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A Contribution to the Identification of Pyrolysis Byproducts in Fluidized Bed Soot and in Pyrocarbon

by

E. Wolfrum, J. Rottmann, I. Büker and H. Nickel

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A CONTRIBUTION TO IDENTIFY PYROLYSIS BY-PRODUCTS IN SOOT OF A FLUIDIZED BED AND IN PYROCARBON

by

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H. Nickel

ABSTRACT

In the frame of developing improved fuel particles, both the pyrocarbon separated in fluidized beds and the resulting soot were studied to their pyrolysis by-products. It was the aim of this study to give a contribution on the knowledge of the separation mechanism of pyrocarbon on fuel kernels during the thermal decomposition of low hydro-carbons.

This study referred to pyrolysis products of acetylene and propylene. The extraction was performed with various methods. The extracts were separated gaschromatographical and mass-spectrometrical; the single components were partially identified. 21 polycyclic and aromatic hydrocarbons were clearly identified in soot. Beyond that pyrocarbon contains still higher-molecular polycycles.

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1. Introduction and Scope of Problem

A promising power reactor for the future is afforded by the helium-cooled high-temperature reactor with spherical or block-shaped fuel elements. Gas temperatures of about 850°C are obtained in these reactors, thus permitting a direct connection to modern steam circuits. Irrespective of the type of fuel elements, the graphite matrix contains the fuel in the form of coated spherical particles (diameter : 500-1000 μm), so-called "coated particles". The oxide or carbide uranium or uranium-thorium kernel is surrounded with one or more pyrocarbon layers of varying structure and density and possibly with an additional silicon carbide layer. Pyrocarbon (PyC) as the result of its low permeability has the property of being impermeable to gaseous fission products and of possessing a high retention capacity in respect of the majority of solid fission products so that it ensures as low as possible a contamination of the coolant circuit (Ref. 1). The HHT (high-temperature reactor/helium turbine) Project, i.e., the development of high-temperature reactors with a helium turbine in the primary circuit and higher coolant gas outlet temperatures, has posed more severe requirements for fission product retention in the coated particles (Ref. 2). It is therefore necessary to improve the properties of the PyC-layers in respect of this requirement.

The pyrocarbon is applied to the fuel kernels in fluidized beds (Fig. 1) by the thermal decomposition of lower hydrocarbons, such as methane, propene, acetylene, etc., in the temperature range between 1200 and 2100°C. Material of different structure

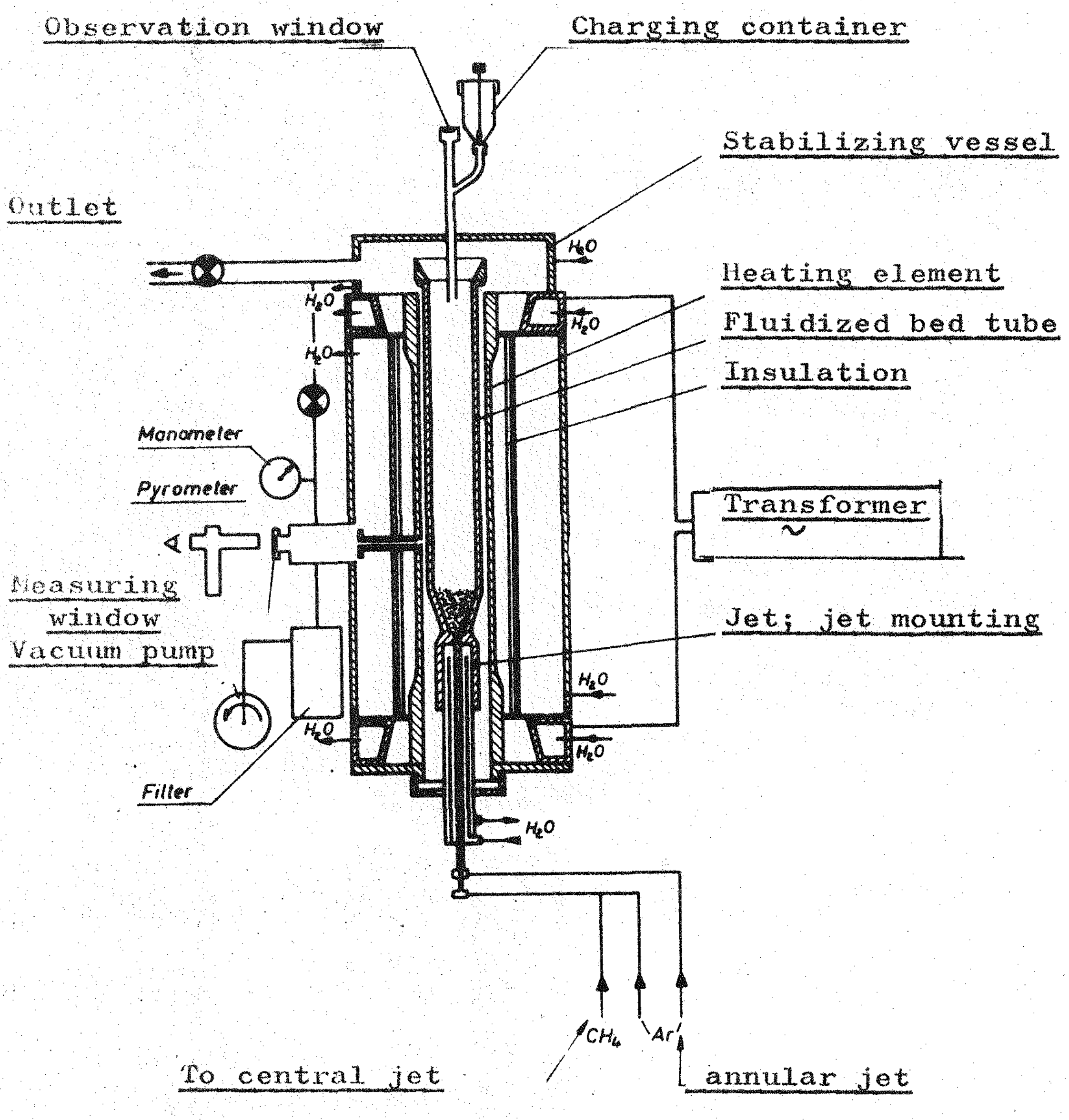


Fig. 1 : Diagram of the fluidized bed installation used (Ref. 1)

is obtained in this way, depending on the nature and concentration of the hydrocarbons and the deposition temperature.

With methane pyrolysis three areas of different PyC structure can be distinguished, depending on the decomposition temperature and the methane concentration : the first area with a laminar, the second with an isotropic and the third with a granular or columnar structure.

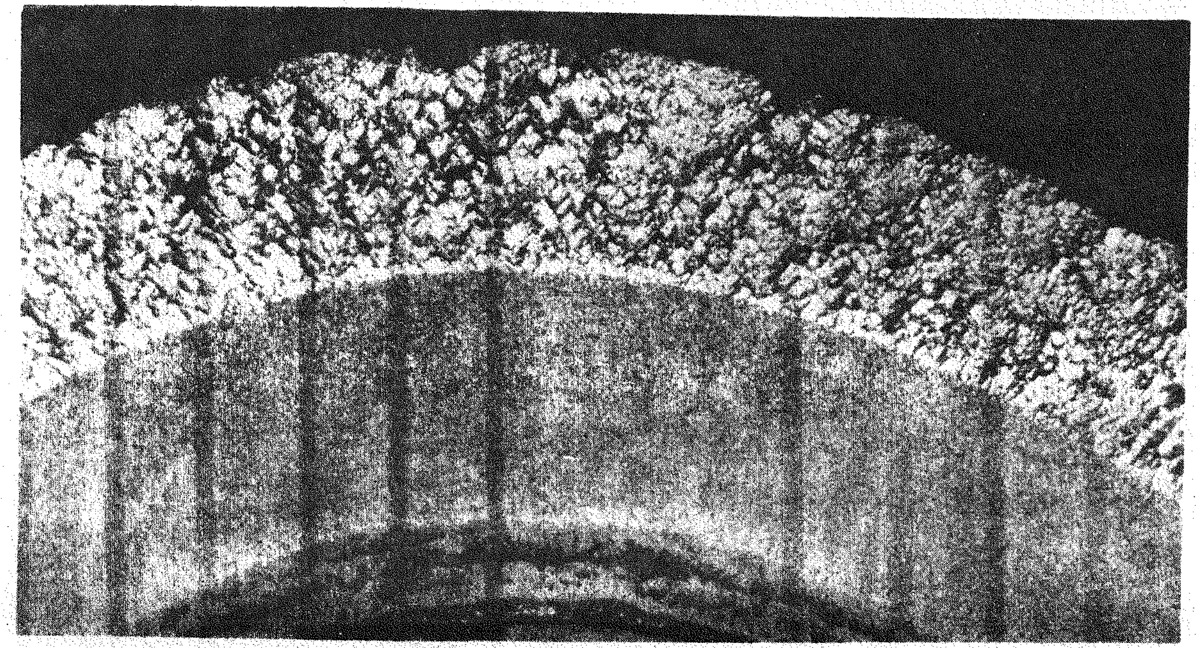
Fig. 2 shows a particle in which these three structures are clearly visible.

On the inside is a porous layer, obtained by the decomposition of acetylene. This is followed by the isotropic layer, which was deposited at 22 v/o methane at coating temperatures between 1500 and 1900°C, and on the outside a columnar layer, which is formed at high pyrolysis temperatures and low methane concentrations.

It is now known that isotropic layers afford the best radiation resistance. The requirement is therefore for the use in the reactor of only coated particles with as far as possible isotropic layers.

Fig. 3 shows, for example, the relation between the coating temperature, the propene concentration and the PyC density, on the one hand, and the pyrocarbon structure on the other (Refs. 1 and 2). It will be seen that pyrocarbon with columnar, densely isotropic, soot-containing isotropic and porous structures are obtained, depending on the coating concentration and the coating temperature. Whereas with methane decomposition pyrolysis temperatures of $>$ 1800°C are required for the deposition of isotropic dense PyC layers suitable for reactor operation, temperatures around 1250°C are sufficient in the case of propene pyrolysis.

Since exact data on the pyrolysis process



Polarized light x 500

Fig. 2 : Metallographic micrograph of a coated fuel particle with isotropic and columnar structure (Refs. 1 and 2)

Structure : First layer : porous, $_{\mathrm{PyC}} = 1$ g/cm^3

Second layer : isotropic, $_{\mathrm{PyC}} = 1.7$ g/cm^3

Third layer : columnar, $_{\mathrm{PyC}} = 2.09$ g/cm^3

Separation conditions :

Porous layer : 1500°C; 50 v/o C_2H_2

Isotropic layer : 1500-1900°C; 22 v/o CH_4

Columnar layer : 1900°C; 5 v:0 CH_4

have not up to now been available, it has only been possible to achieve a directed

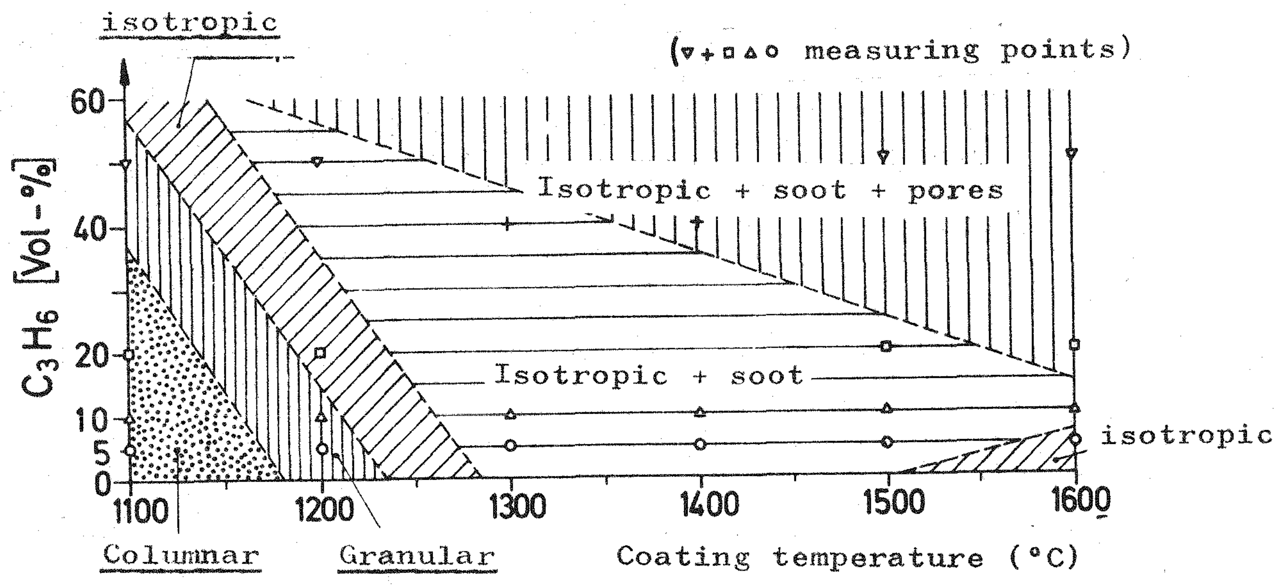


Fig. 3 : Relation between coating temperature, propene concentration, PyC density and pyrocarbon structure (Refs. 1 and 2)

effect on the pyrolysis conditions by empirical means.

Comprehensive investigations, affording an insight into the pyrolysis process during the coating operation, have been carried out by means of model studies (Ref. 3) and mass-spectrometric analyses of gaseous pyrolysis byproducts (Ref. 4) under various reaction conditions.

The aim of this work was :

to detect by means of suitable extraction processes the pyrolysis byproducts present in fluidized bed soots and in pyrocarbon

to separate the extracted compounds and to analyze them by chromatographic and spectroscopic methods.

The nature of the occurring byproducts, the influences exercised on them and the consequent possible changes in the PyC-structure, in conjunction with theoretical considerations and other investigations on a part of the pyrolysis mechanism and coating process, were intended to provide information, which would permit a further optimization of the coating parameters.

2. Theoretical Part

2.1 Review of the Literature on Known Pyrolysis Mechanisms

A summary of known pyrolysis mechanisms is given in the paper by Sütterlin (Ref. 3) on the formation and deposition of PyC from methane in the 1650-2150°C range. The present study, carried out within the framework of investigations on the development of fuel elements for high-temperature reactors, was intended to provide an insight into the mechanism of the coating of nuclear fuel particles with pyrocarbon. The theory developed in this connection will be outlined briefly below.

The pyrolysis of gaseous hydrocarbons has frequently been described as simple decomposition into the elements. This mechanism does not, however, explain the presence of new, lower hydrocarbons, such as ethane, acetylene and poly-ines (Ref. 5) in the resulting gas phase, and also of polycyclic hydrocarbons, which have been detected as byproducts in soot and the presence of which has also been assumed by Mucha and Schreinlechner (Ref. 6) in PyC.

It is also not clear whether a proportion of these pyrolysis products have been formed subsequently as a result of reactions at the active carbon surfaces (Ref. 7).

Investigations aimed at incorporating the higher hydrocarbons in this theoretical principle have described the formation of pyrocarbons from aromatics of increasing molecular weight as quasi-liquid droplets (gas-born droplets) on the hot surfaces. With the fission of methane and hydrogen these droplets coagulate to form larger molecular compounds, corresponding finally to pyrocarbons. However, the decomposition temperatures of the low-molecular intermediate products are so far below the pyrolysis temperature, that their formation would appear to be impossible from the thermodynamic point of view. Since the detection of intermediate radicals during the decomposition process has been confirmed, but a purely radical pyrolysis process is excluded on theoretical grounds, Sütterlin (Ref. 3) has postulated a reaction scheme, which includes both molecular reactions and also radial transformations. According to this model of the so-called pyro-aggregate concept, ions, radicals, excited atoms and excited molecules are formed from the pyrolysis gas molecules with an intensive application of energy. If exchange interactions are possible between these particles, there may be mutual attraction. The combinations, resulting from this attraction, have been designated pyro-aggregates.

It has been possible in this way to construct a reaction mechanism, which fits the experimental results and permits the simultaneous occurrence of radial and molecular reactions.

Furthermore, this concept also clarifies the occurrence and stability of higher-molecular hydrocarbons, the precursors and daughter products of which should no longer exist at the pyrolysis temperatures obtaining. Since PyC is to be regarded as a hydrocarbon large molecule, the hypothesis is based on the pyrocarbon being a product of pyro-aggregates. In the state of coming into being of such a pyro-aggregate the individuality of a single molecule is still so great that one cannot yet speak of a clearly defined structure. Prolongation of the life of the pyro-aggregate is accompanied not only by growth, but also by a relatively high stability, obtained by the coupling of subaggregates and clusters. Such large pyro-aggregates contain already a partially ordered configuration of subaggregates. The question then arises of whether these arrangements are preferably of the chain or cyclic type. Theoretical considerations and calculations have led to the conclusion that more or less marked cyclic arrangements are formed in the subaggregates, depending on the pyrolysis temperature.

Since according to the pyro-aggregate concept the pyrocarbon is produced from "frozen" pyro-aggregates, it was necessary to detect the presence in the pyrocarbon of polycyclic aromatic hydrocarbons (pcAK) of varying molecular weights.

2.2 Review of the Literature on the Analysis of Soots and Pyrocarbon

It has long been known that aromatic hydrocarbons are produced during the pyrolysis of methane, ethane, acetylene, etc. (Refs. 8-11). These pyrolysis products are in part adsorbed soots, provided that the possibility of soot formation is present. They can moreover be concentrated in cold traps, which are connected to the pyrolysis apparatus. Identification of these products in soots has been frequently undertaken in view of the carcinogenic effect of polycyclic aromatic hydrocarbons (Refs. 7, 13, 14). These soots are, however, predominantly of the type produced in flames burning in atmospheric oxygen, so-called diffusion flames, and not in fluidized beds. Pyrolysis products in the soluble fraction of carbon residues, obtained both from diffusion flames and also from the pyrolysis of lower hydrocarbons, have been identified in the same way as the low-boiling compounds, concentrated in cold traps (Ref. 18). These soot-type residues are not, however, identical with the pyrocarbon deposited under fluidized bed conditions.

Initial investigations, aimed at analyzing the organic product compound of PyC, deposited on fuel element particles under fluidized bed conditions, have been carried out by Mucha and Schreinlechner (Ref. 6).

The authors extracted the pyrocarbon, resulting from methane pyrolysis, with m-xylene. No data were given as to whether the extraction was carried out in air or under protective gas. They obtained on evaporation of the solvent (bath temperature : 70°C) not only brown, tarry substances but also white precipitates. Separation was effected by thin-layer chromatography and evaluated under UV light. After application of preparative layer chromatography, the extracts were further investigated by gas chromatography and IR spectroscopy. The following molecular weight ranges were determined for the particular fractions (Table 1) by means of the capillary column used in these investigations.

Deposition conditions of the pyrocarbon	Fraction	Molecular weight range M	Mean molecular weight $\bar{M}$
Temp.: 1800°C	1 (upper)	110-190	140
Methane concentration: 20 v/o	3 (middle)	180-190	180
	5 (start line)	180-240	220

Table 1 : Molecular weight ranges of fractions obtained by thin-layer chromatography after Mucha and Schreinlechner (Ref. 6)

The IR photographs showed that the upper fraction consisted of a mixture of alkylated aromatics, whereas fraction 5 contained predominantly oxidized hydrocarbon with carbonyl groups.

It is evident from Table 2 that the content of extractable substances in the pyrocarbon falls with an increase in the deposition temperature.

Temperature of pyrocarbon deposition °C	Content of extractable substances per g pyrocarbon g	Molecular weight range M	Mean molecular weight $\bar{M}$
1300	0,03 - 0,004	110 - 140	120
1600	0,01 - 0,001	100 - 180	130
1800	0,001 - 0,0002	110 - 240	160

Table 2 : Content and molecular weight ranges of extractable substances in PyC after Mucha and Schreinlechner (Ref. 6)

The molecular weight range had in all cases the same lower limit, whereas the mean molecular weight and also the upper limit rose with an increase in the temperature. The authors assumed that the investigated specimens still contained high-molecular (higher-boiling) substances, which were, however, no longer detectable by gas chromatography under the given experimental conditions.

The presence of oxidized compounds, detected by these authors in a relatively large part of the PyC extracts, is due to the fact that even before deposition of the PyC oxygen was present as an impurity in the pyrolysis gas, as was confirmed by analysis of the waste gasses (0.8 % CO at 1300°C and 1.1 % CO at 1800°C). The hydrogen content was given in both cases as > 97 %. The authors excluded a subsequent oxidation of the PyC extract during the preparation and analysis process, although the proportion of oxygen in the isolated substances was far higher than the figure corresponding to the pyrolysis gas composition.

2.3 Separation and Identification Methods

The separation and identification of pyrolysis products was limited to the polycyclic aromatic hydrocarbons for the reasons given above. These latter possess characteristic absorption peaks in the spectrum range between 200 and 500 mμ (Ref. 19). In addition a large number of these compounds exhibit typical fluorescence bands in the visual range. These two spectral properties have frequently been used for analytical purposes. Their reliability and certainty are however considerably reduced, when complex substance mixtures are present (Ref. 12).

A considerable improvement can be obtained in the detection of pcAK, if the spectral measurements are preceded by one or more separations of the extracted mixtures, using paper, thin-layer or column chromatography (Ref. 20). These methods have the disadvantage, however, that they require a considerable outlay in terms of time, in particular for the production of separation materials having determind activities (Ref. 22). A very much more desirable method appeared to be the gas chromatographic separation and identification of the products. Lijinski et al. (Ref. 21) have, for example, isolated and identified aromatic hydrocarbons in mineral oil, coal tar and other substances, using gas chromatography on silicon oil phases. The sensitivity is in this case high and the analysis time relatively short. Chakraborty and Long (Ref. 14) have also investigated soot specimens from diffusion flames, using gas chromatography. In order to obtain a clear result, these authors used UV absorption spectroscopy for identification of the separated substances. These processes are however restricted to compounds with the given spectral properties, apart from a purely gas chromatographic analysis of the different liquid phases. Other pyrolysis products are therefore not clearly identifiable in the same analytical operation.

2.4 Principle of Work

In the present paper a gas chromatograph/mass spectrometer combination was used for the separation and identification of pyrolysis products from fluidized bed soot and pyrocarbon, as had been used by Oro and Han (Ref. 16) for the identification of methane pyrolysis products. This method has the advantage that it is independent of specifically spectral properties, but possesses in spite of the short analysis time a qualitatively high predictive value. An adverse factor is the high working temperature, required for the gas-chromatographic separation of polycyclid hydrocarbons, which leads to a marked evaporation of the phase. This in turn has an adverse effect on the subsequent mass-spectrometric analysis, especially when operating in the trace range.

A further disadvantage of the high working temperatures is that some authors believe a decomposition of higher pcAK (with 5 or more kernels) to be possible (Ref. 22). The compound coronene (mass 300) is given in almost all cases as the last hydrocarbon to be detected. However, since very much higher masses can also occur during pyrolytic processes, the detection of these compounds is of great interest. A gas-chromatographic separation and identification of such substances has up to now only been possible with difficulty partly due to the absence of equipment and also as a result of the very low concentrations of these compounds in soots and PyC. In order to extend the range of products, detectable by gas chromatography, higher column temperatures and special high-temperature-resistant phases would be necessary.

The application of mass-spectroscopic analysis by means of fractionated specimen evaporation directly on to the ion source of a mass spectrometer under high vacuum conditions, on the other hand, permits the detection of even higher masses. It has the disadvantage, however, that an attribution to definite compounds is problematical. In view of the above considerations, the principle of operation described in Fig. 4, was adopted. It will be used both for the analysis of fluidized bed soot and also for future work in the field of PyC investigations.

The principles of the extraction process used will be given in Section 3.3.1.

3. Experimental Part

3.1 Specimen Material and Sampling

3.1.1 Pyrocarbon

We used as specimen material pyrocarbon layers produced by the pyrolytic decomposition of propene and acetylene on uranium-thorium oxide kernels in a 1 inch fluidized bed.

These two pyrocarbon varieties possess specific properties, which govern their use as coating material in particular cases. The PyC deposited from propene at relatively low temperatures (1300°C) was selected in view of the greater probability in this case of extracting and identifying pyrolysis byproducts.

Table 3 below gives a summary of the specimen material used and the particular deposition conditions.

Batch No.	Kernel Material	Coating gas	Concentration %	Coating temperature °C
PUTO 1012	Uranium-thorium oxide	propene	10	1300
AUTO 846	Uranium-thorium oxide	acetylene	50	1500

Table 3 : Review of the specimen material used

In order to reduce during the extraction any possible catalytic influence of the heavy metals uranium and thorium, which could lead to the decomposition of the polycyclic aromatic hydrocarbons, the pyrocarbon layers were removed from the kernel in a roller breaking mill (Ref. 23) and separated in an air centrifuge.

However, since contamination of the coating layers with uranium and thorium traces has been detected (Ref. 24), a catalytic effect cannot be excluded. This will, however, be unimportant in view of the metal concentrations, which are within the ppm range.

3.1.2 Fluidized Bed Soot

During the pyrolysis of the gaseous hydrocarbons, soot-like components are formed and deposited, depending on the nature and concentration of the hydrocarbons and the decomposition temperature in the fluidized bed. These noncrystalline, soot-like components become embedded in small quantities in the highly dense PyC layers of the particles (Ref. 24), whereas the remainder are deposited on the cooler or cooled parts of the fluidized bed installation and in the waste gas filters. In view of the large surface of these materials, it may be assumed that a large number of pyrolysis byproducts are present in the soots. The water-cooled cover of the fluidized bed installation was selected as the sampling point for the soot specimens (Fig. 1).

A further factor is the constant cover temperature (200 °C) (Ref. 4) and a constant radiation of heat, corresponding to the pyrolysis process, directed on to the growing soot layers over the whole diameter of the cover. This constant temperature would not be obtained in the case of sampling in the cone or in the tube of the coating plant as a result of the marked temperature profile.

3.2 Direct Mass-Spectrometric Investigation of Pyrolysis Byproducts in Fluidized Bed Soots

A gas chromatograph/mass spectrometer combination by the firm VARIAN-MAT, the 100 MS spectrosystem, Model N 101/81 MS, was available for the mass spectrometric analysis. This system includes a CH 7 mass spectrometer with a separate specimen inlet system (Fig. 5, part 10), a VARIAN 1700 Aerograph gas chromatograph and a Series 620 VARIAN Computer with 8 K (16 bit) words core store capacity, the N 101/MS interface for coupling with the CH 7 mass spectrometer, a 9-track digital magnetic tape instrument as program and data store and an operator console typewriter (teletype) for command input and data output.

The spectrum information, delivered by the mass spectrometer, contains the peak intensities and also rounded-off or exact mass values and total current intensities. These can be further processed by normalization, correction, meaning, subtraction or reduction into various forms of presentation, such as spectrum lists, element lists, sign spectra, ion series spectra, gas chromatograms (total current diagrams), mass chromatograms or peak profiles (Ref. 26).

It was possible by means of the separate specimen inlet system (lock system) to heat small quantities of soot to 400°C in a gold crucible and thus to evaporate in fractionated form the substance mixture directly on to the ion source of the mass spectrometer as a function of time or temperature.

It is possible as a result of this investigation :

(1) to obtain a general picture of the mass range of more than 300 mass units (MU), detectable at these heating temperature; this range could no longer be detected by gas chromatography with available agents in view of the high boiling points,

(2) to make an estimate of the relative concentrations of hydrocarbons present, in relation to each other.

3.2.1 Experimental Procedure

1-2 mg of the soot, obtained as a result of the fluidized bed pyrolysis of acetylene or propene, were charged into a gold crucible about 2 mm in diameter and introduced by means of a push rod through the separate inlet system, after evacuation in a pre-vacuum chamber, into the cell of the ion source.

The crucible was then heated continuously from room temperature to 400°C. During this period 20 or 28 mass spectra were recorded. The recorded series of spectra, Nos. 188-216, which were prepared during the heating time of the propene soot, are shown in Table 5.

The operating conditions of the CH 7 mass spectrometer are summarized in Table 4 :

Temperature of Crucible :	Start : 25°C; End : 400°C
Cathode count :	300 µA
Electron energy :	70 eV
Mass range :	20 - 600 ME
Passage time : (including resetting of field)	5 sec
Pressure :	10^{-6} torr
Sensitivity :	10^{-7} A/V

Table 4 : Operating conditions of the CH 7 mass spectrometer

Within the series of spectra recorded, spectrum No. 199 exhibits the highest number of peaks. This spectrum is shown in Fig. 6. Fig. 7 contains for comparison purposes the corresponding spectrum No. 174, which was obtained during the heating process of acetylene soot. These spectra were printed out as line spectra by means of an electrostatic digital plotter.

The peak intensities have been normalized in relation to the peak with the highest intensity in the whole spectrum (≙ basis peak = 100) and corrected for the varying total current intensity.

In order to identify higher masses, which in view of their low concentrations only exhibited weak intensities, the spectra were in each case amplified by a factor of 10, so that the peaks with the highest intensity exhibited the same height as a result of overload.

```
14.8.72 /SPEC#   188/LP/REMARKS : WOLFRUM PROPYL.

 SPEC# PEAKS  IMAX  TMIN  TMAX  LOSS
   188   115 32736   68
   189   110 32736   672
   190    98 32736   656
   191   109 32736   640
   192   123 32736   672
   193   132 32736   688
   194   163 32736   752
   195   179 32736   880
   196   195 32736  1088
   197   209 32736  1216
   198   229 32736  1312
   199   322 32736  1440
   200   250 32736  1344
   201   222 32736  1120
   202   206 32736  1040
   203   207 32736  1040
   204   207 32736  1072
   205   214 32736  1120
   206   205 32736  1104
   207   208 32736  1104
   208   212 32736  1184
   209   222 32736  1344
   210   243 32736  2176
   211   245 32736  2016
   212   247 32736  1792
   213   250 32736  2112
   214   214 32736  1776
   215   208 32736  1856
   216   189 32736   992  2336     0

FIRST SPEC # :    188
LAST  SPEC # :    216
```

Table 5 : Spectrum series recorded : spectra Nos. 188-216, recorded during the heating time of the propene soot

3.2.2 Discussion of the Results

Ghaigneau, Giry and Ricard (Ref. 17) have already carried out mass-spectrometric investigations on soots obtained during the incomplete combustion of heating oil, petrol or wood. The soots were extracted with various solvents and the extracts evaporated in fractioned form on to the ion source of a mass spectrometer at different ionization voltages. The masses obtained were allocated to corresponding hydrocarbon compounds.

Palmer, Voet and Lahaye (Ref. 27) have studied, also by means of mass spectrometry benzene extracts of soots, obtained from diffusion flames of natural gases. In very small traces the mass 646 was still found as the absolute limit.

A direct investigation of volatile components in soots, obtained at various levels in acetylene-oxygen diffusion flames has been carried out by Homann and Wagner (Ref. 5). Although the authors were able in this case to detect masses above 450 MU, no allocation to compounds could be made in these ranges.

In the extraction processes the limit of detectable compounds is governed by the nature of the solvent used. This can be extended by the use of solvent mixtures are however difficult to make up in view of the in general nonspecific solubility properties of some higher pcAK. The direct evaporation of volatile compounds on to the ion source of a mass spectrometer avoids this selection by solvent, with the disadvantage, however, that a trace enrichment is not possible.

Interpretations of mass spectrometric analyses of complex mixtures are, however, known to be extremely difficult and are based on occasions only on assumption. Some adequate predictions can, however, be made by variation of the ionization voltages, since with a lower electron energy the formation of fragments is considerably reduced in the case of aliphatic hydrocarbons and in the case of pcAK virtually no longer occurs (Ref. 5).

However, the reduced electrode current at low electron energies has an adverse effect on the measuring sensitivity affecting particularly the high mass range.

In these investigations an ionization energy of 70 eV (cathode current : 300 µA) was used; although the fragmentation of the compounds was high in this case, it enabled the maximum sensitivity to be obtained. Investigations carried out in the 25 eV range gave only low predictive values, especially in the high mass range.

As is shown by Figs. 6 and 7, the mass spectra of the pyrolysis byproducts from propene and acetylene soot are virtually identical, both in the position of the characteristic mass series and also in the relative intensities. The conclusion may thus be drawn of an identical composition of the pyrolysis products and thus of an identical or at least similar pyrolysis mechanism.

The decrease in the relative intensities at MU 200 indicates a low concentration of these compounds in the soots. A striking feature is provided by the characteristic mass groupings, which occur in both spectra over the whole range.

Ion series spectra were calculated for

identification of characteristic fragmentations, but did not, however, permit any clear prediction.

The group formation disappears at higher masses, but is in both cases identical, so that the masses, recognizable in spectrum No. 199, (Fig. 6) may also be present in the spectrum series of the "acetylene soot".

The masses 414 in the case of "acetylene soot" and 458 in "propene soot" were in each case found in the spectra as the highest mass units. No exact mass calibration could, however, be carried out in this range due to the absence of calibration substances, so that deviations of up to 2 MU have to be expected.

Since virtually every mass was occupied, an allocation even of the highest intensity peaks to definite aromatic or aliphatic hydrocarbon compounds appeared problematical in view of possible fragment superimpositions and was not therefore attempted.

3.3 Solvent Extraction for Specimen Preparation

3.3.1 Selection and Problems in the Selection of Solvents for the Extraction

Apart from the extraction, the selection of the solvent represents a difficult problem. It governs the extent and quality of enrichment of all the compounds in question.

It is apparent from the literature that no specific solvents for the extraction of organic compounds from soot have been used.

Apart from methyl alcohol, for example, relatively unpolar or weakly polar solvents such as benzene, cyclohexane, xylene or chlorobenzene have been used and only rarely solvent mixtures.

The selection of suitable solvents for this problem was made on the basis of satisfying the following conditions :

(1) as wide as possible a solubility spectrum for all compounds present in the soot or PyC,

(2) none of the expected content substances to be regarded as impurities,

(3) no secondary reactions due to reaction with content substances or matrix,

(4) adequate resistance to oxidation.

A wide solubility spectrum is virtually only obtainable by solvent mixtures. We therefore used the ternary mixture cyclohexane (DK : 2.02 at 28°C) dimethylformamide (DK : 36.7 at 25°C and water (DK : 80.3 at 20°C) in a ratio 10 : 9:1 (Ref. 28). The addition of water was intended mainly for the saturation of active centers of the PyC, which could promote a readsorption.

Evaporation of large quantities of solvent up to < 0.5 ml under vacuum conditions inevitably causes an enrichment of the higher-boiling impurities, which complicate considerably any gas chromatographic analysis. We therefore preferred complete evaporation of the solvent under vacuum after the extraction, so that any impurities were reduced to a minimum.

Since the so-called spectroscopically pure solvents used (from the firm Merck, Darmstadt) did not appear to be sufficiently pure, the cyclohexane and dimethylformamide were distilled several times across 1.5 m columns in order to keep the dry residues as low as possible. In this connection, in order to determine the possible presence of residues, 200 ml cyclohexane and 180 ml dimethylformamide were evaporated to 1 ml in the rotation evaporator at 1 torr and 35°C bath temperature and blown dry with argon at room temperature, the residue dissolved in 20 µl and subjected to gas chromatographic analysis. In the event no residual impurities could be detected.

A defect of this solvent mixture was the appearence after 50 hours reflux distillation of a slight saponification of the dimethylformamide into dimethylamine and formic acid. Dimethylamine with a boiling point of 7.4°C does not interfere with subsequent investigations, since it is removed without residue during evaporation under vacuum conditions. Although the boiling point of formic acid, at 100.5°C, is below that of dimethylformamide, it can only be removed with difficulty.

It was found in the extractions of pyrocarbon samples that pyrocarbon has an accelerating effect on the saponification of dimethylformamide. A very much larger quantity of saponification products was for example found than in parallel blank specimens without PyC. In view of the good solution properties of this mixture, however, these disadvantages did not weigh too greatly with us. The solvent mixture was largely resistant to oxidation, in contrast to m-xylene used by Mucha and Schreinlechner (Ref. 6) for the extraction of pyrocarbon specimens.

In our own series of experiments after 4-day reflux boiling of pure m-xylene in air and under daylight, a series of oxidation products such as methylbenzaldehyde and methylbensoic acid were observed, which occurred as white precipitates during evaporation. At the same time the m-xylene turned a yellowish brown. Since the conditions under which the authors (Ref. 7) carried out their extraction are not given, the possibility cannot be excluded that a number of the analyzed pyrolysis byproducts in the pyrocarbon are attributable to oxidation products of the solvent. In the present paper, on the other hand, in order to avoid secondary reactions of the solvent and content substances due to the influence of light and oxygen, all extractions were carried out under an argon atmosphere in a darkroom.

3.3.2 Extraction

Pyrolysis byproducts are in general only present in low concentrations in the specimens for examination. In pyrocarbon in particular the concentrations are in the trace range. Enrichment by means of an extraction process is therefore necessary. Fluidized bed soots can be relatively easily and rapidly extracted by soxhlet extraction. With powdered pyrocarbon, on the other hand, extraction by this technique is subject to many defects. There are two reasons for this. As a result of the relatively great hardness of the pyrocarbon deposited at temperatures above 1300°C, the specimens have to be finely powdered (<50 µm). In consequence passage of the solvent through the material is only to a slight extent possible. As Fischer (Ref. 12) has pointed out, this applies also to finely powdered soots. The author was also able to show that small quantities of benso(a)pyrene are irreversibly adsorbed from benzene solutions, thus showing that polycyclic, aromatic hydrocarbons have a great affinity for soot and coal. Depending on the concentration of the organic substances present, therefore, their identification even where present is not guaranteed. The most effective extraction process must therefore be used, in order to obtain a maximum enrichment.

In the present paper the following extraction procedure was used : quantities of 3 g soot were extracted for 8 h by the Soxhlet technique with 200 ml of a mixture, consisting of cyclohexane, dimethylformamide and water in the ratio 10 : 9 : 1. Glass cylinders with a fritted bottom were used as extraction vessels, in order to avoid any contamination.

For the reasons given above the extraction was carried out under argon as a protective gas and in a darkroom. The solvent was then carefully distilled off by means of a rotary evaporator.

The cyclohexane was first of all completely removed at 14 torr and at room temperature, after which the dimethylformamide-water mixture was concentrated to about 10 ml at 35°C bath temperature and 1 torr. After separation of the suspended substances by centrifugation the solution volume was concentrated under the same conditions to 1 ml, after which the remaining solvent was removed at 30°C bath temperature under normal pressure in an argon stream.

This procedure is necessary, since substances with relatively high vapor pressures, such as naphthalene, and corresponding homologous compounds are present in the extracts. The fiscous residue obtained has a yellowish orange to brown coloring and exhibited intensive fluorescence in the UV range at 365 and 254 µm. A blank specimen was treated in the same way.

Pyrocarbon specimens were reflux extracted for the reasons given above. Comparison investigations had shown that maximum yields were obtained in this way. For this purpose amounts of 50 g PyC were pulverized in a ball mill under argon (< 50 µm) and reflux extracted for 50 h with 400 ml solvent mixture. Evacuation under suction was then immediately effected, in order to avoid readsorbtion. Subsequent processing was as described for the Soxhlet extraction. In contrast to the experience of Mucha and Schreinlechner (Ref. 6), no white precipitates were observed during evaporation of the solvent. The extracts were of a highly viscous consistency and a yellowish brown color. They also exhibited a marked fluorescence under UV light at 365 and 254 µm.

In addition to liquid extraction, a further extraction is possible by the ultrasonic technique. McIver (Ref. 29) has developed a method of this type, whereby organic material can be extracted from rock sediment in a very short time and with high yields. This method is based on the action of an ultrasonic field at a frequency of 50 kHz. The author states that an ultrasonic extraction of 5 minutes duration is equivalent to 3 hours reflux extraction.

This very time-saving and relatively advantageous method was used for the extraction of soot and pyrocarbon, so that maximum extraction times of 1 h in the case of PyC and 10 min for soot could be obtained. Since the effect of an ultrasonic field on the individual components in soot and PyC was not known, the frequency was reduced to 20 kHz and comparison investigations carried out, in order to detect any decomposition reactions.

In the case of soot extracts, as subsequent investigations showed, no changes could be detected in the composition of the main products, in comparison with other extraction processes. Since corresponding investigations on pyrocarbon extracts could not be carried out in view of its largely unknown composition, only extracts, obtained by means of the reflux method, were taken for analysis.

For the ultrasonic extraction 200 ml extraction mixture were added to 3 g of the soot, deposited on the cover of the fluidized bed, and extracted for 10 min at 20 kHz in a simple glass apparatus (Fig. 8), using an ultrasonic plant, by the firm Schoeller and Co., Type KLK 250.

The powdered PyC specimens obtained under the given conditions, were extracted in amounts of 50 g for 1 h with 400 ml solvent under identical conditions. Subsequent processing was as described for the Soxhlet and reflux extraction processes.

Table 6 gives a summary of the yields of extractable material obtained from the soot by the Soxhlet technique and from pyrocarbon by means of reflux extraction under the given conditions.

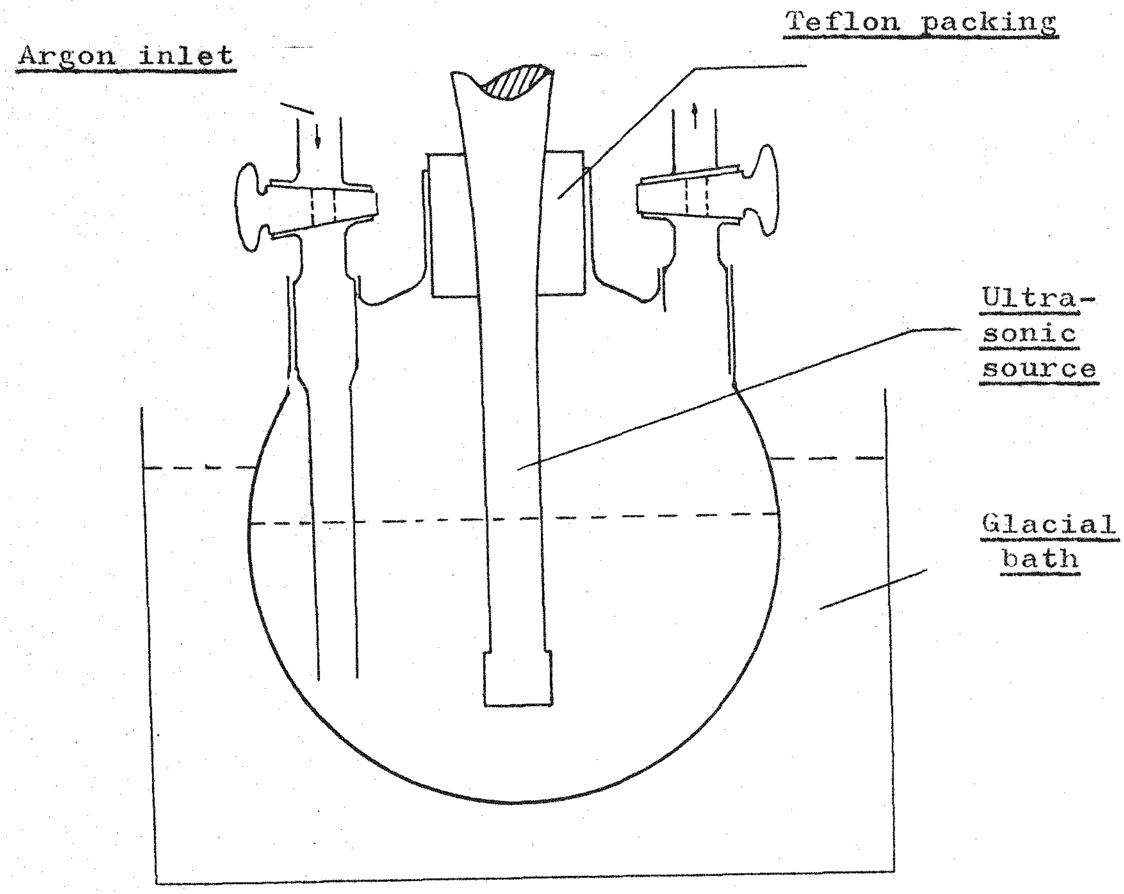


Fig. 8 : Diagram of the device used for the ultrasonic extraction of soot and pyrocarbon

Material	Deposition Temperature °C	Content of Extractable Pyrolysis Byproducts g/g	%
Propene-soot	13oo	o,49	49
Acetylene-soot	15oo	o,17	17
Propene PyC	13oo	o,oo11	o,11
Acetylene PyC	15oo	o,ooo7	o,o7

Table 6 : Content of extractable pyrolysis byproducts in fluidized bed soots and pyrocarbon

3.4 Identification of Fluidized Bed Soot Extracts

3.4.1 Recording of IR and UV Absorption Spectra

In order to detect any carbonyl compounds in the fluidized bed soots, the gas-chromatographically checked solvent-free extracts were examined by means of IR absorption spectroscopy. An infrared lattice spectral photometer, model 421 by Perkin Elmer, was used for recording these spectra. All extracts were measured directly by means of the thin film method immediately after preparation. No absorption bands, characteristic of carbonyl oscillations could be detected either in the propene or in the acethylene soot.

Ultraviolet absorption spectra were recorded for the further characterization of the extracts. These investigations were carried out with the Model SP 800 A instrument by the firm UNICAM. The extracts were measured out with methyl alcohol (spectrally pure, Merck, Darmstadt) in 1 cm quartz cuvettes. Fig. 9 shows the UV absorption spectrum of the "propene soot", which was identical with that of the "acetylene soot".

In order to improve the fine structure of the spectrum, the same extract was dissolved in benzene, separated from insoluble matter and measured out under the same conditions in the transparent spectral range. The spectrum thus obtained is shown in Fig. 9a. It is in this case again identical with the spectrum of the "acetylene soot" extract. The spectra exhibit a structure with absorption peaks at 272.5, 386.5, 318.3 (321.5), 334(375.5), 364, 386 and 431 µm.

3.4.2 Gas-Chromatographic Analysis

The solvent-free extract of the propene and acetylene soots, obtained from 3 g soot by Soxhlet or ultrasonic extraction, was dissolved in 0.5 ml pure benzene, separated from insoluble matter and analyzed by gas chromatography. The residue, easily soluble in polar solvents, was not further investigated in this investigation.

A twin-column gas chromatograph, model 700 by the firm F and M Scientific Corporation with two flame ionization detectors was used for the following analysis. The use of a compensation column was necessary for correction of the base line, since we were working with temperature programming.

We used as separating columns two 24 ft Hi-PAK columns of 1.8" diameter of stainless steel by Hewlett-Packard with SE-52 (methylphenylsilicone rubber) as liquid phase (Ref. 30).

These columns combine the advantage of a high separation capacity (at least 14400 theoretical stages) with a temperature stability up to 300°C. The phase is weakly polar and only to a slight extent specific in relation to the investigated compounds, which are for this reason eluted in the order of their boiling point. A disadvantage is that during the operation the phase is altered in its composition and thus in its chromatographic characteristic as a result of evaporation of the oligomers (Ref. 31).

Table 7 gives the optimal working conditions for gas-chromatographic analysis. Fig. 10

shows the gas chromatograms of the "propene soot" extract with benzene as a solvent under the working conditions given in Table 10.

Columns :	Two 24 ft x 1/8" Hi-PAK stainless steel columns with SE 52
Working conditions :	FID
Helium through flow rates :	30 ml/min, measured at the end of the column at room temperature
Hydrogen flow rate :	30 ml/min
Air flow rate :	400 ml/min
Injector block temperature :	300°C
Detector temperature :	350°C
Furnace temperature, start :	100°C
Furnace temperature, end :	290°C
Heating rate :	2°C/min linear, from 290°C isothermal
Recording rate :	10 mm/min
Quantity of specimen :	2 µl

Table 7 : Operating conditions of the gas chromatograph

Analysis of the gas chromatogram is made by a comparison of the growth retention times of reference substances. An extract of "acetylene soot" was analyzed under identical conditions. Both gas chromatograms were identical in the main products and differed only in the particular quantity ratios of their components.

The gross retention times of the compounds contained in the "propene soot" and "acetylene soot", agreed with the retention times of the following reference substances :

Peak No.	Compound
1	Naphthalene
2	2-Methylnaphthalene
3	1-Methylnaphthalene
4	Diphenyl
5	Acenaphthylene
6	Acenaphthene
7	Fluorene
8	Phenanthrene
9	Anthracene
10	Methylphenanthrene
11	Fluoranthene
13	Pyrene
16, 17	Benzo(a)anthracene and Chrysene
18	Triphenylene
19	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(j)fluoranthene
20	Benzo(e)pyrene
21	Benzo(a)pyrene
22	Pyrylene
23	Benzo(ghi)perylene
25	Coronene

Table 8 : Substances which agree in their retention times with the compounds separated by gas chromatography

The polycyclic aromatic hydrocarbons for reference purposes were obtained from the firms : Th. Schuchardt, Munich; EGA-Chemie KG, Steinheim am Albuch; Fluka AG, Buchs SG (Switzerland) and synthesized compounds from Dr. C. Frischkorn of ZAC of the KFA.

3.4.3 Separation and Identification with a GC/MS Combination

The GC/MS on-line computer combination 100 MS from the firm VARIAN-MAT, described in Section 3.2, was available for the mass-spectrometric analysis.

Table 9 gives the working conditions of the gas chromatograph VARIAN Aerograph 1700, which are identical with the conditions listed in Table 4 for the mass spectrometer.

Column :	24 ft x 1/8" Hi-PAK, stainless steel, with SE-52
Working Conditions :	
Helium flow rate :	30 ml/min (measured at the column outlet at room temperature)
Injection block temperature :	300°C
Furnace temperature, start :	100°C
Furnace temperature, end :	290°C
Heating rate :	10 min isothermal, then 2°C/min, isothermal from 290°C
Quantity of specimen :	3 µl

Table 9 : Operating conditions of the gas chromatograph in the case of GC/MS analysis

A signal analogous to the gas chromatogram gives the total ion count, which was recorded both by a compensation recorder and also with an electrostatic plotter unit (Status 1 model 154).

Fig. 11 shows the total ion current curve of an acetylene soot extract (produced in accordance with Section 3.3.2), expressed by means of an electrostatic plotter. The working conditions are given in Tables 4 and 9. The line working indicates the characteristic number of the mass spectra, which were run every five sec.

During the running time of the gas chromatogram, 840 mass spectra (spectra Nos. 183-1022) were recorded, with registration of the number of peaks and the maximum intensity.

Table 10 gives extracts from the clear text, obtained from the operating sheet recorder, with spectrum numbers, number of peaks and maximum intensity.

Spectra Nos. 266 and 517 with 23 and 83 peaks and intensities of 14800 and 29164 are the mass spectra queried at the highest intensity peak point in Fig. 11. These are the spectra of naphthalene and fluoranthene. They are shown in Figs. 12 and 13.

In this way at the peak maxima of the total ion current chromatogram (Fig. 11) the mass spectra of the substances were queried, evaluated (Ref. 32) and compared with the compounds, revealed by gas-chromatographic analysis. A sample of the extract obtained by reflux extraction of "propene soot" was investigated by the same working procedure.

```
31.7.72 / SPEC  183/LP/REMARKS: WOLFRUM
SPECT  PEAKS   TMAX  TMIN  TMAX  LOSS

 183      6    6825
 184      8    1445   2
 185      8    1521   2

 264      6    7048
 265     15    7520
 266     23   14800
 267     15    8685
 268     10    6974
 269      9    6878

 515     81   32736
 516     78   32736
 517     83   29164  (Range : 10V)
 518     81   18344
 519     79    5991

1021    165   32763
1022    169   32763
```

Table 10 : Spectra Nos. 183-1022, recorded during the running time of a gas chromatogram (extracts)

Both extracts showed an identical composition in regard to the analyzable main products. The following compounds were identified in the propene and acetylene fluidized bed soot by means of gas chromatography and/or mass spectroscopy.

Peak No.	Compound	m/u
1	Naphthalen	128
2	2-Methylnaphthalene	142
3	1-Methylnaphthalene	142
4	Diphenyl	154
5	Acenaphthylene	152
6	Acenaphthene	154
7	Fluorene	166

Peak No.	Compound	m/u
8,9	Phenanthrene and Anthracene	178
10	Methylphenanthrene(s)	192
11	Fluoranthene	202
12	Tetrahydrofluoranthene(?)	202(206)
13	Pyrene	202
14	Dibenzoacenaphthylene(?)	226
15	unknown	226
16,17,18	Benzo(a)anthracene and Chrysene Triphenylene and/or Acepyrene	228
19	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(j)fluoranthene	252
20,21,22	Benzo(e)pyrene, Benzo(a)pyrene Perylene	252
23	Benzo(ghi)perylene	276
24	unknown	276
(25)	Coronene	300

Table 11 : Compounds in propene and acetylene fluidized bed soot, identifiable by means of the GC-MS combination

The last compounds detectable by gas chromatography, coronene of mass 300, was no longer recognizable in the total ion count chromatogram (Fig. 11). For this reason the mass of the molecule ion 300 m/u was queried by means of the computer system in all the mass spectra obtained by fractionated specimen evaporation in accordance with Section 3.2.5. The resulting mass chromatogram of the mass unit 300 is shown in Fig. 14. This shows clearly that coronene was present in the specimen. The smaller peak is due to the presence of higher hydrocarbons in conjunction with the fragment of mass 300.

Fig. 14 : Mass chromatogram of the mass unit 300 in "propene fluidized bed soot"

Fig. 15 shows the structural forms of all the compounds, analyzed in fluidized bed soots.

3.4.4 Discussion of the Results on the Pyrolysis Byproducts in Fluidized Bed Soots

Since the gas-chromatographic analysis of the retention times of reference substances is not sufficient, the separated pyrolysis products from the fluidized bed soot extracts were in addition identified by their mass spectra. The gas-chromatographic separation was carried out by means of highly efficient packed columns. Althouth the separating capacity of these columns is limited, they are sufficient for the separation and identification of the main products in fluidized bed soots.

The use of thin-layer capillaries is to be preferred in view of the coupling with a mass spectrometer, since naturally any overlapping can complicate the interpretation of the mass spectrum or render it impossible (Ref. 30).

A gas-chromatographic separation appears necessary since the spectra of some compounds are so similar that complete mass spectrometric analyses without prior separation cannot produce clear results. Such analyses are only reasonable if as a result of high boiling points or proneness of the compounds to decomposition a gas-chromatographic separation is not possible or appears problematical.

Finally, it has been possible to show that the results obtained by gas-chromatographic analysis agree with the data from the mass spectrometric investigation in the case of the fractionated specimen evaporation of pyrolysis byproducts. It was also found that the compositions of propene and acetylene fluidized bed soot were identical, at least in regard to their identifiable main components.

In the discussion of the gas chromatogram shown in Fig. 10 it was clear that all products following the compound pyrene were only present in low concentrations.

Phenanthrene andanthracene were not separated in view of their structural similarity. Anthracene only appears in the form of a minor shoulder and has a mass spectrum extraordinarily similar to that of phenanthrene.

This shoulder could not be detected in the total ion current chromatogram, but the mass spectra on the sides of the peak confirmed that both compounds were present.

Peak 10 in the same spectrogram probably contains several methylphenanthrenes.

Peak 12 shows on the basis of the mass spectrometric investigation a molecular ion 202 m/u. This may have been the compound tetrahydrofluoranthene (206 MU), which could not, however, be determined beyond doubt due to the absence of a reference substance.

Peak 14 with the molecular ion 226 m/u may have been dibenzoacenaphthylene. Here again the absence of a reference substance prevented any clear finding being reached.

Peaks 16 and 17 were probably due to a mixture of chrysene and benzo(a)-anthracene.

Peak 18 is identical in its retention time with the compound triphenylene. This may, however, have been the compound acepyrene (cyclopenta-cd)pyrene), for which again no reference substance was available. These two peaks were not resolved in the total ion current chromatogram. The molecular ion 228 m/u was detected over the whole peak.

Peak 19 is in all probability a mixture of various benzofluoranthenes with the molecular ion 252 m/u.

Benzo(e)pyrene is screened in the gas chromatogram under the given conditions by benzo(a)pyrene and is only recognizable as a minor shoulder. No resolution was observed in the total ion count chromatogram. The molecular ion 252 m/u was detected over the whole peak.

Peaks 15 and 24 with the molecular ion 226 m/u and 276 m/u could not up to now be identified. Some of the peaks visible in the gas chromatogram were no longer recognisable in the total ion current chromatogram, so that no evaluation has yet been made.

One disadvantage has been that the increasing furnace temperature of the gas chromatograph caused evaporation of the liquid phase on the column. This process caused a considerable increase in the number of background peaks in the mass spectra.

This is clear from the ratio of peak numbers in spectrum No. 266, Fig. 12, naphthalene, with 23 peaks and spectrum No. 517, Fig. 13, fluoranthene, with 83 peaks. In the high-boiling range the substances were only present in low concentrations, so that the background was superimposed over the whole spectrum. It was therefore necessary to adopt the procedure of subtracting the background spectrum of the phase, located in front of a substance peak, from the substance peak over the whole computing program. In this way relatively clear mass spectra were again obtainable.

3.5 Pyrocarbon

3.5.1 Photographs of IR and UV Absorption Spectra

Investigation of the solvent-free extracts of "propene and acetylene pyrocarbon", using IR and UV adsorption spectroscopy, were carried out under the same conditions as those used in Section 3.4 for analysis of the fluidized bed soots.

The IR spectra gave no indications of the presence of carbonyl compounds in contrast to the results of Mucha and Schreinlechner (Ref. 6).

The UV absorption spectrum obtained from the propene pyrocarbon extract with methyl alcohol as a solvent is shown in Fig. 16. In contrast to the corresponding propene soot, no fine structure is apparent from the spectrum and a solution in benzene produced no improvement in this respect.

The UV spectra of "propene and acetylene pyrocarbon" extracts were identical.

3.5.2 Mass Spectrometric Investigation

Pyrocarbon deposited from acetylene was extracted, as described in Section 3.3.2, prepared and then underwent fractionated evaporation (for conditions see Table 4) directly on to the ion source of the mass spectrometer. Fig. 17 shows mass spectrum No. 1015 (range : 10 V) of the acetylene pyrocarbon extract from a series of 173 spectra.

According to Böcker (Ref. 33) no appreciable release rate can be detected as a result of the direct evaporation of possible pyrocarbon components on to the ion source of a mass spectrometer at heating temperatures

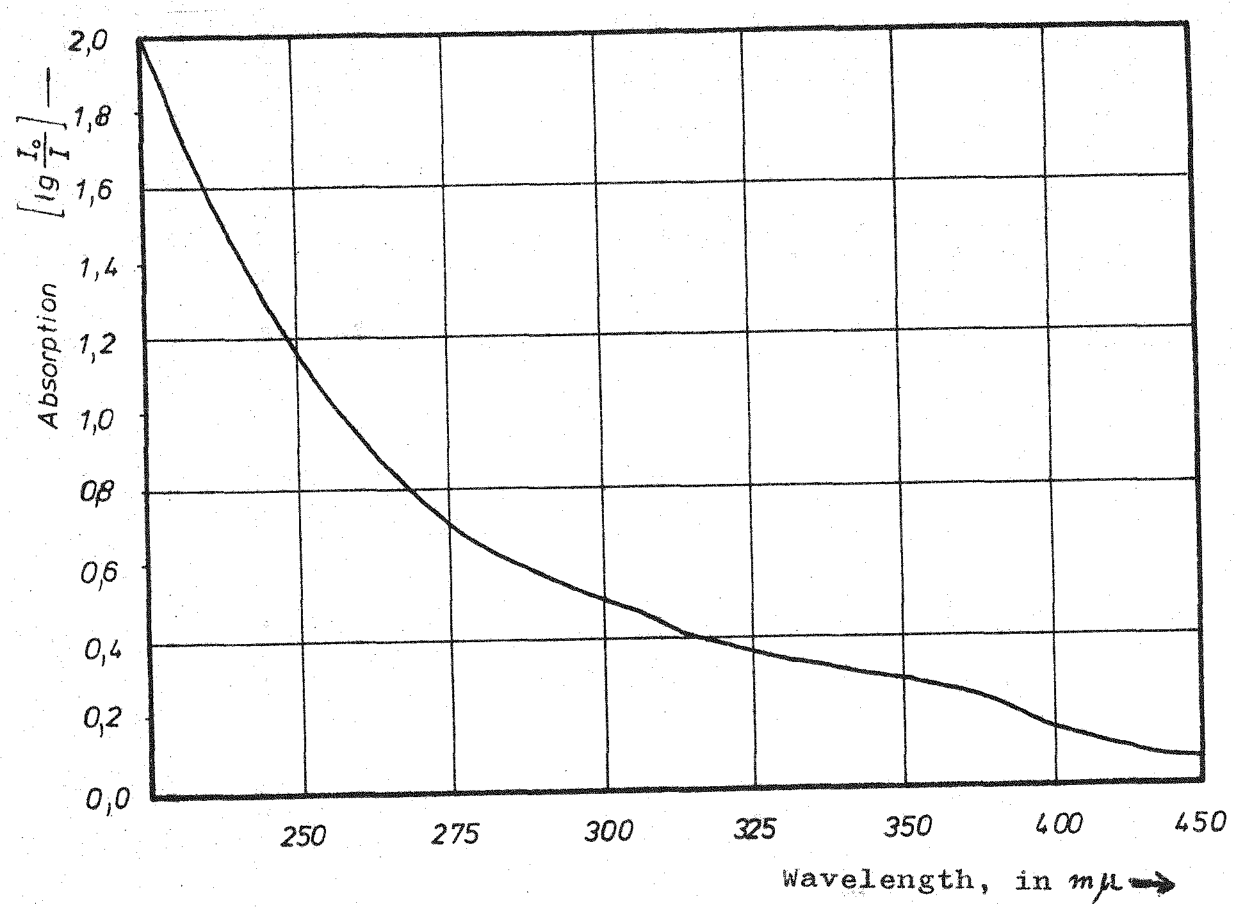


Fig. 16 : UV absorption spectrum of the propene pyrocarbon extract (in methyl alcohol, layer thickness 0.5 cm)

of 400-2100°C and within a mass range of 2-200 MU. On the one hand this result indicates an excessively low concentration of decomposition products in the pyrocarbon in this temperature range and, on the other hand, a gettering of volatile components in the cooled apparatus system cannot be completely excluded.

A concentration of possible PyC components by solvent extraction was therefore regarded as more promising. Whereas soot samples can be directly degassed, the products contained in pyrocarbon are concentrated by solvent extraction and then subjected to fractionated evaporation. Allowing for this factor the following findings may be regarded as valid :

The weight per unit area of the pyrolysis products contained in the soot differs in its mass range from that of the pyrocarbon. Whereas in the soot specimens a clear reduction in the mass coverage was observed from 300 MU onwards and the maximum detectable mass in the case of acetylene soot was 444 MU, a reduction in the mass coverage of the pyrolysis products in acetylene pyrocarbon was only observable from about 450 MU. The maximum detectable mass was in this case 507 MU.

This displacement in the direction of higher masses may have been attributable to the different temperature conditions and the associated mechanism of formation.

3.5.3 Gas-Chromatographic Analysis+)

The solvent-free extract from 50 g propene pyrocarbon, obtained in accordance with Section 3.3.1, was extracted by shaking several times with about 0.5 ml ultrapure benzene and the purified extract concentrated to 0.3 ml in an argon stream. A specimen was separated by means of gas chromatography. The residue, soluble in polar solvents was not further investigated in this paper.

The separation was intended to give a first picture of the number of detectable pyrolysis products and of their boiling points in PyC. A more detailed identification was not carried out. The analysis was carried out with a Hewlett-Packard Model 5750 gas chromatograph with two flame ionization detectors. A compensation column was used for correction of the base line. We used as columns, as in the gas chromatographic investigation of the fluidized bed soot, two HI-PAK columns by Hewlett-Packard with SE-52 as the liquid phase. The working conditions are summarized in Table 12.

Columns :	two 24 ft x 1/8", HI-PAK of stainless steel, with SE-52
Detector :	FID
Range :	10^2
Attenuation :	8
Helium flow rate :	30 ml/min
Hydrogen flow rate :	30 ml/min
Air flow rate :	400 ml/min
Injection block temperature :	300°C
Detector temperature :	350°C
Furnace temperature, start :	100°C
Furnace temperature, end :	290°C
Heating up regime :	2°C/min linear, from 290°C onwards isothermal
Recorder rate :	0.25 inch/min
Quantity of specimen:	3 µl

Table 12 : Operating conditions of the gas chromatograph

The gas chromatogram thus obtained is shown in Fig. 18. A comparison between the gas chromatogram of the pyrolysis byproducts from acetylene soot and the gas chromatogram of compounds from propene pyrocarbon, obtained in this analysis, reveals a very much more frequent occurrence of pyrolysis products with higher boiling points in the pyrocarbon than in the corresponding fluidized bed soot. Compounds also occur in this case having a higher boiling point than coronene.

This displacement towards higher boiling points (masses) is apparent, as already mentioned in Section 3.7, from a comparison of the mass spectra of the pyrolysis byproducts in acethylene soot and acetylene pyrocarbon (Figs. 7 and 17).

An identification of the compounds contained in pyrocarbon will be the subject of further investigation, which will deal in particular with the question of a possible agreement between the pyrolysis products in the two materials.

4. Discussion of the Results

The investigations, which have been carried out, have confirmed that during the coating of nuclear fuel particles with propene and acetylene as pyrolysis gases under fluidized bed conditions polycyclic, aromatic hydrocarbons are formed, which are contained both in the soot and also in the pyrocarbon produced during the same purolysis process. The question then arises of whether the soot-type components (Ref. 24), detected in some pyrocarbon varieties, are in the main carriers of these pyrolysis byproducts.

Of the compounds identified in this paper, aromatic hydrocarbons up to the molecule pyrene have already been detected by Oro and Han (Ref. 16), who obtained these products during the pyrolysis of methane at 1000°C. Higher-molecular compounds have been detected by Chakraborty and Long (Ref. 14) in soots from diffusion flames, the pyrolysis byproducts of which agreed essentially with the compounds in fluidized bed soots. However, these authors identified no compounds having boiling points below that of acenaphthylene, which have however been detected in our investigations. In the present paper, moreover, an additional mass-spectrometric analysis by fractionated specimen evaporation of the pyrolysis byproducts on to the ion source of a mass spectrometer has enabled the number of identifiable compounds to be extended into the boiling range, which could no longer be covered by gas chromatography.

Both the gas-chromatographic and also the mass-spectrometric results from the investigation of fluidized bed soot extracts showed in this case, irrespective of the type of pyrolysis gas used, an identical composition of these extracts.

In experiments, carried out with m-xylene as extraction agent under the action of oxygen, white crystalline precipitates occurred during the evaporation of the solvent, which were identified as oxidation products of m-xylene. For this reason we selected a solvent mixture, which was not sensitive to atmospheric oxygen. In addition the extraction was carried out in an argon atmosphere. This extraction technique again gave rise to a precipitate and the IR spectroscopic analyses still indicated the presence of oxidized compounds with carbonyl groups.

We can, therefore, as anticipated exclude any formation of detectable oxygen-containing hydrocarbons during the pyrolysis process.

In agreement with the results of Mucha and Schreinlechner (Ref. 6), we found with an increasing deposition temperature a clear decrease in the weight fractions of extractable compounds in the pyrocarbons.

After identification of the compounds detectable in the PyC and a comparison with the pyrolysis products adsorbed on the soot it will be possible to reach further conclusions on the chemical processess occurring in the fluidized bed. The possibility is conceivable of changing the compounds, present in the pyrocarbon and soot, both in their composition and also in their relative quantity ratios by a direct action on their mechanism of radical formation (Ref. 34). Gaseous or evaporable additives, which as radical-capturing or radical-forming agents influence the pyrolysis process, would be suitable for this purpose.

The possibly associated change in the structure of the pyrocarbon coatings could provide further information on the formation mechanism and lead to a modification of the reactor engineering behavior of the pyrocarbon.

5. Summary

In the context of the development of improved fuel particles for high-temperature reactors, the pyrocarbon deposited on fuel kernels in fluidized bed and the soot produced during this pyrolysis process have been analyzed for their pyrolysis byproducts.

The aim of this study was to obtain information on possible changes in the pyrocarbon structure due to the influence of the pyrolysis products. It was also intended to provide information

on the deposition mechanism of pyrocarbon during the thermal decomposition of lower hydrocarbons.

The pyrocarbons and fluidized bed soots used were extracted by various methods using a solvent mixture. In the case of acetylene pyrolysis the percentages by weight of extractable pyrolysis byproducts obtained at a deposition temperature in the fluidized bed of 1500°C, were 0.07 % in the pyrocarbon and 17 % in the fluidized bed soot. The corresponding values in the case of propene pyrolysis at a decomposition temperature of 1300°C were 0.11 % for pyrocarbon and 49 % for the soot type of material.

Analysis of the extracts was carried out both by gas chromatography and also by a combination of gas chromatography and mass spectrometry. By means of an additional mass-spectrometric investigation incolving the direct evaporation of the pyrolysis byproducts on to the ion source of a mass spectrometer, the quantity of compounds detectable by gas chromatography was extended into the higher-boiling range.

The extracts from fluidized bed soots possessed an identical composition of pyrolysis byproducts, irrespective of whether they originated from acetylene or propene pyrolysis.

21 polycyclic aromatic hydrocarbons were identified as main products; the mass spectra of 4 further compounds were found.

Polycyclic hydrocarbons with higher boiling points were recorded in a gas chromatographically separated pyrocarbon extract than in extracts from fluidized bed soots. As was to be expected, a qualitative comparison showed that the identified compounds in the soot and pyrocarbon extracts were identical in the lower mass ranges. The higher-molecular polycyclic compounds present in addition in the pyrocarbon are evidence in favor of the assumed pyrolysis mechanism of hydrocarbons, such as the building up of pyrocarbon via low aromatic compounds. The aim of future investigations will be to study this mechanism in quantitative terms.

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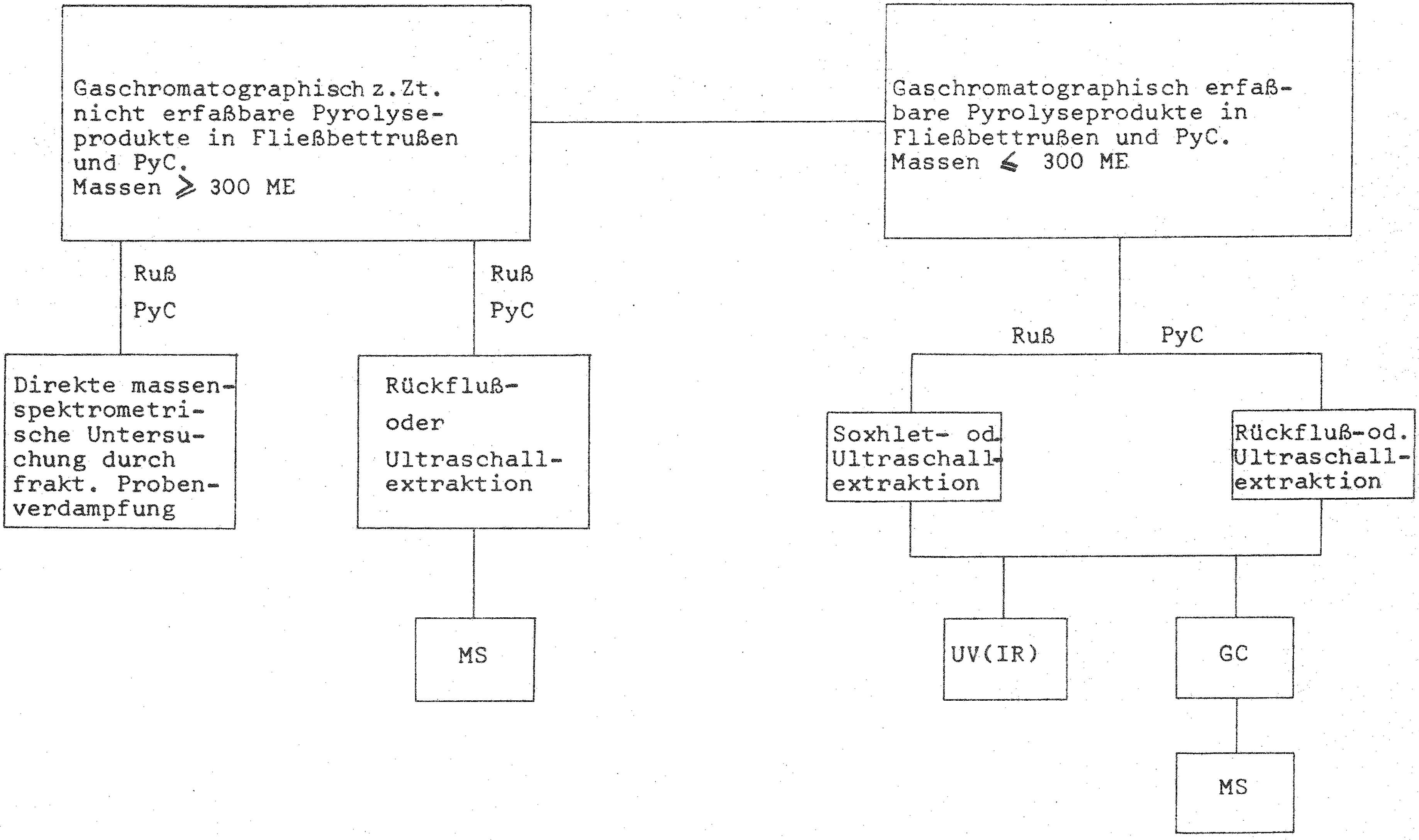


Abb. 4: Arbeitskonzeption

1	Basis Einheit
2	Hochvakuum-Pumpenteil
3	Elektronenstoß-Ionenquelle
4	Emissionsregler
5	Ionenquelle zur Totalstrommessung
6	Collector
7	Multiplier
8	Probeneinlaßsystem
9	GC/MS Interface
1o	Direktes Probeneinlaßsystem für Feststoffe
11	Hochvakuum-Pumpenteil
12	Kompensationsschreiber
13	Galvanometerschreiber
14	Magnetstromregler
15	Vorvakuum

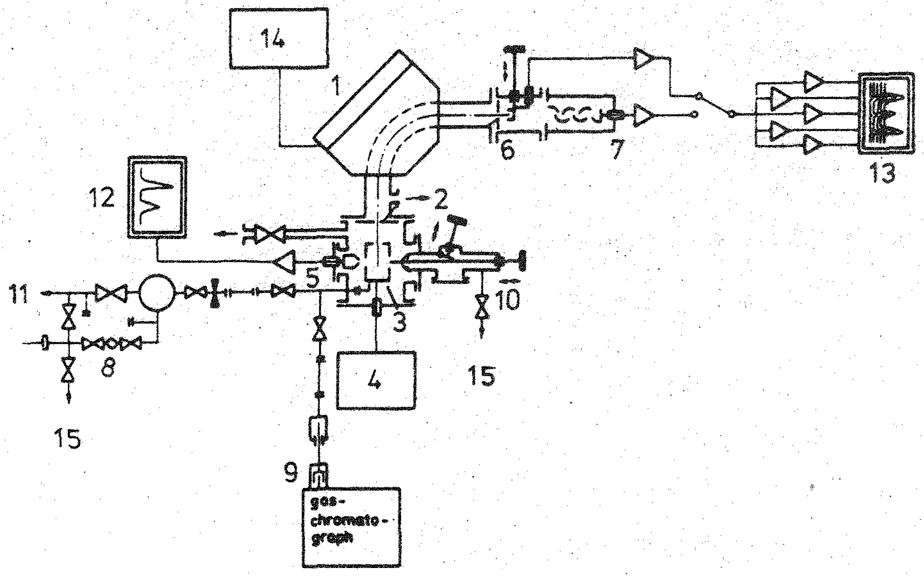


Abb. 5: Schema der verwendeten GC-MS Kombination

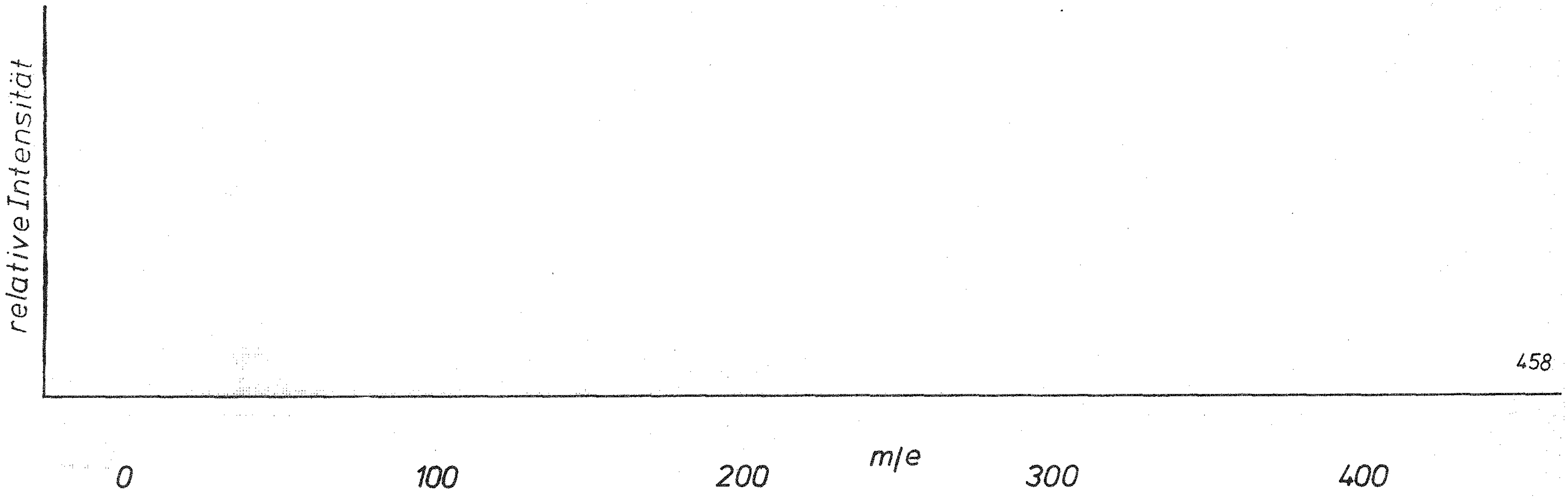


Abb. 6: Massenspektrum der Pyrolysebeiprodukte in "Propen-Ruß"
Arbeitsbedingungen: Tab. 4

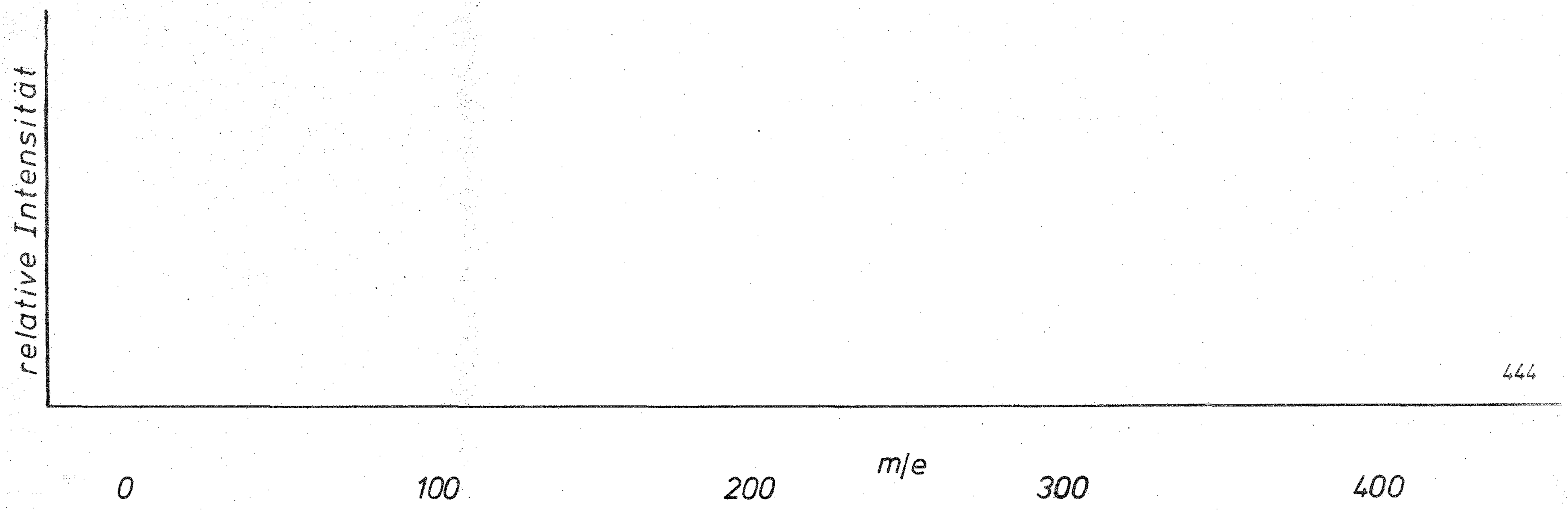


Abb. 7: Massenspektrum der Pyrolysebeiprodukte in "Äthin-Ruß"
Arbeitsbedingungen: Tab. 4

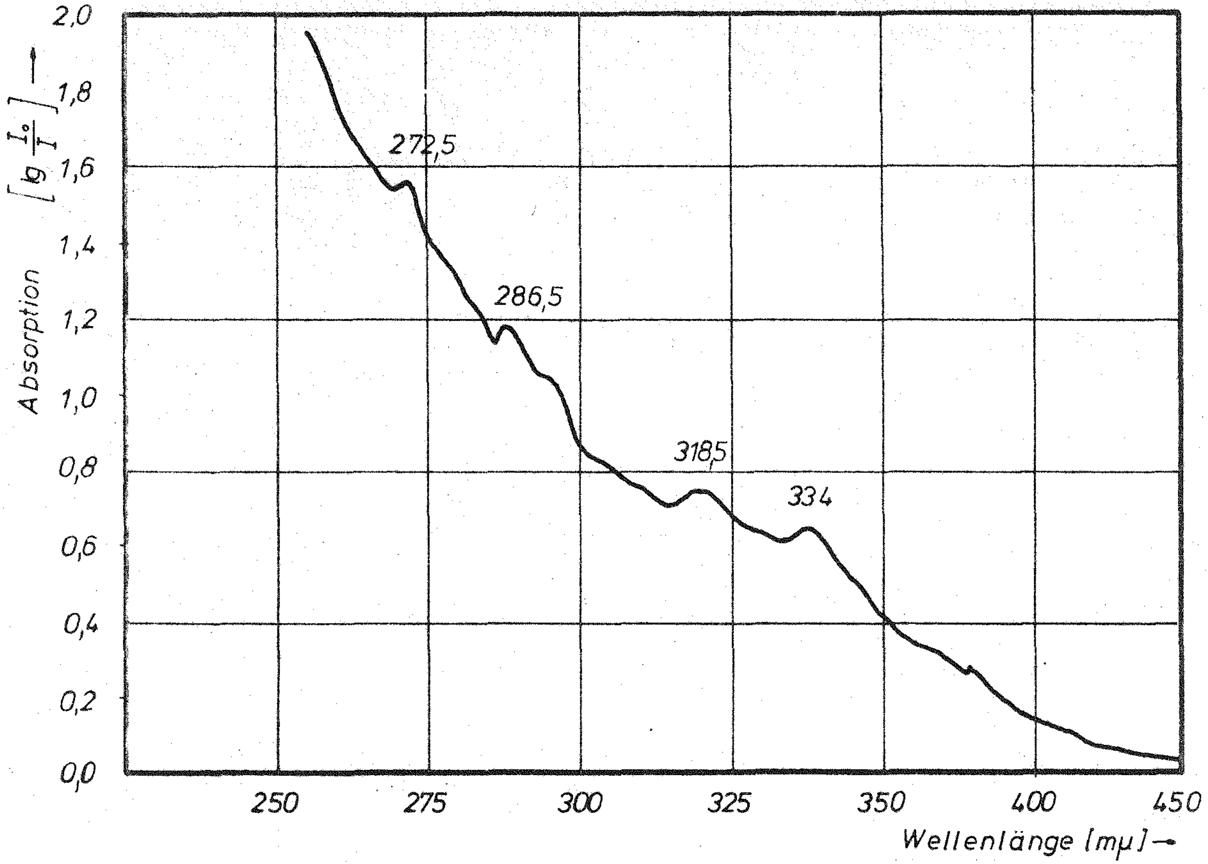


Abb. 9: Ultraviolett-Absorptionsspektrum des "Propen-Ruß"-Extraktes (in Methanol; Schichtdicke 1 cm)

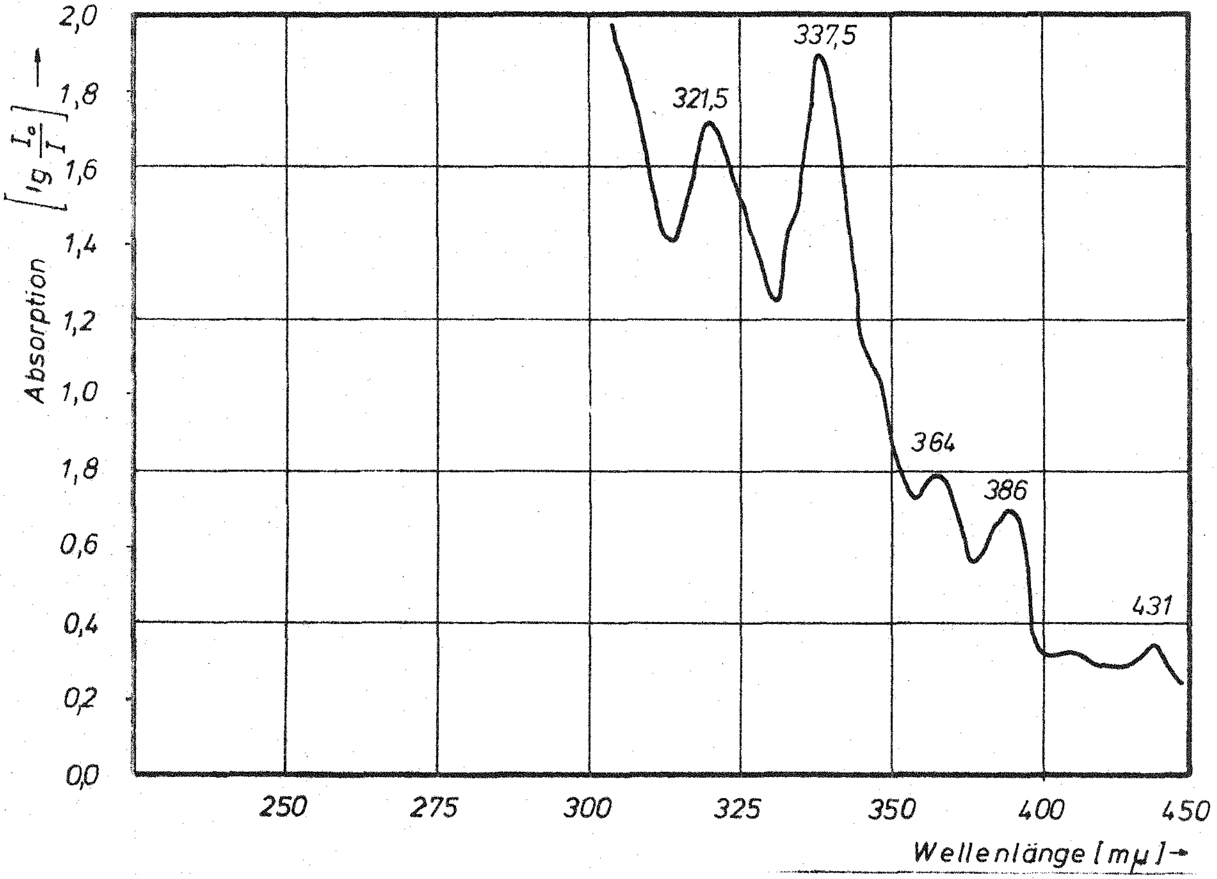


Abb. 9a: Ultraviolett-Absorptionsspektrum des "Propen-Ruß"-Extraktes (in Benzol; Schichtdicke 1 cm)

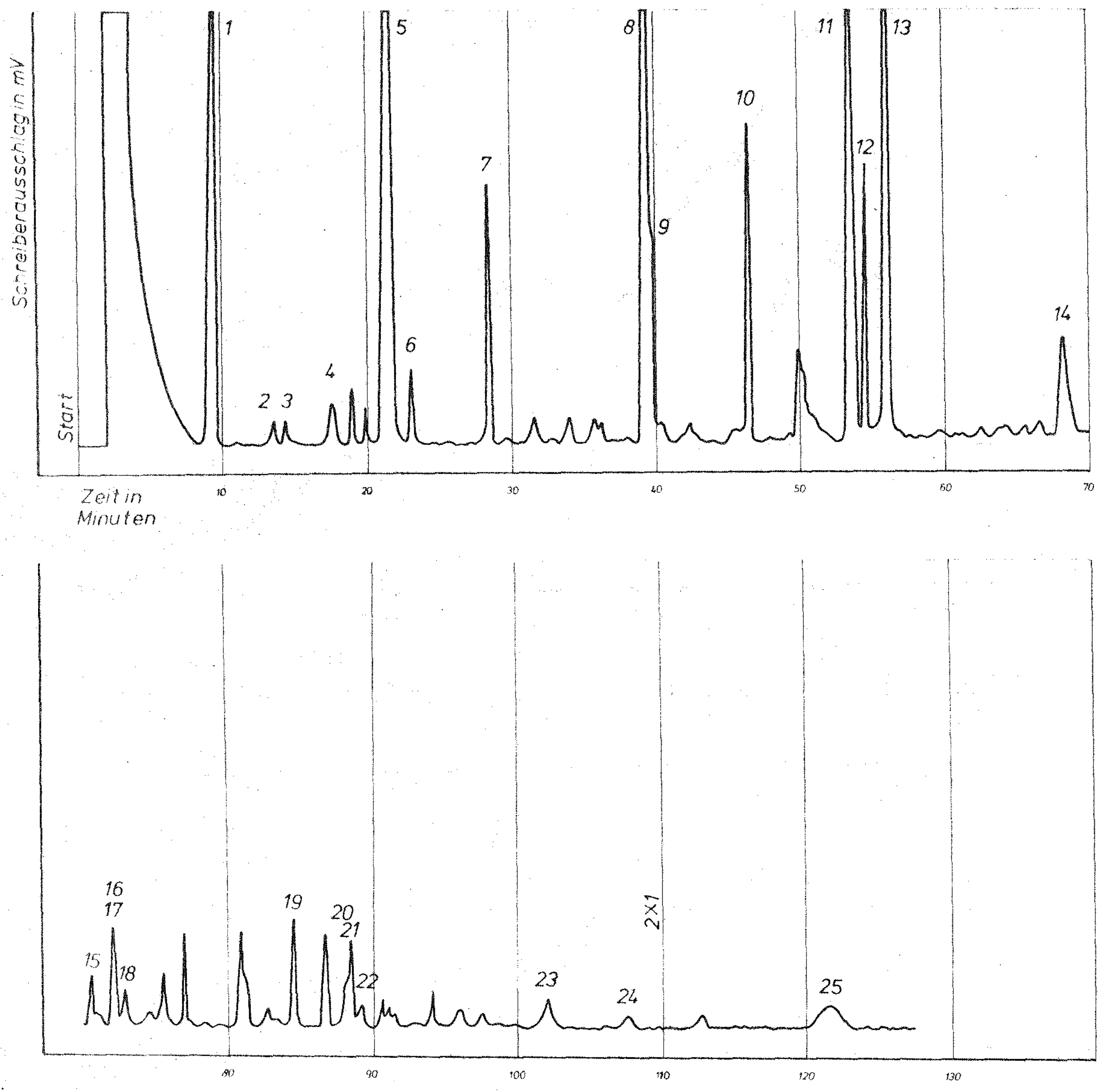


Abb. 10: Gaschromatogramm des "Propen-Ruß"-Extraktes
Arbeitsbedingungen: Tab. 7

Die Nummern der Peaks stimmen mit den in Tab. 8 aufgeführten Verbindungen überein.

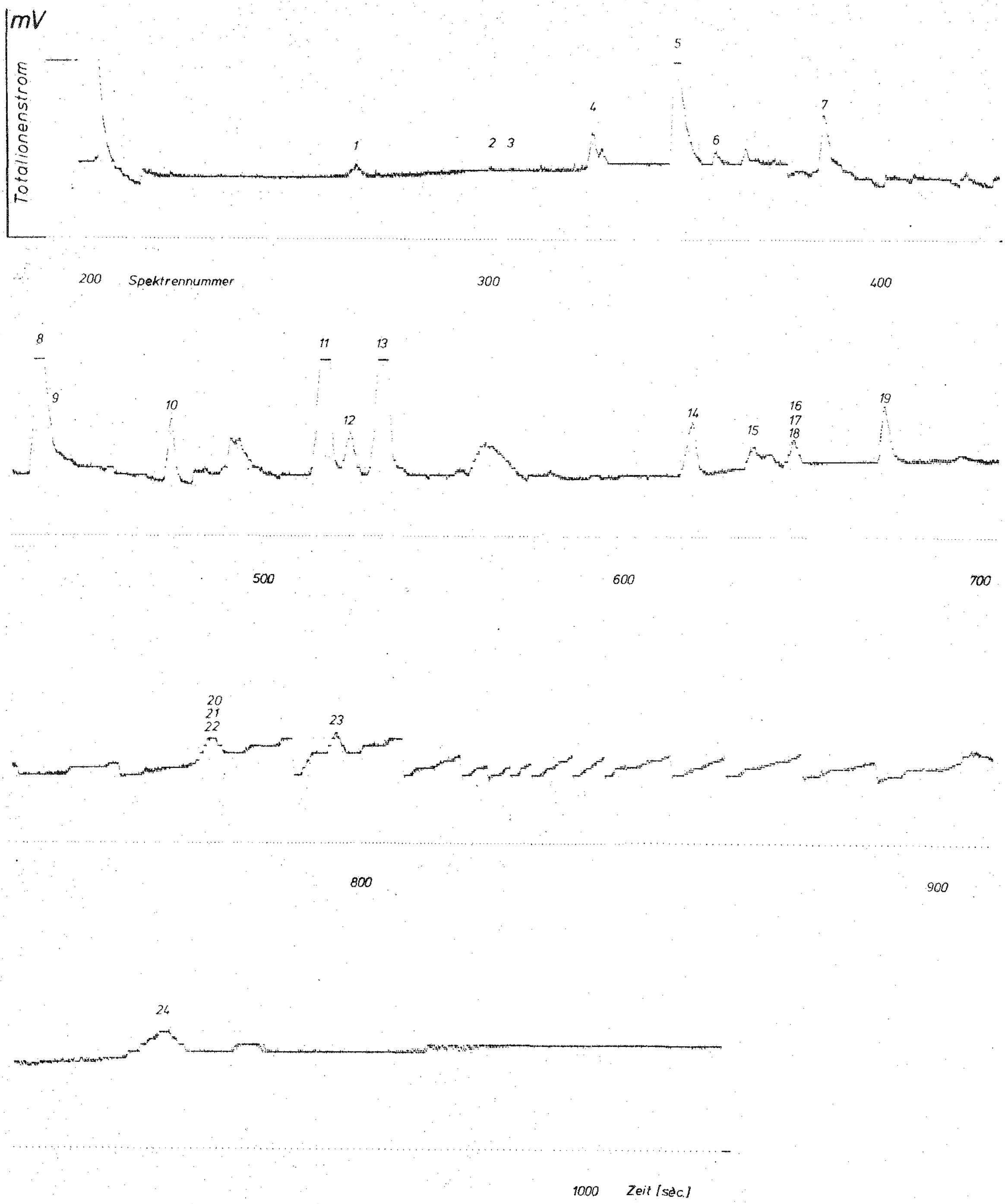


Abb. 11: Totalionenstromplott des "Äthin-Ruß"-Extraktes

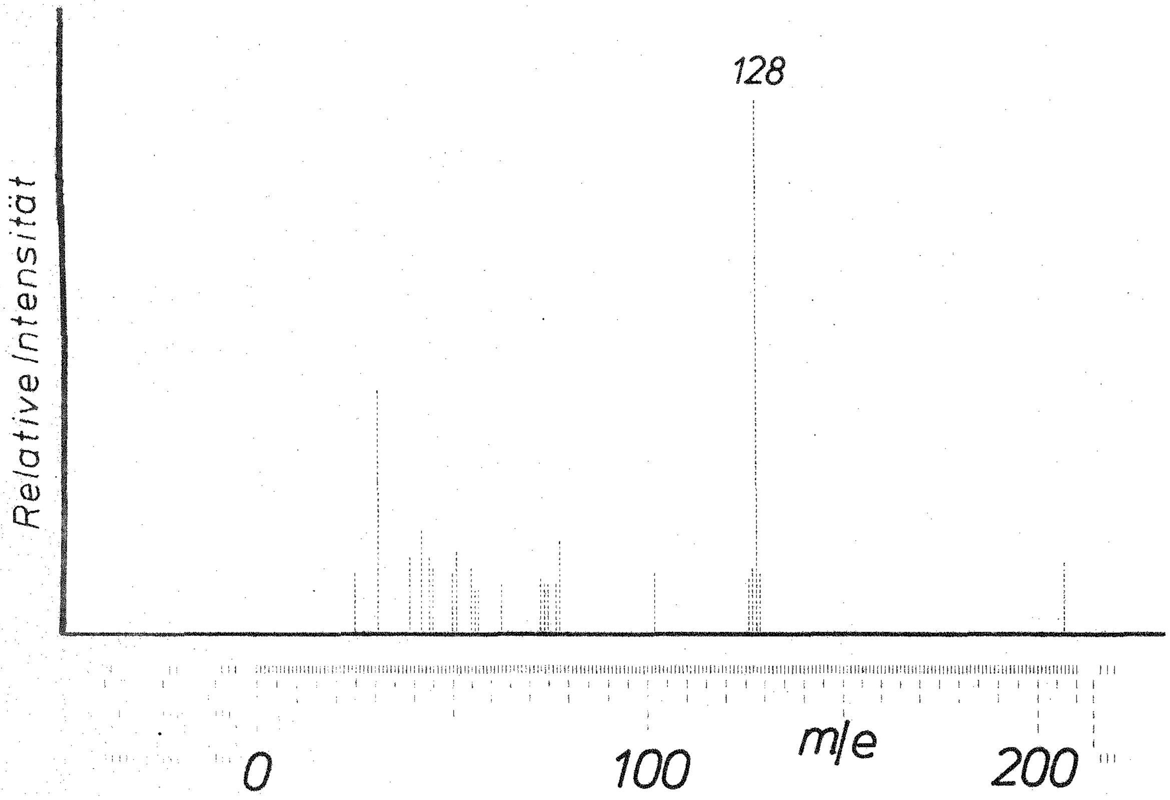


Abb. 12: Spektrum Nr. 266. Verbindung: Naphthalin

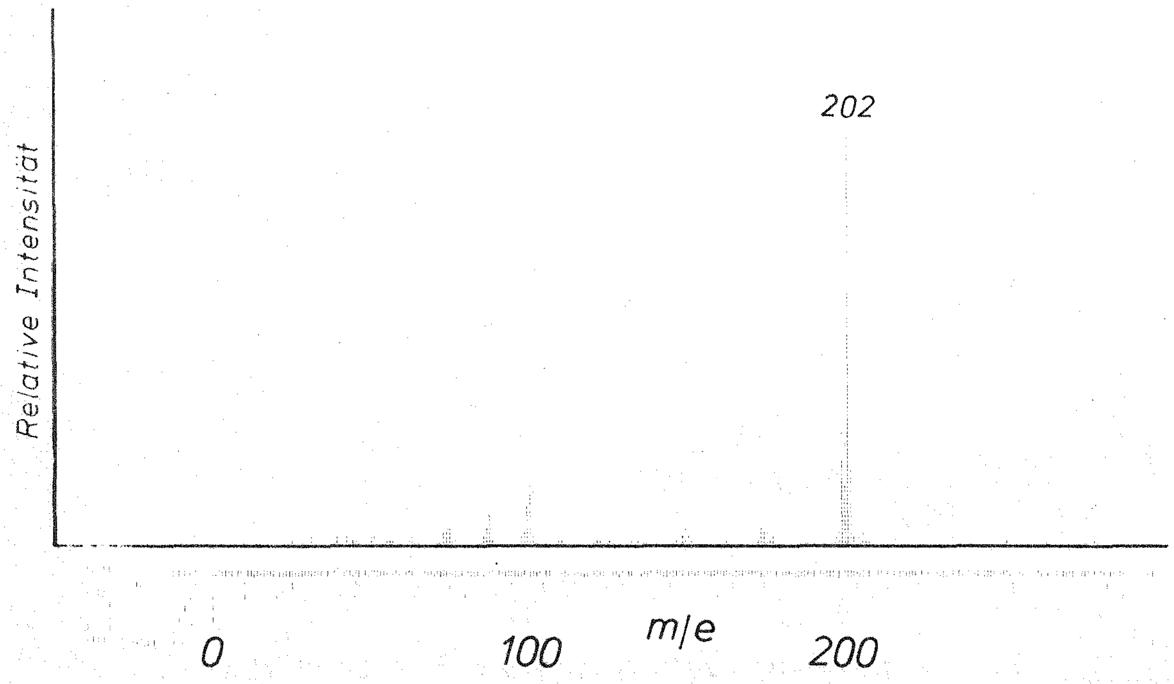
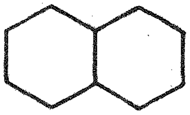
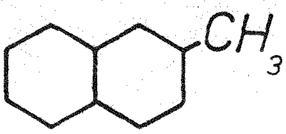


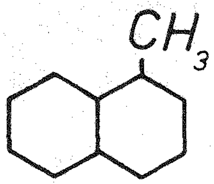
Abb. 13: Spektrum Nr. 517. Verbindung: Fluoranthen



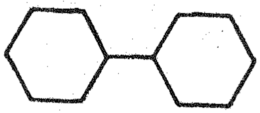
Naphthalin
1



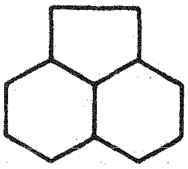
2-Methylnaphthalin
2



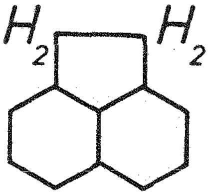
1-Methyl-
naphthalin
3



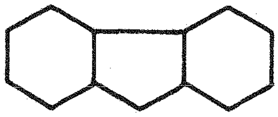
Biphenyl
4



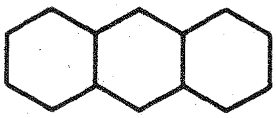
Acenyphtylen
5



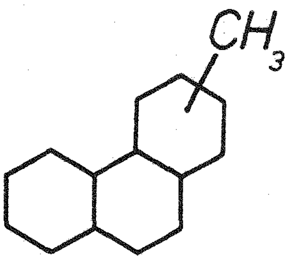
Acenaphten
6



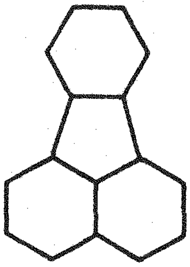
Fluoren
7



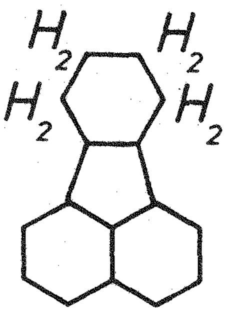
Anthracen
9



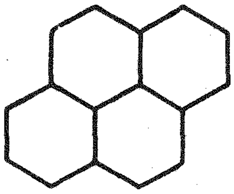
(Methyl-)-Phenanthren(e)
8,10



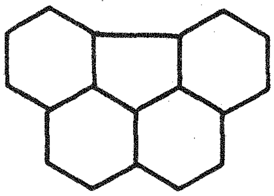
Fluoranthen
11



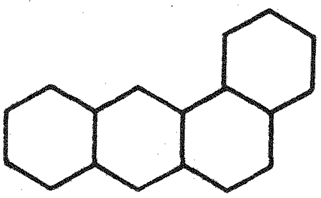
Tetrahydro-
fluoranthen
12(?)



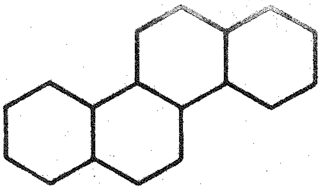
Pyren
13

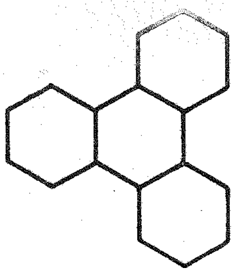


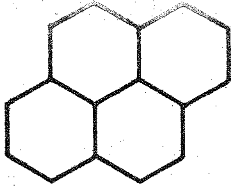
Dibenzoacenaphtylen
14(?)

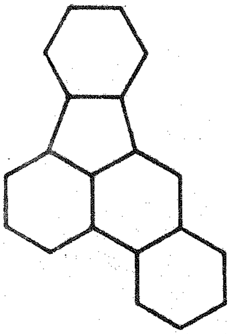


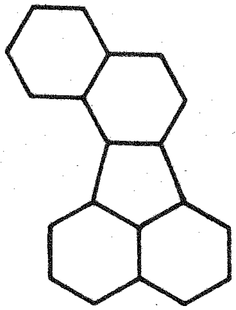
Benzo(a)anthracen
16

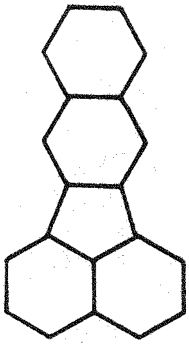

Chrysen
17

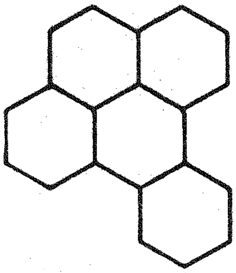

Triphenylen
18

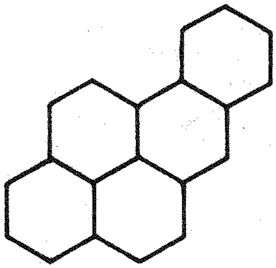

Cyclopenta(cd)pyren
(Acepyren)
18(?)

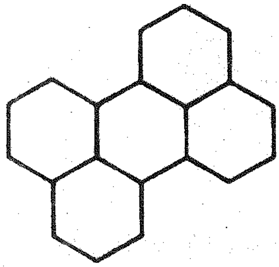

Benzo(b)fluoranthen
19

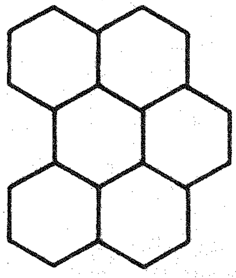

Benzo(j)fluoranthen
19


Benzo(k)fluoranthen
19


Benzo(e)pyren
20


Benzo(a)pyren
21


Perylen
22


Benzo(ghi)perylen
23

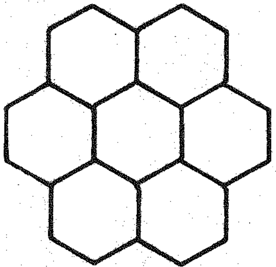

Coronen
25

Abb. 15: Strukturformeln der in Fließbettruß identifizierten Verbindungen

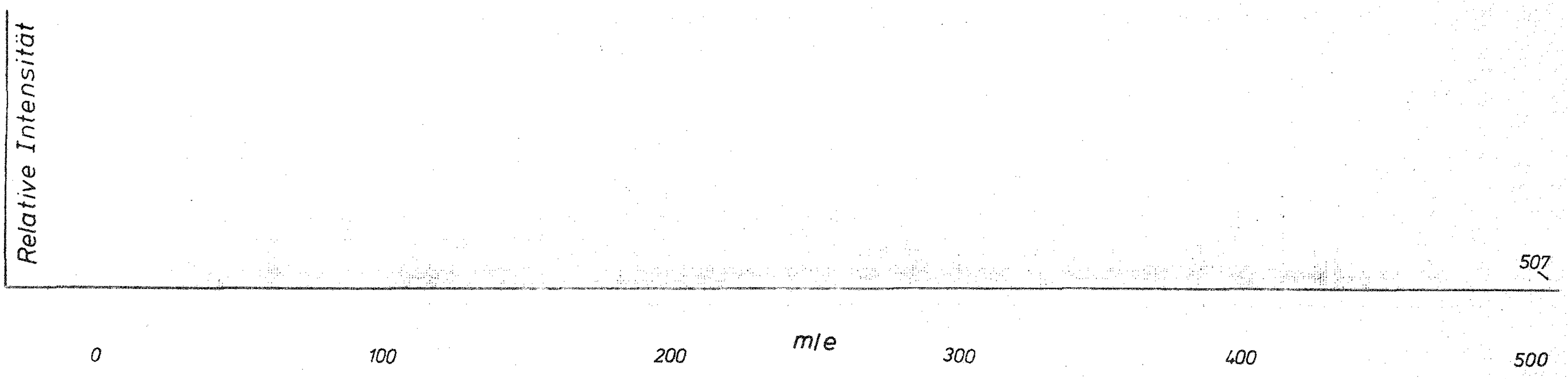


Abb. 17: Massenspektrum des "Äthin-PyC"-Extraktes.
Arbeitsbedingungen: Tab. 4

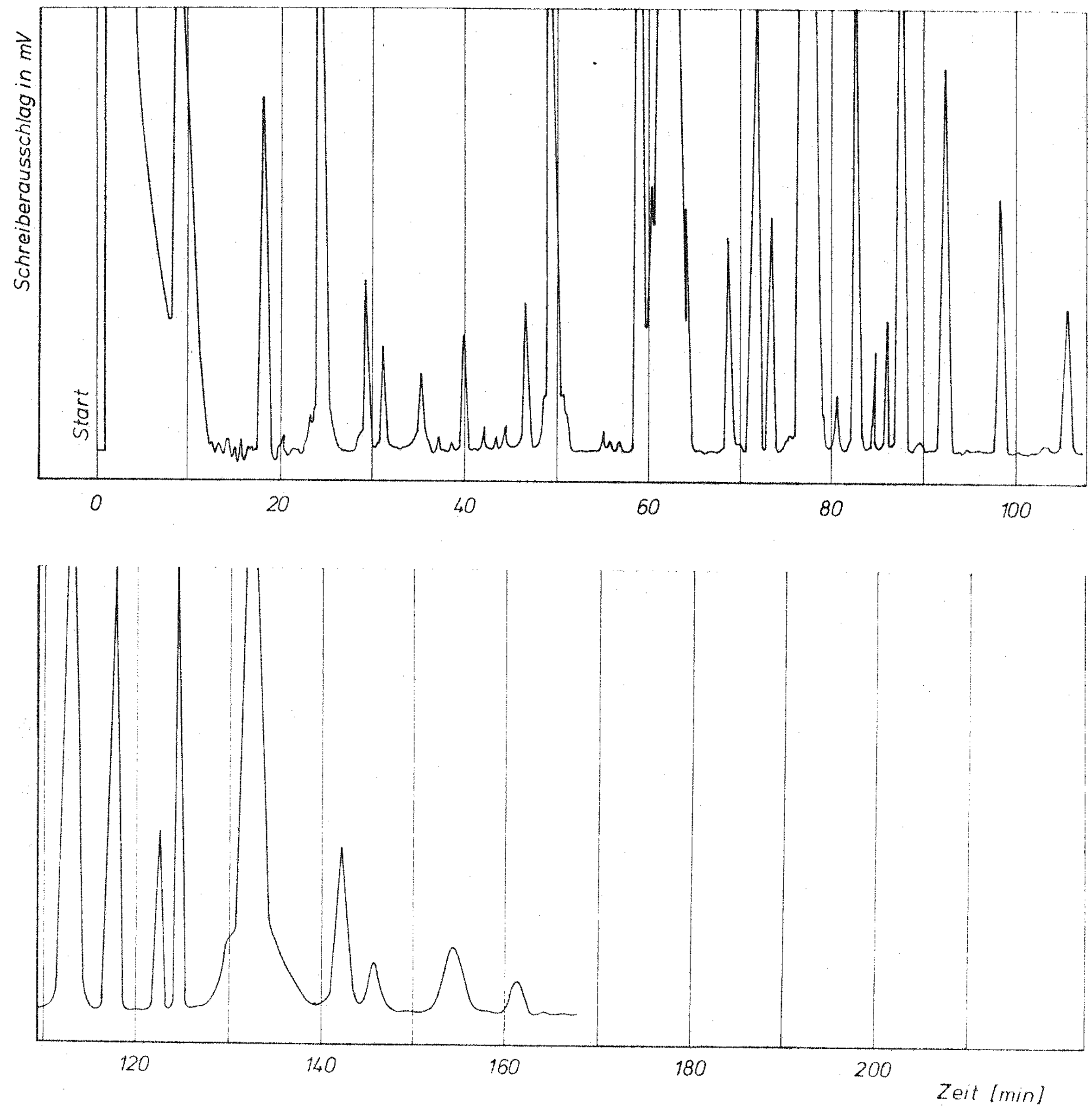


Abb. 18: Gaschromatogramm des "Propen-PyC"-Extraktes. Arbeitsbedingungen: Tab. 13