

CHROM. 16,569

ROUTINE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN CARBON BLACK BY CHROMATOGRAPHIC TECHNIQUES

L. ZOCOLILLO*, A. LIBERTI, F. COCCIOLI and M. RONCHETTI

Dipartimento di Chimica, Università "La Sapienza", Rome (Italy)

(Received January 9th, 1984)

SUMMARY

A method is proposed for the determination of polycyclic aromatic hydrocarbons (PAHs) in carbon blacks. The PAHs are extracted from the carbon black with benzene in a Soxhlet apparatus, purified by silica gel thin-layer chromatography, weighed and analysed by gas and/or high-performance liquid chromatography.

The total PAH and benzo[*a*]pyrene (BaP) concentrations in different types of carbon blacks and in different batches of the same carbon black were determined. It is shown that the distribution of the PAH fraction in different types of carbon blacks is almost the same but there are considerable differences in the total amount of the PAH fraction and the BaP concentration.

INTRODUCTION

The term carbon black refers to a wide range of products obtained by partial combustion or thermal decomposition of hydrocarbons under controlled conditions. The raw materials used in the production of carbon black are mainly liquid hydrocarbons obtained as by-products in petroleum refineries, ethylene plants and coal coking plants. At present most carbon black is produced by the "furnace" process and only small amounts by the "thermal" and "channel" processes¹. In 1980, world production of carbon black was estimated at about 5 million tons. About 93% of the carbon black produced is employed in the rubber industry as a reinforcing agent. It is also used in the ink industry, as an additive to polyolefins and as a pigment.

The interest in carbon black by environmentalists is due to its fine particulate and easily respirable nature and to its tendency to adsorb potentially dangerous levels of organic substances such as polycyclic aromatic hydrocarbons (PAHs) and other polynuclear compounds containing sulphur and oxygen.

The possibility of elution of some PAHs, which are carcinogenic, from carbon blacks is often taken as a criterion for the evaluation of their carcinogenicity²⁻⁵. The conclusions drawn are conflicting. Some workers, considering the drastic conditions necessary for the extraction of PAHs, believe that they are so strongly adsorbed that they are not biologically active. Others, considering the low eluting power of some biological fluids for some carcinogenic PAHs and the long time of contact of the

particles with cellular membranes, have concluded that there is a possibility of transfer of PAHs from carbon black to the membranes and hence the possibility of the development of cancer increases as the amount of carcinogenic substances present increases⁶.

Several methods have been reported for the analysis of carbon black extracts. Employing different types of extraction, such as Soxhlet extraction^{7,8}, vacuum sublimation⁹ or extraction with sonification¹⁰, and different chromatographic techniques, such as gas chromatography (GC) with packed and capillary columns^{11,12} and high-performance liquid chromatography (HPLC) with spectrophotometric and spectrofluorimetric detection¹³, numerous PAHs and sulphur and oxygen-containing compounds have been determined. However, in the work cited, particular aspects of the analytical problem of adsorbed organic compounds were considered and there has not been a systematic study of the evaluation of those parameters which are directly correlated with hazard problems such as the determination of total PAH or benzo[*a*]pyrene (BaP) concentrations, the latter compound being the most important hydrocarbon with respect to carcinogenic activity. An exact evaluation of these parameters is desirable because it should be useful for the routine evaluation of hazards connected with carbon black.

At present the methods available are not suitable for this purpose. The most frequently used method is ASTM Standard Test Method D 1618, in which the transmittance at 425 nm of toluene after contact with carbon black for 1 min at room temperature is measured. In a method proposed by the National Institute for Occupational Safety and Health (NIOSH)⁶, extractable PAHs are determined gravimetrically in the residue after solvent evaporation following room-temperature sonification of a slurry of carbon black in cyclohexane. The extraction efficiency of cyclohexane with respect to BaP is very low. Cyclohexane preferentially desorbs non-aromatic components and only partially desorbs PAHs with less than four rings.

In this paper we propose a method employing selective chromatographic techniques that provides information on PAHs adsorbed on carbon black, in particular the total PAH and BaP concentration, with consideration of results of our previous studies¹⁴⁻¹⁹.

EXPERIMENTAL

Materials

Carbon black. Samples were of the furnace combustion and thermal types. ASTM identification, type and surface area are reported in Table I.

Solvents. Benzene (free from PAHs) was distilled before use. *n*-Hexane, dichloromethane (analytical-reagent grade), tetrahydrofuran and acetonitrile (for HPLC) were used as received.

Silica gel thin-layer chromatographic (TLC) plates. Plates of dimensions 20 × 20 cm were obtained from Merck (Darmstadt, F.R.G.).

Chromatography

GC was carried out with a Dani (Monza, Italy) Model 6800 instrument equipped with a flame-ionization detector and an on-column injector. Separations were carried out on glass columns (70 cm × 0.3 cm I.D.) packed with N,N'-bis-(*p*-

TABLE I
CARBON BLACKS STUDIED

<i>Carbon black (ASTM identification)</i>	<i>Type</i>	<i>Surface area (m²/g)</i>
N 220	ISAF	115
N 326	HAF/LS	80
N 347	HAF/HS	90
N 550	FEF	42
N 660	GPF	36
N 990	MT	10

butoxybenzylidene)- α,α' -bi-*p*-toluidine (BBBT) (Eastman Kodak, Rochester, NY, U.S.A.) on 140–170-mesh glass microbeads (Analabs, North Haven, CT, U.S.A.) pre-treated with sodium dodecylbenzenesulphonate (NaDBS)¹⁴. Nitrogen was used as the carrier gas.

HPLC analysis was performed using a Perkin-Elmer Series 2 instrument with a gradient Series LC-55 UV spectrophotometric and Series LS-5 spectrofluorimetric detectors. A reversed-phase system was used, consisting of a column (16 cm \times 0.4 cm I.D.) packed with a stationary phase consisting of 5 μ m octadecylsilane (ODS)-silica particles (Phase Separations, Queensferry, Clwyd, U.K.). The eluting solvent programme consisted of operating isocratically with acetonitrile–water (60:40) for the first 63 min and then programming to 80% acetonitrile at 0.7%/min.

Method

The extraction method is shown schematically in Fig. 1. A 50-g amount of carbon black was weighed into a thimble and extracted in a Soxhlet apparatus (about 300 extractive cycles) with benzene free from PAHs; 400 ml of the solvent were used and evaporation losses were replaced periodically. The benzene containing the organic fraction was concentrated to about 10 ml in a rotary evaporator, then evaporated to dryness, in the dark, under nitrogen in a weighed container. The residue was placed in a desiccator and dried to constant weight.

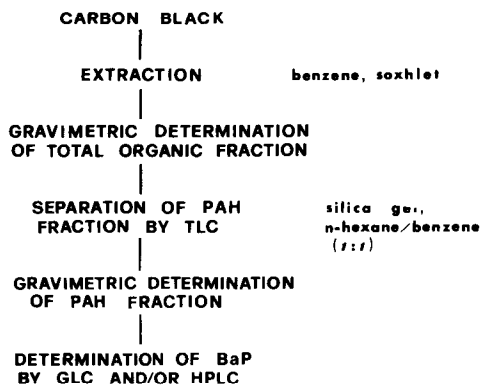


Fig. 1. Outline of the method.

TABLE II

DISTRIBUTION COEFFICIENTS OF A THREE-RING AND A FIVE-RING PAH IN CARBON BLACK-SOLVENT SYSTEMS

500 μg of PAH were equilibrated with 1 g of carbon black N 326 in 5 ml of solvent. Distribution coefficient = $(\mu\text{g PAH/g solvent})/(\mu\text{g PAH/g carbon black}) = \text{ppm}_{(l)}/\text{ppm}_{(s)}$.

Solvent	Phenanthrene	Benzo[<i>a</i>]pyrene
Toluene	1.75	$1.83 \cdot 10^{-2}$
Benzene	$9.4 \cdot 10^{-1}$	$7.3 \cdot 10^{-3}$
Methylene chloride	$5.1 \cdot 10^{-2}$	$7.5 \cdot 10^{-4}$
Cyclohexane	$1.7 \cdot 10^{-2}$	$9.3 \cdot 10^{-6}$

Determination of total PAH and BaP concentration. The organic fraction was dissolved in the minimum possible volume of benzene and applied to a silica gel plate. The plate was developed in *n*-hexane-benzene (1:1) in the dark. After removal of the mobile phase the plate was irradiated for a few seconds with UV light (254 nm). The PAH spot was marked, scraped off, powdered, eluted with about 5 ml of benzene and filtered through a glass frit. The filtrate was evaporated to dryness in the dark under nitrogen in a weighed container and the residue was dried in a desiccator to constant weight. The dried residue was dissolved in tetrahydrofuran and the BaP was determined by GC and HPLC.

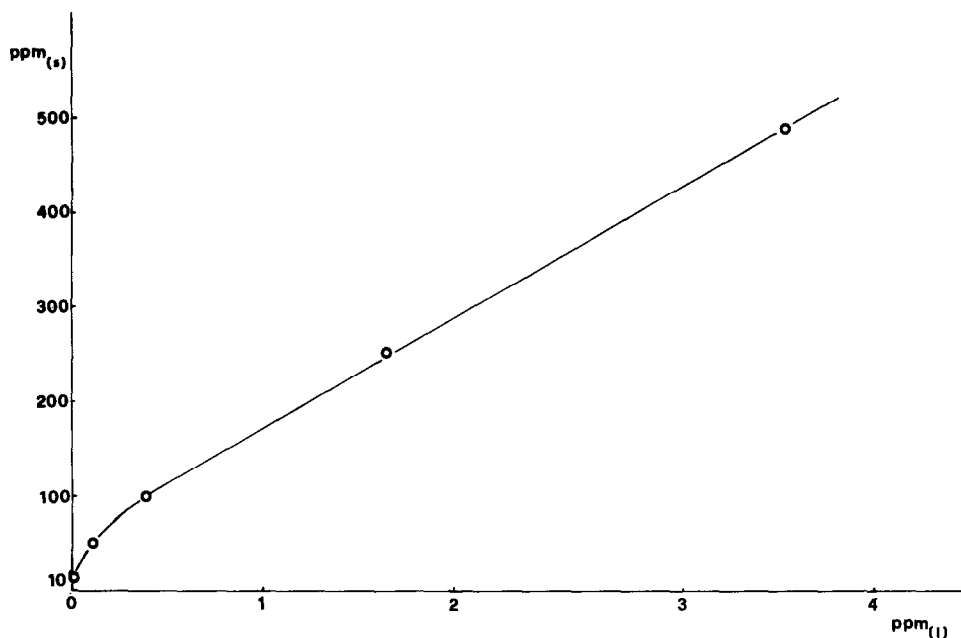


Fig. 2. Plot of BaP concentration in carbon black (N 326) [ppm_(s)] versus BaP concentration in benzene [ppm_(l)].

RESULTS AND DISCUSSION

Extraction

Benzene was selected for its extraction efficiency and for the negligible losses of the volatile organic fraction during evaporation.

The distribution coefficients of phenanthrene and BaP between a carbon black (N 326), free from PAHs, and the solvents more frequently employed in this type of extraction were determined. Table II shows that the distribution coefficient relative to BaP in benzene is 0.4 times that in toluene, whereas it is about 10 times that in methylene chloride and 800 times that in cyclohexane. The percentage of BaP adsorbed increases on decreasing the initial amounts, as shown in Fig. 2, in which is plotted the concentration of BaP in carbon black [ppm_(s)] versus the concentration of BaP in benzene [ppm_(l)]. For concentrations in carbon black above 100 ppm the distribution coefficient is virtually constant.

The number of Soxhlet cycles required to extract the sample depend on these values. For the carbon blacks examined, which differ sufficiently in surface area and amount of PAH adsorbed, for nearly complete extraction about 300 extraction cycles are necessary in a Soxhlet apparatus in which the volume ratio of solvent to solid is about 3. The values reported in Table II and Fig. 2 were obtained by concentration

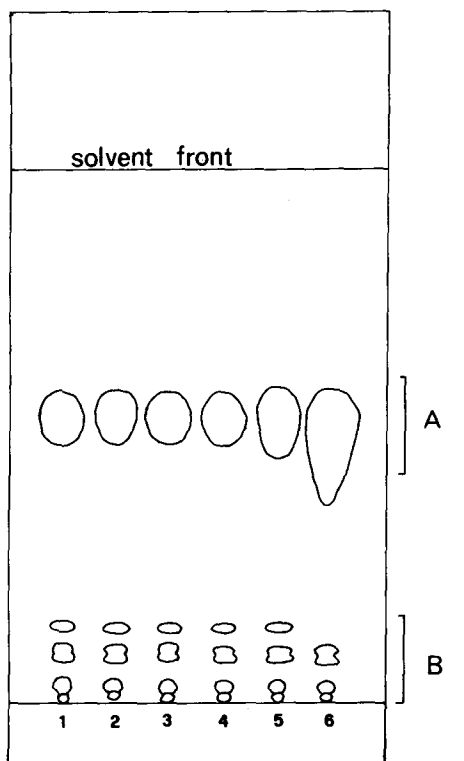


Fig. 3. Thin-layer chromatogram of the benzene extracts of carbon blacks on silica gel. Mobile phase: *n*-hexane-benzene (1:1).

measurements by HPLC with spectrofluorimetric detection in the solvent equilibrated with carbon black.

Determination of total PAH and BaP concentration

Fig. 3 shows the TLC separation of the benzene extracts of the carbon blacks listed in Table I. Fraction A ($R_F = 0.5-0.6$) is composed of PAHs. Fraction B ($R_F = 0-0.2$) contains strongly fluorescent heterocyclic compounds. The fraction composed of saturated aliphatic hydrocarbons ($C_{14}-C_{35}$) ($R_F = 0.9-1$) does not exceed more than 10% of the benzene extract.

Figs. 4 and 5 show chromatograms of the PAH fraction of a carbon black (N 550) obtained on a GLC column and on an HPLC column, respectively. For the determination of BaP (peak 7 in Fig. 4 and peak 4 in Fig. 5) GLC and HPLC gave virtually the same results. The BBT column separated BaP completely from its $C_{20}H_{12}$ isomers (benzofluoranthenes, benzo[e]pyrene and perylene) and also in HPLC there was no interference from other hydrocarbons, as shown the Fig. 6, which shows the UV spectra for peak 4 in Fig. 5(B) and for a peak of pure BaP (99.8%) (A).

The qualitative distribution of the PAH fraction is virtually constant for the

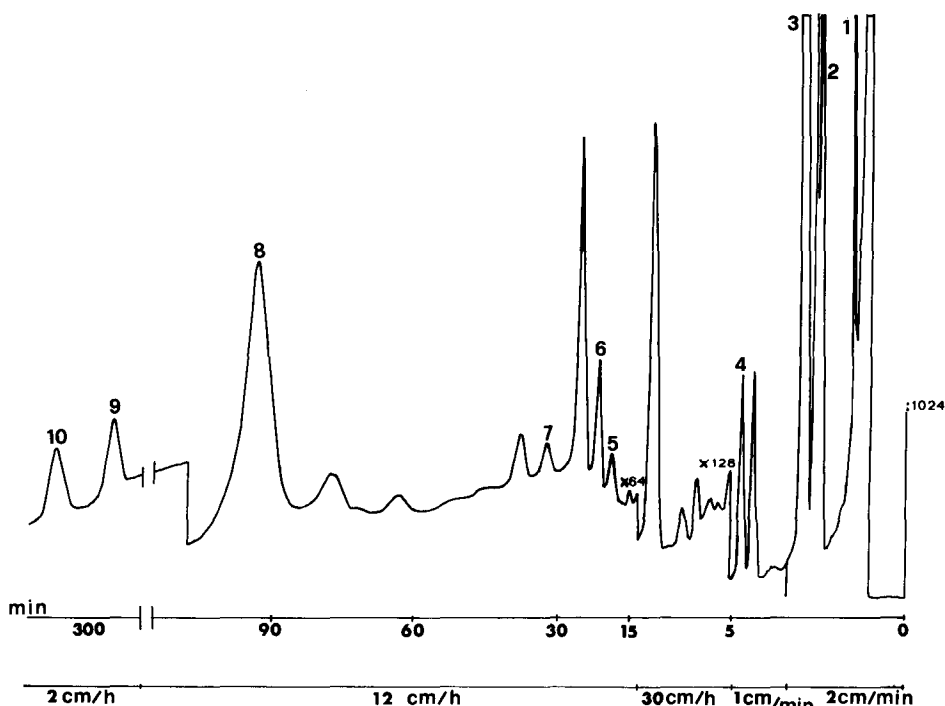


Fig. 4. Gas chromatogram of the PAH fraction of a carbon black (N 550). Glass column (70×0.3 cm I.D.) loaded with 0.05% (w/w) BBT on glass microbeads (140-170 mesh) pre-treated with 0.025% (w/w) NaDBS. Column temperature: 210°C . Injector temperature: 230°C . carrier gas: nitrogen. Flow-rate: 10 ml/min. Flame-ionization detector. Peaks: 1 = phenanthrene; 2 = fluoranthene; 3 = pyrene; 4 = benzo[ghi]fluoranthene; 5 = benzo[b]fluoranthene; 6 = benzo[k]fluoranthene and benzo[e]pyrene; 7 = benzo[a]pyrene; 8 = benzo[ghi]perylene and indeno[1,2,3-cd]pyrene; 9 = dibenzopyrenes; 10 = coronene.

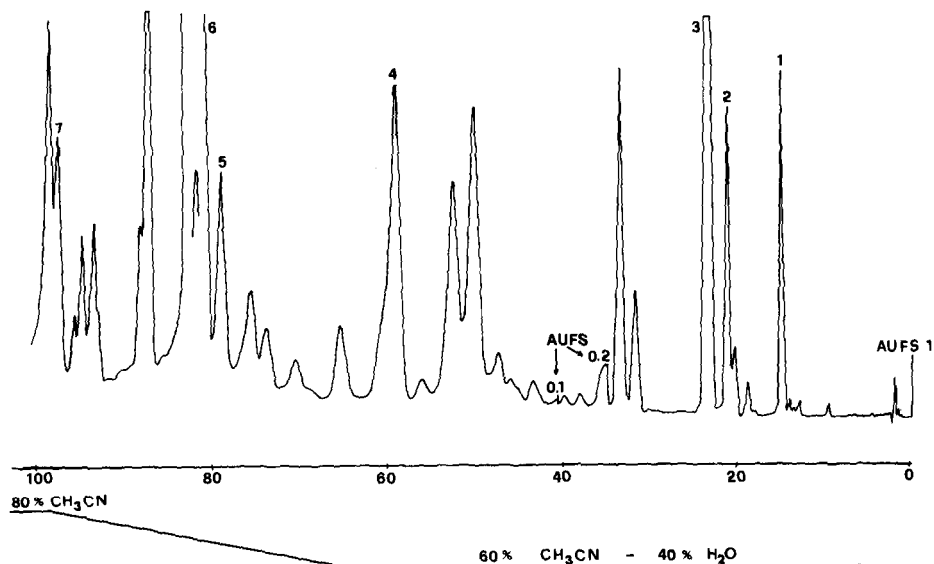


Fig. 5. HPLC trace of a PAH fraction (the same as in Fig. 4) on a reversed-phase column (16×0.4 cm I.D.) packed with $5 \mu\text{m}$ ODS-silica gel. Solvent programme: acetonitrile-water (60:40) for 63 min then to 80% acetonitrile at 0.7%/min. Flow-rate: 1 ml/min. Detector: UV spectrophotometer at 254 nm. Peaks: 1 = phenanthrene; 2 = fluoranthene; 3 = pyrene; 4 = benzo[*a*]pyrene; 5 = indeno[1,2,3-*cd*]pyrene; 6 = benzo[*ghi*]perylene; 7 = coronene.

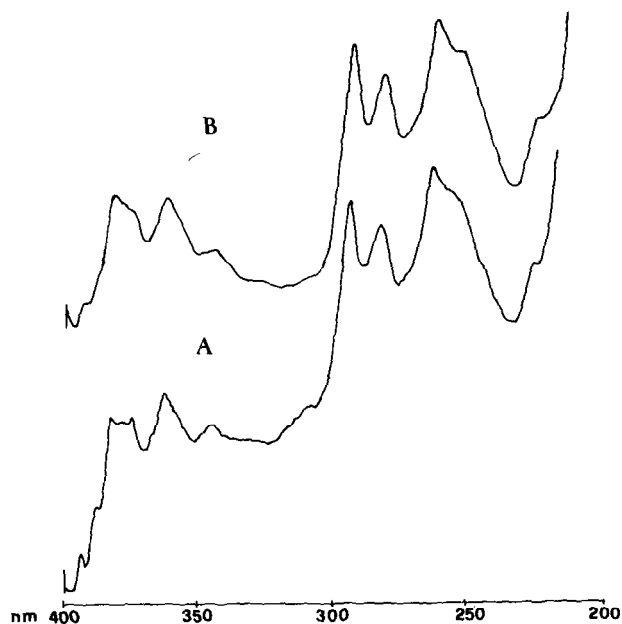


Fig. 6. UV absorption spectra of the BaP peak in Fig. 5(B) and of pure BaP (99.8%) (A).

TABLE III

TOTAL BENZENE EXTRACT, PAH FRACTION AND BaP CONCENTRATIONS (mg/kg) IN CARBON BLACKS

<i>Carbon black</i>	<i>Total benzene extract</i>	<i>PAH fraction</i>	<i>BaP</i>
N 220	172	36	0.04
N 326	225	80	0.18
N 347	343	120	0.50
N 550	610	298	0.14
N 660	620	359	6.10
N 990	8020	2140	35.00

TABLE IV

TOTAL BENZENE EXTRACT, PAH FRACTION AND BaP, CONCENTRATIONS (mg/kg) IN DIFFERENT BATCHES OF CARBON BLACK N 660

<i>Batch</i>	<i>Total benzene extract</i>	<i>PAH fraction</i>	<i>BaP</i>
1	396	250	4.1
2	1062	736	1.2
3	841	614	6.1
4	583	377	9.7
5	620	359	6.1
6	416	200	1.5

different types of carbon black in Table I. In contrast, considerable differences were found in the total amount and in the concentration of each PAH. Tables III and IV report the total organic fraction and BaP concentrations found in the carbon blacks in Table I and in six different batches of one of them (N 660), respectively. These tables show that the PAH fraction is not a constant percentage of the total organic fraction and that the BaP concentration varies widely in the different batches of the same carbon black type.

REFERENCES

- 1 E. M. Dannenberg, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Interscience, New York, Vol. 4, 1978, p. 631.
- 2 H. L. Falk, A. Miller and P. Kotin, *Science*, 127 (1958) 474.
- 3 J. Neal, M. Thornton and C. A. Nau, *Arch. Environ. Health*, 4 (1962) 598.
- 4 W. Kutscher, R. Tomingas and H. P. Weisfeld, *Arch. Hyg.*, 151 (1967) 646.
- 5 W. Kutscher, R. Tomingas and H. P. Weisfeld, *Arch. Hyg.*, 151 (1967) 656.
- 6 *Criteria for a Recommended Standard: Occupational Exposure to Carbon Black*, Department of Health, Education and Welfare (NIOSH), Cincinnati, OH, 1978.
- 7 G. T. Taylor, T. E. Redington, M. J. Bailej, F. Buddingh and C. A. Nau, *Amer. Ind. Hyg. Ass. J.*, 41 (1980) 819.
- 8 G. Locati, A. Fantuzzi, G. Consonni, I. Ligotti and G. Bonomi, *Amer. Ind. Hyg. Ass. J.*, 40 (1979) 644.
- 9 V. R. Stenberg and T. E. Alsberg, *Anal. Chem.*, 53 (1981) 2067.
- 10 W. H. Griest, J. E. Canton, M. R. Guerin, L. B. Yeatts, Jr. and C. E. Higgins, in A. Bjorseth and A. J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons*, Battelle Press, Columbus, OH, 1979, p. 819.

- 11 M. L. Lee and R. A. Hites, *Anal. Chem.*, 48 (1976) 1890.
- 12 A. Gold, *Anal. Chem.*, 47 (1975) 1469.
- 13 P. A. Peadar, M. L. Lee, Y. Hirata and M. Novotny, *Anal. Chem.*, 52 (1980) 2268.
- 14 L. Zoccolillo, G. Goretti and M. Ronchetti, *Chromatographia*, 15 (1982) 757.
- 15 L. Zoccolillo, A. Liberti and D. Brocco, *Atmos. Environ.*, 6 (1972) 715.
- 16 A. Liberti and L. Zoccolillo, *Proceeding of Technical Conference on the Observation and measurement of atmospheric Pollution, Helsinki, July 30-August 4, 1973*, World Meteorological Organisation, Geneva, 1974, p. 79.
- 17 D. Brocco, M. Possanzini and L. Zoccolillo, *Ann. Ist. Super. Sanità*, 9 (1973) 409.
- 18 A. Candeli, G. Morozzi, A. Paolacci and L. Zoccolillo, *Atmos. Environ.*, 9 (1975) 843.
- 19 A. Liberti, G. Morozzi and L. Zoccolillo, *Ann. Chim. (Rome)*, 65 (1975) 573.