THE NATURE OF PARTICULATE MATTER

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ABSTRACT

The origin and the nature of particulate matter which is found in the earth's atmosphere, and which is measured to evaluate air pollution, are discussed. The importance of defining particulate matter in terms of its physical structure and its chemical composition is emphasized.

Attention is drawn to the surface activity of particulate matter and it is shown that, because of its micropore fine structure and its content of metals, particulate matter may act as a catalyst for some reactions, and also as a carrier for any vapour and gas. Ammonia, hydrocarbons and nitrogen oxides, adsorbed on particulates, have been detected and determined.

The compositions of both inorganic and organic fractions of particulates are discussed and a procedure for the systematic analysis of various classes of organic compounds is outlined. The results obtained by thin layer and gas chromatography to elucidate the composition of the organic fraction are presented.

The term 'particulate matter' is defined in a general sense as any solid or liquid matter dispersed in the atmosphere. From a physical standpoint it covers all material which is not molecularly dispersed and which can be included approximately in the range size of about 10 μ–50 Å by disregarding cloud, fog and rain drops and considering only dry air. Larger particles are responsible for the so called atmospheric dust whereas the smaller particles are aerodispersions defined as urban or atmospheric aerosols.

The upper limit coincides with the respirable size of the particles whereas the lower limit approaches the size of a compound, which is molecularly dissolved in the atmosphere and corresponds practically to a cluster of few molecules. Particles of 50 Å or smaller have very short lifetimes because, due to their high mobility, they tend to adhere together becoming rapidly attached to the larger aerosol particles and forming larger aggregates. They can exist in considerable concentrations only if they are produced continuously. Reaction products of gas reactions, small ions or primary particles produced by cosmic radiation are examples.

The large particles are short lived and because of their large mass have a high rate of sedimentation which can be estimated in still air approximately by Stokes' law; particles larger than the mean free path of the gas molecule on the other hand have a constant settling velocity, which is determined by a balance between the gravitational force and the resisting force of aerodynamic drag.

The atmospheric aerosols, thus defined, form a spectrum which is sub-divided for convenience into three groups depending on their size, according to Corn[1] (*Figure 1*). The Aitchen particles which are the smallest (below

Nomenclature				Aitken particles	Large particles	Giant particles
Size range important for :	Air electricity		Large ions			
	Atmospheric optics				Haze particles	
	Cloud physics				Active condensation nuclei	
	Air pollution				Suspended particulate matter	Dustfall

Figure 1. Sizes of particulate matter found in the earth's atmosphere.

0·1 μ radius), larger particles (0·1–1 μ), and the giant particles up to 10 μ. Aerosol particles sometimes carry an electrical charge.

As in the case of the spectrum of electromagnetic waves, different parts of the particle size spectrum are responsible for different phenomena in the atmosphere.

Small ions (below 7×10^{-3} μ radius) and Aitchen particles play a significant role in air electricity by affecting the conductivity of the air and hence other electrical parameters, whereas the large particles are responsible for the scattering of visible light and thus control visibility outside clouds and fog.

As far as pollution is concerned all particles which may be inhaled should however be considered. The origin of aerosols in the atmosphere can be different: they may result from dispersion or from condensation. Dispersion aerosols are formed by the grinding or atomization of solids and liquids and by the transfer of powders into a state of suspension through the action of air currents or vibration. Condensation aerosols are formed both when supersaturated vapour condenses and as a result of reaction between gases leading to the formation of non volatile products. The main difference between these two classes is that dispersion aerosols are in most cases coarser than condensation aerosols and consist of individual or slightly aggregated particles of irregular form; in condensation aerosols solid particles are often loose aggregates of a large number of primary particles. In practice urban particulates originate from both dispersion and condensation; they are made of soot, ash, products of combustion and exhaust gases.

The complexity of a particulate matter requires that its examination be carried from several points of view as its action on man and his environment depends not only on chemical composition but also on physical structure.

Many properties of particulates are dependent on their size: rates of evaporation and of cooling, light scattering, visibility, diffusion, settling and surface activities strongly depend upon size distribution. The particulate size is the most important parameter also in relation to retention and toxic effects of the particulate matter inhaled by the man.

Because of the aggregated nature of atmospheric particles it is important to define the meaning of the particle size. It is well known that examination of air particles by an optical or electron microscope reveals a very irregular shape. The particle size in terms of its diameter is conventionally expressed by assuming the projection of the particle perimeter to be a circle and regarding the particle ideally as a sphere. It has been pointed out however that according to these criteria particle size measurements cannot account for variation in particle density or in particle shape. To overcome this difficulty the geometric radius is sometimes replaced by another quantity related to the aerodynamic behaviour such as the rate of fall of particles in the air, which is indeed a function of the particle weight and of the aerodynamic drag. The Stokes radius is thus defined as a radius of a sphere having the same falling velocity as the particle and a density equal to that of the bulk material; or conventionally the equivalent aerodynamic size of a sphere having the same falling velocity as the particle and a density equal to 1 g/cm^3.

Measurement of particulate matter is usually reported in terms of gravimetric determination ($\mu g/m^3$) or as a number of particles per volume unit with indication of their size distribution and these figures are taken as rough estimates of the pollution of a certain area.

These criteria are well established but it has to be pointed out that particulate matter, because of the wide size spectrum, and the different lifetime of the particules is an unstable system in continuous evolution. Because of this specific characteristic it seems that particulate matter can be described more adequately in terms of an operational property, which also has the advantage of being related to the mechanism of action: the surface area.

The determination of particulate surface area can be carried out with high accuracy by means of gas adsorption, i.e. by measuring the volume of adsorbed gas: it can be accomplished either by the so-called volumetric or BET method by measuring the volume of gas adsorbed at the surface at different pressures in a static system or by a flow dynamic procedure making use of a gas chromatographic technique[2]. The former procedure is well
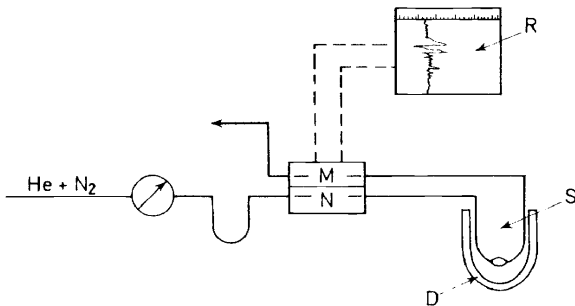

Figure 2. Set-up for the measurement of surface area.

known; the latter, which requires much simpler equipment, has the advantage that it can be used in a routine fashion for this purpose. Its basic principle is briefly outlined: a weighed particulate matter sample, collected by electro-

static precipitation or by other means, is transferred into a suitable vessel and degassed in an inert gas stream.

A helium–nitrogen mixture is passed through the sample and through a thermal conductivity system, made of two measuring cells arranged as is shown in *Figure 2*. M and N are two conductivity cells; they are two sides of a Wheatstone bridge. The gaseous mixture is analysed before and after passing through the sample so that a differential determination is performed.

By cooling the sample (S) in a Dewar vessel (D) adsorption of a certain quantity of nitrogen takes place. Because of the adsorption, there is a decrease in the nitrogen concentration of the gas stream, which passes through the particulate sample and simultaneously a peak appears on the strip chart of the recorder (R).

When the Dewar flask is removed, the temperature increases, desorption of the gas is attained and a new peak, corresponding to an increase of the nitrogen concentration is recorded. Two peaks in the opposite direction are thus obtained, both comprising the same total surface.

By feeding into the gas stream a known quantity of nitrogen a further peak is obtained, which can be used for calibration. The adsorbed or desorbed quantity of nitrogen is always proportional to the surface area; since the surface covered by one ml of nitrogen in a monomolecular layer at the saturation pressure of nitrogen is known, the specific surface area can be determined.

Though in the process of particulate collection some particles may hit each other and larger units might be formed, it is believed that gas adsorption of a system is only slightly affected by the mechanical collision of particles of a system: it has been found that different procedures of collection yield surface area values in fair agreement.

It has been found that the specific surface of particulates collected in urban areas has an average value of 2–$2 \cdot 5$ m^2/g and it may differ considerably from the surface collected in industrial areas. This value refers to the actual surface area of the particulate matter, i.e. to the equilibrium state between adsorption forces of the surface and the gases and vapours in the atmosphere and it includes the irregularities of all particles.

Some information on the adsorption forces of particulate matter may be obtained by measuring the surface area after submitting it to vacuum and to the action of an inert gas flow at various temperature. As is seen from *Table 1* both treatments show that surface area is more than doubled when adsorbed compounds are set free.

Table 1. Surface area of particulate matter.

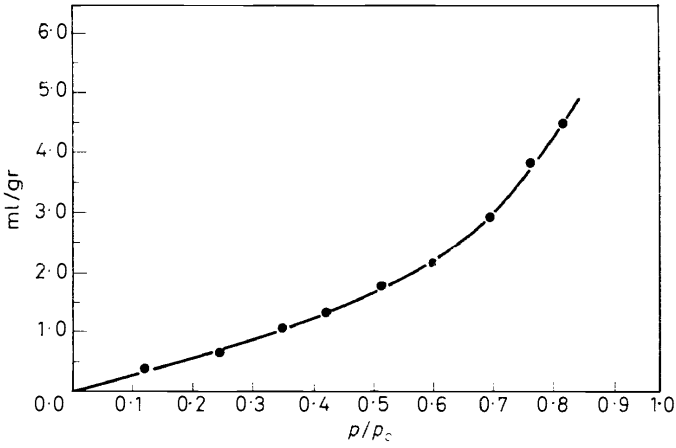| Treatment	Surface area m^2/g
(A) *Particulate matter as such*	2·19
(B) *under vacuum for*: 11 h	3·76
18 h	4·75
(C) *under helium stream for 8 h at*: 130°	2·74
170°	3·65
195°	4·37
215°	5·53

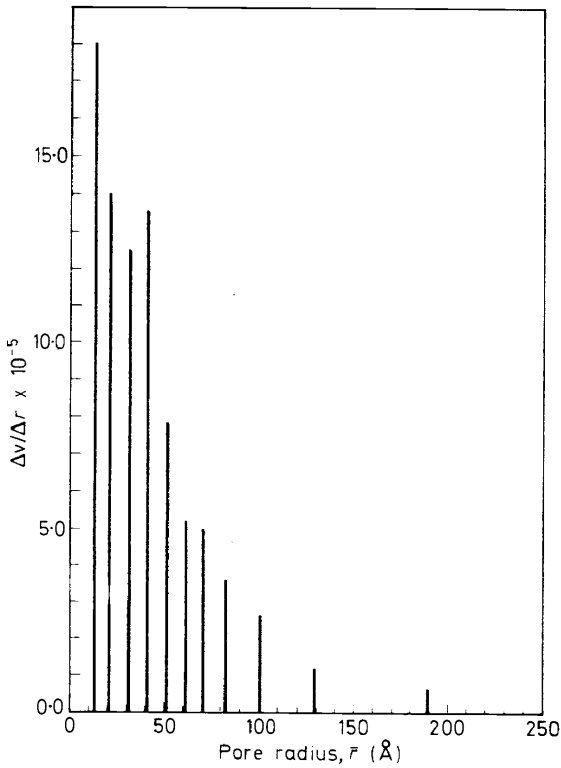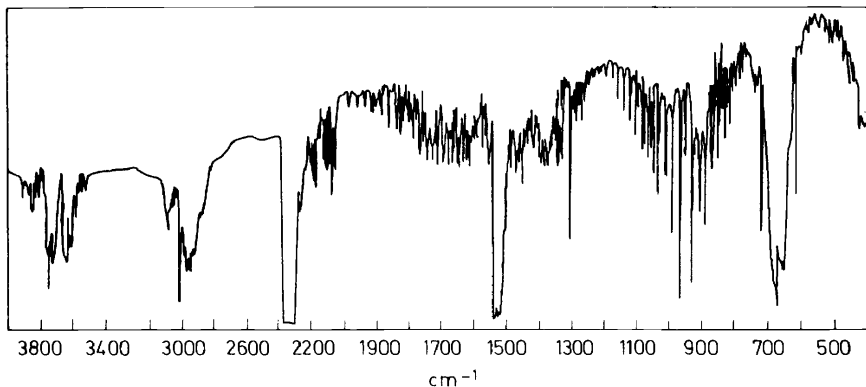*Figure 3*. Isotherm of a sample of urban particulate matter.

Figure 4. Histogram showing pore-volume distribution of particulate matter.

Particulates behave as an adsorption medium and in order to evaluate their properties, it is possible to evaluate their micro-structure by obtaining information regarding the adsorption isotherm. This can be determined by means of the above mentioned technique and it has been found that the adsorption isotherm for most particulate samples has the shape reported in *Figure 3*. From the adsorption isotherm the total pore volume and pore distribution can be calculated; an average volume of about 0·1 ml/g is usually obtained. The histogram relative to the pore distribution of particulates is reported in *Figure 4*: it shows that about 80 per cent of the pores have a pore radius below 100 Å and the greater part of them have a radius between 10 and 40 Å.

The existence of a large number of micropores in particulates means this material might be responsible for physical adsorption as well as for capillary condensation of a great variety of chemical compounds. Evidence for this can be obtained by degassing a particulate sample under vacuum and

Figure 5. IR spectrum of gases desorbed from a sample of urban particulate matter.

collecting compounds set free into a long path (100 m) infrared cell. The IR spectrum of gases desorbed from an urban atmospheric dust is shown in *Figure 5*.

The following compounds have been identified through their specific adsorption bands: carbon dioxide (600–720; 2300–2400 cm^{-1}), carbon monoxide (2100–2200 cm^{-1}), methane (1300; 3000 cm^{-1}), ammonia (800–1050; 900–1000 cm^{-1}), nitrogen monoxide (2200–2300 cm^{-1}), nitro-compounds (1600–1800 cm^{-1}), ethylene 1460 cm^{-1}).

A quantitative determination of these compounds can be carried out by means of the technique described and it has been found that gas concentrations change noticeably from place to place.

In particulates taken in urban areas the range of concentration (in µg/g) was for carbon dioxide 150–300; for carbon monoxide 10–30; for methane 15–60 and for ammonia 30–100.

It is noteworthy that in all samples despite the long degassing time no evidence has been found for the presence of sulphur dioxide though this

pollutant is by far the most abundant in the air. No sulphur dioxide has been detected in any particulate sample either freshly collected or left for some time after sampling. This finding is quite ramarkable as it leads to the conclusion that sulphur dioxide is either oxidized on adsorption or bound by other components which might be present in particulate matter.

It has been shown[3] that in urban dust the sulphur content is about 2–4 per cent in weight; about 80 per cent is present as soluble sulphate whereas the remainder is chemically bound. It is well known that the oxidation of sulphur dioxide is a very slow process becoming more rapid in the presence of a suitable catalyst; it seems that atmospheric dust, because of its micropore structure, may well behave as a catalyst for oxidation to sulphur trioxide.

Particulate matter, besides exerting a chemical action due to its components, has thus two remarkable physicochemical properties: to act as a carrier for a variety of pollutants which are concentrated on its surface and to act as a catalyst for various reactions.

In connection with the activity of dust as a carrier some conclusions can be made about the fate of some pollutants. For instance, it is well established[5] that carbon monoxide is the most abundant gaseous pollutant excluding carbon dioxide; no direct oxidation of carbon monoxide in sunlight has been ever observed and the rate of oxidation by ozone is small for the concentrations present in the atmosphere. Carbon monoxide adsorption by dust may reduce this particular form of pollution; it seems that particulate matter adsorbs carbon monoxide, removing it from the atmosphere and bringing it down to the earth's surface where bacteria are known to oxidize carbon monoxide.

As far as the catalytic action is concerned there is no doubt that it should be attributed to the microporous structure of particulates and to the presence of finely dispersed metals and their salts. After alkali and alkaline earth metals, which are the most abundant, iron and lead are present in the largest concentration, though zinc, manganese, copper, nickel, titanium, vanadium, beryllium, arsenic and others are often present. No definitive range of concentration can be indicated as these figures are strongly influenced in any urban area by city population and by industrial activities.

It is, however, quite important to consider that the different composition of metallic components may strongly influence different reactions in the atmosphere. The availability of atomic absorption spectrometry makes possible the determination of the metals in particulates quite simply and rapidly.

Chloride and sulphate are the two main anions, nitrate is the next, but specific attention is given to particulate fluoride, which is a minor component but quite an effective pollutant.

Knowledge of the inorganic fraction of particulate matter can be obtained quite reliably and the improvement of analytical procedures and the introduction of some techniques such as the use of selective ion electrodes and atomic absorption spectroscopy allow some determinations to be carried out on an almost routine basis.

The evaluation of the organic fraction of particulate matter is far more complicated and efforts made to elucidate it indicate its great complexity.

Organic contaminants are among the most important of all air pollutants as many of them are related to definite diseases.

The removal of organic material from particulates can be carried out by solvents but no solvent is entirely satisfactory, its choice being largely dependent upon the specific class of compounds to be analyzed. It is a common practice to report the total concentration in terms of acetone-soluble or ether-soluble extracts; these data are however of minor interest and to obtain more specific information it is necessary to combine selective extraction with highly sensitive analytical methods.

A full scheme has been suggested by Jacobs[6]; he reports an ether extraction, an acid-base separation and a fractionation by column-chromatography obtained with the use of solvents of different polarity. Another simplified
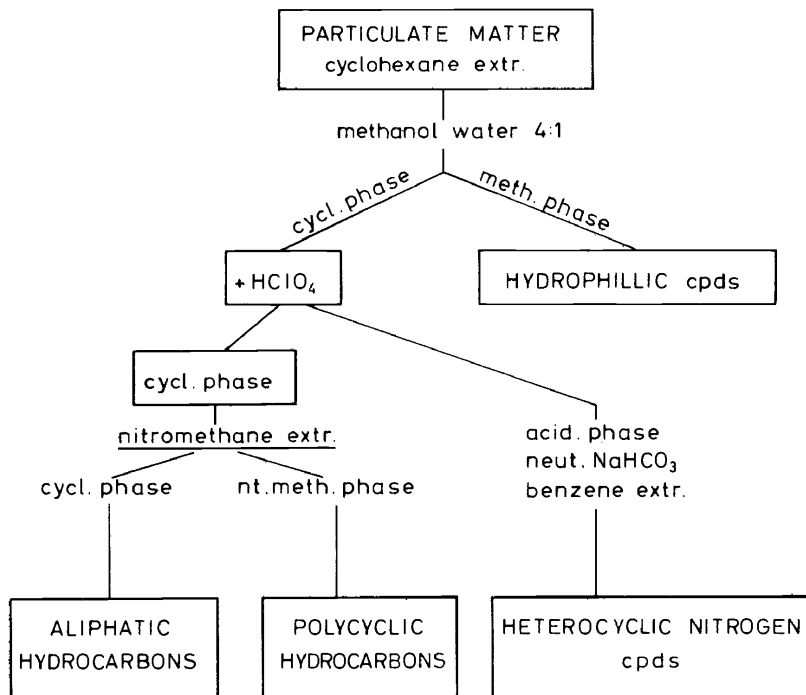

Figure 6. Analytical scheme for the fractionation of organic compounds of particulate matter.

procedure, successfully used to perform the separation, is shown in *Figure 6.* The dust is extracted with cyclohexane and a double liquid–liquid extraction is carried out first with nitromethane and later with methanol.

The following classes of compounds are separated: (a) alkanes (b) poly-cyclic hydrocarbons (c) heterocyclic nitrogen compounds (d) hydrophilic compounds. It should be noted, however, that because of the complex nature of the molecules of the compounds present in a dust, which may have several organic functions, the above scheme does not yield a sharp separation and, as an example, aso-heterocyclic compounds may be found in the

polycyclic hydrocarbons fraction. Thin layer, column and gas-liquid chromatography are generally used for separation of the above fractions and the identification of various compounds can be performed either by means of their spectra or through their chromatographic parameters. The more promising analytical techniques are bi-dimensional thin layer chromatography and gas-liquid chromatography. The greatest value of two-dimensional TLC with mixed solvents is that it allows quick separation and fast characterization, and assay of complicated molecules.

GLC however offers outstanding possibilities in this area; if high resolution columns are used it is possible to obtain a fairly detailed picture of the variety of compounds which are present. Glass capillary columns coated with silicone rubbers are particularly suitable for this investigation.

Information available on various compounds is summarized briefly:

Alkanes: this class of compounds is very abundant; all alkanes with an even and uneven number of carbon atoms with a straight chain from C_{18} up to C_{34} have been identified. It seems that these compounds are normal components of particulate matter as they are found in all samples.

Polycyclic hydrocarbons: this class of compounds has been the object

Table 2. Retention indices (I_{pr}) of polycyclic hydrocarbons at programmed temperature (T_r) on SE-52 column

n	Compound	T_r	I_{pr}
1	naphthalene	102	1173
2	azulene	105	1212
3	diphenyl	109	1262
4	acetylnaphthalene	113	1313
5	acenaphthalene	116	1350
6	fluorene	124	1460
7	*trans*-stilbene	137	1620
8	phenanthrene	143	1695
9	carbazole	154	1838
10	anthracene	160	1850
11	fluoranthene	174	1988
12	pyrene	178	2040
13	1,2-benzfluorene	185	2125
14	3-methylpyrene	189	2173
15	1-methylpyrene	189	2173
16	benz-(m, n, o)-fluoranthrene	199	2297
17	1,2-benzanthracene	204	2358
18	chrysene	207	2397
19	naphthacene	219	2543
20	1,2-benzfluoranthrene	227	2648
21	3,4-benzfluoranthrene	228	2655
22	1,2-benzpyrene	234	2728
23	3,4-benzpyrene	235	2742
24	perylene	237	2766
25	1,3,5-triphenylbenzene	244	2853
26	1,2,5,6-dibenzanthracene	258	3008
27	1,2,3,4-dibenzanthracene	261	3048
28	1,12-benzperylene	278	3230
29	1,2,3,4-dibenzpyrene	281	3270
30	coronene	282	3283

of a great deal of work as the pathogenic action of some of these hydro-carbons has been fully recognized. Systematic investigation by gas-chroma-tography[7] reveals that, by using a high resolution glass capillary column and operating at a programmed temperature, each hydrocarbon has a specific retention index which only overlaps with others in a few cases, as is shown by the values in *Table 2*. As an example, a gas chromatogram of polynuclear hydrocarbons, extracted according to the scheme mentioned, is shown in *Figure 7*. The chromatogram has been recorded by using a hydrogen flame and an electron capture detector: the former reveals all
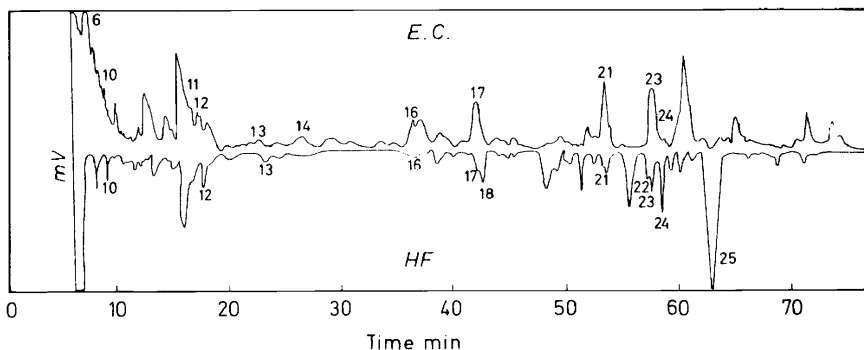
Figure 7. Gas chromatogram of polycyclic hydrocarbons fraction extractor from an atmospheric dust obtained with a hydrogen flame (HF) and an electron capture (EC) detector on a glass capillary SE-52 column. Numbers of the identified compounds as in *Table 2*.

hydrocarbons and yields a response proportional to the relative concentra-tion whereas the latter detects each compound according to its affinity for electrons. The selective response may be a further clue to the identification of polycyclic hydrocarbons.

Peak number of *Figure 7* corresponds to compounds listed in *Table 2*; it appears that several compounds still need to be identified. Some of the unknown peaks might be due to the alkylated derivatives of the polynuclear aromatic hydrocarbons and polynuclear ring-carbonyl type detected by Sawicky *et al.* by column and thin layer chromatography[8].

Attempts to develop standard analytical procedures for this class of compounds have been made and a tentative ASTM method[9] restricted to a limited number of hydrocarbons has been recently described. The analytical procedure consists of a benzene extraction, followed by alumina column chromatography with pentane and diethyl ether as solvents; identification and quantitative determination is carried out in pentane solution by ultra-violet spectrophotometry.

Heterocyclic-compounds: a large number of these compounds have been detected in particulates by means of paper, thin layer and gas chromatography. Furthermore for the heterocyclic nitrogen compounds it has been shown[10] that, by using high resolution glass capillary columns and working at a programmed temperature, identification and separation of the compounds listed in *Table 3* has been achieved:

640

Table 3. Azo-heterocyclic compounds detected in particulate matter

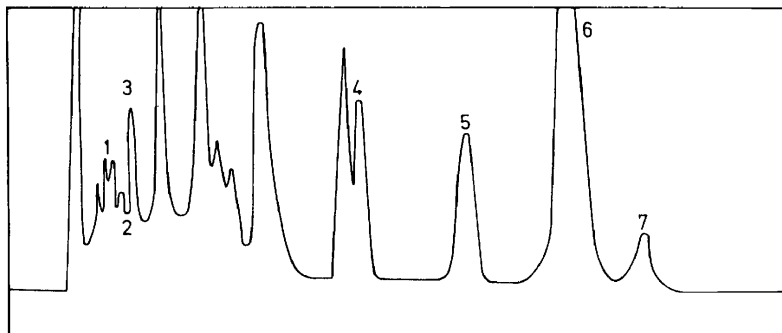| 1. 3,4-benzoquinoline	7. 8,12-dimethylbenzo-(a)acridine
2. 3-methylacridine	8. 1-azafluoranthene
3. 2-methylcarbazole	9. 1-azapyrene
4. benzo-(c)-acridine	10. 10-methylbenzene-(a)-acridine
5. 9-2(2-pyridyl)anthracene	11. 10-methylbenzene-(c)-acridine
6. 10-dimethylbenzo-(c)-acridine	

Figure 8. Gas chromatogram of heterocyclic nitrogen compounds extracted from particulate matter obtained on a glass capillary column coated with SE 52 at 180°. Peak numbers refer to compounds listed in *Table 3.*

A typical chromatogram of particulates extracted according to the procedure described above, is reported in *Figure 8.* This chromatogram also shows the presence of several compounds which are not identified. The great complexity of these particle extracts appears also from the results obtained with the use of bi-dimensional thin layer chromatography where only a limited number of compounds have been identified[11].

Hydrophilic compounds: no systematic investigation has been carried out on this class of compounds which seem to be of minor importance in relation to human health, as organic acids, aldehydes and phenols have only been found in small amounts.

It is necessary to emphasize that particulate matter composition varies considerably from place to place and depends strongly on the quality of air in various areas. As far as the organic fraction is concerned it must be pointed out that all classes of the above compounds are always present in particulates but major differences have been observed not only in the absolute content but also in the qualitative composition. As an example tetracyclic ring compounds are normally present in the atmosphere but their alkyl derivatives, which have a higher carcinogenic activity, are found only in particulates from industrial sources and not in most urban samples. No systematic investigations have been carried out to define these differences, the main limitation being the difficulty of analysing such complex mixtures.

It seems that the development of techniques involving a combination of gas chromatography and mass spectrometry, and their systematic application to the evaluation of the organic fraction of particulate matter, might give

a clear identification of all organic pollutants and clear up the variety of the problems which have been outlined.

This paper attempts to emphasize the importance which should be given to particulate matter in the study of air pollution. Air quality criteria for particulate matter have been established through evaluation of effects and through toxicological studies and epidemiological appraisal[12]. A better knowledge of particulate matter is still a challenging problem for every chemist; it is necessary to elucidate its composition more thoroughly, to know its behaviour and to understand the reactions which are taking place in the air. In this way it should be possible to contribute to a very important goal: human health and the welfare of our environment.

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