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# Influence of Elemental Sulfur on the De-Novo-Synthesis of Organochlorine Compounds from Residual Carbon on Fly Ash

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## Abstract

Thermal experiments between 300°C and 500°C were performed with fly ash of a municipal waste incineration plant which had been spiked with elemental sulfur. The influence of elemental sulfur on the heterogeneous carbon-decomposition and the de-novo-synthesis of polychlorinated compounds was investigated. Compounds such as polychlorinated dibenzodioxins, dibenzofurans, benzenes, benzo- and dibenzothiophenes, $Cl_4$-thiophene, $Cl_4$-thienothiophene, $Cl_7$- and $Cl_8$-phenylthiophene were quantified. Apart from those, other intermediate structures were determined. These compounds are mainly aromatics with a vinyl- or butadienyl-group, stabilized by perchlorination. In detail, the compounds are $Cl_7$- and $Cl_8$-styrene, $Cl_{10}$-vinylnaphthalenes, $Cl_{10}$-phenylbutadiene, $Cl_{10}$-octatetraene, $Cl_{10}$-bis-butadienylsulfides and $Cl_{12}$-stilbenes. ©1998 Elsevier Science Ltd. All rights reserved

## Key Words

de-novo-synthesis, fly ash, carbon, sulfur, intermediate structures, PCDD, PCDF, PClBz, chlorinated bezo- and dibenzothiophenes, stilbenes, vinyl- and butadienyl-compounds

## Introduction

In municipal waste incineration plants, a large variety of polychlorinated trace compounds are formed in the exhaust gas system. Since the discovery of PCDD/F on fly ash of municipal waste incinerators [1], the research on incineration processes indicated, that the "de-novo-synthesis" [2] is suitable to explain the observations. In this theory, a new formation of polychlorinated compounds occurs as heterogen catalytic reactions [3] in the cooling zone between 250° and 350°C on the surface of the fly ash. The educts are carbonaceous material, oxygen and anorganic chloride with mineral components as catalysts. The carbonaceous material on fly ash is a source for the formation of polychlorinated organic compounds during the metal-catalyzed degradation [4,6]. Parallel to the decomposition of the carbon, a decrease of the TOX (total organic halogen) and an increase of the EOX (extractable organic halogen) takes place [6]. The surface of the macromolecular carbon and the adsorbed crack-products are partly stabilized against oxidation to $CO_2$ by chlorination [7,8]. Stieglitz et.al. [12] found, that $^{13}C_{12}$-PCDD/PCDF are formed via de-novo-synthesis by heterogen catalyzed decomposition of $^{13}C$-carbon on fly ash at 300°C.

The objective of this work was to investigate the formation of polychlorinated structures during the metal-catalyzed decomposition of the macromolecular carbon. In good approximation, the oxidation of the carbon can be described as a combination of two reactions [6]. In the course of these reactions, a series of polychlorinated compounds are formed as by-products and released. In this paper, the influence of different amounts of elemental sulfur on fly ash, added before thermal treatment, is discussed. In this connection, we investigated the change of the activity of the metal catalyst and the kinetics of the carbon oxidation, by the presence of sulfur. Besides PCDD / PCDF / PClBz, the influence on the formation of several other halogenated compounds was determined. Further on, the ability of sulfur to react with instable cracking products of the macromolecular carbon structure e.g. butadienes, styrenes, is discussed.

## Experimental

Materials, thermal treatment, clean-up: Fly ash from an electrostatic precipitator of a MWI-plant (4,26 % carbon) was used in this study. The inhomogeneous material was ground and refluxed five times with cyclohexane and benzene, filtered and dried under reduced pressure (0,15 mbar) at room temperature for 48 hours. Then, 1 to 3% elemental sulfur (99,999% Merck) was added to the fly ash. For all samples, thermal treatment was performed for 30, 60, 120 and 240 min.. The samples were treated in a vertical quarz tube with a frit at the bottom using an ascending flow of wet synthetic air (50 ml/min.; 30,8 mg/l $H_2O$) at 350°, 400° and 450°. Two impingers (benzene, cyclohexane) were used for collecting volatile organic compounds. The residue was extracted for 24 hrs. with $CCl_4/CH_2Cl_2$ (9:1) under reflux. The clean-up of the extraxt and the solution of the washing bottles was done separately. For removing the sulfur, the solutions were extracted with TBAH (tetrabutylammonium-hydrogensulfate) and natriumsulfite [5]. After thermal treatment and clean-up, the residual carbon was determined by total oxidation at 850°C and catalytic conversion to $CO_2$. The quantification occurs by infrared detection and the contents of carbonates was subtracted. Further sample preparation is described elsewhere [2,3].

Analysis: For the separation of all compounds of interest, a gaschromatographic separation (column DB-5; 30m; i.d. 0,32mm; $d_f$=0,25 µm; splitless injection (1µl $CCl_4$); T-program 60°C - 2min., then 5°/min. to 280°C, 280°C - 20min.) in combination with different detectors was used. Because, there are no $^{13}C$-standards for all compounds, thianthren was selected as internal standard for quantification, since there is no formation of thianthren at thermal treatment of fly ash. Further on, the element-specific analysis of organohalogen-sulfur-compounds with GC/AES (atomic emission spectrometry) was carried out using the sulfur-channel at 181nm and thianthren as internal standard.

Measurements: In our studies, the following measurements were carried out:

- Apart from PCDD / PCDF / PClBz, the other compounds were quantified with a combination of gaschromatograph - atomic emission spectrograph, HRGC / AES, (HP-5921 A-5890 series) and thianthren as internal standard, using the sulfur- and the carbon-channel at 181nm and 193nm.
- To determine the substance specific response factors of these compounds, relative to thianthren, the HRGC/MSD-SIM-mode was used (HP-5890 series II, HP-5970 MSD).
- The identification of the compounds occurs with HRGC/MS (Finnigan Mat. Mod. 4500)
- For the analysis of all samples at trace levels, the HRGC/MSD-SIM-mode was used.
- The regular monitoring of the internal standards occurs with HRGC/AES.

## Results and Discussion

### 1. Oxidative decomposition of residual carbon

In previous studies, the kinetics of the residual carbon decomposition was described in good approximation [6] by a combination of two first order reactions. The decomposition of residual carbon on fly ash by annealing with 1% elemental sulfur in the temperature range from 350°C to 450°C is presented in fig. 1:

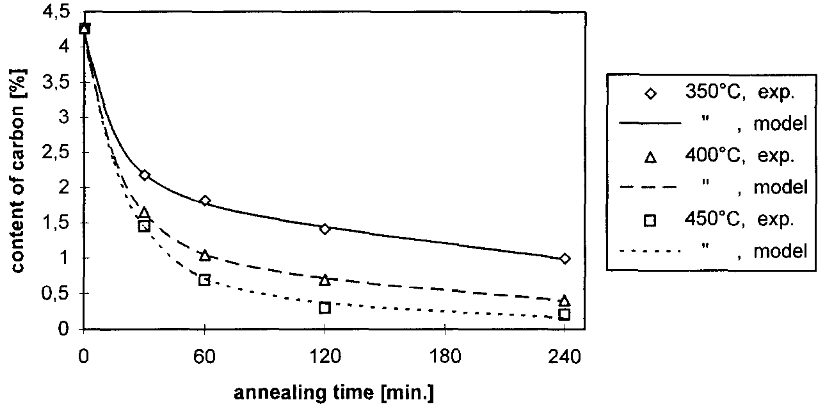


**Fig. 1**: Kinetics of the residual carbon decomposition on fly ash with 1% elemental sulfur

The parameters a and b represent the initial fractions of the residual carbon ($c_0$) which are decomposed fast ($k_1$) or slowly ($k_2$) to $CO_2$ and volatile organic compounds. For the fly ash with 1% elemental sulfur, a parametric regression of the measured concentration of residual carbon after thermal treatment was performed and the reaction constants are given in table 1:

Table 1: Reaction constants for decomposition of residual carbon on fly ash with 1% elemental sulfur

| reaction constants | 350°C | 400°C | 450°C |
|---|---|---|---|
| a | 0,51 | 0,70 | 0,80 |
| b | 0,49 | 0,30 | 0,20 |
| $k_1$ [$min.^{-1}$] | 0,067 | 0,057 | 0,050 |
| $k_2$ [$min.^{-1}$] | 0,0031 | 0,0048 | 0,0073 |

The differential scanning calorimetry of the fly ash samples with amounts of sulfur up to 3% shows, that the characteristic peak temperature at maximum reaction is constant at 347°C. However, we determined the residual carbon of all samples after thermal treatment and found higher residual carbon concentrations with ascending amounts of elemental sulfur. Therefore we suppose, that the added sulfur has no influence on the peak temperature at maximum decomposition of carbon. We found, that the fraction a, which decomposed fast by a metal catalyzed mechanism is increased from 51% to 80 % with increasing temperatures. However, the reaction constant $k_1$ of the fast reaction is reduced, $k_2$ is increased with increasing temperatures from 350°C to 450°C. Compared to our previous studies [6], the reaction constants of the residual carbon decomposition are changed, in the presence of sulfur on fly ash.

## 2. Formation of polychlorinated compounds from residual carbon

After thermal treatment (120 min.) and clean-up of fly ash, added with different contents of elemental sulfur before thermal treatment, a series of polychlorinated compounds are quantified such as polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF), benzenes (PClBz), benzothiophenes (PCBT), dibenzothiophenes (PCDBT), $Cl_4$-thiophene ($Cl_4$-T), $Cl_4$-thienothiophenes ($Cl_4$-Th-T), $Cl_7$- and $Cl_8$-styrene ($Cl_7$-Sty, $Cl_8$-Sty), $Cl_8$-dihydrobenzothiophene ($Cl_8$-DHBT), $Cl_{10}$-octatetraene ($Cl_{10}$-OT), $Cl_{10}$-phenyl-thiophene ($Cl_{10}$-PT), $Cl_{10}$-bisbutadienylsulfides ($Cl_{10}$-BBS), $Cl_{10}$-vinylnaphthalenes ($Cl_{10}$-VN), $Cl_{10}$-phenylbutadiene ($Cl_{10}$-PB) and the $Cl_{12}$-bisphenylethenes ($Cl_{12}$-BPE).

In table 3, 4 and 5, the total amounts of the determined concentrations of PCDD/PCDF/PClBz and the further chlorinated compounds and in fig. 2,3,4, the GC/MS full-scan spectra of some polychlorinated compounds are presented.

To compare the formation of all quantified compounds from residual carbon, the concentrations are transformed in molar values of organic carbon (sum = 100%). The data in table 2 represented the relative content of organic carbon for each compound class. The further chlorinated sulfur compounds (further Cl-S-comp.) are $Cl_4$-Th-T, $Cl_4$-T, $Cl_8$-PT, $Cl_8$-DHBT and the $Cl_{10}$-BBS. The other chlorinated compounds (other Cl-comp.) are $Cl_7$-Sty, $Cl_8$-Sty, $Cl_{10}$-PB, $Cl_{10}$-OT, $Cl_{10}$-VN and the $Cl_{12}$-BPE.

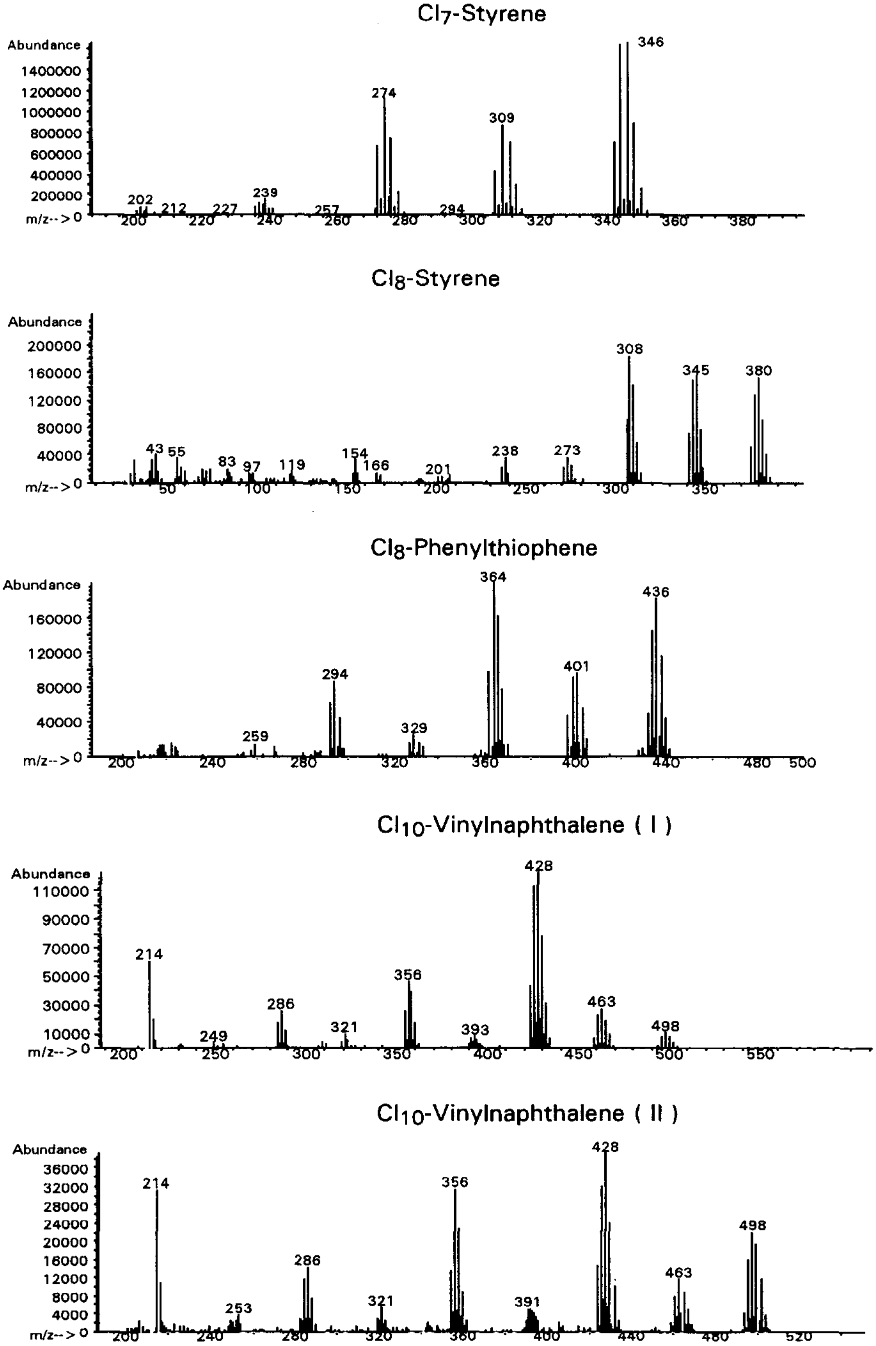
Table 2: Fraction [%] of the quantified compounds related to residual carbon on fly ash in dependence of the sulfur content and the annealing temperature

| experimental conditions | PClBz | PCDD | PCDF | PCBT | PCDBT | further Cl-S-comp. | other Cl-comp. |
|---|---|---|---|---|---|---|---|
| 350°C ; 1% S; air | 83,9 | 2,9 | 9,4 | 3,4 | 0,10 | 0,34 | 0,01 |
| „ ; 2% S; air | 80,1 | 6,7 | 9,6 | 2,9 | 0,49 | 0,14 | 0,13 |
| „ ; 3% S; air | 63,2 | 12,1 | 15,5 | 5,9 | 1,54 | 0,89 | 0,84 |
| 400°C ; 0% S; air | 90,7 | 0,7 | 5,4 | 1,8 | 0,16 | 0,07 | 1,19 |
| „ ; 1% S; air | 76,9 | 4,1 | 15,5 | 3,0 | 0,22 | 0,15 | 0,13 |
| „ ; 2% S; air | 72,7 | 7,6 | 14,4 | 4,1 | 0,52 | 0,47 | 0,09 |
| „ ; 3% S; air | 65,1 | 9,5 | 15,5 | 6,4 | 1,89 | 1,34 | 0,24 |
| „ ; 0% S; He | 56,1 | 1,1 | 1,3 | 22,6 | 1,85 | 1,62 | 15,42 |
| 450°C ; 1% S; air | 80,3 | 2,2 | 14,3 | 2,7 | 0,29 | 0,08 | 0,10 |
| „ ; 2% S; air | 81,2 | 3,3 | 13,1 | 2,2 | 0,15 | 0,05 | 0,02 |
| „ ; 3% S; air | 77,8 | 4,5 | 13,3 | 3,7 | 0,61 | 0,12 | 0,01 |

Besides the PClBz / PCDD / PCDF / PCBT / PCDBT, we report about the formation of polychlorinated intermediate structures from residual carbon on fly ash.

### 2.1 Formation of PCDD/PCDF:

With increasing contents of elemental sulfur, more PCDD / PCDF are formed. The concentrations obtained in the experiments with fly ash, added with different contents of elemental sulfur, are presented in table 3. We show, that with increasing contents of sulfur on fly ash, the $Cl_4$-DD to the $Cl_8$-DD and the $Cl_7$-DF / $Cl_8$-DF are increased.



$Cl_7$-Styrene

$Cl_8$-Styrene

$Cl_8$-Phenylthiophene

$Cl_{10}$-Vinylnaphthalene ( I )

$Cl_{10}$-Vinylnaphthalene ( II )

**Fig. 2:** Mass spectra of $Cl_7$-Styrene, $Cl_8$-Styrene, $Cl_8$-Phenylthiophene, $Cl_{10}$-Vinylnaphthalenes

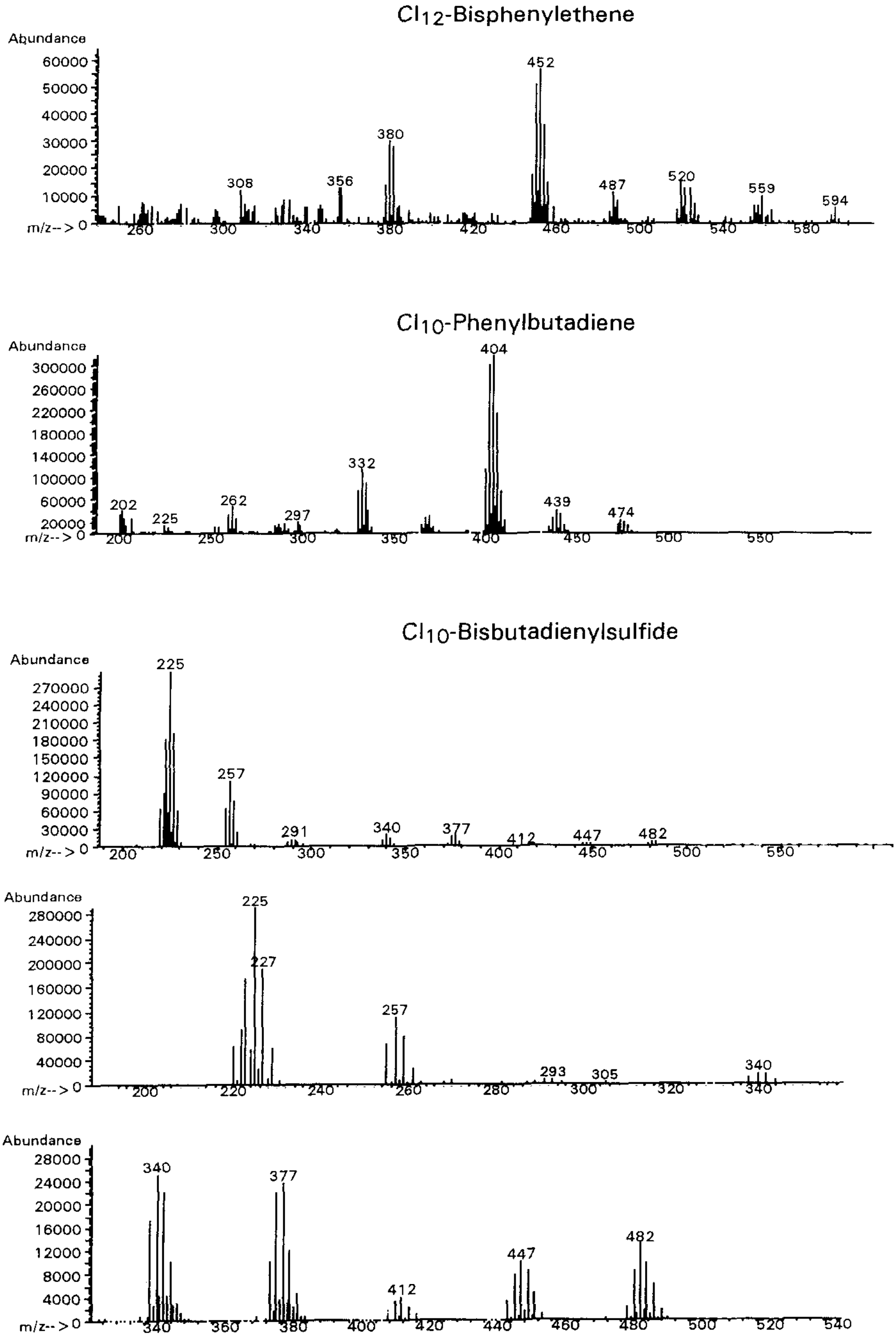
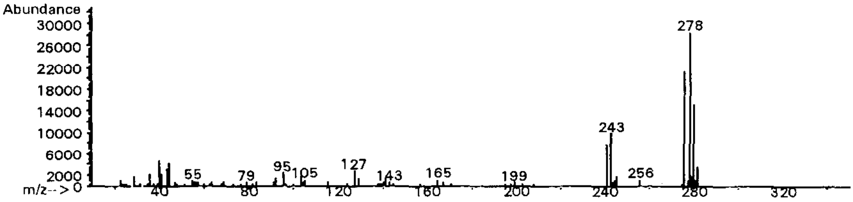
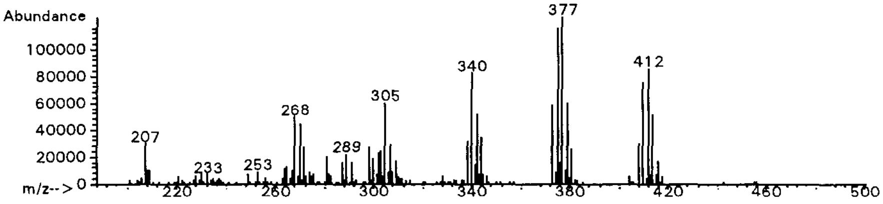


**Fig. 3:** Mass spectra of $Cl_{12}$-Bisphenylethene, $Cl_{10}$-Phenylbutadiene ,$Cl_{10}$-Bisbutadienylsulfide

$Cl_4$-Thienothiophene



$Cl_8$-Dihydrobenzothiophene



$Cl_{10}$-Octatetraene

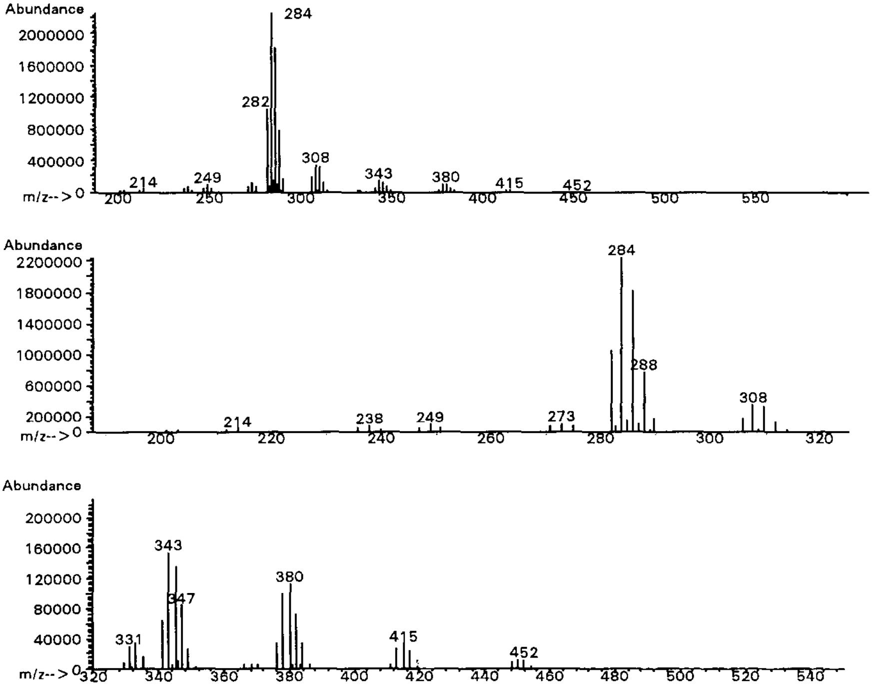


**Fig. 4:** Mass spectra of $Cl_4$-Thienothiophene, $Cl_8$-Dihydrobenzothiophene, $Cl_{10}$-Octatetraene

Table 3: Formation of PCDD / PCDF [ng/g fly ash] in dependence of the sulfur content at 350°, 400° and 450°C

| experimental conditions | $Cl_4$-DD | $Cl_5$-DD | $Cl_6$-DD | $Cl_7$-DD | $Cl_8$-DD | PCDD |
|---|---|---|---|---|---|---|
| 350°C ; 1% S; air | 247 | 774 | 963 | 570 | 193 | 2747 |
| „ ; 2% S; air | 563 | 2219 | 2976 | 2086 | 561 | 8404 |
| „ ; 3% S; air | 292 | 1500 | 2467 | 2148 | 987 | 7395 |
| 400°C ; 0% S; air | 74 | 162 | 188 | 147 | 66 | 638 |
| „ ; 1% S; air | 416 | 715 | 889 | 401 | 132 | 2552 |
| „ ; 2% S; air | 298 | 1022 | 1541 | 790 | 233 | 3883 |
| „ ; 3% S; air | 365 | 1083 | 1783 | 1270 | 605 | 5105 |
| „ ; 0% S; He | 0,7 | nn | 0,7 | 1,5 | 1,4 | 4,3 |
| 450°C ; 1% S; air | 114 | 233 | 201 | 92 | 35 | 675 |
| „ ; 2% S; air | 122 | 293 | 363 | 143 | 27 | 948 |
| „ ; 3% S; air | 91 | 322 | 411 | 295 | 98 | 1217 |

| experimental conditions | $Cl_4$-DF | $Cl_5$-DF | $Cl_6$-DF | $Cl_7$-DF | $Cl_8$-DF | PCDF |
|---|---|---|---|---|---|---|
| 350°C ; 1% S; air | 1753 | 3204 | 2392 | 756 | 46 | 8151 |
| „ ; 2% S; air | 2549 | 4506 | 2172 | 1506 | 137 | 10869 |
| „ ; 3% S; air | 1592 | 3592 | 1527 | 1343 | 271 | 8325 |
| 400°C ; 0% S; air | 1258 | 1373 | 792 | 967 | 159 | 4550 |
| „ ; 1% S; air | 2815 | 2879 | 2286 | 647 | 128 | 8755 |
| „ ; 2% S; air | 1289 | 2277 | 2202 | 865 | 110 | 6742 |
| „ ; 3% S; air | 1769 | 2195 | 2276 | 1013 | 239 | 7491 |
| „ ; 0% S; He | nn | 1,3 | 1,3 | 1,9 | nn | 4,5 |
| 450°C ; 1% S; air | 990 | 1425 | 1159 | 428 | 77 | 4078 |
| „ ; 2% S; air | 830 | 1141 | 1163 | 395 | 37 | 3567 |
| „ ; 3% S; air | 708 | 1172 | 809 | 520 | 91 | 3300 |

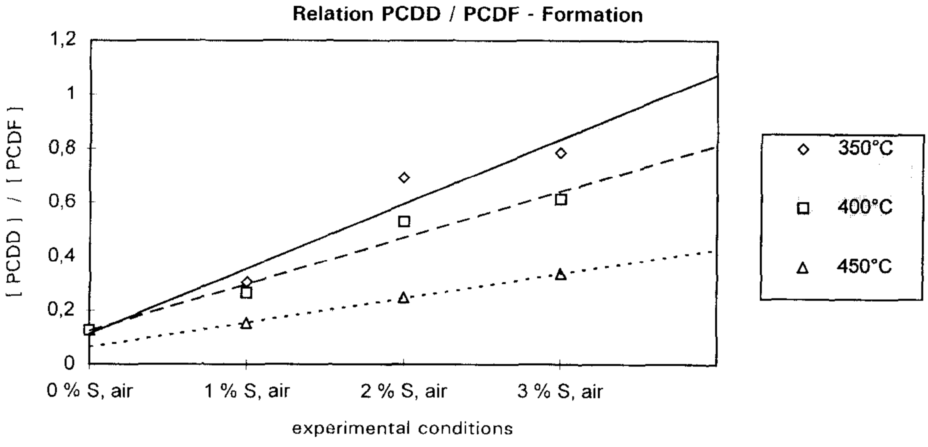
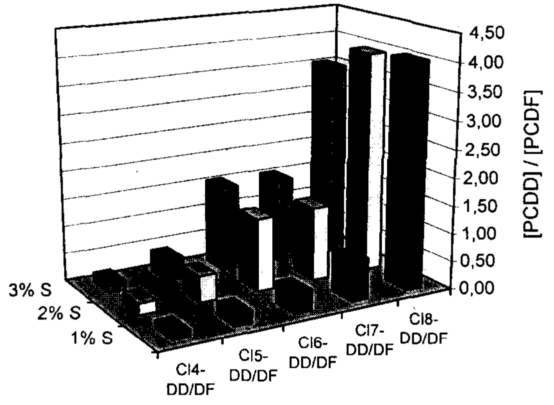
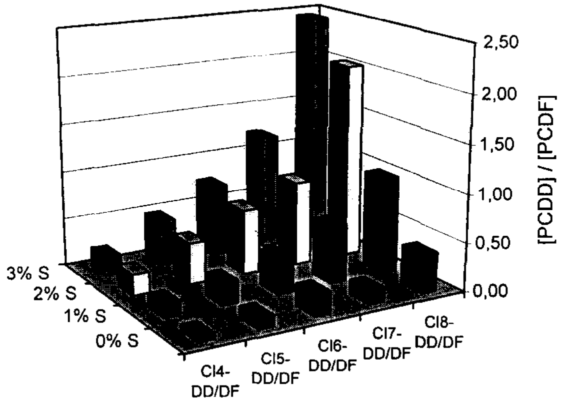


**Fig. 5:** The molar ratio PCDD / PCDF in dependence of different contents of elemental sulfur on fly ash

Molar PCDD / PCDF - Ratio in the Formation on Fly Ash at 350°C



Molar PCDD / PCDF - Ratio in the Formation on Fly Ash at 400°C



Molar PCDD / PCDF - Ratio in the Formation on Fly Ash at 450°C

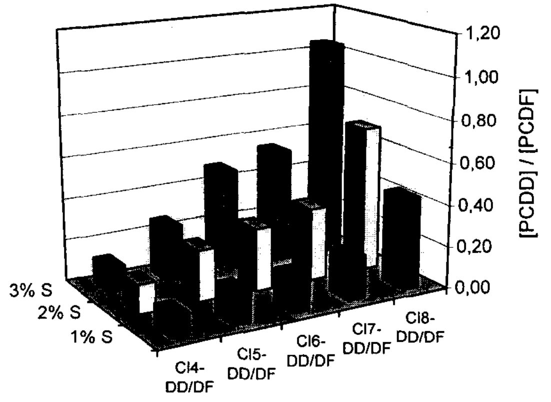


**Fig. 6:** The molar ratio of PCDD / PCDF - formation on fly ash in dependence of different contents of elemental sulfur

To compare the formation of PCDD and PCDF, the concentrations are transformed in molar values. In fig. 5, the ratio of the total PCDD / PCDF - formation is presented. As seen from fig. 5, the ratio of total PCDD / PCDF formation is increased, with increasing contents of elemental sulfur.

In detail, the ratio of formation of $Cl_4$-DD / $Cl_4$-DF to the $Cl_8$-DD / $Cl_8$-DF is shown in fig. 6.

At 350°C (fig. 6), the ratio of the PCDD / PCDF-formation is increased from the tetra to the heptachloro-isomers, with increasing sulfur contents, and a maximum change for the hexachloro-isomers could be observed. The ratio for the octachloro-isomers is nearly not influenced.

At 400°C (fig. 6), the situation is changed. Altogether, the ratio of PCDD / PCDF-formation is reduced, compared to 350°C. The higher the rate of chlorination, the higher is the ratio of PCDD / PCDF-formation, which is increased with increasing contents of elemental sulfur.

The situation at 450°C (fig. 6) show, that the stability of the determined PCDF is still higher, compared to the PCDD. However, with increasing contents of elemental sulfur, the formation of PCDD compared to PCDF is increased too.

## 2.2 Formation of PClBz:

As seen from table. 2, with increasing sulfur content on fly ash, the formation of PClBz in relation to the rest of the quantified polychlorinated compounds is decreased. The experimental data, after thermal treatment of the fly ash (120 min.) and clean up, are presented in table 4:

Table 4: Formation of PClBz [ng/g fly ash] in dependence of the sulfur content at 350°, 400° and 450°C

| experimental conditions | $Cl_2$-Bz | $Cl_3$-Bz | $Cl_4$-Bz | $Cl_5$-Bz | $Cl_6$-Bz | PClBz |
|---|---|---|---|---|---|---|
| 350°C ; 1% S; air | 24001 | 24793 | 17221 | 4940 | 5441 | 76396 |
| „ ; 2% S; air | 24448 | 30479 | 28166 | 9588 | 4971 | 97652 |
| „ ; 3% S; air | 2964 | 8788 | 16532 | 7999 | 4835 | 41118 |
| 400°C ; 0% S; air | 29271 | 21864 | 15854 | 6854 | 3796 | 77639 |
| „ ; 1% S; air | 11925 | 17550 | 11349 | 3923 | 2442 | 47189 |
| „ ; 2% S; air | 8456 | 10717 | 11568 | 3695 | 2230 | 36666 |
| „ ; 3% S; air | 6289 | 10429 | 11183 | 4198 | 2889 | 34988 |
| „ ; 0% S; He | 77 | 47 | 23 | 26 | 12 | 185 |
| 450°C ; 1% S; air | 6104 | 7056 | 7135 | 3483 | 1172 | 24950 |
| „ ; 2% S; air | 7087 | 5989 | 6523 | 2970 | 886 | 23455 |
| „ ; 3% S; air | 3873 | 5881 | 7474 | 3162 | 1115 | 21505 |

Further details about the influence of elemental sulfur on fly ash on the formation of the $Cl_2$- to the $Cl_6$-isomers are illustrated in fig. 7.

At 350°C we recognize, that with increasing sulfur content, the maximum of formation is shifted to the $Cl_4$-isomeres by reduced concentrations. We suppose, that especially the formation of the lower chlorinated isomeres is influenced.

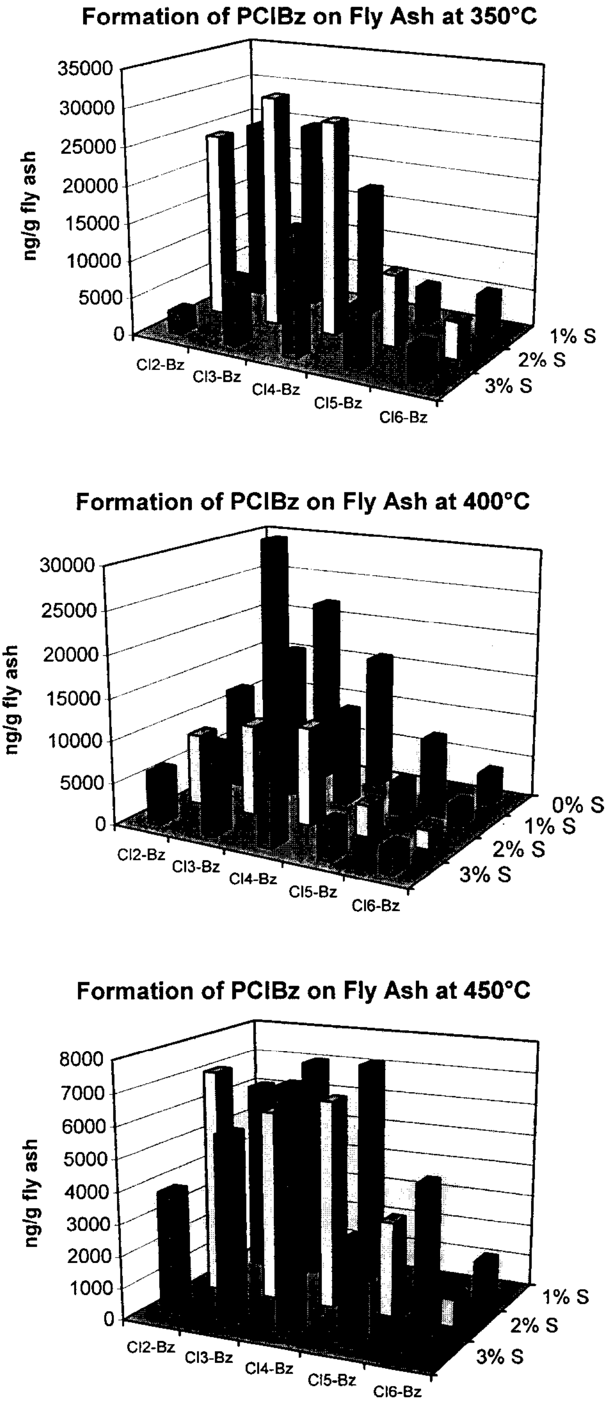


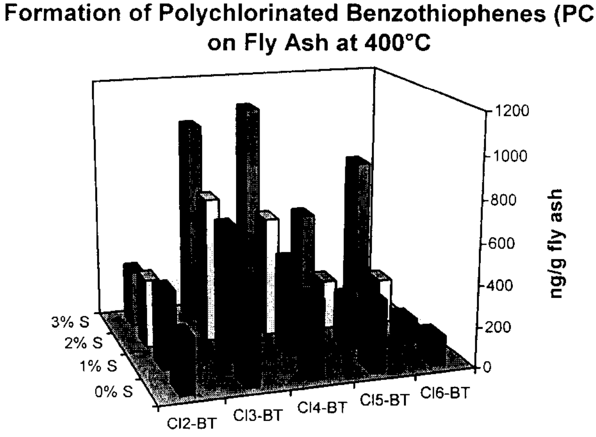
**Fig. 7:** Formation of PClBz on fly ash in dependence of different contents of elemental sulfur at 350°, 400° and 450°C

At 400°C (fig. 7), the formation of $Cl_2$- and $Cl_3$-benzenes decreases, especially from the change of the used fly ash without sulfur to such with 1% sulfur. Generally, the concentrations are usual lower than at 350°C.

The effect at 450°C is clearly reduced and from the $Cl_4$- to the $Cl_6$-isomer, the formation is almost not influenced.

### 2.3 Formation of polychlorinated organosulfur-compounds:

The polychlorinated benzothiophenes (PCBT) were the quantified sulfur-compounds (table 5) with the highest concentrations, by polychlorinated dibenzothiophenes (PCDBT). In contrast, the formation of tetrachlorothienothiophene ($Cl_4$-Th-T) and the decachlorobisbutadienylsulfides ($Cl_{10}$-BBS) is preferably increased with increasing sulfur content on fly ash. Table 5 show, that the maximum of formation of polychlorinated benzothiophenes (PCBT) is at 350°C, similar to the polychlorinated dioxins and furans, the trichloro- to the pentachloro- isomers being dominant. The strongest influence of sulfur on the formation of polychlorinated sulfur compounds occurs at 400°C. The experimental data at 400°C are presented for the PCBT in fig. 8, for the PCDBT in fig. 9 and for further chlorinated sulfur compounds in fig. 10. For the PCBT, the maximum of formation is shifted from the trichloro- to the tetrachloro- isomers by increasing concentrations and a strong influence on the formation of the $Cl_6$-BT occurs.



Formation of Polychlorinated Benzothiophenes (PCBT) on Fly Ash at 400°C

**Fig. 8**: Formation of polychlorinated benzothiophenes (PCBT) on fly ash in dependence of different contents of elemental sulfur at 400°C

Compared with the polychlorinated benzothiophenes (PCBT), the maximum of formation for the polychlorinated dibenzothiophenes (PCDBT) is shifted to higher temperatures (table 5). With increasing amounts of elemental sulfur on fly ash, the relation of PCBT/PCDBT-formation is decreased from 10-40 (0% S) down to 5-6 (3% S), by increasing concentrations of both compound classes. The maximum of formation for the PCDBT (fig. 9) is shifted from the tetra- to the hexachloro- isomers. In analogy to the general tendency, that higher sulfur content leads to increased formation of polychlorinated compounds, we show for the PCDBT a strong increase on the formation of the $Cl_7$- and $Cl_8$-DBT.

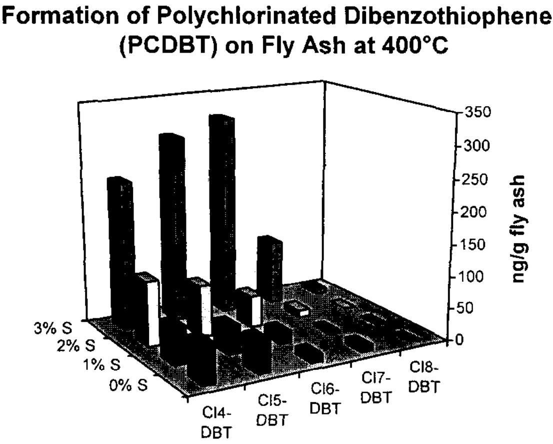


**Fig. 9**: Formation of polychlorinated dibenzothiophenes (PCDBT) on fly ash in dependence of different contents of elemental sulfur at 400°C

With increasing contents of sulfur, the $Cl_4$-thienothiophenes ($Cl_4$-Th-T) and the $Cl_{10}$-bisbutadienylsulfides are preferably formed at 400°C (table 5). The macromolecular carbon structure of the fly ash is the source for the formation of polychlorinated aromatic structures during the metal catalyzed degradation of the carbonaceous material [2,3,4,6,8,10,12]. In these reactions, polychlorinated cracking products may react with sulfur on the surface of the carbonaceous particles, e.g. by cyclization with simultaneous input of sulfur. So the sulfur may be a reagent for catching polychlorinated precursors of the de-novo-synthesis [9,11]. A second possibility of forming chlorinated sulfur compounds is the gas phase reaction of instable cracking products of the carbonaceous material with sulfur. Increasing concentrations of polychlorinated thiophenes, benzothiophenes, dibenzothiophenes, phenylthiophenes and bisbutadienylsulfides indicated, that sulfur is involved in reactions with polychlorinated butadienes, styrenes, biphenyls and phenylbutadiene.

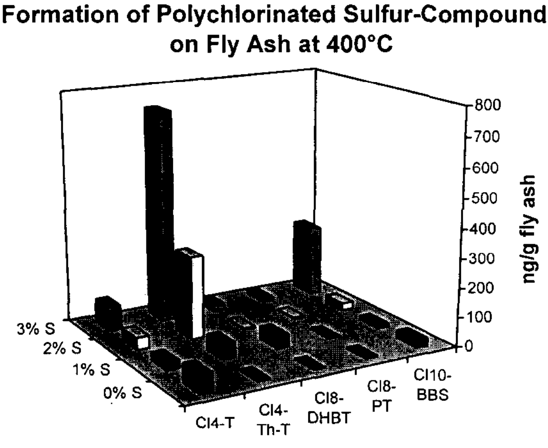


**Fig. 10**: Formation of polychlorinated sulfur compounds on fly ash in dependence of the sulfur content at 400°C

Table 5: Formation of polychlorinated sulfur-compounds in dependence of the sulfur content at 350°, 400° and 450°C [ng/g fly ash]

| compound | **350°C** | | | **400°C** | | | | **450°C** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1% S | 2% S | 3% S | 0% S | 1% S | 2% S | 3% S | 1% S | 2% S | 3% S |
| $Cl_2BT$ | 273,0 | 311,1 | 259,0 | 275,4 | 381,5 | 335,5 | 277,2 | 86,0 | 89,4 | 45,1 |
| $Cl_3BT$ | 1004,5 | 1200,6 | 1090,8 | 495,2 | 653,5 | 704,2 | 989,6 | 208,1 | 226,9 | 408,5 |
| $Cl_4BT$ | 1194,9 | 1181,3 | 1126,6 | 386,0 | 464,0 | 585,0 | 1060,1 | 316,5 | 226,9 | 272,5 |
| $Cl_5BT$ | 543,5 | 726,3 | 718,8 | 353,7 | 243,9 | 244,0 | 495,2 | 203,2 | 73,2 | 211,0 |
| $Cl_6BT$ | 311,9 | 227,2 | 427,2 | 146,1 | 122,6 | 221,6 | 749,9 | 69,4 | 34,0 | 88,1 |
| PCBT | 3327,8 | 3646,5 | 3622,4 | 1656,4 | 1865,5 | 2090,3 | 3572,0 | 883,2 | 650,4 | 1025,2 |
| $Cl_4DBT$ | 38,4 | 166,9 | 217,0 | 61,0 | 57,3 | 101,4 | 233,0 | 20,7 | 17,2 | 45,4 |
| $Cl_5DBT$ | 30,5 | 218,8 | 278,5 | 50,5 | 43,4 | 79,3 | 292,0 | 33,8 | 15,5 | 57,7 |
| $Cl_6DBT$ | 14,2 | 157,0 | 281,3 | 11,8 | 18,8 | 48,6 | 314,5 | 24,3 | 6,7 | 42,7 |
| $Cl_7DBT$ | 3,0 | 22,1 | 77,9 | 9,5 | 4,3 | 10,9 | 100,9 | 6,7 | 1,0 | 7,4 |
| $Cl_8DBT$ | 0,0 | 0,3 | 6,0 | 0,2 | 0,2 | 0,1 | 8,2 | 0,4 | 0,2 | 0,3 |
| PCDBT | 86,1 | 565,1 | 860,7 | 133,0 | 124,0 | 240,3 | 948,6 | 85,9 | 40,6 | 153,5 |
| $Cl_4$-T | 46,3 | 38,9 | 50,8 | 65,0 | 30,3 | 42,9 | 82,1 | 6,0 | 6,9 | 11,1 |
| $Cl_4$-Th-T | 421,6 | 190,5 | 441,4 | 4,5 | 55,1 | 283,9 | 730,7 | 4,2 | 6,1 | 31,5 |
| Cl8-DHBT | 5,0 | 2,1 | 25,0 | 2,9 | 45,0 | 3,6 | 21,1 | 11,6 | 1,8 | 0,9 |
| Cl8-PT | 1,8 | 5,9 | 16,7 | 3,8 | 4,1 | 5,2 | 12,5 | 3,1 | 0,7 | 1,2 |
| $Cl_{10}$-BBS | 2,5 | 20,4 | 304,0 | 28,1 | 12,0 | 24,9 | 247,0 | 20,1 | 8,4 | 7,1 |
| Total | 477,2 | 257,8 | 837,9 | 104,3 | 146,5 | 360,5 | 1093,4 | 45,0 | 23,9 | 51,8 |

## 2.4 Formation of organic sulfur compounds on fly ash at 540°C

After thermal treatment of the same fly ash with 1% sulfur at 540°C and clean up, a series of unchlorinated sulfur compounds are preferably formed. The identification occurs with HRGC/MS, the quantification with HRGC/AES and thianthren as internal standard, using the sulfur channel at 181nm. Fig. 11 show the HRGC/AES-chromatogram of the extract.

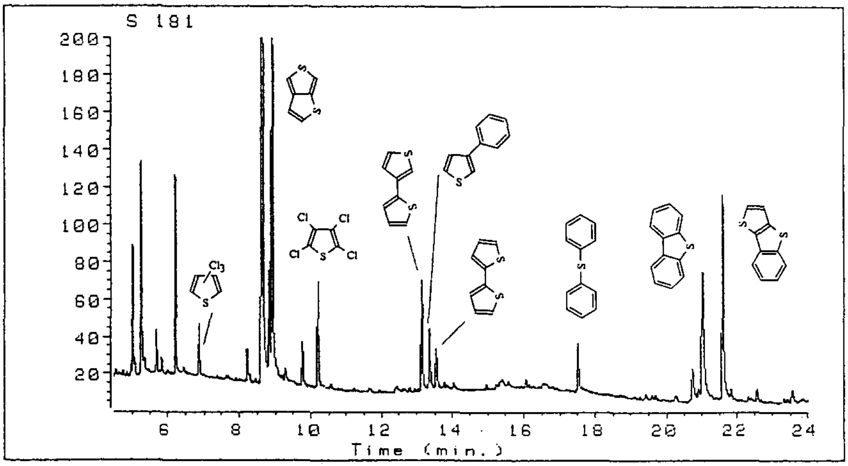


**Fig. 11:** HRGC/AES-chromatogram (S-181 nm) of organosulfur compounds from annealing fly ash with 1% sulfur at 540°C

The compounds are identified as 3,4-b-thienothiophene, 2,2'-bithiophene, 2,3'-bithiophene, dibenzothiophene, bisphenylsulfide, 3-phenylthiophene, and thieno-(3,2-b)-benzothiophene and chlorothiophenes. The results of the quantification are presented in table 6:

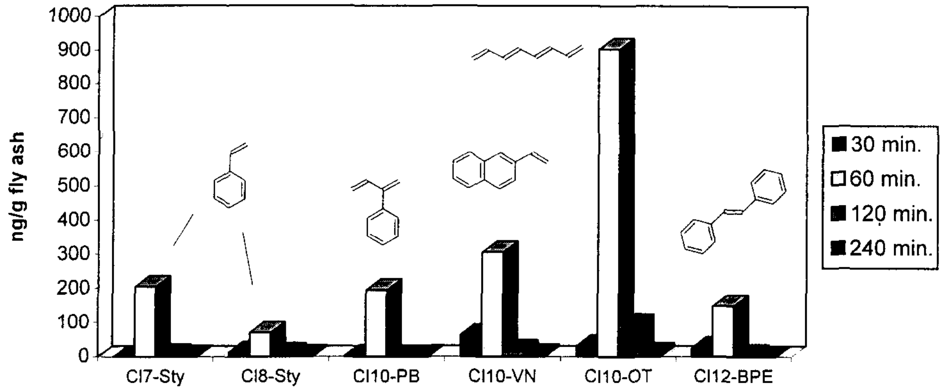
Table 6: Formation of organosulfur compounds on fly ash at 540°C, with 1% sulfur added

| compound | ng/g fly ash |
|---|---|
| 2,3'-bithiophene | 2,62 |
| 2,2'-bithiophene | 1,06 |
| dibenzothiophene | 11,47 |
| 3-phenylthiophene | 2,64 |
| bisphenylsulfid | 2,57 |
| $Cl_3$-thiophenes | 1,92 |
| $Cl_4$-thiophene | 5,36 |
| 3,4-b-thienothiophene | 9,90 |
| thieno-(3,2-b)-benzothiophene | 6,49 |
| sum | 44,03 |

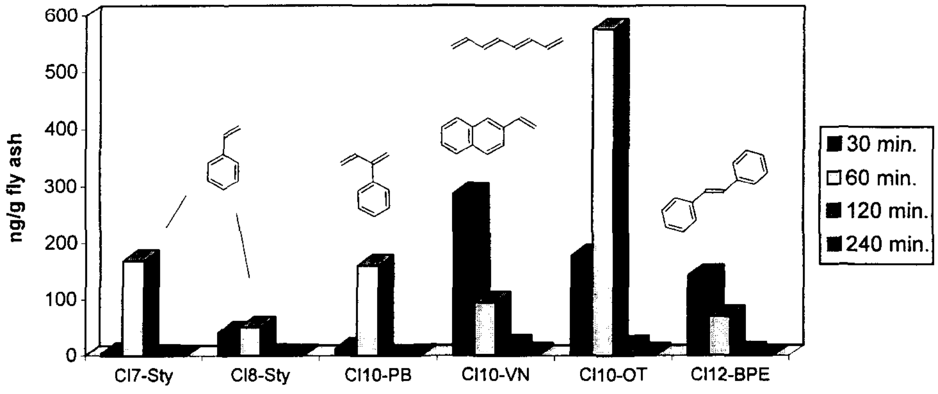
## 2.5 Formation of polychlorinated intermediate compounds:

As by-products of the oxidative decomposition, polychlorinated intermediate de-novo-products are formed and released [9]. The maximum of formation of these intermediate organic structures occurs after 60 min. reaction time [11]. After that, a decrease to concentrations in the range of the detection limit takes place and conversion to other polychlorinated compounds (PCDD, PCDF, PClBz) may be possible.

As seen from fig. 12, it is interesting to know, that at 450°C, the maxima of formation for the $Cl_{10}$-vinylnaphthalene and the $Cl_{12}$-bisphenylethene is shifted to 30 min. reaction time in correlation with the heterogen catalytic decomposition of the macromolecular carbon on fly ash.



Formation of Polychlorinated Intermediate Compounds by De-Novo-Synthesis at 400°C



Formation of Polychlorinated Intermediate Compounds by De-Novo-Synthesis at 450°C

**Fig. 12:** Formation of polychlorinated intermediate compounds by de-novo-synthesis from particulate carbon on fly ash with 1% elemental sulfur, in dependence of the annealing time

## Conclusions

- By addition of elemental sulfur to the fly ash before thermal treatment, an influence on the heterogeneous metal-catalyzed oxidation of the carbon is observed. With increasing temperatures, the reaction konstant $k_1$ of the fast reaction is reduced in the presence of sulfur. From this it is indicated that by the presence of sulfur, the catalytic activity of the fly ash with regard to the oxidation is changed. Parallel, the rate for the second reaction ($k_2$) is higher than without sulfur and its importance is increasing at higher temperatures.

- Parallel to the heterogeneous metal catalyzed degradation of the carbonaceous material on fly ash to $CO_2$, the macromolecular carbon structure is decomposed to intermediate aromatic and aliphatic structures as by-products, which are stabilized by perchlorination on the surface and released.

- The formation of intermediate structures (aromatics with vinyl- and butadienyl groups, stabilized by perchlorination) with the carbon decomposition between 300° and 450°C shows, that the de-novo-synthesis [2] is suitable to explain the observations. The clear maximum of formation of these compounds occurs after 60 min. reaction time. This indicated, that these structures are primarily formed. After that, a rearrangement to thermodynamic or kinetic more stable compounds (e.g. PCDD, PCDF) with a maximum of formation after 240 min. may occurs.

- Increasing amounts of sulfur on the fly ash leads to other compositions of the crack-products and the formation of PClBz, especially the $Cl_2$- and $Cl_3$- isomers is reduced. In contrast, the formation of PCDD is preferred compare to that of PCDF. This indicated, that both compound classes are formed from different precursors.

- The addition of sulfur to the fly ash leads to increasing amounts of chlorinated thiophenes, benzothiophenes, dibenzothiophenes, phenylthiophenes and $Cl_{10}$-bis-butadienylsulfides. This indicates, that intermediate aromatic and aliphatic structures with carbon-chlorine bonds may react with sulfur under dimerization or cyclization. So the sulfur may be involved in reactions of polychlorinated butadiens, styrenes, biphenyls and phenylbutadienes.

- With increasing contents of elemental sulfur on fly ash, a shift on the formation of higher chlorinated de-novo products is observed. This indicates an influence on the carbon decomposition with an increase of the lifetime of the macromolecular carbon surface, where the precursors are adsorbed, chlorinated and released.

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