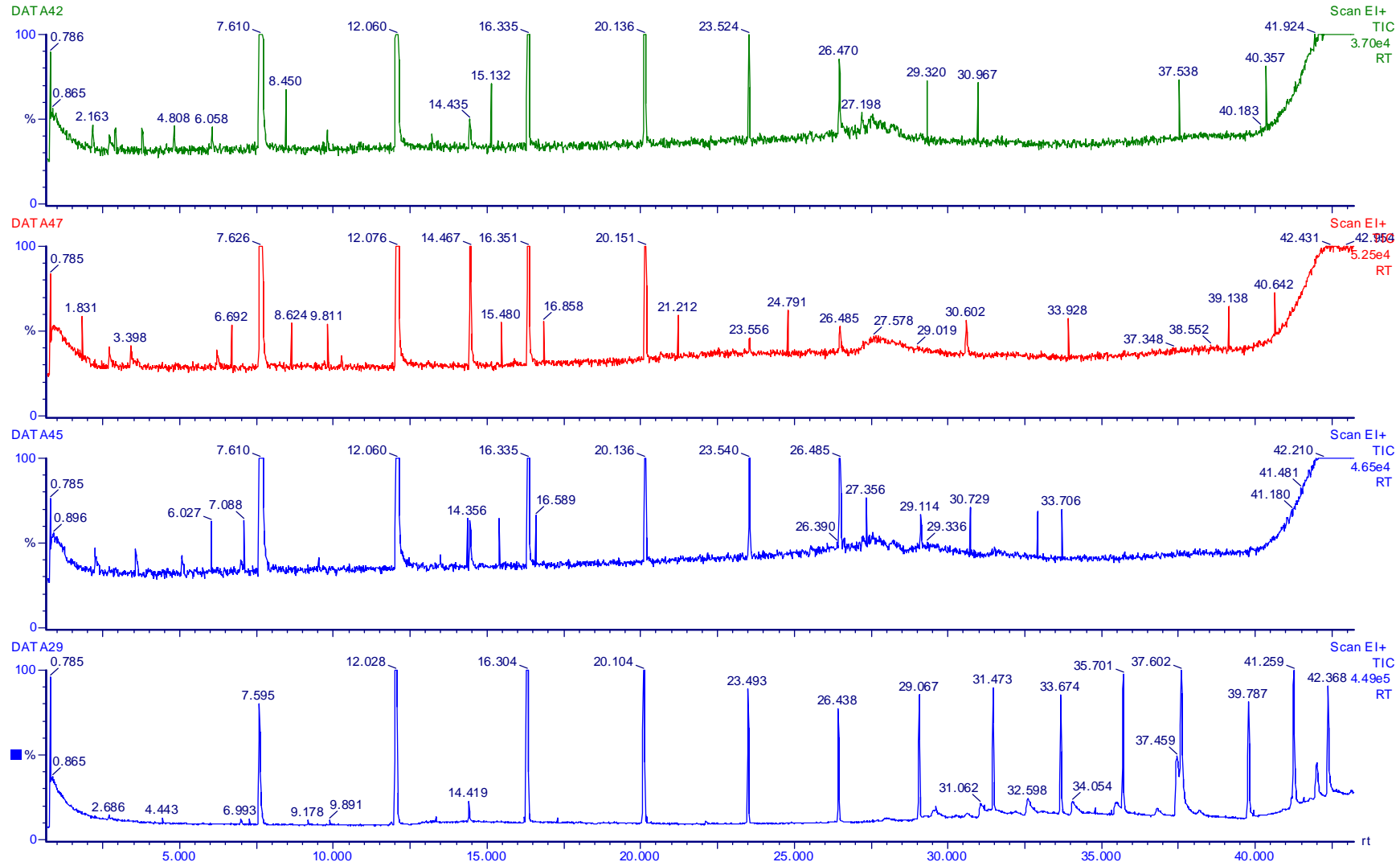
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Picture 6.2-15: Background chromatogramm

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

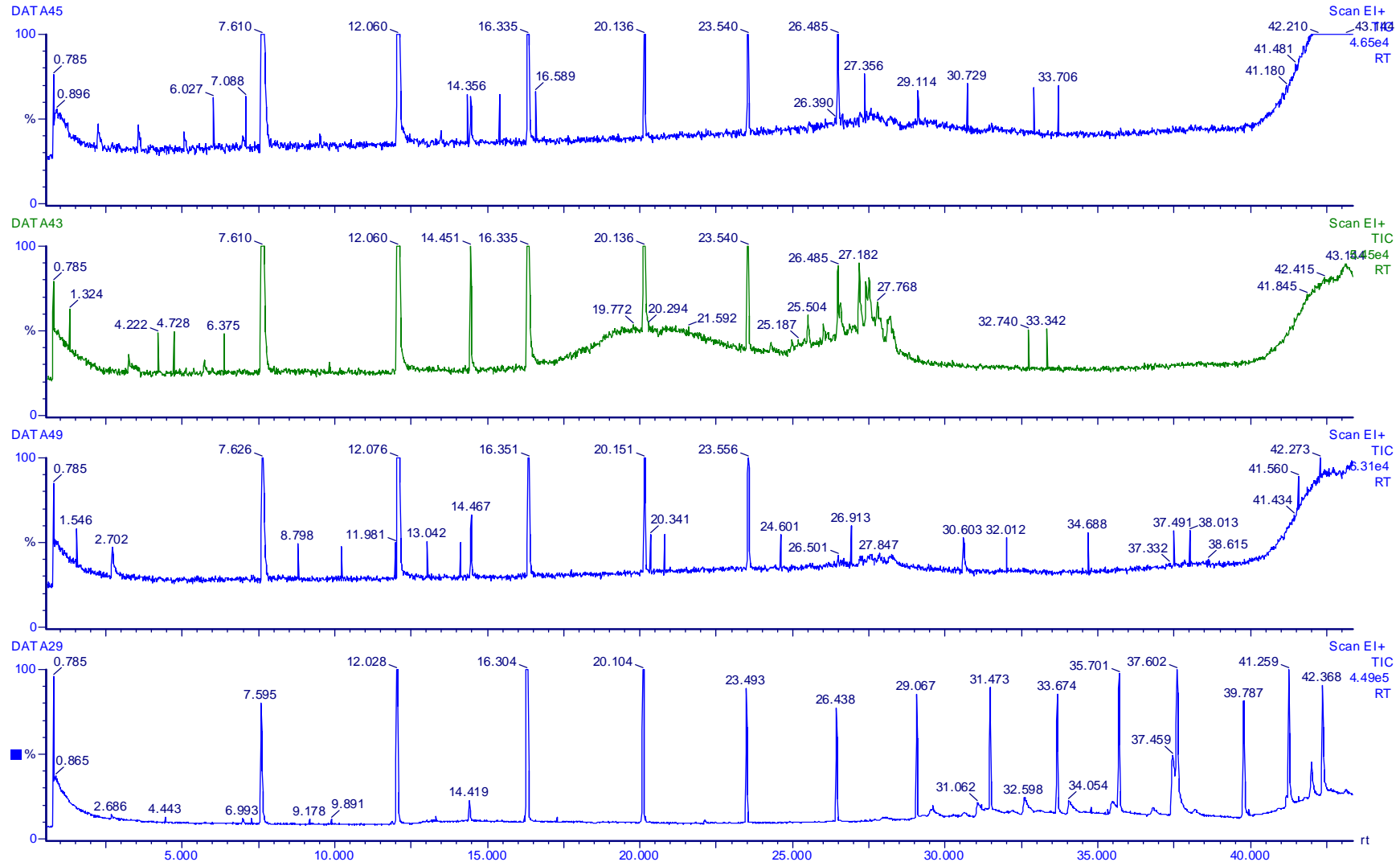
Acquired on 15-Dec-2004 at 18:26:38



Picture 6.2-16: Chromatograms of soot / condensate; Data 42: Kerosene; Data 47: Neoplen + Kerosene; Data 45: Neoplen; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

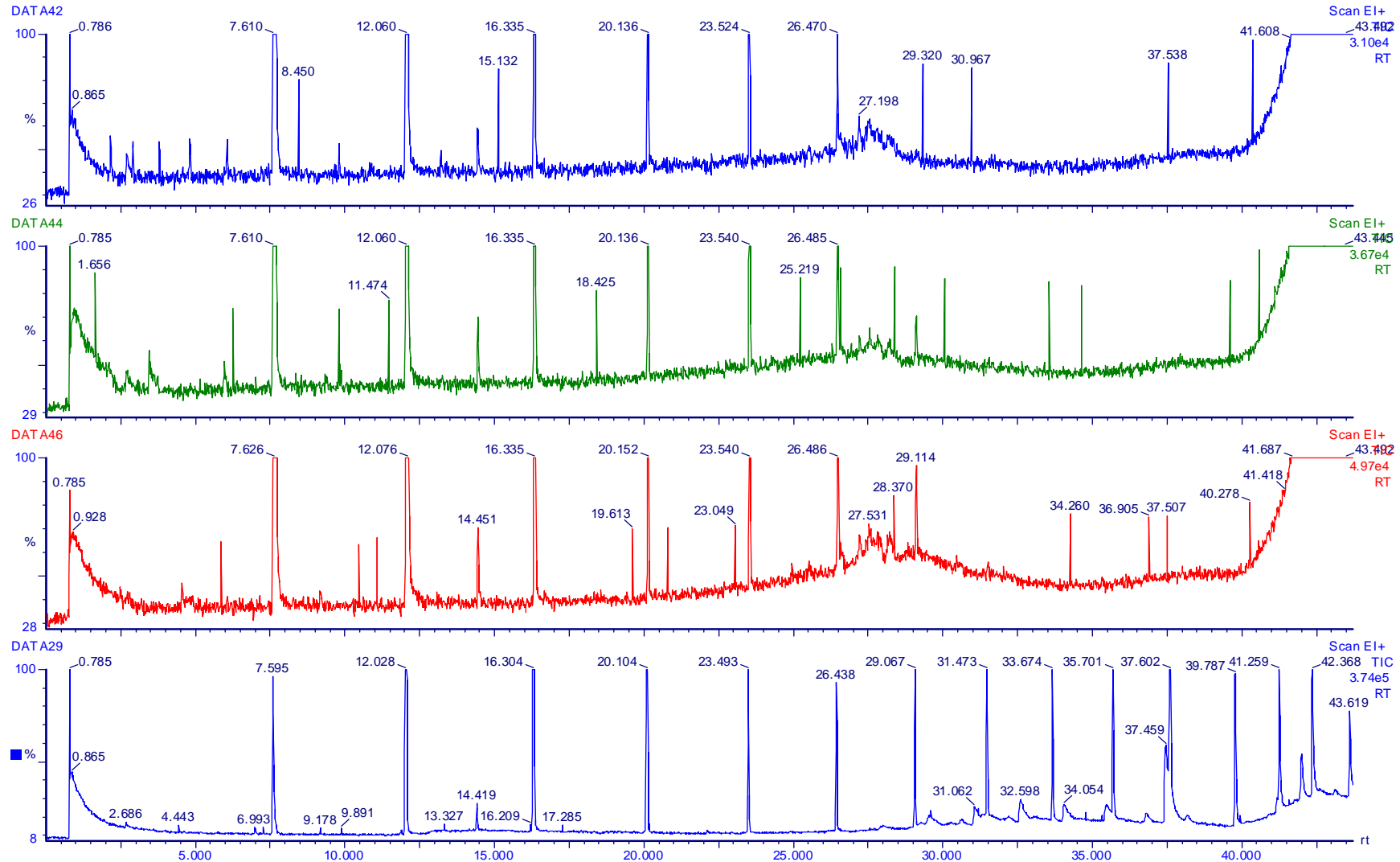
Acquired on 15-Dec-2004 at 18:26:38



Picture 6.2-17: Chromatograms of soot / condensate; Data 45: Neopolen; Data 43: BBQ- lighter; Data 49: Neopolen + BBQ- lighter; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

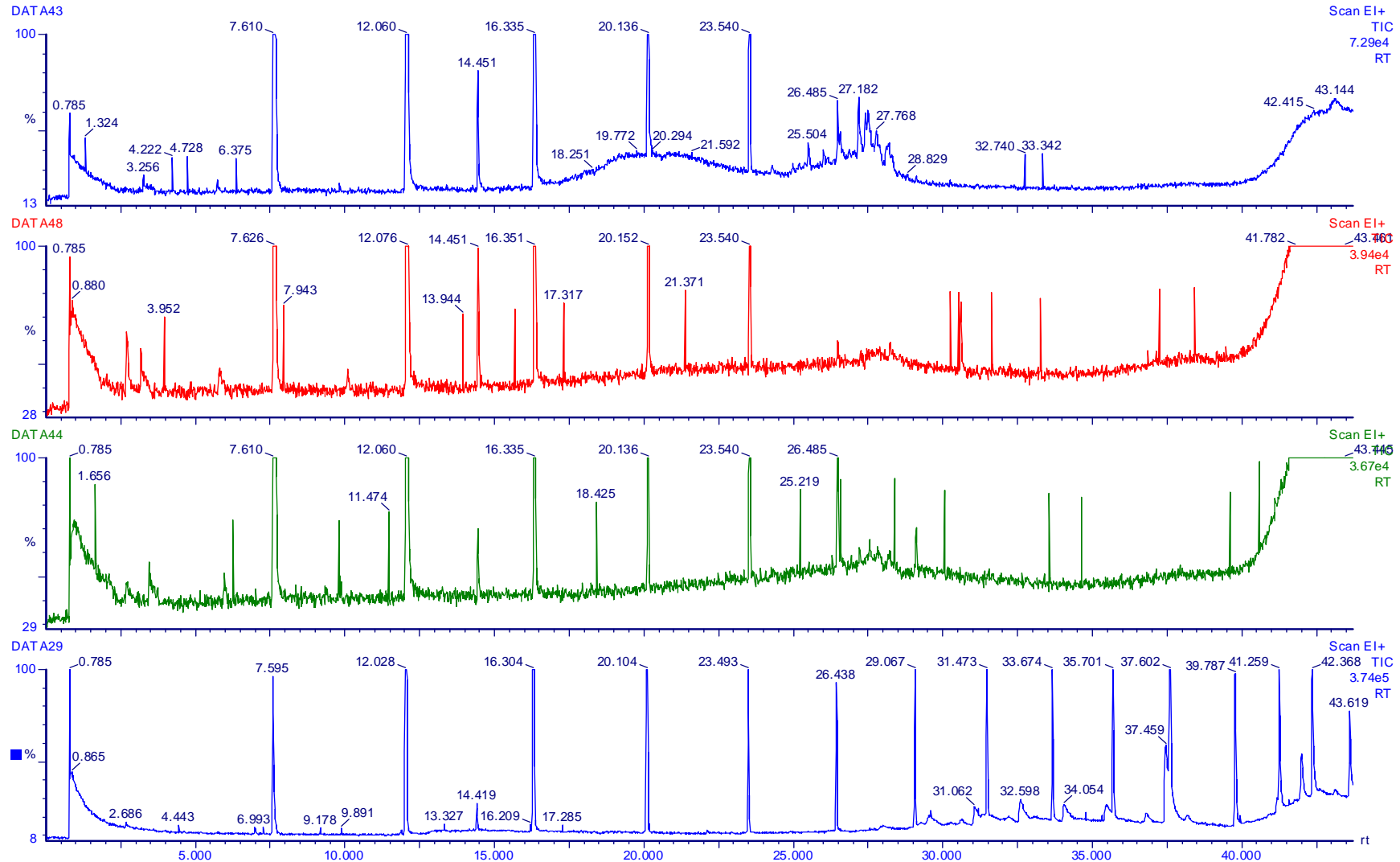
Acquired on 15-Dec-2004 at 18:26:38



Picture 6.2-18: Chromatograms of soot / condensate; Data 42: Kerosene; Data 44: Polyurethane foam; Data 46: Kerosene + Polyurethane foam; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

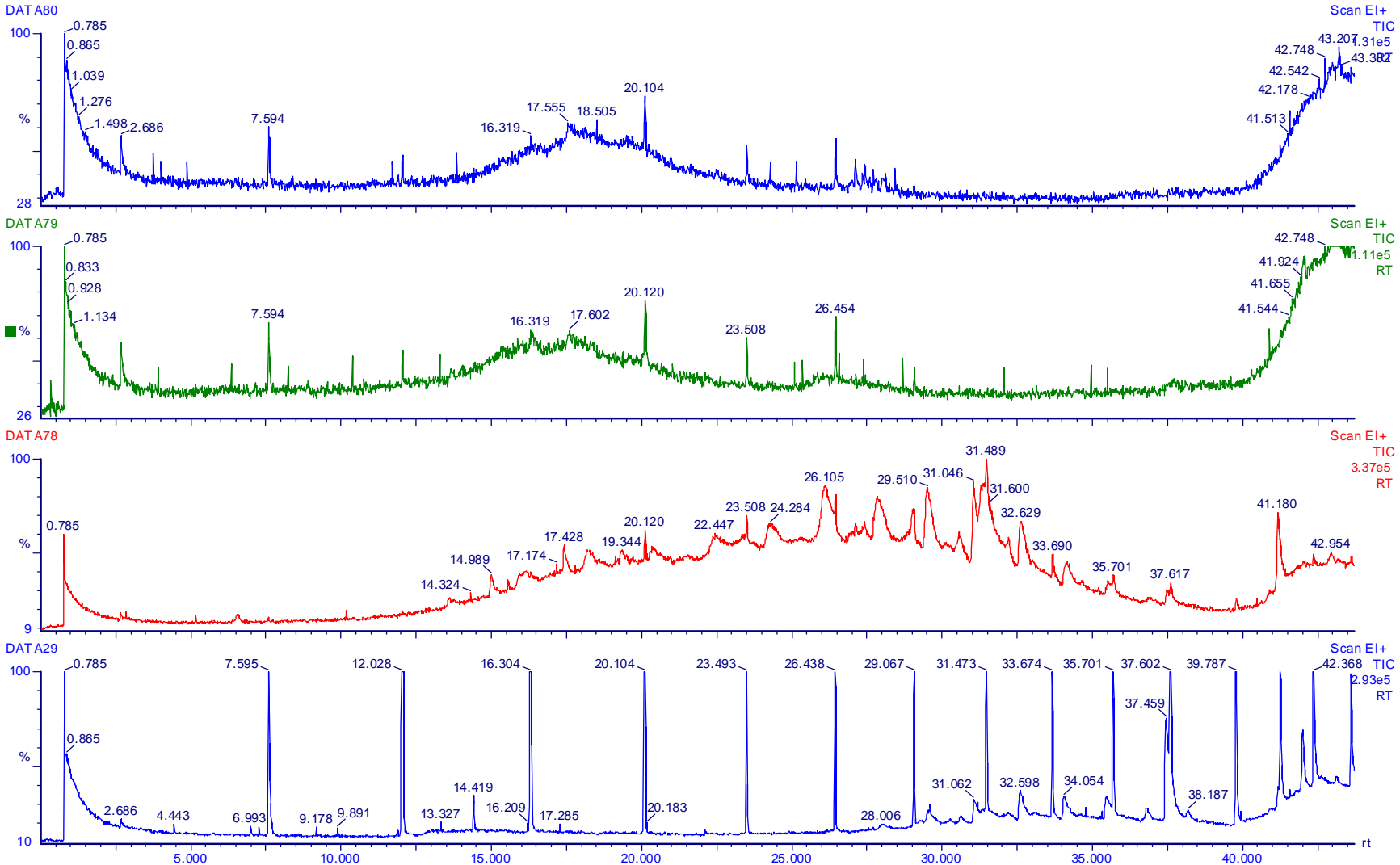
Acquired on 15-Dec-2004 at 18:26:38



Picture 6.2-19: Chromatograms of soot / condensate; Data 43: BBQ- lighter; Data 48: BBQ- lighter + Polyurethane foam; Data 44: Polyurethane foam; Data 29: Background

Sample ID: BASF TDI MD long term comb. with BBQ Lighter, soot, cond. see Data49

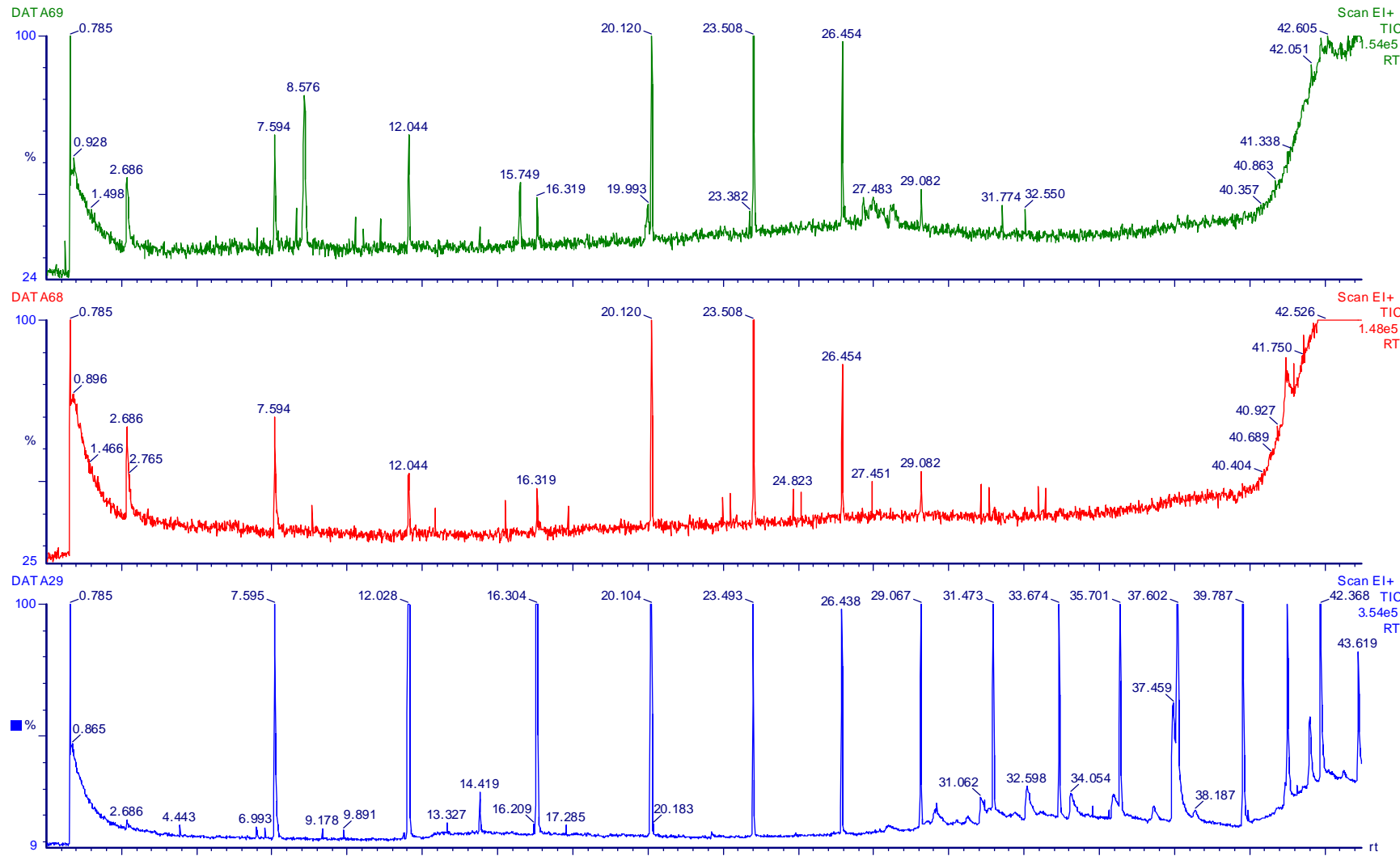
Acquired on 14-Jan-2005 at 12:42:07



Picture 6.2-20: Chromatograms of soot / condensate of the long term combustion;
Data 80:BBQ- lighter; Data 79: BBQ- lighter + Polyurethane foam; Data 78: Polyurethane foam; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

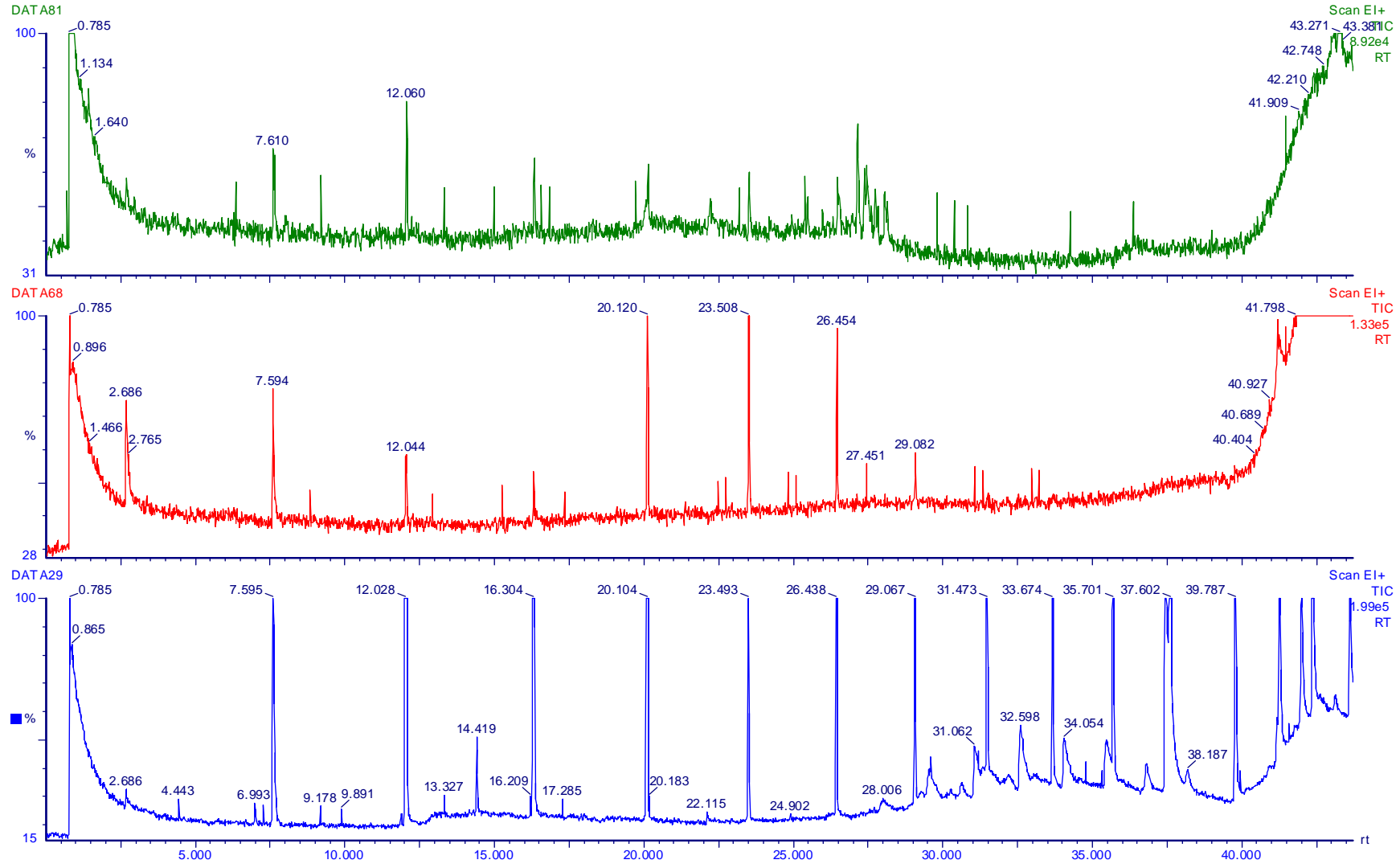
Acquired on 15-Dec-2004 at 18:26:38



Picture 6.2-21: Chromatograms of soot / condensate; Data 69: Lacknafta + Polyurethane foam; Data 68: Polyurethane foam; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

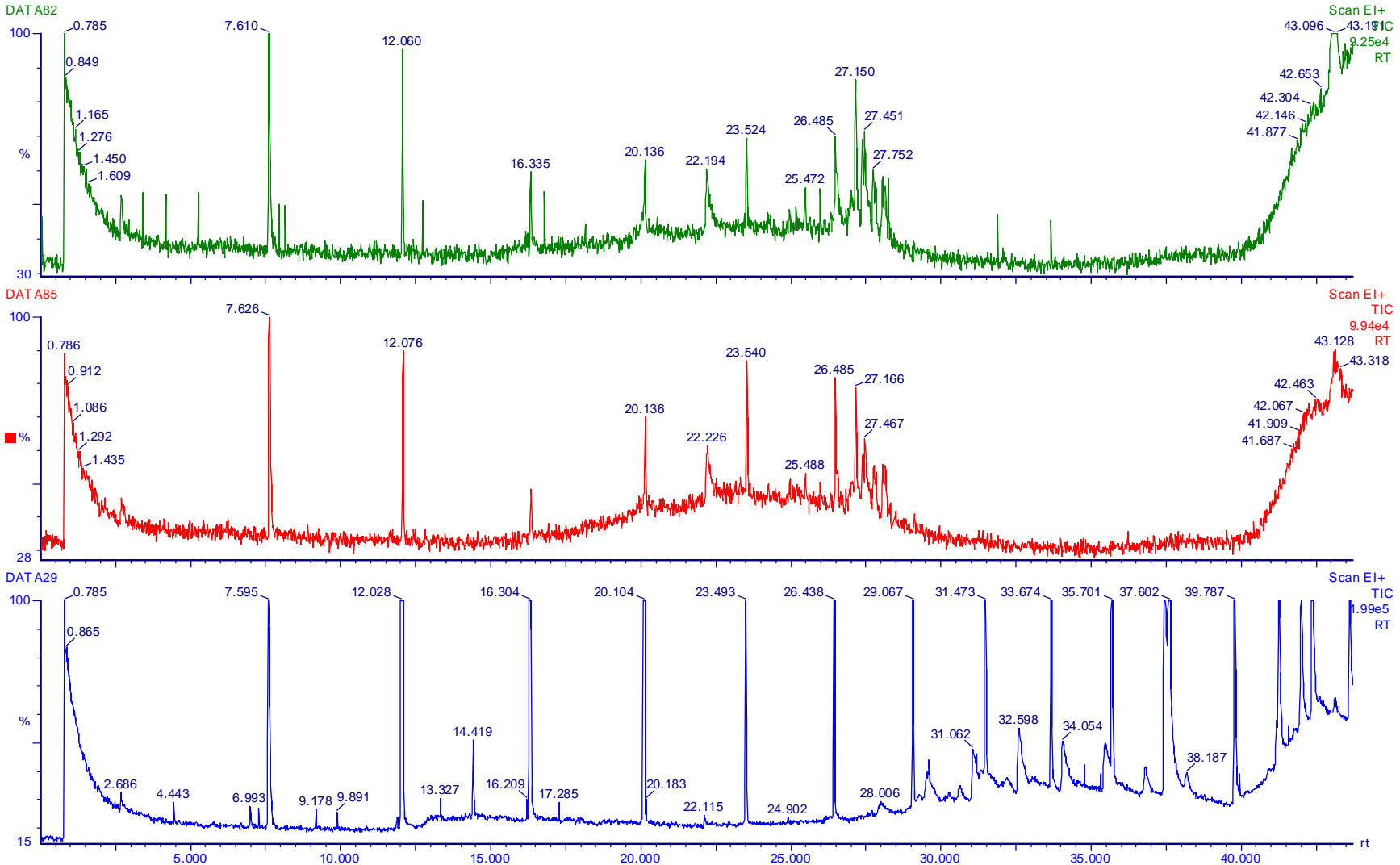
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Picture: 6.2-22 Chromatograms of soot / condensate; Data 81: Heptane + Polyurethane foam; Data 68: Polyurethane foam; Data 29: Background

Sample ID: BASF Neopolen Block, LTH, soot, cond. see Data 49

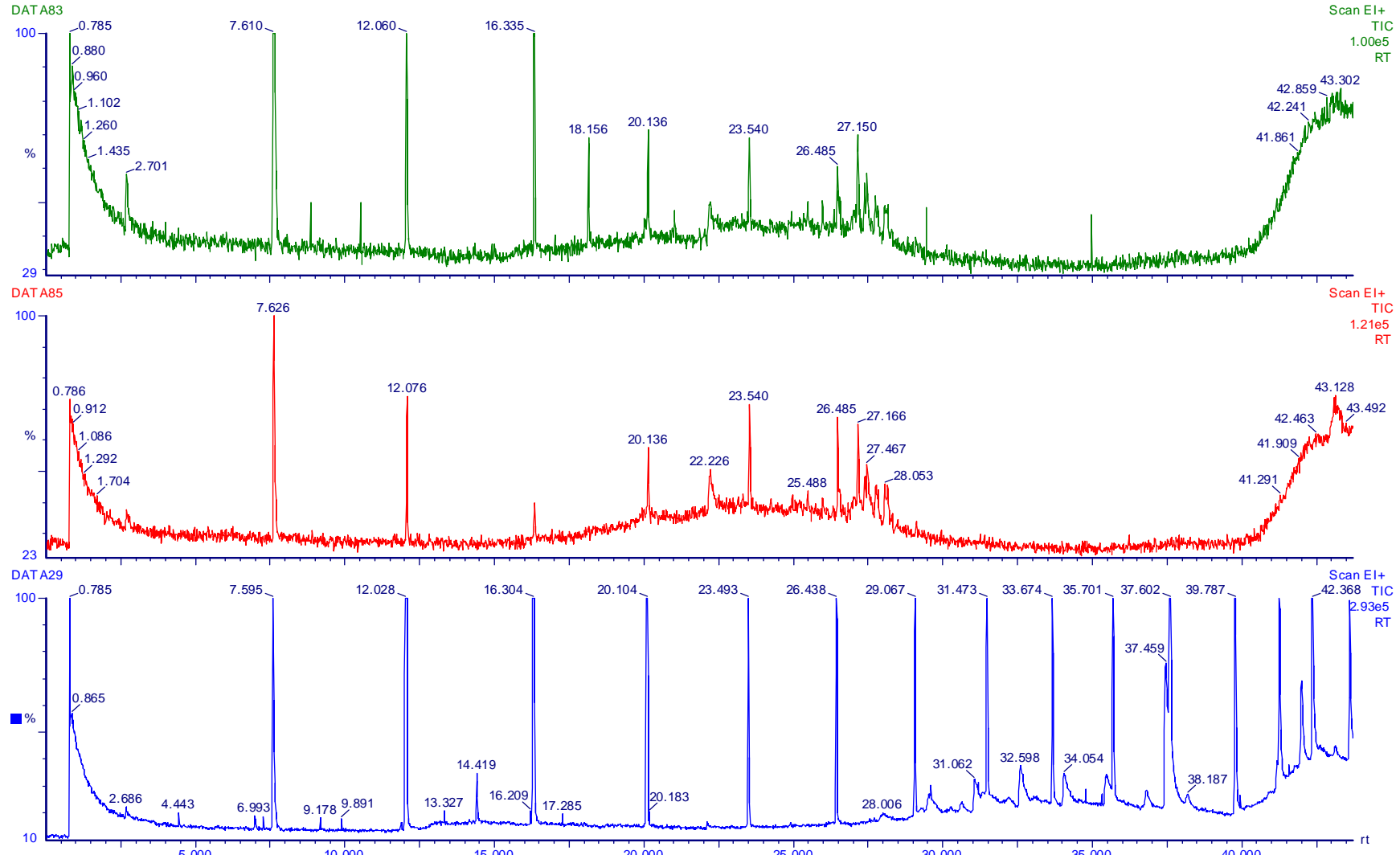
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Picture 6.2-23: Chromatograms of soot / condensate; Data 82: Neopolen + Lacknafta; Data 85: Neopolen; Data 29: Background

Sample ID: Background Sample Glass, Tape, Glasswool,
with Vacuum, 100µm PDMS, 1min

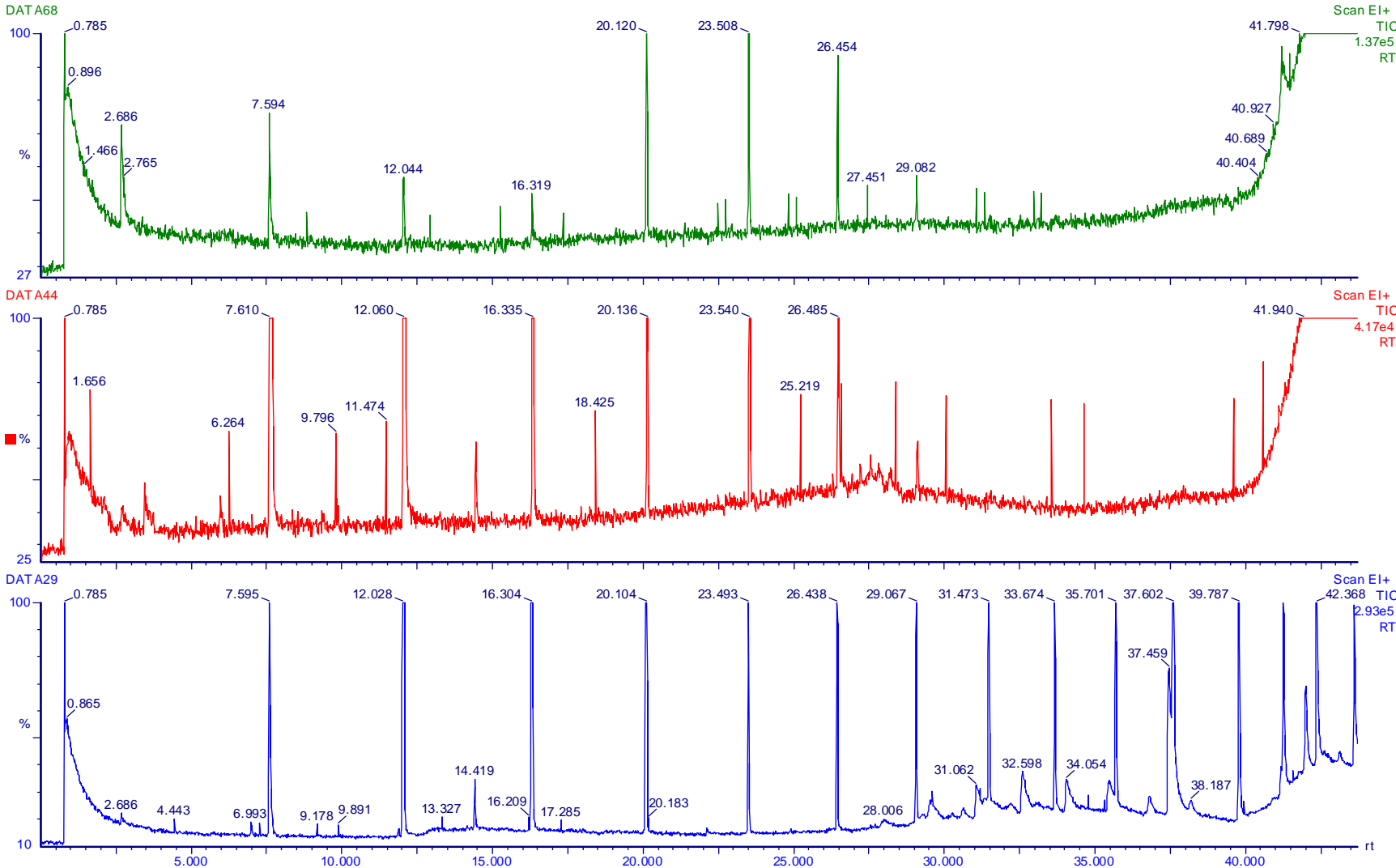
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Picture 6.2-24: Chromatograms of soot / condensate; Data 83: Neopolen + Heptane; Data 85: Neopolen; Data 29: Background

Sample ID: Soot of TDI Foam, sgl. Comb. Vac., Filter, 100my PDMS 20min in Line

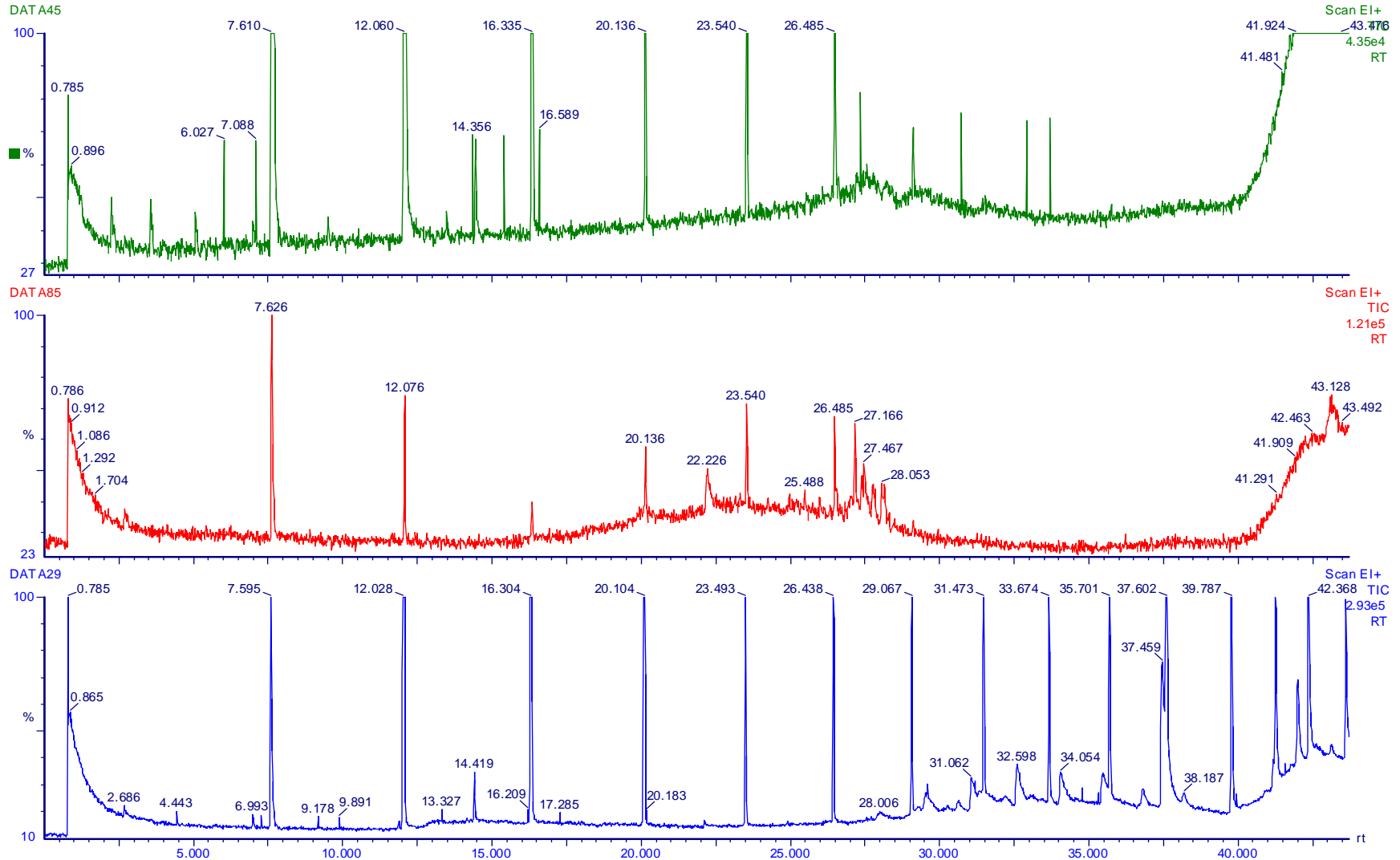
Acquired on 22-Dec-2004 at 14:22:20



Picture 6.2-25: Chromatograms of soot / condensate; Data 68: Polyurethane foam in third scale; Data 44: Polyurethane foam in lab scale; Data 29: Background

Sample ID: Soot of Neoplen, sgl. Comb. Vac., Filter, 100my PDMS 20min in Line

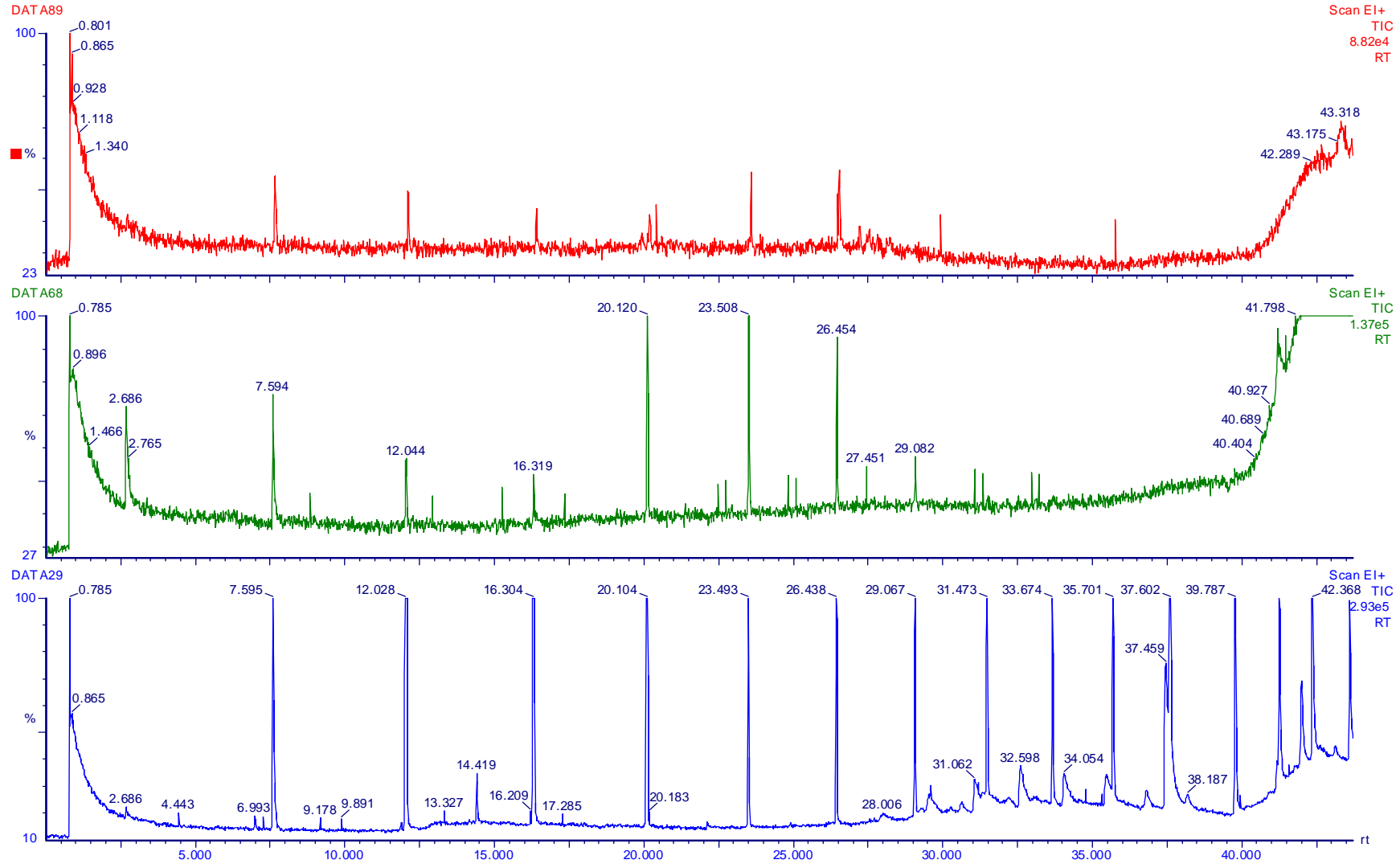
Acquired on 22-Dec-2004 at 15:36:20



Picture 6.2-26: Chromatograms of soot / condensate; Data 45: Neoplen in lab scale; Data 85: Neoplen in third scale; Data 29: Background

Sample ID: Volvo 245 1984 Model, seat + Heptane, LTH, cond. see Data 49

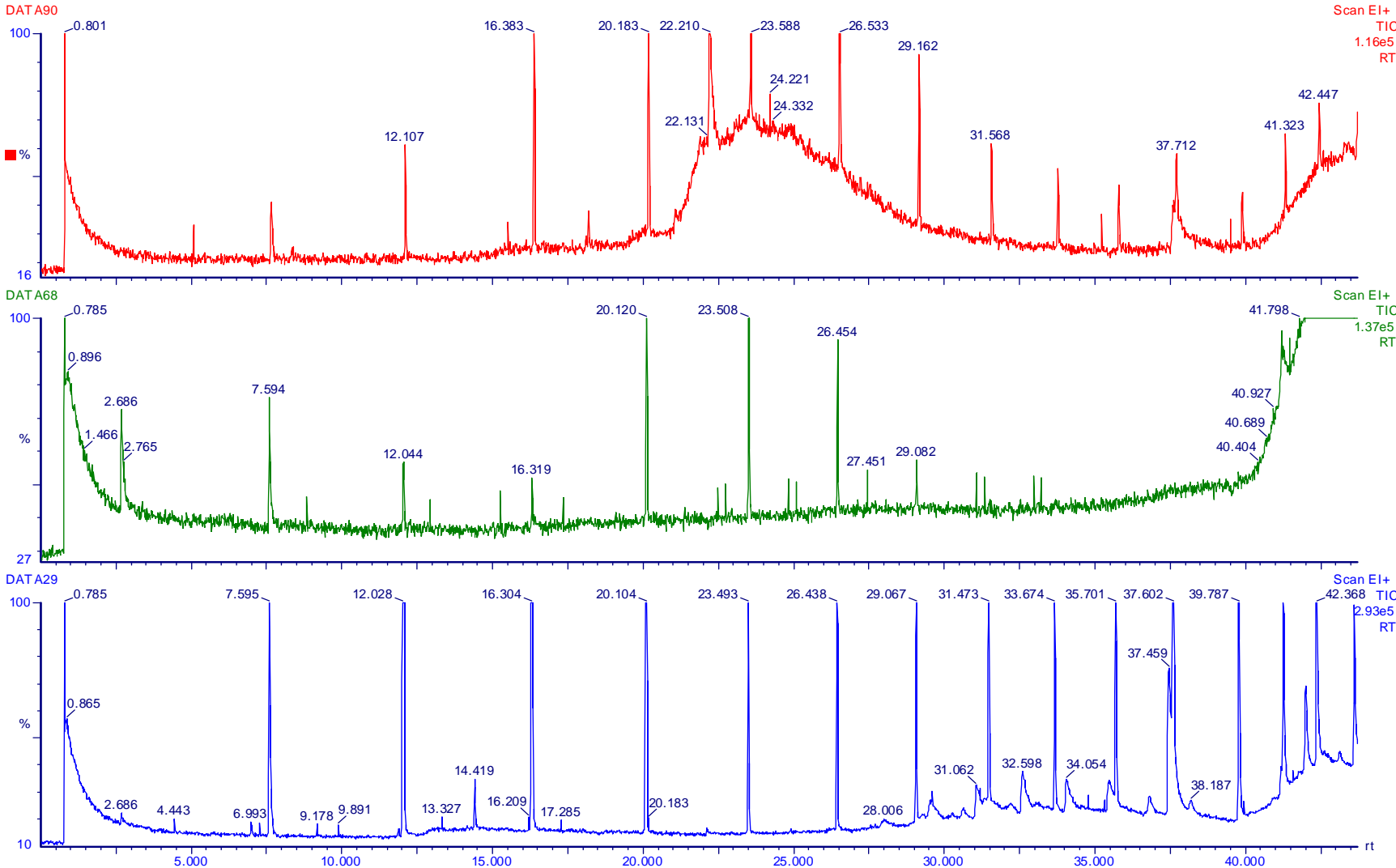
Acquired on 18-Jan-2005 at 16:57:08



Picture 6.2-27: Chromatograms of soot / condensate; Data 89: Volvo 245 seat, Model 1985 + Heptane; Data 68: Polyurethane foam in third scale; Data 29: Background

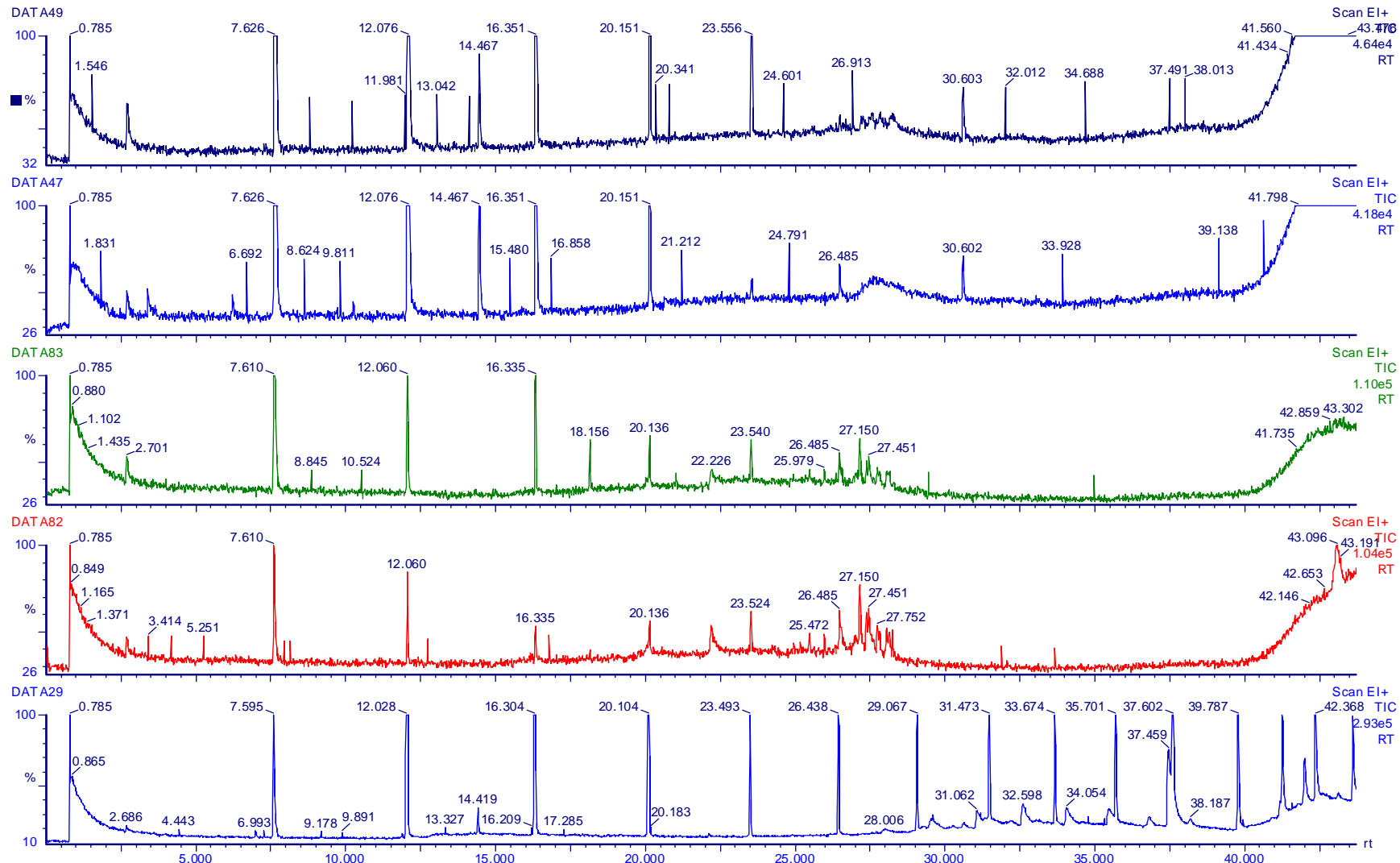
Sample ID: Volvo 245 1984 Model, seat + Lacknafta, LTH, cond. see Data 49

Acquired on 18-Jan-2005 at 18:33:12



Picture 6.2-28: Chromatograms of soot / condensate; Data 90: Volvo 245 seat, Model 1985 + Lacknafta; Data 68: Polyurethane foam in third scale; Data 29: Background

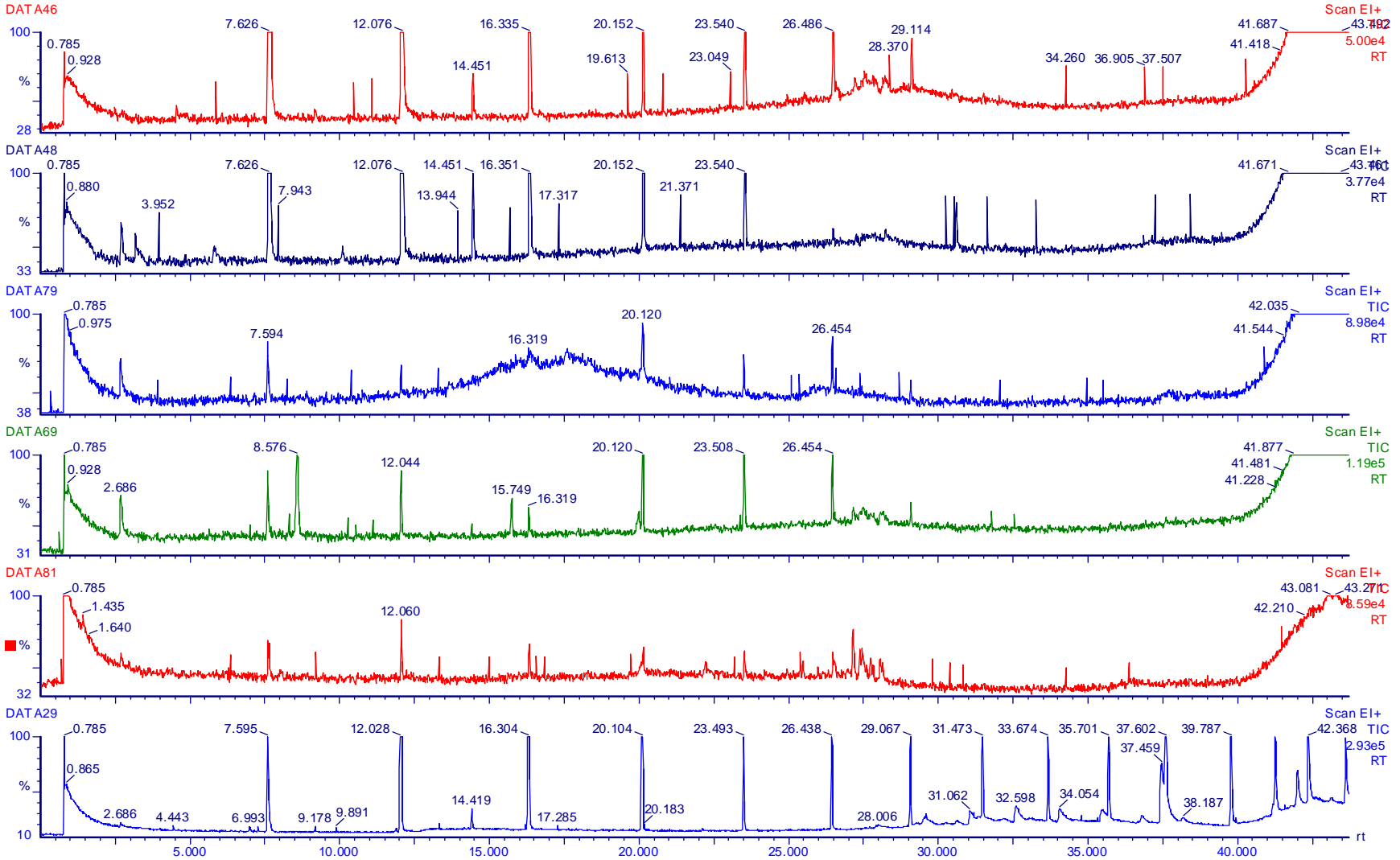
Sample ID: Soot of Neoplen+ BBQ Lighter Vac., Filter, 100my PDMS 20min in Line Acquired on 22-Dec-2004 at 20:17:01



Picture 6.2-29: Chromatograms of soot / condensate; Data 49: Neoplen + BBQ- lighter; Data 47: Neoplen + Kerosene; Data 83: Neoplen + Heptane; Data 82: Neoplen + Lacknafta; Data 29: Background

Sample ID: BASF TDI LTH Heptane, soot, cond. see Data 4

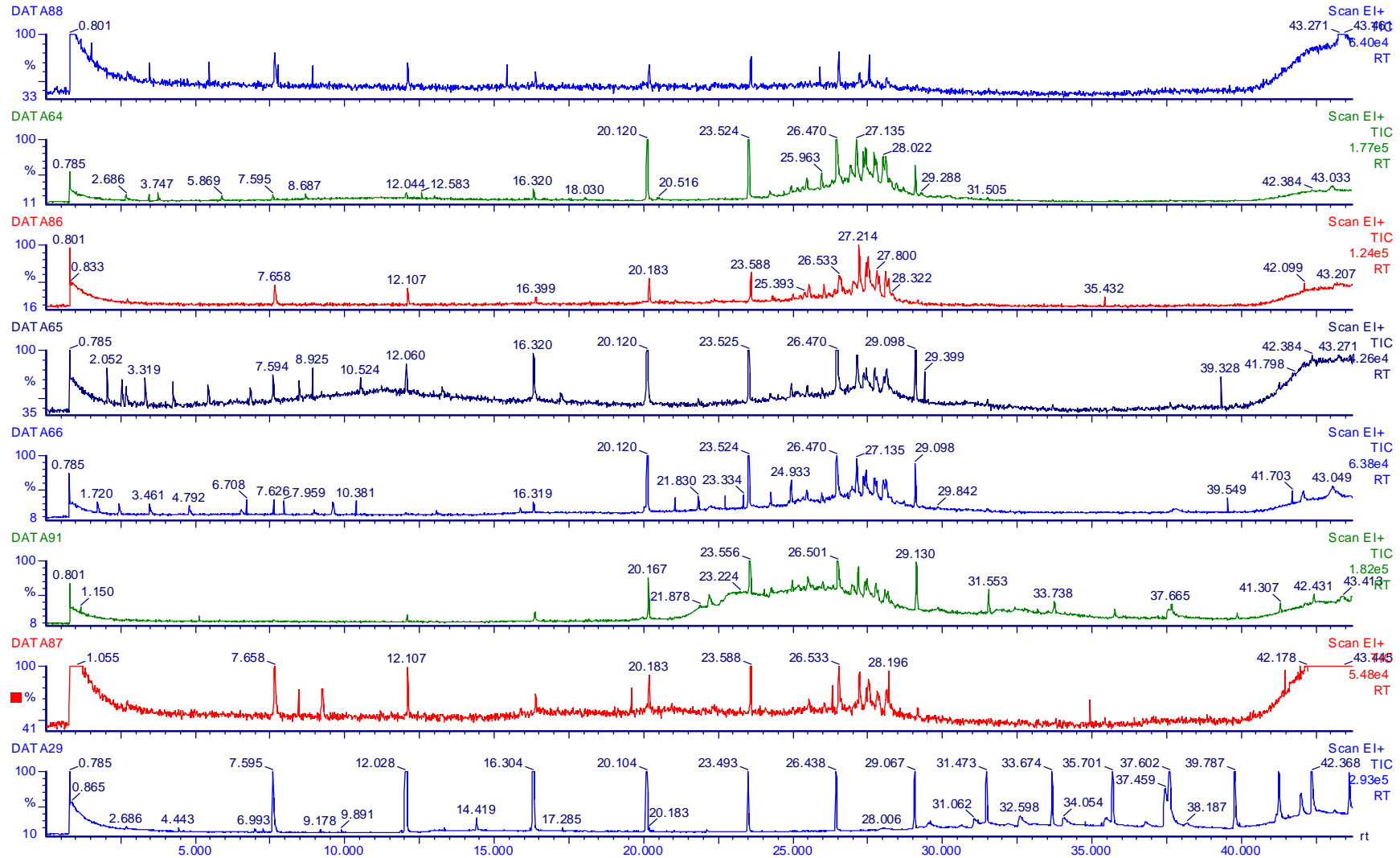
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Picture 6.2-30: Chromatograms of soot / condensate; for clarification see table 6.2-7 on page 74

Sample ID: 46-1-2, cond. see Data 49

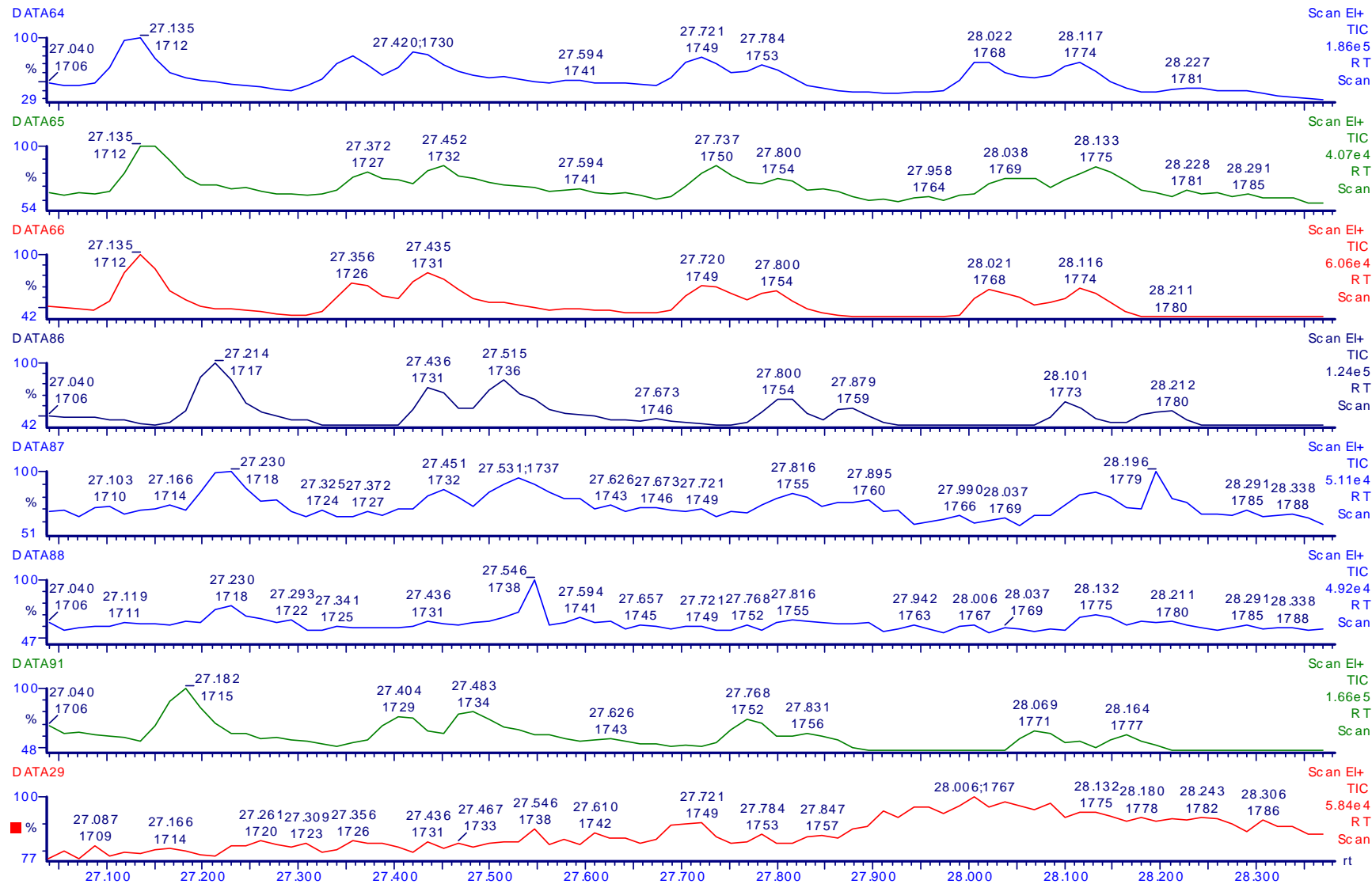
Acquired on 18-Jan-2005 at 13:12:10



Picture 6.2-31: Chromatograms of soot / condensate; for clarification see table 6.2-8 on page 74

Sample ID: Background Sample Glass, Tape, Glass wool,

Acquired on 15-Dec-2004 at 18:26:38



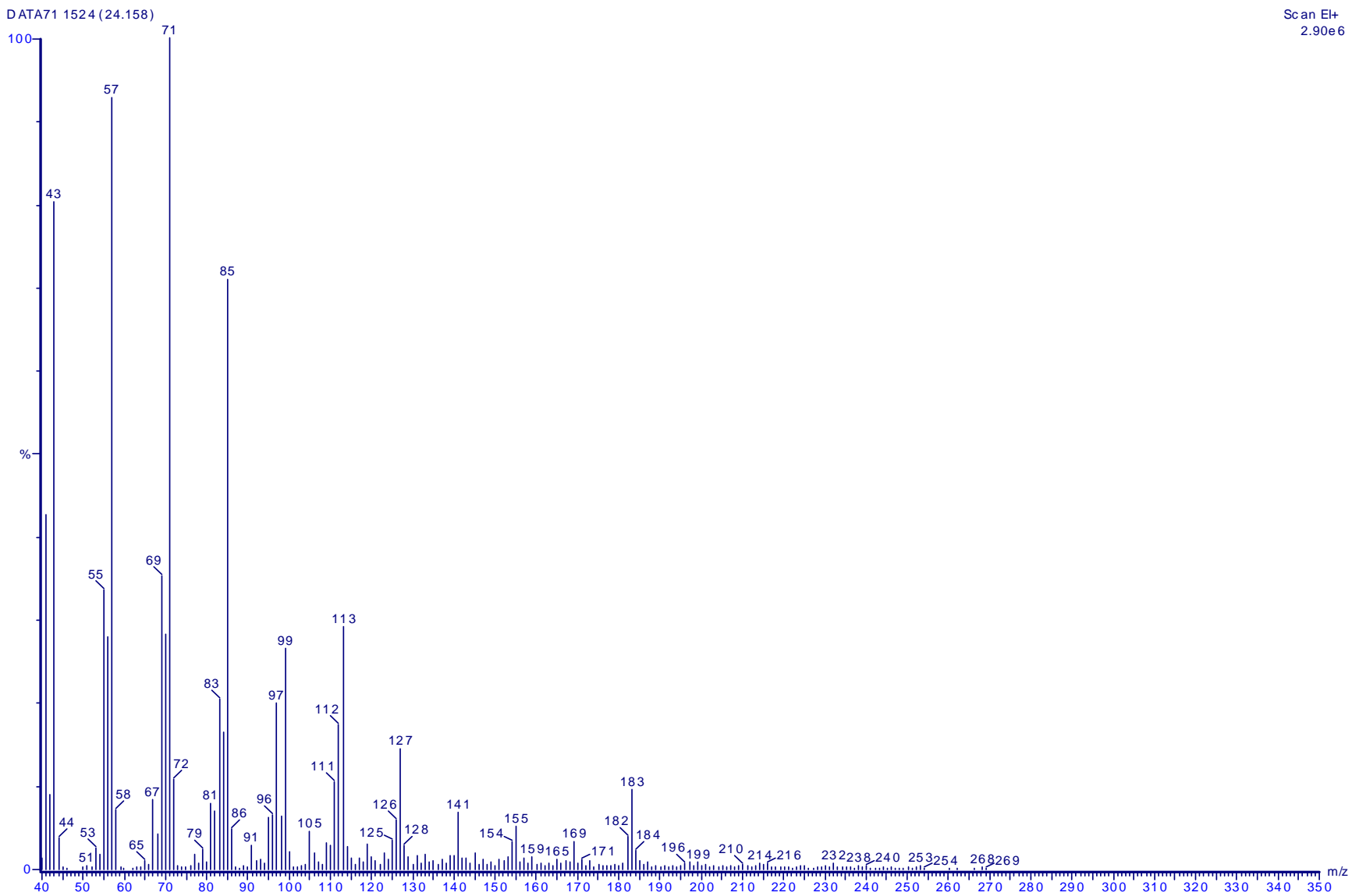
Picture 6.2-32: Section from picture 6.2-31; for clarification see table 6.2-8 on page 74

Table 6.2-7: Clarification for picture 6.2-30 on page 71

GC / MS-File	Clarification
Data 46	Polyurethane foam + Kerosene; Data 48: Polyurethane foam + BBQ- lighter
Data 79	Polyurethane foam + BBQ- lighter from long term combustion test
Data 69	Polyurethane foam + Lacknafta
Data 81	Polyurethane foam + Heptane
Data 29	Background

Table 6.2-8: Clarification for pictures 6.2-31 and 6.2-32 on pages 72 and 73

GC / MS-File	Car model	Clarification
Data 88	Opel Kadett, Model 1975	Sample from window pane taken after the test was finished with glass wool
Data 64	Saab 900 Gli, Model 1984	Sample from window pane taken after the test was finished with glass wool
Data 86	Saab 900 Gli, Model 1984	Sample collected during the test with glass wool and the sampling unit
Data 65	Volvo V70 Kombi, Model 2004	Sample collected during the test with glass wool and the sampling unit
Data 66	Volvo V70 Kombi, Model 2004	Sample from window pane taken after the test was finished with glass wool
Data 91	Volvo V70 Kombi, Model 2004	Sample collected during the test with glass wool and the sampling unit
Data 87	Volvo XC 90, Model 2003	Sample collected during the test with glass wool and the sampling unit
Data 29		Background chromatogram



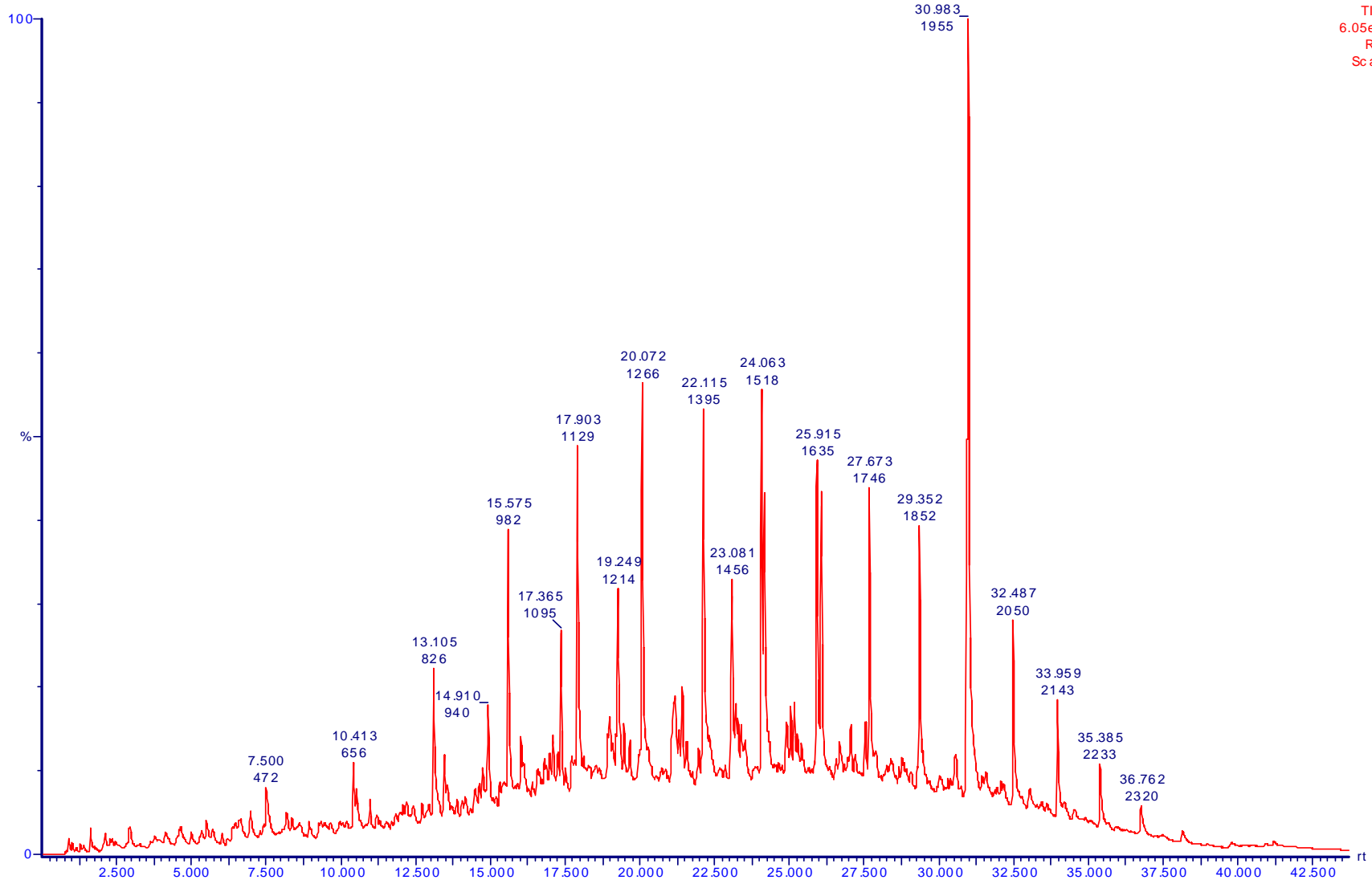
Picture 6.2-33: Mass spectra of the peak at retention time 24,158 min from a sample of diesel fuel

Sample ID: Diesel Fuel, 5s sampling, other cond. see DATA49

Acquired on 11-Jan-2005 at 20:41:08

DATA71

Scan El+
TIC
6.05e7
RT
Scan



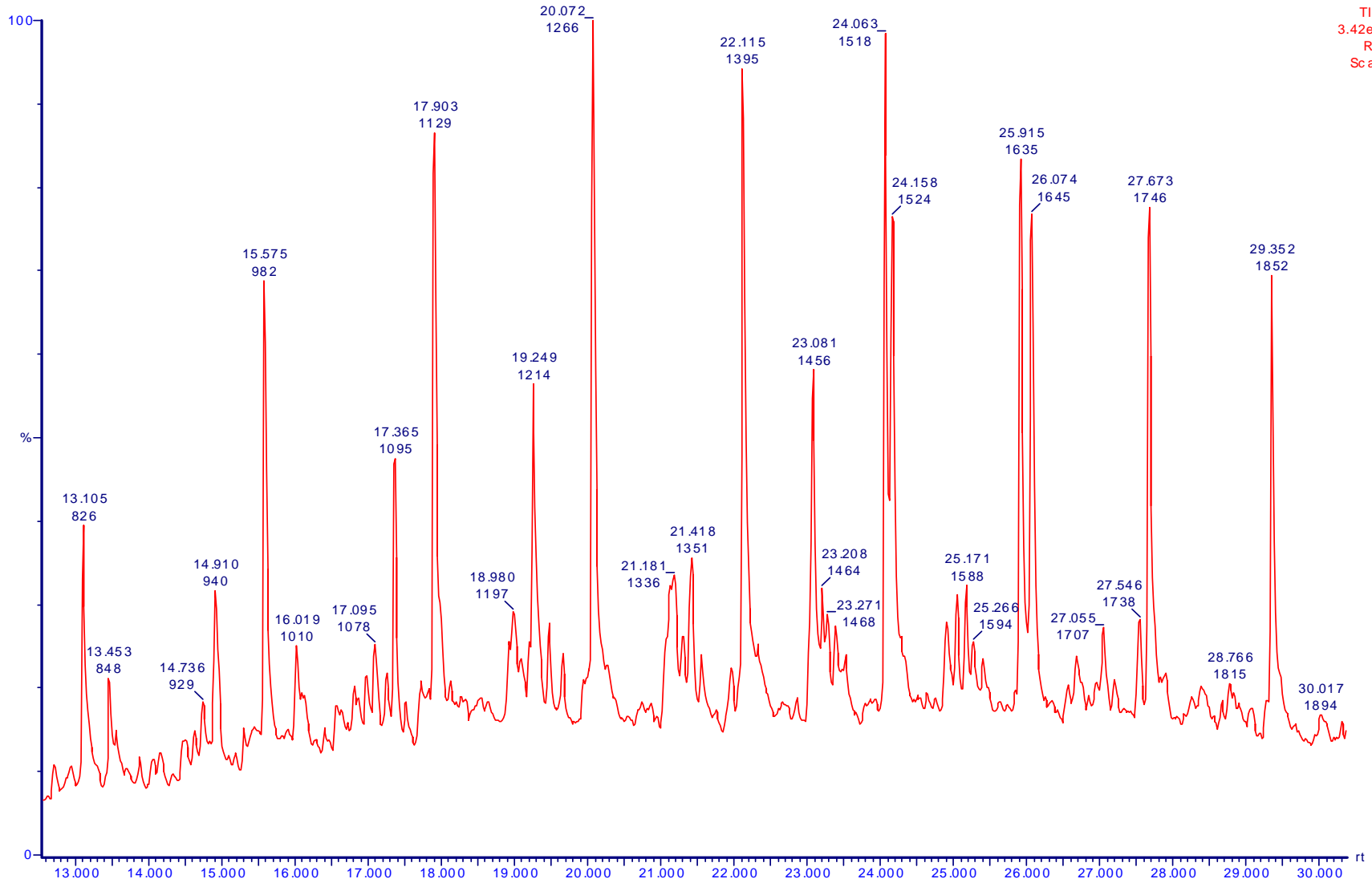
Picture 6.2-34: Chromatogram of non-combusted diesel fuel

Sample ID: Diesel Fuel, 5s sampling, other cond. see DATA49

Acquired on 11-Jan-2005 at 20:41:08

DATA71

Scan El+
TIC
3.42e7
RT
Scan



Picture 6.2-35: Section from picture 6.2-34

