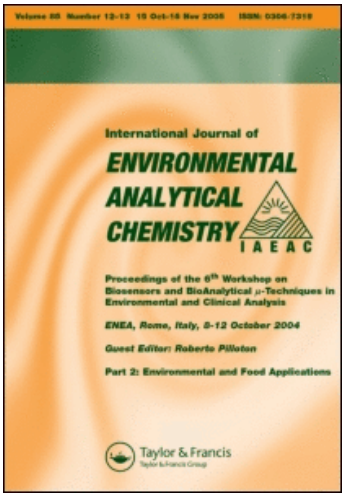

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Ozonolysis Products of Benzo[A]Pyrene With Capillary Gas Chromatography Mass Spectrometry and Liquid Chromatography Mass Spectrometry

R. Koeber[a]; J. M. Bayona[b]; R. Niessner[a]
[a] Institute of Hydrochemistry, Technical University of Munich, Munich, Germany [b] Department of Environmental Chemistry, C.S.I.C. Barcelona, Barcelona, Spain

To cite this Article Koeber, R. , Bayona, J. M. and Niessner, R.(1997) 'Analysis of Ozonolysis Products of Benzo[A]Pyrene With Capillary Gas Chromatography Mass Spectrometry and Liquid Chromatography Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 66: 4, 313 — 325
To link to this Article: DOI: 10.1080/03067319708028372
URL: http://dx.doi.org/10.1080/03067319708028372

Intern. J. Environ. Anal. Chem., Vol. 66, pp. 313-325
Reprints available directly from the publisher
Photocopying permitted by license only

ANALYSIS OF OZONOLYSIS PRODUCTS OF BENZO[A]PYRENE WITH CAPILLARY GAS CHROMATOGRAPHY MASS SPECTROMETRY AND LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

R. KOEBER[a], J. M. BAYONA[b] and R. NIESSNER[a, *]

[a] *Institute of Hydrochemistry, Technical University of Munich, Marchioninistrasse 17, 81377 Munich, Germany;* [b] *Department of Environmental Chemistry, C.S.I.C. Barcelona, Jordi Girona 18–26, 08034 Barcelona, Spain*

(Received 13 Februay 1997; In final form 25 March, 1997)

Various chromatographic techniques coupled with mass spectrometry were used for the analysis of polar products after ozonolysis of benzo[a]pyrene (BaP), including CGC-HRMS, thermospray-LC-MS and APCI-LC-MS. The simulation of atmospheric degradation of benzo[a]pyrene by ozone was carried out on glass fiber filters and BaP-coated soot. The drawback of GC/MS is the low sensitivity for these analytes, the advantages are the higher separation performance and the possibility of electron impact (EI) spectra. In comparison, APCI-LC-MS is by far more sensitive with detection limits in the absolute picogram range, despite the lack of structural information. No qualitative difference between the ozonolysis products of BaP deposited on glass fiber filters or soot surfaces was observed. Reaction products consist mainly of quinones and carboxylic acids. A number of compounds cannot be identified yet and require further investigation. With the APCI-LC-MS, the formation of BaP degradation products was confirmed on real samples of air particulate matter.

Keywords: Benzo[a]pyrene degradation, ozone, APCI-LC-MS, GC-HRMS, particulate matter

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAH) are known as strong, ubiquitous carcinogens and mutagens, formed by natural diagenetic processes or anthropogenic (e.g. burning of fossil fuels in power and heat generation, industry or traffic) processes [1]. PAHs occur in fossil fuels, tobacco smoke, sediments and airborne particulates. It has been demonstrated that PAHs require metabolic activation in order to induce

* Corresponding author: Fax: +49–89–70957999.

carcinogenicity [2,3]. Among the PAHs, benzo[*a*]pyrene (BaP) has been studied most extensively. Derivatives of BaP are formed by enzymatic activation or conjugation [4,5] in biological systems or by reactions with chemical agents like NO_2, SO_2, O_3 and with or without light under atmospheric conditions [6,7].

Particle-adsorbed compounds are exposed to a variety of gaseous pollutants in urban atmospheres. The pathways for the degradation of PAH depend on the seasonal conditions: the degradation by nitrogen oxides and sulfur oxides plays an important role during winter time due to low temperatures and low irradiation intensities, whereas photochemical reactions with oxygen and secondary air pollutants like ozone, peroxyacetylnitrate, hydroxyl and hydroperoxyl radicals are more important in summer [7]. The reaction between BaP and ozone under preparative conditions was reported 35 years ago [8], with the BaP quinones (BaP-1,6-dione, BaP-3,6-dione, BaP-6,12-dione) being the main products. Van Cauwenberghe et al. reported the formation of several oxidized compounds like carboxylic acids, aldehydes and phenols [9] after exposure of BaP to ozone on glass fibre filters. The formation of the highly carcinogenic BaP-4,5-epoxide in laboratory experiments was discovered by Pitts et al. [10].

Despite the fact that there is considerable research on the degradation of BaP under simulated atmospheric conditions [6, 11-12], there is a lack of knowledge about the composition and fate of degradation BaP products adsorbed on particles.

Besides the ability to analyze PAH with LC-MS [13], this technique offers the possibility to examine highly polar derivatives without the limitations occurring in GC/MS: under LC conditions, thermally labile compounds and those of low volatility can be analyzed easily. Unlike in GC-MS no derivatization is required for very polar compounds. The lower separation efficiency of LC compared to GC results in the need for a highly selective detection method like mass spectrometry. In the last few years, coupling devices for LC-MS have become more reliable and its application range has been considerably extended, especially in biochemical, biomedical [14] and environmental analysis [15].

Preliminary results with thermospray-LC-MS showed that extracts of BaP treated with ozone are dominated by the BaP quinones (m/z = 282). Other intense peaks show molecular ions with m/z = 284 and m/z = 316. An intercomparison study between the TSP and the APCI interface under the same conditions [16] showed that in TSP the base peaks of substituted BaP derivatives are the molecular ions, except polyhydroxy derivatives, which are dominated by $[M\text{-}nH_2O]^-$ peaks. Limitations of the TSP interface in comparison to APCI are the lower sensitivity and less fragmentation processes. In APCI, usually more fragmentation occurs due to cone induced dissociation. No structural information could be obtained with TSP.

EXPERIMENTAL

Materials

HPLC-grade water, methanol, acetonitrile were obtained from Merck (Darmstadt, Germany). Benzo[*a*]pyrene was obtained from Sigma (St. Louis, MO). Benzo[*a*]pyrene metabolites (BaP-1,6-dione, BaP-3,6-dione, BaP-6,12-dione) were purchased from Midwest Research Institute (Kansas City, MO). (N, N', N)-l-methyl-3-nitro-1-guanidine was obtained from Aldrich Chemical Co. (Milwaukee, WI).

Apparatus

LC was performed with a Hewlett Packard 1090 Liquid Chromatograph (Palo Alto, CA) with a diode array detector. For the LC separation, a Vydag 201TP54 4.6 × 250 mm (Hesperia, CA) RP 18 column was used. Acetonitrile – water (40:60) was held for the initial 15 min, with a subsequent linear gradient to 90 % acetonitrile over 15 min. Each analyte was dissolved in acetronitrile at a concentration of 0.1 mg/ml. Usually, a flow-rate of 1ml/min was used.

Atmospheric Pressure Chemical Ionization (APCI). A VG Platform from Fisons Instruments (Manchester, UK) equipped with a standard atmospheric pressure ionization (API) source was used. The APCI interface consists of a heated nebulizer probe and the standard atmospheric pressure source equipped with a corona discharge pin. The source and probe temperature were set to 180°C and 500°C, respectively. The full scan range was from m/z = 250 to 350. The corona discharge voltage was 2.5 kV, the cone voltage was 20 V and the HV lens voltage was set to 0.2 kV.

Capillary Gas Chromatography High Resolution Mass Spectrometry. A Hewlett Packard HP 5890 Series II gas chromatograph (Hewlett Packard, Palo Alto, CA) was connected to a VG AutoSpec mass spectrometer with a resolution of 10.000 using a 60 m × 0.25 μm i.d. (0.1 mm film thickness) DB–5 column (J&W Scientific, Folsom, CA). The MS was operated at the electron impact mode with an electron energy of 40 eV with a trap current of 800 μA. A mass scanning range of m/z = 100 – 350 was set at 1.1 scan/s. Carrier gas used was ultrahigh purity helium (grade 5.6). The initial oven temperature was 90°C, immediately ramped to 220°C at 15°C/min and to 310°C at 2°C/min and held for 20 min. The temperature of the splitless injector and the GC/MS interface was 270°C.

Sample preparation

Aerosol generation and measurement

Carbon-particles were produced with a commercial generator based on a spark discharge between two carbon electrodes [17] (GfG 1000, Palas GmbH, Karlsruhe, Germany). Weingartner et al. [18] observed for this particular aerosol a fractal dimension of approximately $D_f = 2$, which is quite similar to urban aerosols [19]. Particle distributions were characterized with a commercial differential mobility particle sizer (DMPS), which combines an electrostatic classifier (EC) (TSI Model 3071, TSI Inc., St. Paul, Minnesota, USA) and an ultrafine condensation particle counter (UCPC) (TSI Model 3025). A second condensation nucleus counter (CNC) (TSI Model 3020) was employed to count the monodisperse concentrations.

Ozone generation and detection

Ozone is generated by photodissociation of O_2 using UV-radiation from a Hg-line source [20]. The generator consists of a 10 cm long polished aluminum cylinder with an elliptical cross-section. For optimum illumination a Hg-lamp with an emission maximum at 185 nm (Model L 937-02, Hamamatsu, Herrsching, Germany) was placed in one focal line, while an UV-transparent flow-tube (Type Suprasil, Schott, Mainz, Germany) resided in the second focal line. During operation either pure O_2 or pressurized air was flushed through the flow tube. The O_3 concentration was measured with a commercial O_3-analyzer based on an UV-absorption based system (Ansyco, Karlsruhe, Germany). Both ozone-analyzers were calibrated according to German VDI Standard Guideline No. 2468 (1978) based on the oxidation of KI to I_2.

Sample preparation and clean-up

Glass fibre filters (GF/C Whatman, Maidstone, UK) were spiked with 2 mg BaP, dissolved in acetonitrile, under a nitrogen stream in dimmed illumination in order to avoid any reaction under ambient conditions. Soot-loaded filters were prepared by mixing the carbon aerosol with BaP vapor in a ring-gap nozzle [21] and a subsequent aerosol sampling. BaP is vaporized by heating the solid inside a glass bulb placed in a temperature controlled oil bath, under a stream of nitrogen (2 l/min). The BaP concentration can be controlled by the temperature of the oil bath. The BaP molecules adsorb onto the aerosol particle surfaces in the subsequent condensation section which is controlled to 5°-10°C. The BaP-coated carbon aerosol is then collected on a glass fiber filter. Real samples of particulate matter were collected in the outskirts of Munich (Grosshadern) for 24 hours with a low volume sampler GS 050 (Derenda, Berlin, Germany) at a flow rate of 2.3 $m^3\ h^{-1}$.

The dry spiked filters were exposed to a stream of 1 ppm ozone for between half an hour to 4 hours (60 μg to 480 μg ozone). The filters were extracted in 4 ml of a mixture of toluene/dichloromethane/methanol (1:1:1) in an ultrasonic bath for 15 minutes. The extracts of the spiked glass fibre filter experiments needed a clean-up step in order to remove the excess of unreacted BaP: the extracts were evaporated to 100 μl, applied to little silica column (0.5 g) and successively eluted with 5 ml of toluene, dichloromethane and methanol, respectively. BaP elutes in the toluene fraction, whereas the degradation products elute in the methanolic fraction. For GC/HRMS analysis, some of these methanolic fractions were evaporated to dryness and treated for 30 minutes with 0.5 ml diazomethane in dimethylether.

RESULTS AND DISCUSSION

Capillary Gas Chromatography High Resolution Mass Spectrometry (CGC-HRMS).

The chromatogram of the reaction products is dominated by the BaP-6,12-dione, BaP-1,6-dione and BaP-3,6-dione (all m/z = 282), which can be distinguished by their different retention times and mass spectra (see **Table I**). These quinones show the typical sequential loss of two times CO (m/z = 254 and m/z = 226), see **Figure 1**. When the extracts are treated with diazomethane to the acidic compounds, an interesting artifact occurs: the quinones react with diazomethane to give methylated (m/z = 296) and dimethylated (m/z = 310) quinones, which show again loss of two CO molecules. After treatment of the pure quinones with diazomethane, one methylated and one dimethylated quinone of the BaP-1,6-dione and the BaP-3,6-dione, respectively, are formed. The BaP-6,12-dione forms two methylated and two dimethylated quinones, which can be determined in the spiked filter extracts. Additionally, the formation of methyl-BaP (m/z = 266) by methylation of unreacted BaP was confirmed. Usually, the formation of methylated aromatic compounds is the side reaction of diazomethane with aromatic rings, but with increasing amount of rings it becomes the main pathway instead ring extension. This artifact has to be kept in mind when analyzing derivatized samples.

Table I lists the peaks before and after derivatization analyzed by GC/HRMS. The information additionally gained by high resolution is the sum formula obtained by accurate mass measurement. Without derivatization, mostly carbonyl derivatives can be analyzed, e. g. the mentioned BaP quinones and benzanthracene-7-one (m/z = 230). Two isomers with m/z = 246 show losses of [M-28-29]+, matching very well with the data of a annellated coumarine reported by König et al. [22]. The pathways to these coumarines and to the

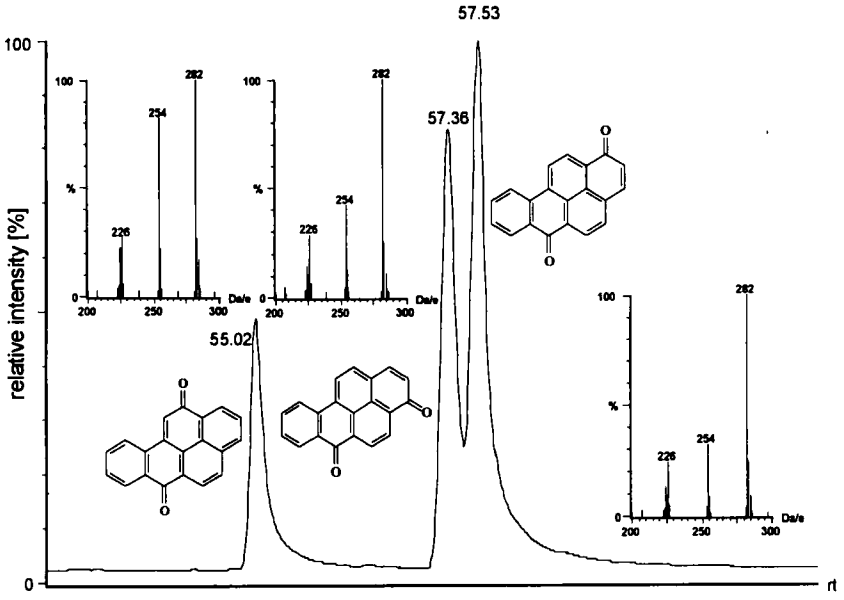

FIGURE 1 Separation of three BaP quinones after ozonolysis by GC/HRMS. The isomers can be distinguished by their different mass spectra and retention times

benzanthracene–7-one is not clear, because in both cases one ring of the five-ring system of BaP seems to be eliminated. Several isomers of a compound with m/z = 270 show the same fragmentation pattern, leading to the assumption that these structures are lactones, too. Another possible structure is a quinone structure, but the loss of CO and CHO is more typical for aromatic lactones than for quinones which usually show a two-fold loss of CO. The presence of the lactone, however, is of toxicological interest. Is has been reported that this compound is a highly active promutagen [23]. Similar lactones by ozonolysis have been reported in the case of pyrene [24] and phenanthrene [25].

The peaks at m/z = 284 and loss of $[M-28]^+$ and $[M-29]^+$ followed by another loss of $[M-29-29]^+$ indicate the presence of corresponding hydroquinones of the three BaP quinones (m/z = 282). The latter can show hydration in the MS under the used conditions, resulting in an additional high abundant m/z = 284 peak. After derivatization, the presence of benzanthracene-7-one-3,4-dicarboxylic methylester (m/z = 346) and another dicarboxylic methylester (m/z = 360) can be determined. Two peaks with m/z = 282 show loss of a methyl group, followed by loss of CO, indicating aromatic methoxy compounds. These could have been formed by methylation of different isomers of hydroxy-BaP.

TABLE I Degradation products of benzo[a]pyrene after ozonolysis analyzed by GC/HRMS

retention time	*main peaks*	*formula*	*tentative identification*
42.22	230 (100), 202 (30), 200 (25)	$C_{17}H_{10}O$	7H-benz[de]anthracen-7-one
45.08	246 (100), 218 (40), 189 (50)	$C_{17}H_{10}O_2$	annellated coumarine
47.30	270 (100), 242 (20), 213 (55)	$C_{19}H_{10}O_2$	lactone/quinone
47.33	246 (100), 218 (70), 189 (80)	$C_{17}H_{10}O_2$	annellated coumarine
48.38	336 (100), 335 (95), 307 (15), 279 (15), 251 (25), 238 (20), 226 (20)		
48.47	246 (100), 218 (80), 189 (70)	$C_{17}H_{10}O_2$	annellated coumarine
48.57	270 (100), 242 (20), 213 (50)	$C_{19}H_{10}O_2$	lactone/quinone
49.26	270 (100), 242 (20), 213 (50)	$C_{19}H_{10}O_2$	lactone/quinone
50.54	270 (100), 242 (80), 213 (80)	$C_{19}H_{10}O_2$	lactone/quinone
51.26	336 (85), 335 (100), 307 (10), 279 (10), 251 (20), 238 (10), 226 (15)		
52.40	270 (100), 242 (80), 213 (60)	$C_{19}H_{10}O_2$	lactone/quinone
53.00	270 (100), 242 (85), 213 (45)	$C_{19}H_{10}O_2$	lactone/quinone
53.06	300 (40), 285 (100), 257 (50), 229 (20), 200 (40)	$C_{20}H_{12}O_3$	
54.09	290 (100), 261 (50), 242 (100), 234 (15), 224 (25), 213 (60)		
55.02	282 (100), 254 (85), 226 (30)	$C_{20}H_{10}O_2$	BaP-6, 12-dione
55.48	284 (70), 256 (100), 255 (90), 239 (60), 226 (80)	$C_{20}H_{12}O_2$	BaP-hydroquinone
56.16	284 (60), 256 (80), 255 (100), 239 (50), 226 (60)	$C_{20}H_{12}O_2$	BaP-hydroquinone
56.39	314 (25), 286 (100), 255 (50), 239 (70), 226 (60)		
57.02	314 (30), 286 (100), 255 (50), 239 (70), 226 (40)		
57.36	282 (100), 254 (40), 226 (30)	$C_{20}H_{10}O_2$	BaP-3,6-dione
57.53	282 (100), 254 (35), 226 (25)	$C_{20}H_{10}O_2$	BaP-1,6-dione
	additional peaks after derivatization with diazomethane		
48.07	304 (15), 273 (100), 245 (20), 217 (20), 189 (20)	$C_{19}H_{12}O_4$	ester
53.29	282 (70), 267 (35), 239 (100)	$C_{21}H_{14}O$	methoxy-BaP
54.01	282 (95), 267 (100), 239 (45)	$C_{21}H_{14}O$	methoxy-BaP
54.18	294 (65), 279 (100), 263 (10), 251 (90), 250 (95), 224 (15)	$C_{22}H_{14}O$	
57.31	328 (20), 300 (75), 283 (15), 271 (15), 255 (85), 239 (50),, 226 (100),	$C_{22}H_{16}O_3$	
58.03	328 (25), 300 (75), 283 (15), 271 (15), 255 (85), 239 (50), 226 (100),	$C_{22}H_{16}O_3$	
58.23	346 (40), 315 (100), 287 (25), 272 (40), 256 (30), 228 (15), 216 (25), 200 (20), 188 (25)	$C_{21}H_{14}O_5$	benzanthrone-3,4-dicarboxylic methylester
60.16	360 (80), 329 (100), 301 (301), 270 (25), 257 (15), 242 (15), 229 (10), 213 (20)	$C_{22}H_{16}O_5$	dicarboxylic methylester

However, there are still several peaks which cannot be identified yet although well resolved mass spectra of these unknown compounds are obtained. Despite the high separation performance and obtainable structural information by electron impact spectra, the major drawback of GC-MS is the low sensitivity for these analytes. For example, the absolute detection limits for the three BaP quinones are at the low nanogram range with GC/HRMS, whereas the detection limits in APCI-LC-MS are at the low picogram range [16] .

APCI-LC-MS. Previous studies with BaP metabolites [16] showed that the APCI interface is by far more sensitive than thermospray-LC-MS, usually by two to three orders of magnitude. In order to detect also minor abundant degradation products, the experiments were started with high amounts of BaP (2 mg) but decreased later to levels more in line with those in ambient. This was carried out by BaP-coated soot aerosols, which were collected on glass fiber filters and exposed to ozone. Furthermore some real samples of air particulate matter were analyzed to prove the applicability of the used technique for environmental samples.

Glass fiber filters. Chromatograms of extracts obtained by the reaction on glass fiber filters show a series of abundant peaks, see **Figure 2.** Some additional hidden peaks can be detected after evaluation of single ion chromatograms. As

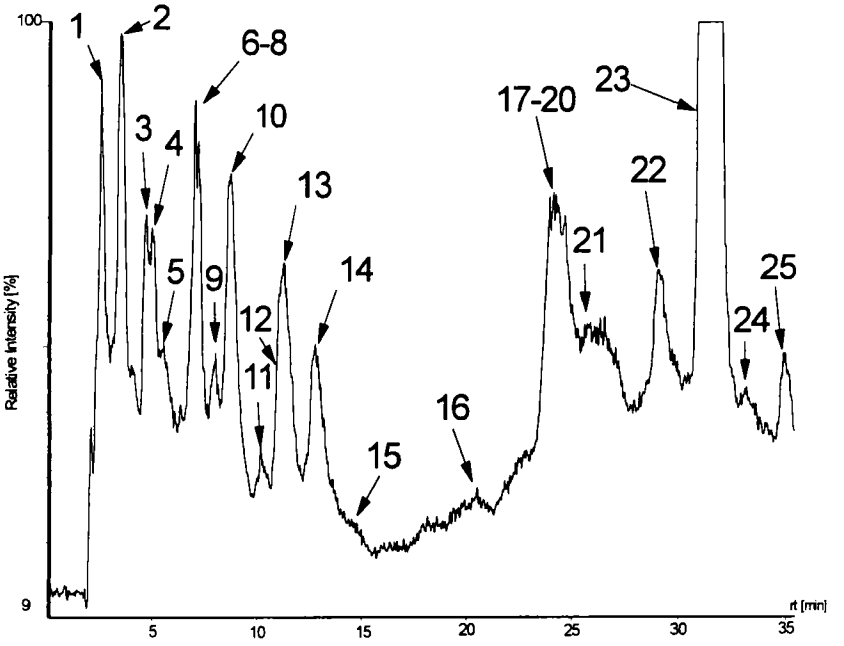

FIGURE 2 APCI-LC/MS total ion chromatogram of an extract of ozonized BaP. The peaks are listed in Table II

reported recently [16] , metabolites of BaP analyzed under these conditions show usually only the molecular ion $[M]^-$ or in the case of some hydroxy derivatives the quasimolecular ion $[M-H]^-$. The samples analyzed show in general only scarce fragmentation, which is due to the soft ionization technique and the high stability of the aromatic molecules. **Table II** lists all peaks of a typical sample of an extract of reaction products obtained by reaction of ozone with BaP on a glass fiber filter. We suggest that the early eluting peaks 1, 2, 4 and 5 are carboxylic acids, peak 2 being benzanthracene-7-one-3,4-dicarboxylic acid, which was reported to be formed by ozonolysis of BaP [8]. Peak 4 is most likely a homologous dicarboxylic acid [7]. The acids are formed by a ring opening process in which the ozone molecule attacks a double bond forming ozonides. These decompose to aldehydes which are further oxidized to carboxylic acids. Peak 6 to 8 consist of three different isomers, presumably being the corresponding hydroquinones of the later eluting main products, the three BaP quinones. They are not separated under these conditions and coeluted in peak 23, but they can be separated under different elution conditions [12, 16]. In this case this was not a drawback, because the aim was to get more information about the less abundant highly polar compounds. For the other peaks, no chemical structures can be suggested yet. Peak 23 consists of BaP-1,6-dione, BaP-3,6-dione and BaP-6,12-dione, which are the only, commercially available reference substances which are formed in the oxidative degradation process of BaP. This means that for the further investigations of these degradation processes reference standards will have to be prepared and more characterization is only possible in a larger preparative scale.

Pitts et al. reported a reaction yield of 0.07% to 0.5% for the carcinogenic BaP-4,5-epoxide by ozonolysis of BaP under similar conditions [10], which means that approximately 1 μg to 10 μg in the sample or 0.2 μg to 2 μg in one injection volume should be present. The BaP-4,5-epoxide could not be confirmed despite the low absolute detection limit of 50 pg.

The major advantage of the technique applied is the excellent sensitivity for these analytes. Despite the fact that there is still a lack of knowledge about chemical structures of unknown compounds, it can be stated that in principle they can be analyzed by APCI-LC-MS. In order to prove this statement, experiments with lower concentrations were carried out with soot samples.

Soot and real samples. A polydisperse or monodisperse carbon aerosol generated by a soot generator was coated with BaP, collected on a glass fiber filter and ozonized like the samples before. In this case, the BaP concentrations were much lower, so the clean-up step was not necessary. **Figure 3** shows chromatograms in which the different extracts with and without the soot matrix are compared. The BaP concentrations were approximately 200 μg for the glass fiber filter, 20 μg for the polydisperse and 1 μg for the monodisperse soot filter before the ozona-

TABLE II Degradation products of benzo[a]pyrene after ozonolysis analyzed by LC-UV-APCL/MS

peak No.	*ret. time*	*MS peaks*	*UV peaks*	*tentative identification*
1	2.6	300 (20), 299 (50), 298 (60), 282 (100), 254 (15)	222 nm (100), 272 nm (75)	carboxylic acid
2	3.5	318 (20), 300 (70), 299 (30), 298 (70), 282 (100)		benzanthrone–3,4-dicarboxylic acid
3	4.7	304 (20), 286 (100)		
4	4.9	332 (100)		
5	5.1	318 (20), 300 (80), 299 (40), 298 (70), 282 (100)	230 nm (100), 265 nm (100)	isomere of peak 2
6	7.0	284 (100)	$\lambda_{max1} < 220$ nm, $\lambda_{max2} = 252$ nm	BaP-hydroquinone
7	7.1	284 (100)	coeluting with peak 6	BaP-hydroquinone
8	7.2	284 (100)	coeluting with peak 6	BaP-hydroquinone
9	8.1	338 (15), 316 (100), 282 (40)		
10	8.7	286 (30), 285 (100) 258 (20)		
11	10.2	300 (30), 282 (100)		
12	11.0	336 (40), 335 (30), 334 (100)		
13	11.2	316 (20), 300 (100), 274 (15), 258 (10)		
14	12.8	316 (30), 300 (100), 274 (15), 258 (15)	$\lambda_{max} = 274$ nm	
15	14.6		$\lambda_{max} = 273$ nm	
16	20.7		253 nm (100), 271 nm (65) sh	
17	23.8	316 (100)		
18	24.0	298 (100)		
19	24.4	316 (100)		
20	24.6	298 (100)		
21	25.0	348 (50), 346 (100), 330 (40)		
22	29.1	286 (40), 285 (100)		
23	31.4	282 (100)	$\lambda_{max} < 220$ nm, 255 nm (100), 263 nm (90), 284 nm (80), 297 nm (95), 346 nm (30), 363 nm (50), 383 nm (50)	BaP–1,6-dione, BaP–3,6-dione. BaP–6,12-dione
24	35.0	318 (30), 317 (30), 316 (100), 282 (50), 267 (20)		
25	36.6	318 (30), 317 (30), 316 (100), 282 (50)		

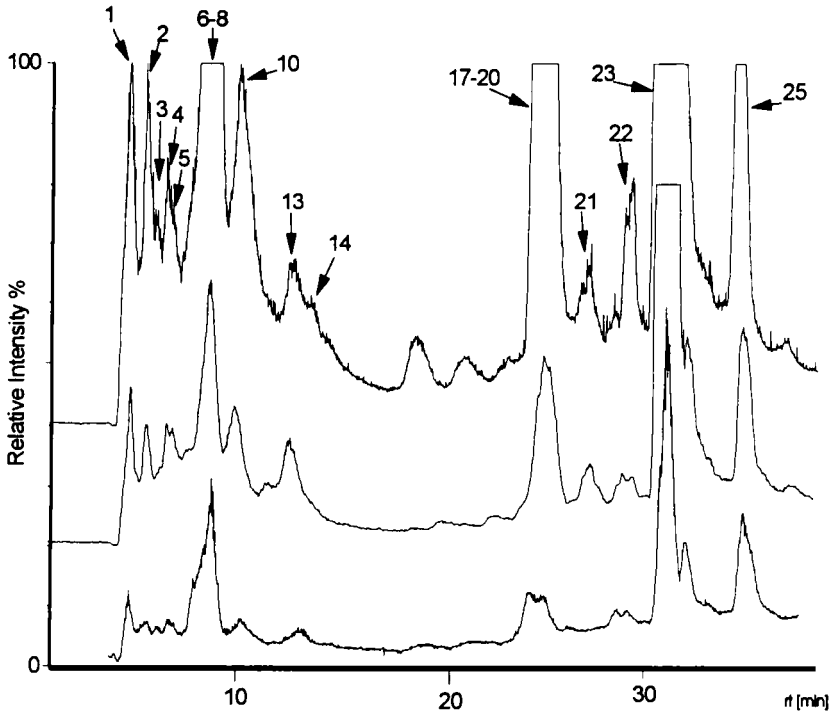

FIGURE 3 Comparison of different matrices coated with BaP. The upper chromatogram represents 2 mg BaP on a glass fiber filter, the chromatogram in the middle is obtained by reaction of 200 µg BaP on polydisperse soot and the lower chromatogram represents the reaction of 1 µg BaP on monodisperse soot with d_p = 100 nm. The peaks are listed in Table II

tion. The results show that the soot matrix has no inhibiting effect on the formation of the degradation products, moreover, the chromatogram of the monodisperse soot filter demonstrates the suitability of the technique with regard to the low concentrations applied. The same reaction takes place on the soot filters as on the glass fiber filters.

In order to prove the applicability of the technique, APCI-LC-MS was used for the analysis of air particulate matter for environmental samples. The filter were collected at a low polluted site in the outskirts of Munich. In these samples, two peaks with m/z = 284 and m/z = 282 were determined, being identical with Peak 6 to 8 and Peak 23 of the glass fiber filters (see **Figure 4**). By using a different gradient with a higher content of organic solvent, the quinones can be separated sufficiently. The fact that these degradation products of BaP were found in a minor contaminated area show that APCI-LC-MS is a powerful tool for the trace analysis of PAH metabolites in environmental samples.

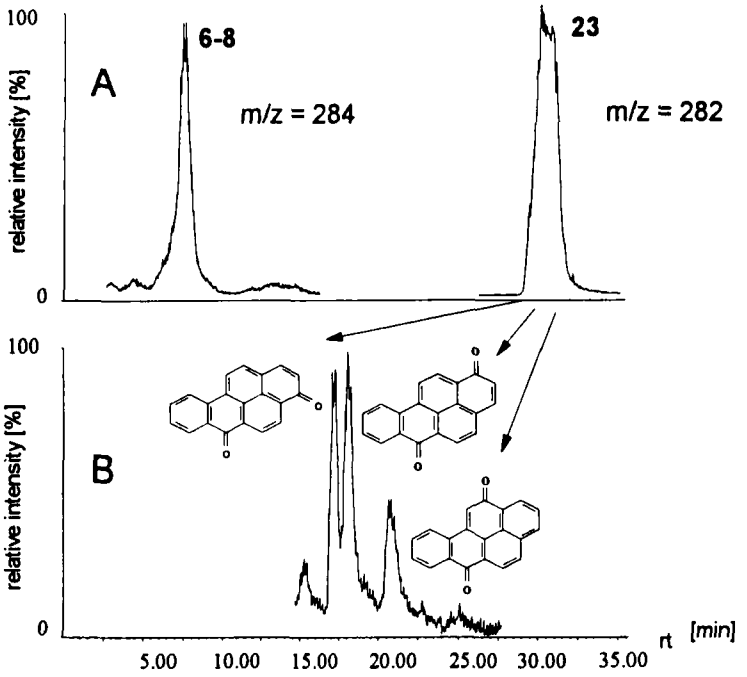

FIGURE 4 Confirmation of BaP derivatives on air particulate matter. A and B represent real samples collected in the outskirts of Munich. A is the APCI chromatogram under the discussed LC conditions in time scheduled single ion monitoring. The first peak is the identical with peaks 6 to 8 in table II, the second peak is identical with peak 23, the three BaP quinones. B represents another sample under different LC conditions (methanol - water (80:20) for 8 min., linear gradient to 90:10 methanol - water over 12 min) under which the quinones are separated

Acknowledgements

R. Alonso, R. Chaler and S. Vollmuth are thanked for technical assistance. A. Scherzinger is thanked for the possibility to evaluate the UV spectra at Hexal Pharma. R. K. is a recipient of a grant of the ENVIROTRACE program of the Commission of the European Communities (Contract No. ERXCHRXCT 920039). The financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] A. Bjørseth, T. Ramdahl, *Handbook of Polycyclic Aromatic Hydrocarbons*, Vol. 2, (Dekker, New York, 1985).

[2] D. M. Jerina and J. W. Daly, *Science*, **185**, 573–582 (1974).

[3] I. B. Weinstein, A. M. Jefferey, K. W. Jenette, J. H. Blotstein, R. G. Harvey, C. Harris, H. Antrup, H. Kasai and K. Nakanishi, *Science*, **183**, 592–595 (1976).

[4] Y. Ishimura, T. Iizuka, I. Morishima and O. Hayaishi, in: H. V. Gelboin and P. O. P. Ts'o, (Editors) *Polycyclic Hydrocarbons and Cancer,* (Academic Press, New York, 1978), Vol. 1.
[5] L. F. Chasseaud, *Adv. Cancer Res.*, **29,** 175–274 (1979).
[6] J. N. Pitts, *Environ. Health Persp.*, **47,** 115–140 (1983).
[7] K. A. van Cauwenberghe, in A. Bjørseth and T. Ramdahl, (Editors.), *Handbook of Polycyclic Aromatic Hydrocarbons* (Dekker, New York, 1985), Vol. 2.
[8] E. J. Moriconi, B. Racoczy and W. F. O'Connor, *J. Am. Chem. Soc.*, **83,** 4618– 4623 (1961).
[9] K. A. van Cauwenberghe, L. van Vaeck and J. N. Pitts, *Adv. Mass Spectrom.*, **8B,** 1499–1507 (1979).
[10] J. N. Pitts, D. M. Lokensgard, P. S. Ripley, K. A. van Cauwenberghe, L. van Vaeck, S. D. Shaffer, A. J. Thill and W. L. Belser, *Science,* **210,** 1347–1349 (1980).
[11] J. N. Pitts, H.-R. Paur, B. Zielinska, J. Arey, A. M. Winer, T. Ramdahl and V. Mejia, *Chemosphere,* **15,** 675–685 (1986).
[12] F. Valerio, M. Pala and C. Borgogni, *Intern. J. Environ. Anal. Chem.*, **38,** 343–349 (1990).
[13] J. F. Anacleto, L. Ramaley, F. M. Benoit, R. K. Boyd and M. A. Quilliam, *Anal. Chem.*, **67,** 4145–4154 (1995).
[14] E. Gelpi, *J. Chromatogr.*, **703**, 59–80 (1995).
[15] J. Slobodnik, B. L. M. van Baar and U. A. Th. Brinkman, *J. Chromatogr.*, **703,** 81–121(1995).-
[16] R. Koeber, J. M. Bayona and R. Niessner, Comparison of Liquid Chromatography Mass Spectrometry Interfaces for the Analysis of Polar Metabolites of Benzo[a]pyrene, *Fres. J. Anal. Chem.*, **359,** 267-273 (1997).
[17] C. Helsper, W. Mölter, F. Löffler, C. Wadenpohl, S. Kaufmann and G. Wenninger, *Atmos. Env.*, **27A,** 1271–1275 (1993).
[18] E. Weingartner, U. Baltensperger and H. Burtscher, *J. Aerosol Sci.*, **26,** 667–668 (1995).
[19] K. A. Katrinak, P. Rez, P. R. Perkes and P. R. Buseck, *Environ. Sci. Technol.*, **27,** 539–547 (1993).
[20] B. Eliasson and U. Kogelschatz, *Ozone Sci. Eng.*, **13,** 365–362 (1991).
[21] R. Niessner, *Sci. Total Environ.*, **36,** 353–362 (1984).
[22] J. König, E. Balfanz, W. Funcke and T. Romanowski, *Anal. Chem.*, **55** 599–603 (1983).
[23] S.Amin, S. S. Hecht, E. La Voi and D. Hoffmann, *J. Med Chem.*, **22,** 1336–1340 (1979).
[24] J. N. Pitts, D. M. Lokensgard, W. Harger, T. S. Fischer, V. Mejia, J. Schuler, G. M. Scorziell and Y. A. Katzenstein, *Mutat. Res.*, **103,** 241–249 (1982).
[25] J. R. Patel, I. R. Politzer, G. W. Griffin and J. L. Laseter, *Biomed Mass Spec.*, **5,** 664–670 (1978).