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Journal of Chromatography A, 878 (2000) 171–181

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of basic nitrogen-containing polynuclear aromatic hydrocarbons formed during thermal degradation of polymers by high-performance liquid chromatography–fluorescence detection

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Received 7 October 1999; received in revised form 14 February 2000; accepted 16 February 2000

Abstract

A method for the simultaneous determination of 22 nitrogen-containing polynuclear aromatic hydrocarbons (PAHs) (15 azaarenes and seven amino-PAHs) in the gaseous products of the thermal degradation of polymers is described. After desorption and clean-up using cation-exchange chromatography (PRS cartridge) the samples were analyzed by HPLC–FD. The validation was carried out with real nylon 6 combustion samples. The recoveries of the compounds are in the range of 89–99% for the extraction and 91–100% for the clean up procedure. The detection limits ranged from 7 to 160 pg. The high recovery values, due to the quick and efficient clean-up procedure, resulted in low relative standard deviations (with the exception of acridine and 2-aminoanthracene <5%). The applicability of the method is also investigated for the determination of the *N*-PAHs in a pyrolysis sample.

Keywords: Thermal degradation; Azaarenes; Polynuclear aromatic hydrocarbons; Polymers

1. Introduction

The formation of polynuclear aromatic hydrocarbons (PAHs) and polychlorinated aromatic compounds during combustion or pyrolysis of synthetic polymers has been published by many authors in recent years. Less information is available on nitrogen-containing PAHs, which include e.g., the basic and neutral aza-heterocyclic hydrocarbons (azaarenes) and the amino-PAHs.

Several azaarenes have been found to be very mutagenic to *Salmonella typhimurium*, in some cases more than their corresponding parent hydrocarbons [1–4]. Many of the azaarenes also show carcinogenic activity [5] and toxicity to alga [6] and *Daphnia magna* [7]. The azaarenes emanate from many combustion sources and therefore they have become widespread in the environment [8–11]. The *N*-heterocyclic PAHs have been determined in the aerosol of urban atmosphere [8,12], in river and lake sediments [13] or in sewage sludges [14]. As a result of pyrolysis or incomplete combustion of organic matter [15], azaarenes have also been detected in charcoal-grilled meat [16,17].

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00266-1

Amino-PAHs are mentioned in the literature as compounds of synthetic fuel materials as coal and shale derived petroleum substitutes [18]. They show very high mutagenic activity. 2-Aminonaphthalene produces more mutagenic activity than benzo[*a*]-pyrene and, e.g., 3-aminopyrene exhibits an activity more than 50-times that of benzo[*a*]pyrene [19].

So far, the building of nitrogen-containing PAHs during the pyrolysis or thermolysis of nitrogen-containing plastics still has not been well studied. The *N*-PAHs are partially formed only in traces. These facts demand a special method for the determination of the *N*-PAHs in thermal degradation products and the object in this investigation was the development of a method to determine nitrogen-containing PAHs in the gaseous products of the thermal degradation products of nitrogen-containing plastics. Recoveries, detections limits and applicability of the method have been studied.

2. Experimental

2.1. Chemicals and materials

Nylon 6 (polycaprolactame) was obtained from EGA (Steinheim, Germany). Bond-Elut propyl sulfonic acid (PRS 500) column was from Analytichem International (ICT, Basel, Switzerland).

Acetonitrile (HPLC-grade), methanol (Pestanal) and dichlormethane (Pestanal) were provided by Riedel-de Haën (Seelze, Germany).

Adsorberharz Amberlite XAD-4 (20–50 mesh) and tris(hydroxymethyl)aminomethane z.A. were from Merck (Darmstadt, Germany).

The Tris buffer used for the liquid chromatography (LC) analysis was a tris(hydroxymethyl)-aminomethane solution (0.02 mol/l) adjusted with 1 *M* HCl to pH 6.9.

The silanized glass fiber wadding was obtained from Machery and Nagel (Düren, Germany).

Standard substances: 1-aminonaphthalene, 2-aminonaphthalene (95%), 2-aminoanthracene (96%), 2-aminofluorene (98%), 9-aminophenanthrene (96%), 6-aminochrysene (97%), benzo[*h*]quinoline (97%), phenanthridine (98%), 7,10-dimethylbenz[*c*]acridine and 7,9-dimethylbenz[*c*]acridine were purchased from Aldrich (Steinheim, Germany). 4-Azafluorene (99.9%), 1-azafluoranthene (99%), 4-azapyrene (99.5%) and dibenz[*c,h*]acridine (99.4%) were from Institut für PAH-Forschung (Greifenberg, Germany). Acridine (>98%) was obtained from Merck, 1-aminopyrene (>98%) from Fluka (Germany) and benzo[*f*]quinoline (>95%) from Ultra Scientific (North Kingstown, UK).

Standard stock solutions of 100 ng/μl in acetonitrile were used for further dilution. They were made by dissolving 10 mg of each compound in 100 ml acetonitrile.

Benz[*a*]acridine, benz[*c*]acridine, dibenz[*a,j*]acridine and dibenz[*a,c*]acridine, dibenz-[*a,h*]acridine were obtained as solutions 10 ng/μl in acetonitrile from Ehrenstorfer (Augsburg, Germany).

A list of compounds is given in Tables 1 and 2.

2.2. Instruments

High-performance liquid chromatography (HPLC) with fluorescence detection (FD)–spectrophotometric detection was carried out with a Hewlett-Packard (Waldbronn, Germany) Series 1100 HPLC system and a Hewlett-Packard Fluorescence Detector 1046 A. Liquid chromatographic separations were performed on a Vydac-PAH column 250×4.6 mm.

2.3. Sample

The gaseous combustion samples were produced in a German VCI-Oven [20].

Combustion conditions: the Nylon 6 (~20 mg) was filled in a quartz dish and introduced into the combustion chamber. The combustion was carried out at 800°C in an air stream at 135 ml/min. The volatile or semi-volatile products (like the PAH derivates) were collected on XAD-resin (340 mg). The sampling device was water cold. The efficiency of the adsorption of semi-volatile organic compounds has already been investigated [21].

2.4. Desorption

The gaseous compounds were extracted from the XAD resin ultrasonically (for 15 min) by treatment with 8 ml dichloromethane (DCM). The solution was separated from the resin by filtration over silanized

Table 1
Structures, abbreviations and fluorescence data of azaarene compounds

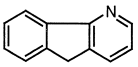
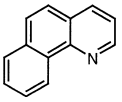
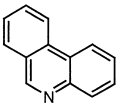
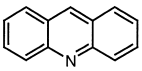
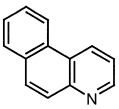
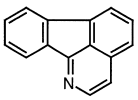
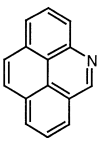
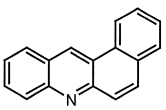
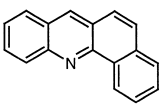
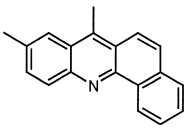
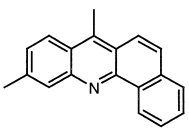
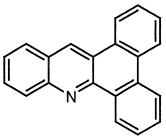
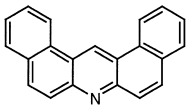
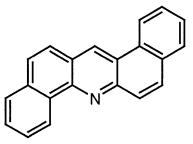
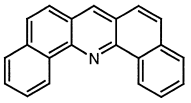
Compound	Abbreviation	Structure	Fluorescence maxima [Ex; Em wavelength (nm)]
4-Azafluorene	4-Afl		247; 330
Benzo[*h*]quinoline	B[*h*]q		263; 364
Phenanthridine	Phen		246; 365
Acridine	Acr		247; 420
Benzo[*f*]quinoline	B[*f*]q		266; 364
1-Azafluoranthene	1-Aflu		280; 463
4-Azapyrene	4-Apy		270; 385
Benz[*a*]acridine	B[*a*]a		279; 404
Benz[*c*]acridine	B[*c*]a		285; 407
7,9-Dimethylbenz[*c*]acridine	7,10-Dmeb[*c*]a		285; 412
7,10-Dimethylbenz[*c*]acridine	7,10-Dmeb[*c*]a		285; 405

Table 1. Continued

Compound	Abbreviation	Structure	Fluorescence maxima [Ex; Em wavelength (nm)]
Dibenz[*a,c*]acridine	Db[*a,c*]a		275; 388
Dibenz[*a,j*]acridine	Db[*a,j*]a		291; 410
Dibenz[*a,h*]acridine	Db[*a,h*]a		290; 408
Dibenz[*c,h*]acridine	Db[*c,h*]a		292; 405

glass fiber wadding, which was rinsed with an additional 2 ml DCM.

2.5. Clean-up

Azaarenes and amino-PAHs are basic compounds (excluding carbazol and indol derivates). This property could be used for the separation from the neutral PAHs, which are present in a much higher quantity. One possibility for this separation is liquid–liquid extraction [4,22]. But in comparison to liquid–liquid partitions with acids, better recoveries (especially for larger compounds) are obtained using ion-exchange chromatography [10]. Solid-phase extraction provides an improvement over the use of a large column [16]. We decided to perform the separation on a 500 mg propylsulfonic (PSR) cartridge.

The DCM extract was applied to a PSR 500, preconditioned with 4 ml DCM and rinsed with additional 4 ml DCM. The dripping rate was regulated under the gentle pressure of a stream of nitrogen. This DCM fraction eluted contained the PAHs, cyanoarenes and neutral azaarenes.

The basic azaarenes remained in the PRS. They were eluted with 2 ml methanol–ammonia (9:1) in a 5-ml measuring flask after drying the column under a stream of nitrogen. The measuring flask was filled up with acetonitrile. The basic character of the solution did not disturb the determination by HPLC–FD. This procedure avoided the step of evaporation and thus bad recoveries of the more volatile compounds.

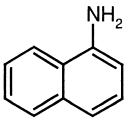
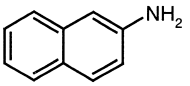
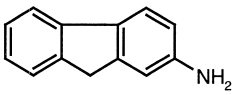
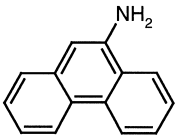
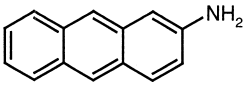
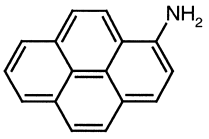
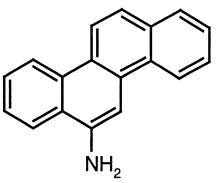
3. Results and discussion

3.1. LC analysis

3.1.1. Azaarenes

A C_{18} stationary phase was used, which is specially made for the separation of PAHs. The azaarenes behave on a C_{18} column similarly to the PAHs. Several acetonitrile–water or acetonitrile–Tris buffer, pH 6.9 mobile phases, including various solvent gradients, were tested to separate 15 azaarenes. For an optimal fluorescence of the amines the pH value of the mobile phase should be situated if possible

Table 2
Structures, abbreviations and fluorescence data of amino-PAH compounds

Compound	Abbreviation	Structure	Fluorescence maxima [Ex; Em wavelength (nm)]
1-Aminonaphthalene	1-Anaph		243; 429
2-Aminonaphthalene	2-Anaph		243; 408
2-Aminofluorene	2-Aflu		288; 370
9-Aminophenanthrene	9-Aphen		250; 443
2-Aminoanthracene	2-Aanth		260; 495
1-Aminopyrene	1-Apyr		360; 440
6-Aminochrysene	4-Achr		270/430

over pH 7, but to avoid hydrolysis of the stationary phase only mobile phases with a pH value <7.0 should be used. Thus the Tris buffer, pH 6.9 represents a compromise [23]. The optimum separation of all compounds was obtained using the conditions specified in the legend of Fig. 1. Fig. 1 shows a chromatogram of a standard solution mix (injected 1 ng of each compound) under working conditions. Only the separation of benzo[*h*]quinoline and phenanthridine was unsuccessful. With other mobile phases (e.g., acetonitrile–water gradient systems) the separation of benzo[*h*]quinoline and

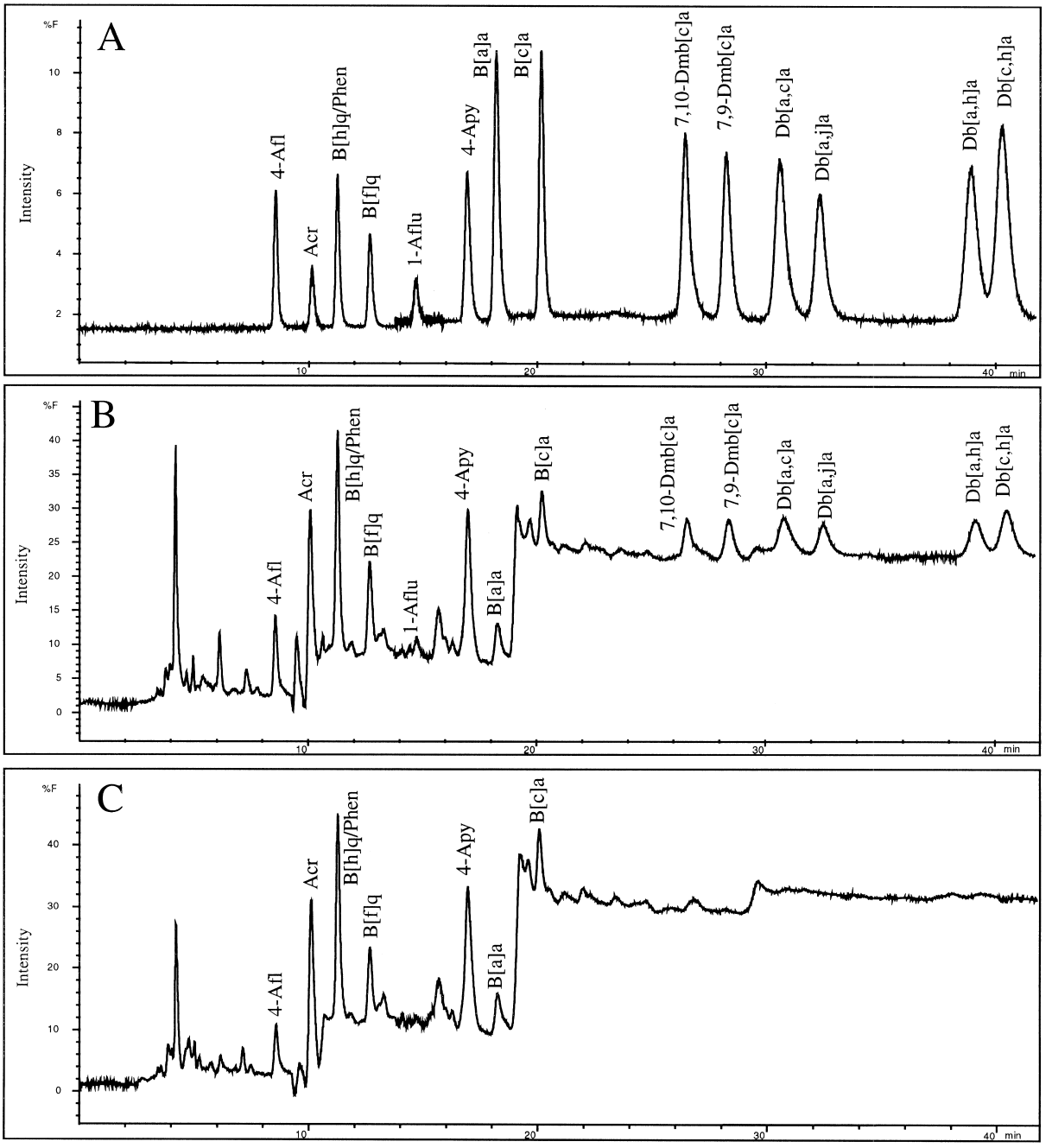


Fig. 1. Chromatograms of azaarenes by HPLC with fluorescence detection. Vaydac-PAH column 250×4.6 mm, mobile phase: 0–16.0 min: acetonitrile–Tris buffer (40:60) to acetonitrile–Tris buffer (70:30), 16.0–43.0 min acetonitrile–Tris buffer (70:30) to acetonitrile–Tris buffer (75:25), flow-rate: 1 ml/min, temperature: 30.7°C, fluorescence detection: 0–9.2 min: Ex. 246 nm, Em: 330 nm, PmtGain 14; 9.2–10.7 min: 247 nm, 380 nm, 15; 10.7–13.7 min: 263 nm, 364 nm, 13; 13.7–15.9 min: 280 nm, 463 nm; 16, 15.9–19.2 min: 270 nm, 385 nm, 14; 19.2–24.5 min: 280 nm,. 405 nm, 14; 24.5–30.0 min: 285 nm,. 409 nm, 14; 30.0–34.0 min: 275 nm, 388 nm, 14; 34.0–45 min: 290 nm, 408, 13. (A) Standard solution: 1 ng of each compound injected, (B) real combustion sample of nylon 6 spiked with 0.5 μg of each compound, (C) real pyrolysis sample of nylon 6 unspiked.

phenanthridine succeeded easily, but separation of the other compounds was not possible. The separation can also be performed with an isocratic mobile phase of acetonitrile–Tris buffer, pH 6.9 (40:60).

Calibration plots for the azaarenes were found to be linear ($r>0.999$) in the range of working concentrations [0.06 ng (0.25 ng for 1-azafluoranthene)–6 ng injected]. We found detections limits for the azaarenes between (0.0062 and 0.16 ng) based on a signal-to-noise ratio of 3:1 (see Table 3).

3.1.2. Amino-PAHs

We tried to separate seven different amino-PAHs using the Vydac-PAH column. These compounds have a more polar character, so we had to modify the mobile phase. A good separation was achieved with the gradient program indicated in the legend of Fig. 2. A chromatogram of a standard solution mix (injected 1.25 ng of each compound) under working conditions is shown in Fig. 2. If operated with mobile phases of water–acetonitrile mixtures, bad reproducibility of the response factors (run-to-run) was achieved, due to the strong pH dependency of the amino-PAHs. With a Tris buffer (pH 6.9) good reproducibility was obtained. The calibration plots for the amino-PAHs were nearly linear ($r>0.999$) in the range of working concentrations (0.03–2.5 ng and 0.1–25 ng for 1- and 2-aminonaphthalene injected, respectively). The detections limits for the amino-PAHs between 0.053 and 0.0070 ng based on a signal-to-noise ratio of 3:1 are shown in Table 4.

Table 3
Detection limits of azaarenes

Azaarene	Detection limit (ng injected)[a]
4-Afl	0.024
Acr	0.055
B[*h*]q/Phen	0.0073
B[*f*]q	0.011
1-Aflu	0.16
4-Apy	0.020
B[*a*]a	0.011
B[*c*]a	0.011
7,10-Dmb[*c*]a	0.014
7,9-Dmb[*c*]a	0.012
Db[*a*,*c*]a	0.014
Db[*a*,*j*]a	0.023
Db[*a*,*h*]a	0.0095
Db[*c*,*h*]a	0.0062

[a] 10 μl injected.

3.2. Desorption

The effectiveness of the desorption was examined, as 340 mg of the XAD resin was spiked with 500 ng of each analyte (50 μl of standard solutions 10 ng/μl; solvent: DCM). The small amount of DCM was evaporated immediately and then the resin treated as mentioned above ($n=5$). The solutions were filtrated into 10-ml measuring flasks and filled up with DCM. For comparison, standard solutions ($n=5$) were made (10 ml DCM), which contained the same concentrations of the compounds as the desorption solutions (referred to recoveries of 100%). For the HPLC analysis it was necessary to change the solvent to acetonitrile. From each solution (desorption and standard) we took 1 ml, evaporated the DCM under a stream of nitrogen and dissolved the analytes in 500 μl acetonitrile. The solutions were analyzed by HPLC–FD. The recoveries of each compound were calculated:

$$\text{recovery (\%)} = \frac{\text{average concentration of the desorption solution}}{\text{average concentration of the standard solution}} \cdot 100$$

The recoveries of the azaarenes after the desorption procedure ranged from 94 to 99% and the recoveries of the amino-PAHs from 84 to 93%.

3.3. Clean-up procedure study

In order to check the suitability of the clean-up procedure, the PSR step was studied for all compounds. Experiments were performed taking samples of a mixture of the reference standards. A 10-ml volume of DCM was spiked with 2.5 μg of each azaarene and with 0.5 μg of each amino-PAH. The details of the clean-up procedure are mentioned above. The recovery values calculated by an external standard ranged for the azaarenes from 94 to 100% and for the amino-PAHs from 91 to 96%. The fast and efficient clean-up make it possible to find all *N*-PAHs at high levels.

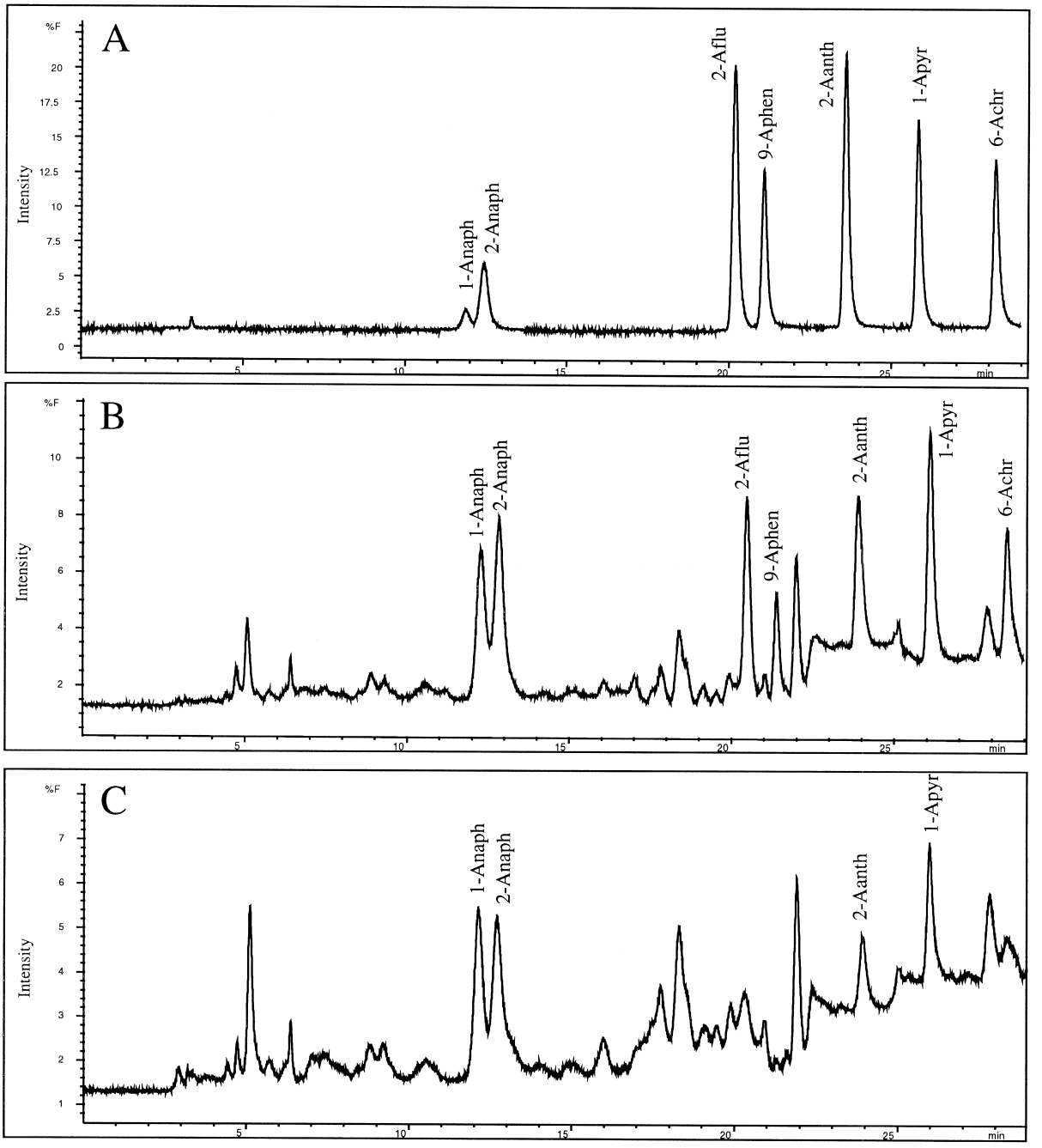


Fig. 2. Chromatograms of amino-PAHs by HPLC with fluorescence detection. Vydac-PAH column 250×4.6 mm, mobile phase: 0–35 min acetonitrile–Tris buffer (30:70) to acetonitrile–Tris buffer (80:20), flow-rate: 1 ml/min, temperature: 30.7°C, fluorescence detection: 0–17.0 min: Ex. 273 nm, Em. 415 nm, PmtGain 14; 17.0–21.0 min: 288 nm, 370 nm, 14; 21.0–22.5 min: 250 nm, 443 nm, 14; 22.5–25.0 min: 260 nm, 495 nm, 14; 25.0–27.5 min: 360 nm, 440 nm, 14; 27.5–30 min: 270 nm., 430 nm, 14. (A) Standard solution 1.25 ng injected, (B) real combustion sample of nylon 6 spiked with 0.5 μg of each compound, (C) real pyrolysis sample of nylon 6 unspiked.

Table 4
Detection limits of amino-PAHs

Amino-PAH	Detection limit (ng injected)[a]
1-Anaph	0.0883
2-Anaph	0.0313
2-Aflu	0.0070
9-Aphen	0.0117
2-Aanth	0.0071
1-Apyr	0.0102
6-Achr	0.0082

[a] 5 μl injected.

3.4. Analysis of a combustion sample

The method was applied to the determination of basic azaarenes and amino-PAHs in a real combustion sample. The compounds were quantified by the standard addition method. The gaseous combustion products of six identically executed burns in the VCI-oven were spiked with 0.5, 1, 1.5, 2, 2.5 and 3 μg of the analytes after desorption. The samples were treated using the clean-up method described in the Experimental section and analyzed by HPLC–FD. Figs. 1 and 2 show the chromatograms of a spiked sample (0.5 μg). The measured concentrations of the six spiked samples were analyzed by linear regression.

The simultaneous analysis of basic azaarenes and amino-PAHs in the basic fraction of a combustion sample is possible. The detection of the individual substances occurs with an excitation (Ex) and emission (Em) wavelength optimal for each substance, therefore the probability of disturbances is reduced. The polarity and the fluorescence data of the basic azaarenes and the amino-PAHs differ strongly, so that no interferences were expected. Only acridine and 1-azafluoranthene have fluorescence data similar to the appropriate amino-PAHs. The fluorescence detection of acridine was adjusted to minimize disturbance from aminophenanthrenes with possible similar retention times. The experiment did show that the acridine is built in a much higher quantity than aminophenanthrene, so the determination of acridine was undisturbed; 1-azafluorananthene was not detected.

The results of the calibration experiment showed a good precision of the method and the relative standard deviations were very low (see Tables 5 and 6). The ordinate intercepts of the calibration straight lines showed the original concentrations of the analytes of the sample (see Tables 5 and 6).

In general the use of an internal standard is efficient for each chromatographic determination. In the case of burning samples it is difficult to exclude definitely the building of an certain isomer during a thermal degradation process. To avoid such a sys-

Table 5
Relative standard deviations (RSDs) and original concentration of the spiked nylon 6 sample of the azaarenes

Azaarene	RSD (%)	Concentration of the combustion sample (mg/g)[a]	Concentration of the pyrolysis sample (mg/g)
4-Afl	3.2	0.031	0.032
Acr	9.3	0.390	0.360
B[*h*]q	1.8	0.120	0.110
Phen	4.2	0.091	0.150
B[*f*]q	3.6	0.071	0.079
1-Aflu	4.5	n.d.	n.d.
4-Apy	3.8	0.096	0.096
B[a]a	2.8	0.015	0.012
B[*c*]a	3.3	0.021	0.019
7,10-Dmb[*c*]a	2.0	n.d	n.d.
7,9-Dmb[*c*]a	3.0	n.d.	n.d.
Db[*a*,*c*]a	2.2	n.d.	n.d.
Db[*a*,*j*]a	2.6	n.d.	n.d.
Db[*a*,*h*]a	1.5	n.d.	n.d.
Db[*c*,*h*]a	0.9	n.d.	n.d.

[a] Referred to the original weight of nylon 6.
n.d. = Not detected.

Table 6
Relative standard deviations (RSDs) and original concentration of the spiked nylon 6 sample of the amino-PAHs

Amino-PAH	RSD (%)	Concentration of the combustion sample (mg/g)[a]	Concentration of the pyrolysis sample (mg/g)
1-Anaph	3.2	0.22	0.19
2-Anaph	3.3	0.058	0.053
2-Aflu	3.1	n.d.	n.d.
9-Aphen	1.1	n.d.	n.d.
2-Aanth	7.6	0.0089	0.0063
1-Apyr	1.6	0.014	0.013
6-Achr	1.7	0.0090	n.d.

[a] Referred to the original weight of nylon 6.
n.d. = Not detected.

tematic fault, we decided to determine by an external standard.

The basic fraction of an unspiked combustion sample (produced under the same conditions as the spiked samples) was evaporated to dryness and resolved in 100–200 μl acetonitrile and analyzed by gas chromatography–mass spectrometry (GC–MS). The presence of 4-azafluorene, acridine, benzo[*h*]quinoline, phenanthridine, 4-azapyrene, benz[*c*]acridine and 1-aminonaphthalene were confirmed. The concentration of the other compounds detected by HLPC–FD were below the detection limits of our GC–MS system (scan-mode).

Figs. 1 and 2 also shown an unspiked sample originate from the pyrolysis of nylon 6 in a VCI-Oven at 800°C. The conditions were similar to the conditions of the combustion, but the pyrolysis takes place in a nitrogen stream. The results are presented in Tables 5 and 6. The concentrations of the determined compounds are quite similar to results obtained for the combustion sample using the standard addition method. The applicability of the method for the determination of the *N*-PAHs in a pyrolysis sample also could be shown.

4. Conclusion

The method described above was developed to analyze basic nitrogen-containing PAHs in the gaseous combustion products of plastics. The clean-up necessary for the determination is efficient and fast with easy handling. The determination with HPLC–FD is very sensitive and has low limits of detection (for most of the compounds <15 pg).

The method enabled us to determine several azaarenes and amino-PAHs, which are known for their mutagenic and carcinogenic potential.

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