Environment Protection Engineering

Vol. 18 1992 No. 1–2

LIDIA WARZECHA*, BEATA JANOSZKA*,
DANUTA BODZEK*

SEPARATION AND ANALYSIS OF BIOLOGICALLY ACTIVE NITROGEN DERIVATIVES OF POLYCYCLIC AROMATIC HYDROCARBONS FROM AIRBORNE PARTICULATE MATTER

The dichloromethane extracts from airborne particulate matter collected in highly industrialized region of Upper Silesia were investigated. Using the column chromatography filled with Al_2O_3 and silicic acid as the stationary phases, the fraction of azaarenes has been separated. The silicic acid column chromatography combined with the reduction of the nitroarenes in $KBH_4/CuCl_2$ system and derivatization with pentafluoropropionic acid anhydride yielded an enriched nitro fraction. Nitroarenes present in this fraction as pentafluoropropyl amides and also the azaarene fraction were analysed by GC–MS system. Some nitroarenes and azaarenes were identified on the basis of comparisons of mass spectral data of standard compounds. Especially, the mass spectra of fluoroamide derivatives of nitroarenes have characteristic fragment ions $(M\text{-}147)^+$, $(M\text{-}147\text{-}27)^+$ that provide the best information for their identification.

1. INTRODUCTION

Polyaromatic air pollutants containing nitrogen in their molecules comprise several classes of organic compounds, i.e., nitroarenes, carbazoles and azaarenes. Because of high biological activity of the majority of nitro compounds and azaarenes and the resulting health hazards, particularly in industrial regions, much attention has lately been paid to the problems of analysis of these compounds.

The presence of nitroarenes and azaarenes in the organic pollutants of air is the result, first of all, of fuel and waste burning [1], [2]. A significant source of nitro compounds are the gas-phase atmospheric reactions of two- to four-ring polycyclic aromatic hydrocarbons (PAH) with N_2O_5 and/or with the OH radicals in the presence of NO_x [3], [4].

---

* Silesian Medical Academy, Faculty of Medicine, Department of Chemistry, 41-808 Zabrze, ul. Jordana 19, Poland.

A marked dependence has been found between mutagenetic capabilities of the extracts separated from airborne particulate matter or diesel exhaust gases and the presence of nitroarenes and azaarenes in the extracts studied [5], [6]. It should be noted that nitroarenes are hazardous chemicals to people's health not only because of their genotoxic action, but also on account of a possibility of their transformations to more toxic derivatives as a result of decomposition reactions, or processes of metabolic activation [7].

Since extracts of airborne particulate matter are complex multicomponent mixtures of various classes of organic compounds, the analytical methods of nitroarenes and azaarenes comprise several steps: separation of the concentrates of these compounds, preliminary separation, identification analysis and quantitative determination. The separation of azaarenes and nitroarenes from the extracts is carried out, first of all, by means of high-performance liquid chromatography [8] or column liquid adsorption chromatography [9]. In the identification and quantitative determinations of nitrogen compounds, GC–MS system was found to be the most useful technique [10]. Also gas chromatography with nitrogen selective detectors is a very effective method for these purposes [11]. In liquid chromatography methods applied to nitroarenes analysis, a significant progress has also been made mainly thanks to the use of on-line reduction of nitroarenes to amines and fluorescence detection [12], [13]. The results of our studies concerning the separation and identification of nitroarenes and azaarenes from airborne particulate matter of Upper Silesia (a region of the highest ecological hazard in Poland) have been presented in this paper. The column adsorption chromatography with the subsequent use of aluminium oxide and silicic acid as the stationary phases and GC–MS system have been used as the basic analytical methods.

2. EXPERIMENTAL

2.1. SAMPLE ORIGIN

Two averaged samples of airborne particulate matter taken in a few towns of Upper Silesia during the summer and winter seasons were analysed. Airborne particulate matter was collected on glass fiber filters and then extracted in Soxhlet apparatus with methylene chloride according to a procedure described earlier [14].

2.2. CHEMICALS

Silicic acid (Mallinckrodt, 100 mesh powder) and neutral aluminium oxide (90 Merck, Brockman Activity II–III) were used as the stationary phases in chromatographic separation. Analytical-grade organic solvents (dichloromethane, *n*-hexane, benzene, chloroform, THF, ether, ethanol) were used as the eluents. The model compounds including polycyclic aromatic hydrocarbons, nitroarenes, aminoarenes, azaarenes and oxygen compounds were obtained from Aldrich Chemical Co., Sigma Chemical Co. and Fluka AG. Copper (II) chloride, $NaBH_4$, triethylamine and pentafluoropropionic anhydride (PFPA) (Aldrich, 99%) were used to receive the fluoroamide derivatives.

2.3. ANALYTICAL SYSTEM

The glass open columns of dimensions as follows: 30 cm × 1.8 cm (for silicic acid) and 30 cm × 1.1 cm (for Al_2O_3) have been used for preparative chromatographic separations. A Shimadzu mass detector (Model QP 2000) with a data system was used for mass spectrometric identification. The ion source EI was operated at 70 eV and the temperature of 300°C. A Shimadzu gas chromatograph (Model A-14) was connected to the mass detector. This instrument was equipped with a fused silica capillary column CPB-5 (25 m × 0.20 mm i.d., 0.25 μm film thickness). Aliquots of samples of 1μl volume were injected with stream splitting at the ratio of 1:50. The temperatures in this instrument were set as follows: injection port – 270°C, interface – 300°C. The carrier gas was helium of the flow velocity equal to 1.2 $cm^3 \cdot min^{-1}$. During GC–MS analysis, the oven temperature was held at 60°C for 3 min and then temperature was programmed: for fluoroamide derivatives – from 60°C to 280°C (4°C/min), 280°C (for 5 min); for azaarenes from 60°C to 280°C (5°C/min), 280°C (for 10 min); for carbazoles – 60°C (for 3 min), from 60°C to 220°C (25°C/min), from 220°C to 280°C (4°C/min), 280°C (for 10 min).

The UV-Vis absorption spectra were recorded by spectrophotometer UV-Vis, model Specord (Carl Zeiss, Jena).

2.4. SEPARATION OF NITROARENE FRACTION – PREPARATION OF AMIDES

The analytical procedure of separating nitroarene fraction from the extracts has been presented in figure 1. Two extracts and mixtures of standards representing various organic pollutions of the atmosphere, i.e. pyrene, benzo(*a*)pyrene, 9-nitroanthracene, 2-nitronaphthalene, 2-nitrofluorene, 1-nitropyrene, acridine, anthrone, 2-naphthol and aminoanthraquinone, were separated according to this procedure.

The course of separation of the standard mixtures was controlled by registration of UV-Vis spectra of the 3 cm^3 eluates received from a column. On the basis of the spectrograms, the eluates were combined into fractions containing the particular classes of compounds. Separations were carried out in columns packed with silicic acid which contained 5% of water. Earlier, silicic acid had been dried at 150°C for 24 hours, and next, after an addition of water, shaked for 24 hours. About 50 mg of the extract was dissolved in methylene chloride combined with 0.5–1 g of silicic acid and, after evaporation of the solvent, introduced into the column previously packed with a stationary phase. Nitroarene fraction was eluted with a mixture of *n*-hexane–benzene (1:1).

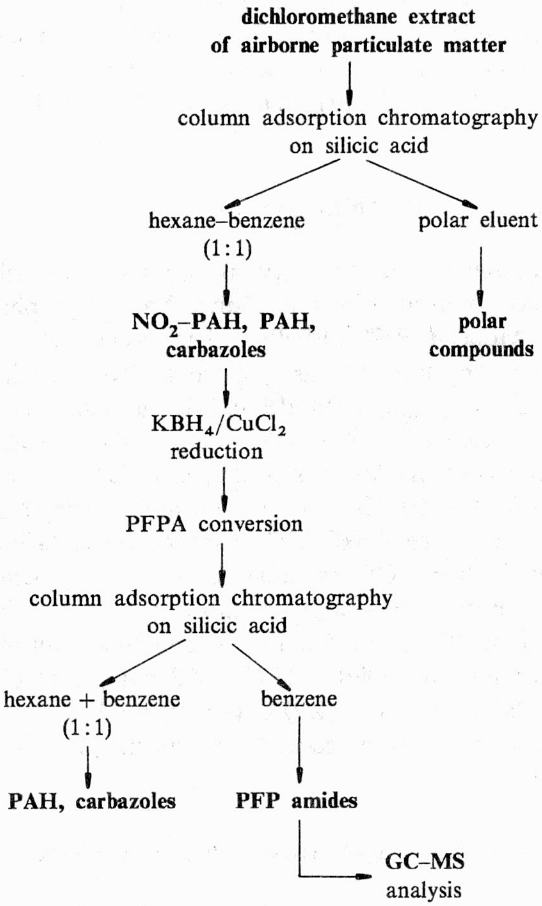

Fig. 1. Isolation of nitroarenes from particulate extracts
NO_2–PAH – nitro polycyclic aromatic hydrocarbons; PAH – polycyclic aromatic hydrocarbons;
PFPA – pentafluoropropionic anhydride; PFP amides – pentafluoropropylamide derivatives

The reduction of nitroarenes to aromatic amines as well as acylation of amines to fluoroamide derivatives were conducted according to procedure used by CAMPBELL et al. [15]. The fraction of fluoroamide derivatives was separated on silicic acid using the following eluents: a mixture of *n*-hexane–benzene (1:1) for elution of the fraction containing polycyclic aromatic hydrocarbons and carbazoles; benzene for the elution of amide fraction.

2.5. SEPARATION OF AZAARENE FRACTION

A diagram of the analytical procedure is given in figure 2. The diagram has been based on the paper by LATER et al. [16], [17] referring to analysis of nitrogen

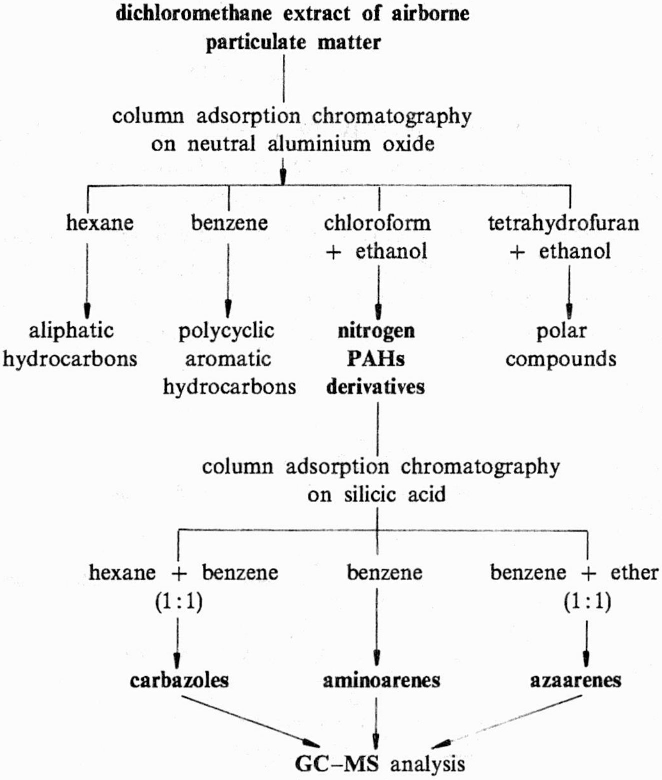

Fig. 2. Isolation of nitrogen compounds from particulate extracts

compounds in coal liquids. In the first step of analysis, there were separated some mixtures of standards containing anthracene, benzo(*a*)pyrene, carbazole, dibenzcarbazole, 2-aminofluorene, acridine, phenanthroline, 1-naphthol and 9-hydroxyphenanthrene. The course of the elution was controlled by means of a spectrophotometer UV-Vis. Aluminium oxide activated at 130°C for 12 hours was used. The adsorbent prepared in this way contains the optimum amount of water, i.e., about 1.1% [18]. About 300 mg of the extract, after being dissolved in chloroform, was combined with 3 g of aluminium oxide and, after evaporation of the solvent, introduced to a column containing 3 g of packing. Elution was carried out in turn with *n*-hexane, benzene, chloroform with an addition of 0.75% vol. of ethanol and a mixture of ethanol–THF. The fraction eluted with chloroform, containing nitrogen derivatives of PAH, was fractionated on silicic acid into three classes of compounds: carbazoles (elution with a mixture of *n*-hexane–benzene), aminoarenes (elution with benzene) and azaarenes (elution with a mixture of benzene–ether).

3. RESULTS AND DISCUSSION

3.1. NITROARENES

Because of great polar similarity between nitroarenes, PAH, carbazoles and moderately polar oxygen compounds, the separation of nitro compounds by means of liquid chromatography from complex extracts is very difficult. The diagram used by us and presented in figure 1 made possible an efficient separation of nitroarenes from the extracts of airborne particulate matter. The use of chromatographic separation on silicic acid leads to the separation of nitro compounds from more polar components which are more strongly adsorbed by stationary phase.

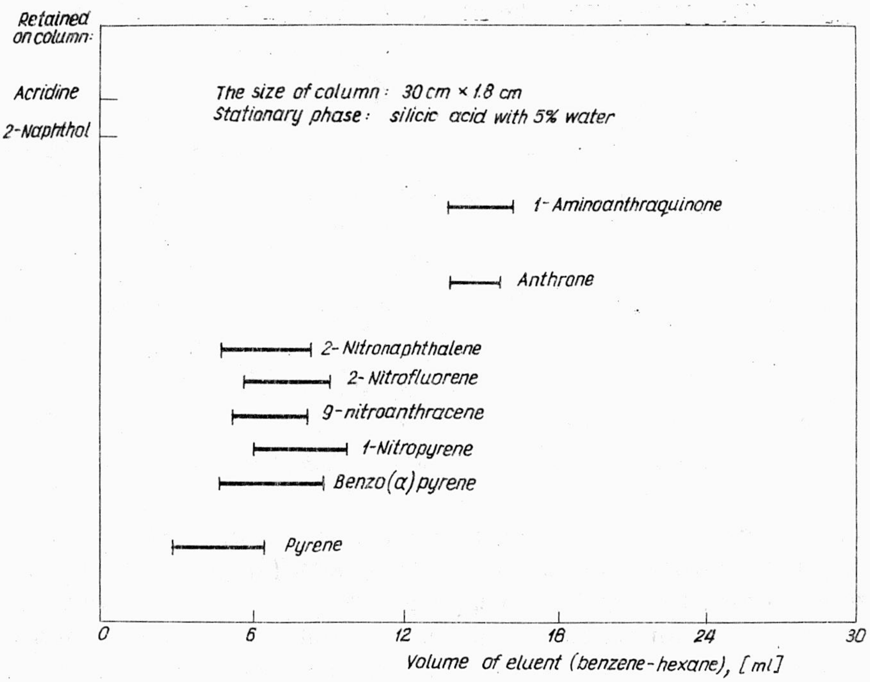

Fig. 3. Diagram of elution volumes of standard mixture separated by using silicic acid adsorption chromatography

The diagram of elution (figure 3) of the standard mixtures shows that the process conditions enable an effective separation of the moderately polar fraction containing among other things the nitroarenes from the remaining components.

The reduction of nitroarenes to amines, the subsequent acylation of anhydride with pentafluoropropionic acid (figure 4) and separation of these derivatives on silicic acid allow obtaining the amide concentrate without carbazoles and PAH. The data presented in table 1 point to a relatively good degree of conversion of the standard nitroarenes into amide derivatives, amounting on the average to 80%.

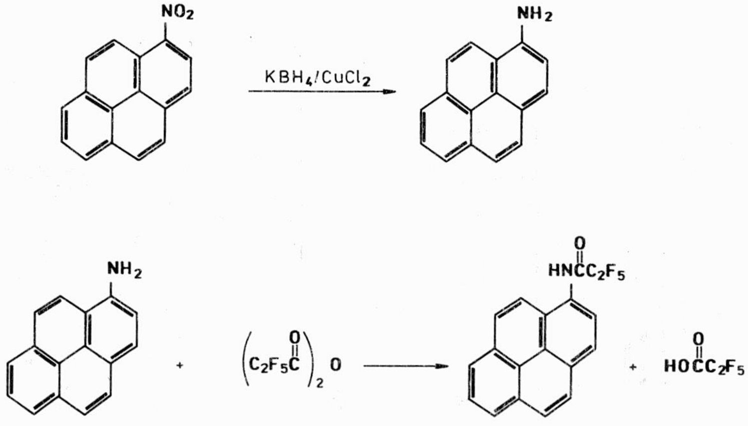

Fig. 4. Conversion of nitroarenes to pentafluoropropylamides

Table 1

Reduction and acylation yields
of selected nitroarene standards

Nitrocompound	Yield (%)
2-nitronaphthalene	80
9-nitroanthracene	82
2-nitrofluorene	78
1-nitropyrene	80

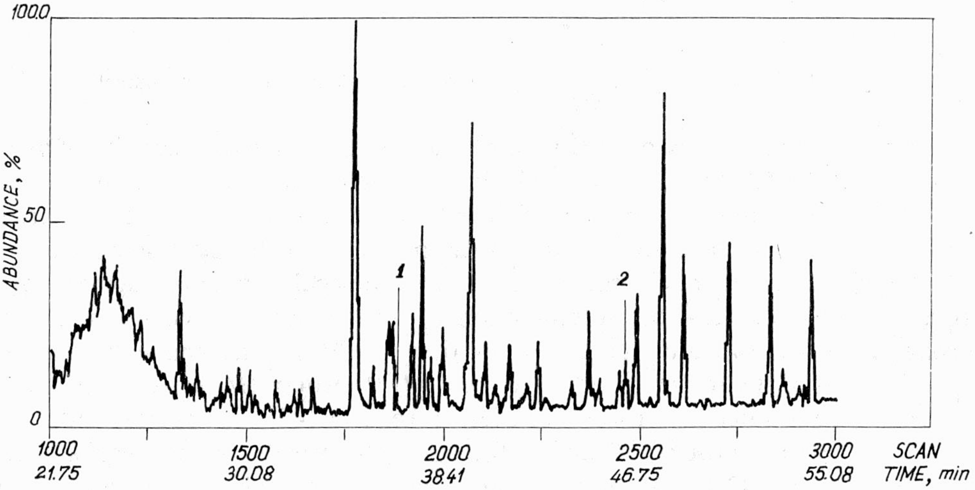

Fig. 5. Total ion chromatogram of pentafluoropropylamides isolated from winter sample extract
1 – 2-nitrofluorene, *2* – 1-nitropyrene

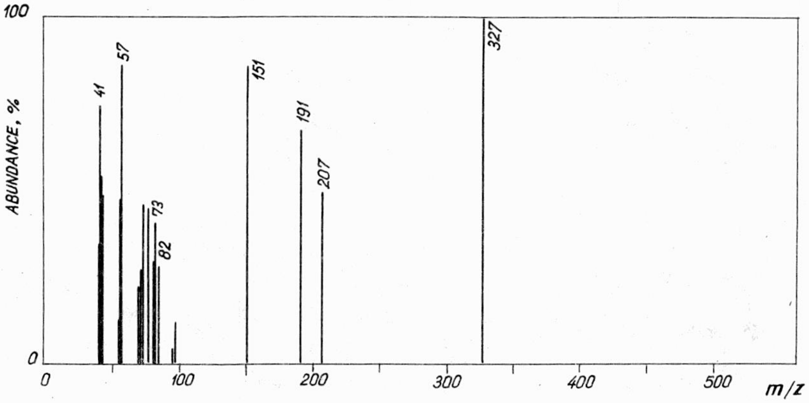

Fig. 6. Mass spectrum of 2-nitrofluorene fluoroamide derivative (winter sample)

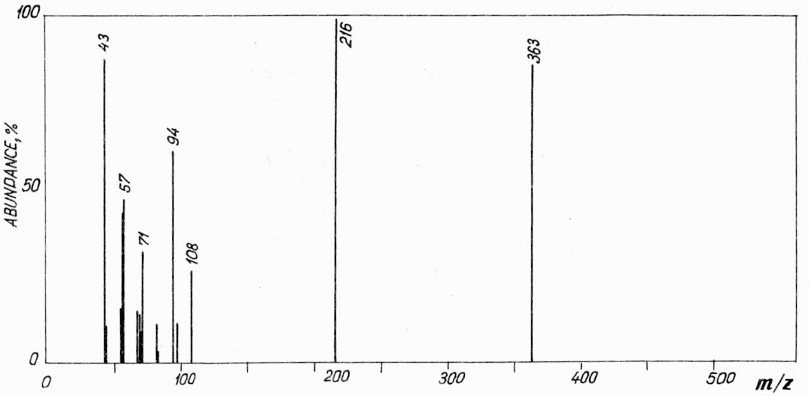

Fig. 7. Mass spectrum of 1-nitropyrene fluoroamide derivative (winter sample)

A significant problem associated with nitroarene analysis is the necessity of using suitably sensitive detection. The use of GC–MS system for identification of nitro compounds as a result of the analysis of their amide derivatives enabled a nitroarene identification beyond all doubt thanks to the presence (in the mass spectra of the amides) of characteristic peaks corresponding to a molecular ion and fragment ions. It is a very distinct peak of molecular ion of fluoroamide. Molecular weight of fluoroamide is by 146 amu greater than that of the parent amine because of a substitution of hydrogen atom with the PFP group $(M–H + C_3F_5O)^+$ or $(M + 146)^+$. Two other major ions are present, i.e., $(M–147)^+$ ion corresponding to the loss of the PFP group and giving the molecular weight of the unsubstituted aromatic amine $(M–C_3F_5O)^+$ and second fragment ion resulting from the loss of HCN $(M–C_3F_5O–HCN)^+$ or $(M–147–27)^+$.

In figure 5, the total ion chromatogram of amide fraction from the winter extract is presented. The mass spectra of the amides of 2–nitrofluorene and 1–nitropyrene identified in this sample are given in figures 6 and 7 – these compounds are dominant in the nitroarenes detected in the extracts of airborne particulate matter by other authors [19]. In the summer sample, no nitroarenes were found.

3.2. AZAARENES, CARBAZOLES

Column chromatography with Al_2O_3 as stationary phase was used to separate this group of PAH derivatives (figure 2). The use of aluminium oxide allows efficient separation of organic mixtures which are distributed between classes of compounds, depending on the kind of the heteroatom present in the polycyclic aromatic structure of the molecule [20]. The fraction separated in this way and eluted with chloroform contains a mixture of nitrogen derivatives of PAH. Its separation on silicic acid leads to a selective separation of carbazole, aminoarene and azaarene fractions.

The effectiveness of the applied procedure of chromatographic separation in the system Al_2O_3–silicic acid was confirmed by the results of GC–MS analysis of the particular fractions from the separation of a mixture of standards (table 2).

The use of an analytical procedure presented in figure 2 for the separation of the extracts tested made it possible to separate, in the first step, the fraction of aliphatic hydrocarbons, PAH, nitrogen derivatives of PAH and fraction of polar compounds.

The fractions obtained as a result of separation of the concentrate of PAH nitrogen derivatives on silicic acid (figure 2) were subjected to GC–MS analysis.

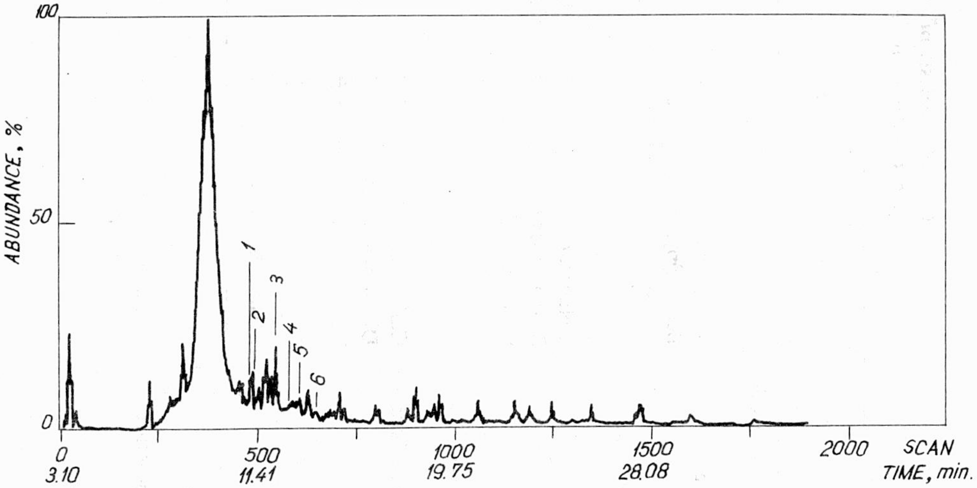

Fig. 8. Total ion chromatogram of carbazole fraction separated from winter sample extract
1 – carbazole, *2* – 9-nitrosocarbazole, *3* – 2-methylcarbazole,
4 – 9-methylcarbazole, *5* – 9-ethylcarbazole, *6* – 9-(1-methylethyl)carbazole

Table 2

GC–MS analysis of fractions from chromatographic separation of standard mixture in aluminium oxide/silicic acid system (fig. 2)

Eluent	Standard	Mol wt	Retention time (min)	*m/z*, relative abundance				
Aluminium oxide				$(M)^+$				
Benzene	Anthracene	178	10.83	178(100)				
	Benzo(*a*)pyrene	252	24.03	252(100)				
THF–ethanol				$(M)^+$	$(M–CO)^+$	$(M–COH)^+$	$(M–COH_2)^+$	$(M–COH_3)^+$
	1-Naphthol	144	21.61	144(100)	116(40)	115(94)	114(5)	113(8)
	2-Hydroxyphenanthrene	194	35.48	194(100)	–	–	–	–
Silicic acid				$(M)^+$	$(M–HCN)^+$	$(M–H_2CN)^+$	$(M–H_3C_3N)^+$	
n-Hexane–benzene	Carbazole	167	11.16	167(100)	140(14)	139(2)	114(2)	
	Dibenzocarbazole	267	29.16	267(100)	240(5)	239(2)	214(2)	
				$(M)^+$	$(M–H)^+$	$(M–HCN)^{+\cdot}$	$(M–H_2CN)^+$	$(M–NH_2)^+$
Benzene	1-Aminofluorene	181	45.46	181(100)	179(9)	154(35)	153(45)	165(5)
				$(M)^+$	$(M–HCN)^+$	$(M–H_2CN)^+$	$(M–H_3C_3N)^+$	
Benzene–ether	Acridine	179	28.08	179(100)	152(14)	151(11)	–	
	Phenanthroline	180	28.60	180(100)	153(10)	152(13)	127(4)	

Table 3

GC–MS analysis of carbazole fraction separated from winter and summer extracts

Compound	Retention time (min)	*m/z*, relative abundance						
		$(M)^+$	$(M{-}CH_3)^+$	$(M{-}C_2H_5)^+$	$(M{-}HCN)^+$	$(M{-}H_2CN)^+$	$(M{-}H_3C_3N)^+$	$(M{-}N)^+$
Carbazole	11.88	167(100)	–	–	140(11)	139(13)	114(3)	153(0.5)
9-Nitrosocarbazole[a]	11.20	167(100)[b]	–	–	140(13)	139(18)	114(4)	–
2-Methylcarbazole	12.05	181(100)	–	–	154(5)	153(5)	128(3)	–
9-Methylcarbazole[a] (probably)	12.86	181(100)	–	–	–	–	–	–
9-Ethylcarbazole	13.18	195(100)	180(53)	166(5)	–	167(10)	–	181(8)
9-(1-methylethyl)carbazole[a]	14.00	209(100)	194(71)	165(11)	–	–	–	195(14)

[a] Absent in summer sample.

[b] Ion formed after loss of nitroso group.

Table 4

GC–MS analysis of azaarene fraction separated from winter and summer extracts

Compound	Retention time (min)	m/z, relative separated abundance				
		$(M)^+$	$(M\text{–}HCN)^+$	$(M\text{–}H_2CN)^+$	$(M\text{–}H_3C_3N)^+$	$(M\text{–}N)^+$
Quinoline or isoquinoline	13.96	129(100)	102(34)	101(8)	76(8)	–
Benzo(*h*)quinoline	28.58	179(100)	152(15)	151(16)	126(9)	–
Phenanthridine or benzo(*f*)quinoline	29.13	179(100)	152(13)	151(20)	–	–
Benzo(*c*)quinoline	30.81	180(83)	152(100)	151(26)	–	–
9-Methylacridine	31.23	193(100)	–	165(13)	–	–
1-Azafluoranthene[a] or 4-azapyrene	34.81	203(100)	176(25)	–	150(24)	–

[a] Absent in winter sample.

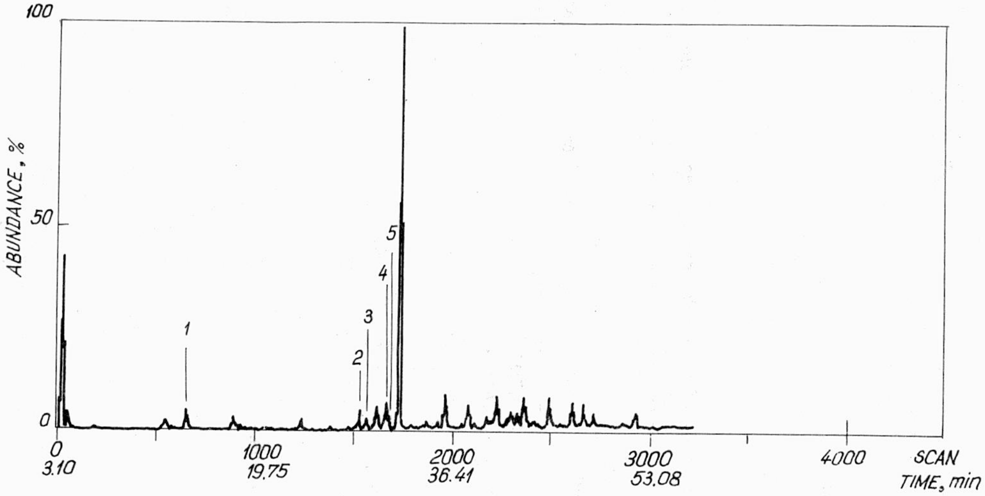

Fig. 9. Total ion chromatogram of azaarene fraction separated from winter sample extract
1 – quinoline or isoquinoline, *2* – benzo(*h*)quinoline, *3* – phenanthridine or benzo(*f*)quinoline, *4* – benzo(*c*)quinoline, *5* – 9-methylacridine

In the fraction eluted with *n*-hexane–benzene mixture, constituting 2% of the extracts tested, carbazole and its alkyl derivatives were identified (table 3). In figure 8, the total ion chromatogram of carbazoles fraction from the winter sample is presented. The aminoarenes were not found in the fraction eluted with benzene from both analysed extracts.

In table 4, there are presented the azaarenes identified in the fraction eluted with a mixture benzene–diethyl ether, the content of which in both extracts was about 10%. The identification analysis of carbazoles and azaarenes was based on the detection of the peaks in the mass spectra. These peaks give evidence of the presence of a nitrogen atom in the compound molecule. The presence of a fragment ion (M-14), corresponding to the removal of nitrogen, is rarely observed in the mass spectra of these components. The most characteristic fragment ions in nitrogen compounds are the ions originating as the result of the removal of the following groups: CH=N $(M\text{-}27)^+$, CH=NH $(M\text{-}28)^+$ and CH=N-CH=CH $(M\text{-}53)^+$ [2]. In figure 9, the total ion chromatogram of the azaarene fraction from the winter sample is presented.

Of the azaarenes identified, two- and three-ring compounds are dominant in both extracts. Four-ring azafluoranthene or azapyrene was found only in the summer sample. The azaarenes listed in table 6 are compounds exhibiting muta- and cancerogenic biological activities, particularly quinoline, benzoquinoline and phenanthridine [6].

4. CONCLUSIONS

The applied analytical procedure allowing conversion of nitrocompounds into fluoroamide derivatives enables an identification of biological active nitrofluorene and nitropyrene in a complex mixture of organic air pollutants containing also PAH, carbazoles and oxygen derivatives of PAH.

Two-step column adsorption chromatography in the system of Al_2O_3–silicic acid, used for the separation of nitrogen derivatives from the extracts of airborne particulate matter, made it possible to obtain fractions containing the individual classes of polycyclic nitrogen compounds. As a result of analysis of these fractions in the system GC–MS, carbazole and its alkyl derivatives, as well as two- and three-ring azaarenes were identified. Any substantial differences in the composition of the heterocompounds fractions separated from the winter and summer samples were not found.

The experiments were carried out within the framework of project No. 6028891.01 financed in the years 1991–1992 by the Polish State Committee for Scientific Research.

REFERENCES

[1] SCHUETZLE D., *Sampling of vehicle emissions for chemical analysis and biological testing*, Environ. Health Perspec., Vol. 47 (1983), pp. 65–80.

[2] GRIMMER G., JACOB J., DETTBARN G., NAUJACK K.W., *Determination of polycyclic aromatic hydrocarbons, azaarenes and thiaarenes emitted from coal-fired residential furnaces by gas chromatography/mass spectrometry*, Fresenius Z. Anal. Chem., Vol. 322 (1985), pp. 595–602.

[3] ATKINSON R., AREY J., ZIELIŃSKA B., ASCHMANN S.M., *Kinetics and nitro-products of the gas-phase OH and NO_3 radicals – initiated reactions of naphthalene – d_8, fluoranthene – d_{10} and pyrene*, Int. J. Chem. Kinet., Vol. 22 (1990), pp. 999–1014.

[4] AREY J., ATKINSON R., ASCHMANN S.M., SCHUETZLE D., *Experimental investigation of the atmospheric chemistry of 2-methyl-1-nitronaphthalene and a comparison of predicted nitroarene concentrations with ambient air data*, Polycyclic Aromatic Compounds, Vol. 1 (1990), pp. 33–50.

[5] PITTS J.N., Jr., *Nitration of gaseous polycyclic aromatic hydrocarbons in simulated and ambient urban atmospheres: a source of mutagenic nitroarenes*, Atmospheric Environment, Vol. 21 (1987), pp. 2531–2547.

[6] LA VOIE E.J., DOLAN S., LITTLE P., WANG C.X., SUGIE S., RIVERSON A., *Carcinogenicity of quinoline, 4- and 8-methylquinoline and benzoquinoline in newborn mice and rats*, Fd. Chem. Toxic., Vol. 26, (1988), pp. 625–629.

[7] FU P.P., CHOU M.W., BELAND F.A., *Effects of nitro substitution on the in vitro metabolic activation of polycyclic aromatic hydrocarbons*, [in:] *Polycyclic aromatic hydrocarbon carcinogenesis: structure–activity relationships*, Vol. II (1988), pp. 37–65, ed. by S.K. Yang, B.D. Silverman, CRC Press, Boca Raton.

[8] PAPUTA-PECK M.C., MARANO R.S., SCHUETZLE D., RILEY T.L., HAMPTON C.V., PRATER T.J., SKEWES L.M., JENSEN T.E., RUEHLE P.H., BOSCH L.C., DUNCAN W.P., *Determination of nitrated polycyclic aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection*, Anal. Chem., Vol. 55 (1983), pp. 1946–1954.

[9] JÄGER J., *Detection and characterization of nitroderivatives of some polycyclic aromatic hydrocarbons by fluorescence quenching after thin-layer chromatography: application to air pollution analysis*, J. Chromat., Vol. 152 (1978), pp. 575–578.

[10] SCHUETZLE D., HAMPTON C.V., *Gas chromatography/mass spectrometry in air pollution studies*, [in:] *Mass spectrometry in environmental sciences*, ed. by F.W. Karasek, O. Hutzinger, S. Safe, Plenum Publ. Corp., pp. 159–193 (1984).

[11] BOSCH L.C., CHAN T.L., DUNCAN W.P., GIBSON T.L., JENSEN T.L., MERMELSTEIN R., PERRY M., POLLE C.F., ROSENKRANZ H.S., RUEHLE P.H., SCHUETZLE D., TOMKINS B.A., WHITE C.M., *Nitrated polycyclic aromatic hydrocarbons*, ed. by A. Hüething, Heidelberg 1985.

[12] MAC CREHAN W.A., MAY W.E., Anal. Chem., Vol. 56 (1984), pp. 625–628.

[13] TEJADA S.B., ZWEIDINGER R.B., SIGSBY J.E., *Fluorescence detection and identification of nitroderivatives of polynuclear aromatic hydrocarbons by on-column catalytic reduction to aromatic amines*, Anal. Chem., Vol. 58 (1986), pp. 1827–1834.

[14] BODZEK D., LUKS-BETLEJ K., WARZECHA L., TYRPIEŃ K., *Investigations on the selection of extraction solvent for recovery of organic matter from air pollution samples*, Chemia Analityczna, Vol. 35 (1990), pp. 693–710.

[15] CAMPBELL R.M., LEE M.L., *Capillary column gas chromatographic determination of nitro polycyclic aromatic compounds in particulate extracts*, Anal. Chem., Vol. 56 (1984), pp. 1026–1030.

[16] LATER D.W., LEE M.L., WILSON B.W., *Selective detection of amino polycyclic aromatic compounds in solvent refined coal*, Anal. Chem., Vol. 54 (1982), pp. 117–123.

[17] LATER D.W., ANDROS T.G., LEE M.L., Anal. Chem., Vol. 55 (1983), pp. 2126–2132.

[18] LATER D.W., LEE M.L., *Chromatographic methods for chemical and biological characterization of polycyclic aromatic compounds in synfuel materials*, pp. 44–73, [in:] *Advanced techniques in synthetic fuels analysis*, Ch. 4, Technical Inf. Center, U.S., Dep. of Energy, Oak Ridge TN (1983).

[19] ZIELIŃSKA B., AREY J., ATKINSON R., MCELROY P.A., *Nitration of acephenanthrylene under simulated atmospheric conditions and in solution and the presence of nitroacephenanthrylene (S) in ambient particles*, Environ. Sci. Technol., Vol. 22 (1988), pp. 1044–1048.

[20] LATER D.W., LEE M.L., BARTLE K.D., KONG R.C., VASSILAROS D.L., *Chemical class separation and characterization of organic compounds in synthetic fuels*, Anal. Chem., Vol. 53 (1981), pp. 1612–1620.

WYDZIELANIE I ANALIZA BIOLOGICZNIE AKTYWNYCH AZOTOWYCH POCHODNYCH WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH Z PYŁOWYCH ZANIECZYSZCZEŃ POWIETRZA

Poddano analizie dichlorometanowe ekstrakty z pyłowych zanieczyszczeń powietrza w rejonie Górnego Śląska. Frakcję azaarenów wyodrębniano za pomocą chromatografii kolumnowej, stosując Al_2O_3 i kwas krzemowy jako fazy stacjonarne. Aby wydzielić nitroareny, zastosowano również chromatografię na kwasie

krzemowym. Połączono ją z redukcją tych związków w układzie $KBH_4/CuCl_2$ i acylowaniem bezwodnikiem kwasu pentafluoropropionowego. Nitroareny obecne w tej frakcji jako pentafluoropropyloamidy oraz frakcję azaarenów analizowano w systemie GC–MS. Porównując widma masowe wzorców i analizowanych próbek, zidentyfikowano kilka nitroarenów i azaarenów. Obecność w widmach masowych fluoroamidowych pochodnych nitroarenów charakterystycznych jonów fragmentacyjnych $(M\text{-}147)^+$, $(M\text{-}147\text{-}27)^+$ umożliwiło jednoznaczną identyfikację nitrozwiązków.

ВЫДЕЛЕНИЕ И АНАЛИЗ БИОЛОГИЧЕСКИ АКТИВНЫХ АЗОТНЫХ ПРОИЗВОДНЫХ ПОЛИЯДЕРНЫХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ ИЗ ПЫЛЕВЫХ ЗАГРЯЗНЕНИЙ ВОЗДУХА

Проанализированы дихлорметанные экстракты из пылевых загрязнений воздуха в районе Верхней Силезии. Фракцию азааренов выделили с помощю колончатой хроматографии, применяя Al_2O_3 и кремневую кислоту в качестве стационарных фаз. Чтобы выделить нитроарены, применили также хроматографию на кремневой кислоте. Ее связали с редукцией этих соединений в системе $KBH_4/CuCl_2$ и ацилированием ангидридом пентафторпропионовой кислоты. Нитроарены, присутствующие в этой фракции в качестве пентафторпропиламидов, а также фракцию азааренов анализировали в системе GC–MS. Сравнивая масс-спектры образцов и анализируемых пробок, идентифицировали несколько нитроаренов и азааренов. Присутствие в масс-спектрах фторамидных производных нитроаренов характерных фрагментационных ионов $(M\text{-}147)^+$, $(M\text{-}147\text{-}27)^+$ дало возможность однозначной идентификации нитросоединений.