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Chemical characterization of atmospheric particles

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Abstract. In the characterization of complex environmental materials such as atmospheric particulate matter, analytical specificity is required to account for the many dimensions of information present in the sample. These dimensions include size, morphology, elemental composition, inorganic and organic chemical speciation, all to be performed on either single particles or on the population (or bulk sample) basis. Various techniques were developed for such measurements, including a number of bulk analysis procedures, methodologies for microscopical analysis of individual particles, and a variety of procedures for organic/inorganic chemical speciation.

1. INTRODUCTION

The air is a complex mixture of gaseous, liquid and solid components. The solid component of this aerosol is referred to as airborne particles or dust. It can be of natural or anthropogenic origin and it varies widely in respect to its concentration in the environmental air, its overall chemical composition, the homogeneity, the size, shape and morphology of the particulate constituents. The particulates in the air have a profound influence on environmental health, on corrosion and conservation of man-made materials, on the atmospheric visibility, and finally on the earth's climate. They act effectively as condensation nuclei or as catalysts for reactions taking place in the atmosphere, hence they influence the presence of a number of chemicals.

Assessment of the potential environmental and toxicological effects of particulate matter in the atmosphere requires a detailed chemical and physical characterization of the particles. The most important distinction between individual particles is their size; it ranges from well into the submicroscopical size range to "giant" particles of several hundred micrometer in diameter. It are the smallest particles, with the highest surface-to-volume ratio, that are the most important entities in many respects.

In this chapter we will treat, without going into any detail, some aspects of the particulate component of the air, its characteristics such as size and morphology, then the sampling of particles from the atmosphere for detailed study in the laboratory and finally some aspects of the analytical chemistry. The analytical study includes the determination of elemental composition, inorganic and

organic chemical speciation on particle collections and the characterization of individual particulates. A detailed description of this subject can be found in a number of textbooks (Buffle and van Leeuwen, 1992, Spurny, 1986).

2. COMPOSITION OF AIR PARTICULATE MATTER

2.1 Classes of atmospheric particles.

The environmental impact of atmospheric particles is dependent on their chemical and physical properties, and on their lifetimes and abundances. A number of particle formation processes occur that result in the *direct* release of particles, e.g. dust storms (e.g. mineral dust) or emissions by vegetation (e.g. pollen).

These generate predominantly "large" particles (with diameters 10 μm or more) which tend to give rise to rapid sedimentation, hence the effects tend to be geographically localised. On the other hand, particles formed *indirectly* in combustion processes or in secondary gas-to-particle conversion reactions (e.g. in photochemical smog or in the condensation of plant emanations), are small (1 μm or less); they have long lifetimes (up to several weeks) and hence may travel over large distances (up to 10,000 km) and to high altitudes (ca. 20 km). They may be of a more general, even a global, concern. Small particles tend to coagulate to micron sized dimensions, larger particles (above a few micrometers) tend to disappear from the gas phase through sedimentation. The residence time of particles in the atmosphere, hence, is related to their size, the particle size of greatest importance is that between 0.1 and 10 μm .

An input/removal diagram for aerosol mass as constructed by Whitby and Cantrell (1976) is shown in Figure 1. It shows the major formation mechanisms of small particles from high temperature processes (volcanism, natural fires, anthropogenic and industrial processes); the composition of these primary aerosol particles is quite diverse. Small particles also result from homogeneous nucleation from gases and vapors e.g. by photochemical conversion of reactive hydrocarbons (natural or industrial emissions), or oxidation of precursors such as sulfur dioxide. Coagulation quickly transforms these fine aerosol particles to larger particles. The coarse particles and their formation mechanisms and its sink through sedimentation are also shown with a peak around 10 μm . Large particles are easier to allocate to specific origins than the small ones as they usually preserve at least partly the original structure and composition of the source material.

Figure 1 also shows (in an idealised way) the resulting *particle size distribution* with a typical three humped distribution. Many realistic aerosol size distributions follow a log-normal distribution. Junge (1955) established his famous power law in 1955 describing particle number concentration by:

$$dN / d(\log r) = Cr^{-\beta}$$

The constant C depends upon the number of particles and β is the slope of the size-distribution curve. There are many studies in which researchers have tried size-distribution fits and also related aerosol sizes with their source of origin. Noll and Pilat (1971) observed complete size distribution in the size range 0.1-100 μm radius and found average slopes of 2.3 between 5 and 25 μm and 6.7 between 40 and 100 μm . The general applicability of the power law concept follows from Figure 2 where the particle distributions with size is compared between typical city air and several classes of clean room facilities.

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

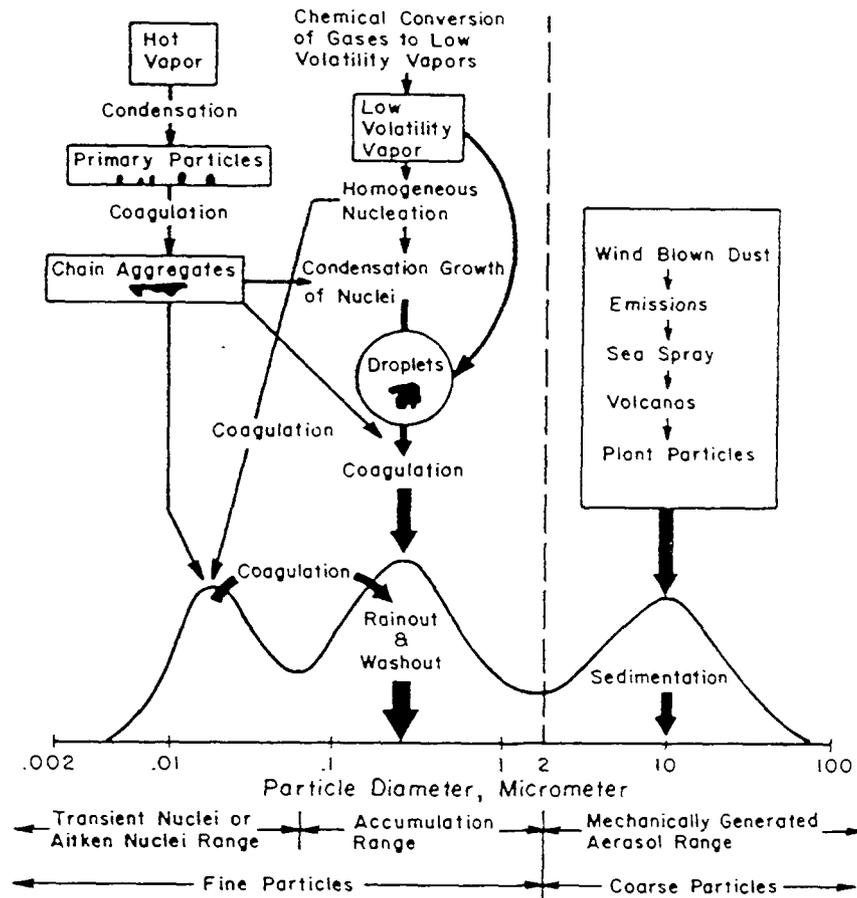


Figure 1: Idealization of the atmospheric aerosol surface area distribution showing the principal modes, main sources of mass for each mode, and the principal processes involved in injecting mass in each mode as well as primary removal mechanisms (Buffle and van Leeuwen, 1992).

Monomodal with one maximum, or polymodal distributions with two or more maxima occur. The size distribution can also be expressed as a mass distribution or as the distribution of a given component. Common ways to summarise the distribution are the arithmetic mean radius, r_m , (half the particles have a radius smaller than r_m), and the mass median diameter, D_m (the dividing point 50% above 50% below in mass).

For direct particle production the natural component (sea salt particles produced by the bubble bursting in the ocean, windblown dust, volcanic emissions and forest fires) dominates the man-made production processes (various industrial processes, power consumption and transport related activities) on a global scale. Manmade production of particulates through secondary processes is of more or less the same order of magnitude as the natural production. The combined global production particles from sulphates, nitrates and hydrocarbons as gaseous precursors is a few megaton per year (Prospero, 1984).

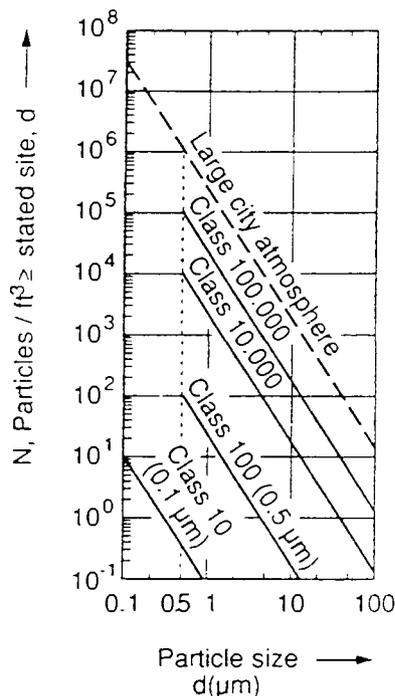


Figure 2: Upper limit to permitted number of particles $N(d)$ per cubic foot (contamination level) as function of particle size d , in various cleanroom categories. Class 100 (0.5 μm) means that not more than $N = 100$ particles, with $d = 0.5 \mu\text{m}$ or greater, and not more than, for instance, about 20 particles with $d = 1 \mu\text{m}$ or greater may occur per cubic foot. The proximate contamination level in a large city's atmosphere is included.

2.2 Composition of air particulate matter

The atmospheric aerosol has a very complex and variable composition. Particulate matter amounts to more than 50 % of all air pollutants. More than 70 elements as well as a whole range of organic compounds have been identified in it using a number of advanced analytical methods.

Anthropogenic emissions are dominated by sulfates (as a secondary aerosol), while natural emissions are dominated by sulfates, sea salt and dust.

Carbonaceous aerosol derives primarily from hydrocarbon emissions and from combustion processes, both of which have significant natural and anthropogenic sources. The elemental (non-organic) composition of particles from combustion of coal, fuel oil, gasoline and wood (gaseous fuel generates little aerosol) and various industrial processes have been intensively studied.

As is evident from the previous comments that air particulate matter is by no means an homogeneous batch of particles with a closely similar composition. Airborne particles have a widely varying composition, aerodynamic dimension and shape. This suggests the analysis of particles as a function of particle size following the separation of the particulates in several particle size categories. The ways to separate particles according to their size will be discussed briefly in a following paragraph. Alternatively analysis may be attempted on single microscopical particles. A number of microanalytical techniques are used for single particle characterization. Sometimes even

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

the surface predominance (or depletion) can be inferred by using surface sensitive methods. In fact, particles of microscopical dimensions when studied in detail may show that they are complex aggregates with locally differently composition and structure, result of complex formation processes.

Atmospheric particles collected near the earth's crust may be expected to have the earth crust or the sea as a major natural source and reflect the composition of them. Particles emitted in various industrial processes may contain information on the source composition. Comparison of the aerosol composition with that of the source is, hence, relevant and the *enrichment factor* (EF) is used for such comparisons, as for example :

$$EF_x = (X/A)_a / (X/A)_c$$

where X is one element in the aerosol (subscript a) or in the crust (subscript cr). Aluminium is chosen in this example as a normalisation element with high abundance and negligible enrichment.

EF can be identified for any given element in a system comparing the aerosol with the ocean (e.g. with Na as reference), a particular emission process (e.g. coal burning), etc.

Figure 3 shows an example with the enrichment of a number of elements in the urban aerosol and the emissions from different power plants. The enrichment of a number of elements is striking. Some of them might be used as a tracer : e.g. Se with an high EF in the power plant emissions looks attractive for this purpose in Figure 3. As a result of condensation from the gas phase the more volatile elements are enriched at the particle's surface.

Elemental carbon or *black carbon* (BC) has long been recognized as an important component of the total atmospheric aerosol. Marine and terrestrial particulate matter have been found to contain these carbonaceous particles with the largest concentrations being obtained from urban air samples, where it normally resides in the smaller size fractions. The ratio of elemental to total carbon (elemental + organic, OC) have been found to be strongly dependent on the source.

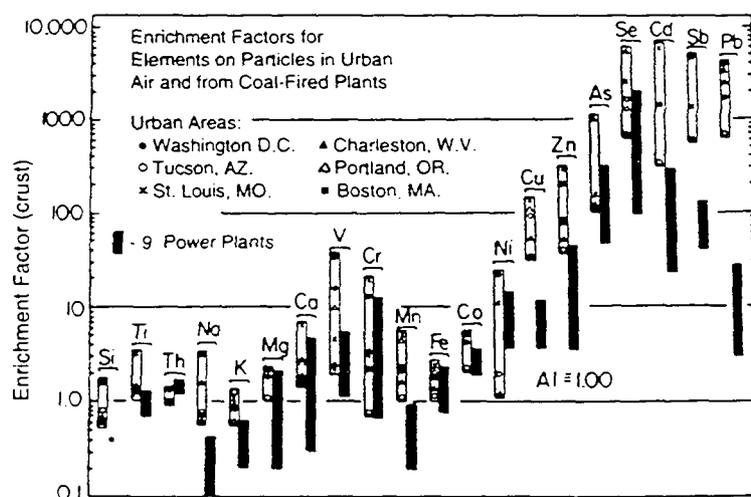


Figure 3: Enrichment factors with respect to crustal abundances for elements attached to urban particles from (•) Washington, D.C. (○) Tucson, AZ (×) St. Louis, MO, (▲) Charleston, WV (△) Portland, OR, and (■) Boston, MA. (Gordon G.E. et al. , 1981).

Elemental carbon is a significant cause of light extinction. With its high specific absorption of solar radiation black carbon has important direct and indirect radiative and possibly climatic effects. The relative chemical inertness of carbon coupled to its predominantly submicrometer size suggests that it may act as a tracer for sources of combustion-type aerosols over long path distances in the atmosphere.

Particulate organic carbon (*carbonaceous particles*) retains structural clues of source specific biosynthesis processes ("molecular markers"). In contrast combustion carbon, which passed through a gaseous/free radical state generates a specific imprint for combustion processes with polymerization reactions leading to *polyaromatic hydrocarbons* (PAHs) as shown in Figure 4.

	Mass (amu)	Compound	
1	252 [*]	benzo[a]pyrene ^{a,b}	1
2		benzo[e]pyrene ^{a,b}	2
3		perylene ^{a,b}	3
4		benzo[k]fluoranthene ^{a,b}	4
5	276 [*]	anthanthrene ^{a,b}	5
6		dibenzo[a,c]anthracene ^a	6
7		benzo[ghi]perylene ^{a,b}	7
8	300 [*]	coronene ^{a,b}	8
9	306 [*]	a benzo[thiophene]	9
10	326 [*]	dibenzo[a,ghi]perylene	10
11	350 [*]	benzo[a]coronene	11
12	362 [*]	a benzo[thiophene]	12
13	374 [*]	dibenzo[a,bc]coronene	13
14	380 [*]	a benzo[thiophene]	14
15	398 [*]	ovalene	15
16	404 [*]	a benzo[thiophene]	16
17	424 [*]	benzophenanthrocoronene	17
18	448 [*]	benzo[a]ovalene	18
19	472 [*]	dibenzo[a,bc]ovalene	19
20	496 [*]	circumanthracene	20
21	520	circum[pyrene]	21
22	546	benzo[a]circumanthracene	22
23	570	dibenzo[a,bc]circumanthracene	23
24	594	circum[tetracene]	24
25	620	tribenzo[a,bc,h]circumanthracene	25

a - confirmed by HPLC analysis
b - confirmed by GC/MS analysis
* - confirmed by direct insertion EI and CI MS analysis

Figure 4 : PAHs found by laser microprobe mass spectrometry in oil retort soot. (Mauney T. et al., 1984).

2.3 Data treatment

In order to develop rational and effective strategies for improving air quality, it is necessary to have an understanding of the relationship between the pollutant sources and their impact at *receptor* sites. Source or dispersion models predict the concentrations of pollutants at a receptor site using diffusion models with emission inventories and meteorological data. Receptor models infer source contributions at receptor sites using statistical models with data taken at the receptor site (Gordon, 1988).

Receptor modelling has frequently been used to determine possible sources of pollution in many sites. E.g. Gray et al. (1986) developed and operated a fine-particle monitoring network in Los Angeles in 1982. They found that particulate carbon emissions were the principal contributors to

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

fine carbonaceous concentrations and accounted for about 40 % of the total mass. Pratsinis et al. (1988) found that about half of the fine aerosol mass and two-thirds of the carbonaceous aerosols can be attributed to motor vehicle emissions during high pollution days in 1983 at Duarte, a residential Los Angeles site. In addition, they showed atmospheric chemistry and even background aerosol (e.g. soil dust) can have significant contributions to the non-black carbonaceous aerosol. The complete set of observations (samples), as well as seasonal subsets of the data were examined using correlation coefficients and *principal component analysis* (PCA). PCA is frequently used for identifying pollutant sources affecting the air quality. PCA attempts to explain the variance of a large set of intercorrelated variables (the observed air quality data) with a smaller set of independent variables (the principal components). This procedure is advantageous because detailed information regarding atmospheric chemistry and meteorology is not required. The initial set of principal components generated by PCA are not readily interpretable. The first principal component is created to explain as much of the variance as possible. The second principal component tries to explain as much of the remaining variance as possible and so on. This analysis results in a number of possible distinct sources being grouped together. PCA is one method of a collection of qualitative and quantitative techniques for data analysis which collectively termed *factor analysis* (FA). There is a considerable literature on this topic (Martens and Naes, 1989). *Chemical mass balance* (CMB) methods are designed to apportion aerosol mass of each sample quantitatively amongst a number of contributing sources. This is possible if each source is characterized by a specific chemical pattern (as in Fig. 3) and provided there are at least as many variables as sources. Table I shows the results obtained by principal component analysis on a 34 sample set of trace elemental data for 6 fractions of size separated air particulate matter in the altiplano in Bolivia. Five distinct components explain the variability of the concentrations : soil derived dust, particles related to biological processes (forest fires or agricultural burning?) plus three components with unknown origin labelled as sulfur, lead and calcium because of the predominance of these elements.

Table I : Percentage variance in the data of the different size fractions of remote aerosol explained by the identified components (F. Adams, 1983).

Fraction μm	Variance explained by component				
	Soil	Sulphur	Lead	Calcium	Burning
16-8	64.9	12.9	14.2	-	-
8-4	58.9	16.5	15.8	-	-
4-2	57.0	19.8	7.7	8.4	-
2-1	54.6	19.6	12.9	-	-
1-0.5	31.3	27.3	8.9	7.7	18.5

3. SAMPLING OF PARTICULATE MATTER FROM THE AIR

Different methods of separation of particles from the air use sedimentation, electrostatic or inertial collection, centrifugation, or filtration. *Filter sampling* in so-called high volume samplers, is often used and is still prescribed in most official standard procedures as it is easy, straightforward and cheap. Filters can collect almost all sizes of particles. The simplest filter materials are porous filters (e.g. cellulose) which can be extracted after sampling with organic solvents, water and acid solutions for

subsequent organic and inorganic analysis. Alternatives are membrane filters composed of thin films of porous polymers (e.g. Millipore and Nuclepore with a controlled pore size). The bulk aerosol collected with filtration samplers depends, however, on their design characteristics; the cut-off diameter of the larger particles is especially poorly defined. It has become common to equip such samplers with a special inlet system, so that an upper cut-off (e.g. 15 μm or 10 μm) is established. To provide such cut-off values or even lower ones e.g. 5 μm , *cyclone* preseparators are often employed.

The diameter of non-spherical particles is operationally defined as the *aerodynamic particle diameter* (d_{ae}), the diameter of an hypothetical sphere of unit density with the same settling velocity as the particle under consideration.

Any discussion of environmental standards and measurements implies the use of terms such as total dust or *total suspended particulate* material (TSP). Common bulk samplers do not collect all sizes with equal probability and accidental selection characteristics depend strongly on the speed and direction of any external wind. Actual sampling conditions thus play an important role in defining the aerosol sampled. Filter sampling is also affected by various sources of error : direct errors in air volume or flow rate, air leaks in the sampling train, wrong calibrations, sample losses during and after sample collection, wrong estimates of filter blanks, contaminations. Sampling errors are often more important than analytical errors.

Filter materials are often selected on the basis of their purity as blank problems otherwise would affect the analytical results unless the particles are removed from the filter substrates. Hence, for inorganic analysis a pure (from trace elements) cellulose type filter material is often preferred for routine applications whereas glass fiber filters are used for organic analysis because they are free from organic contaminants. Cellulose or glass fiber filters tend to sample the particulate matter into the inside of the filter. Membrane filters, on the other hand, act as screens and collect the particle at their outer surface. Filter collection systems have practically no capability of resolving the particle size distribution. "Two filter" sampling trains exist but have a limited use. They consist of e.g. a combination of a Nuclepore filter with pore size in the range of 5-8 μm , and in series another filter with much smaller pore size (e.g. 0.4 μm). This difficulty in sampling according to size precludes measurements in terms of the "*inhalable particulate matter*" i.e. the fraction of the size population likely to penetrate the human respiratory tract. Technological advances towards increased burning efficiency of fossil fuel and better control mechanisms for stack emissions decrease large particles emissions considerably, hence, increase the relative importance of the particles in the respirable range. Of the collection systems with capability of size classification, *inertial impactors* are most popular. The schematic working principle is shown in Figure 5. There are many designs base on the same underlying principle : an aerosol jet is forced to change its direction and particles too large for following the streamlines are collected by impingement on a collection plate. In *virtual* impactors the same principle is used to separate particles according to their inertia in two parallel streams where they remain airborne and can be separated by e.g. filtration. *Cascade impactor* arrangements use this principle repeatedly to collect particles in several (typically 6-8) size fractions.

The cut-off size of any impactor stage can be calculated from the geometric, fluid and particle diameters. Theory shows that properly designed impactor stages will provide sharp classification between particles above a certain d_{ae} which are collected and smaller particles which are not. Disturbing effects may be due to interstage losses (particles deposited on surfaces other than the impactor plates), particle re-entrainment (bounce-off or blow-off in the airstream) and inlet losses. Table II shows a practical example of the importance of particle size classification where the mass median diameter is used to calculate the fraction deposited in several respiratory regions of the lung.

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

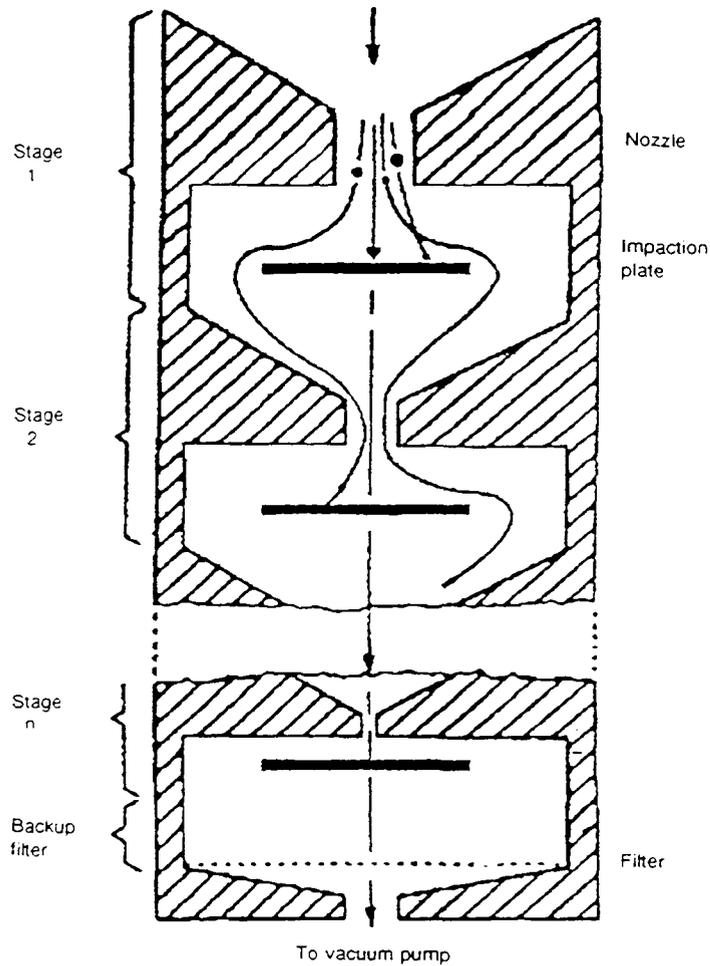


Figure 5 : Design of a cascade impactor. Three stages of aerodynamic flow are shown. The last stage is usually a membrane filter.

Whereas normal impactors are designed to provide sharp cut-offs, in some cases it is desirable for the cut-off to be a specific function of particle size e.g. simulating the retention of the human lungs of respirable dust. Figure 6 shows an example. Another commonly used concept is "PM 10" (a US Federal Reference of inhalable dust) to sample particulate matter below $10\ \mu\text{m}$. In the same way e.g. PM 2.5 refers to the atmospheric aerosols with $d_{ae} < 2.5\ \mu\text{m}$; TSP is commonly defined as $d_{ae} < 30\ \mu\text{m}$. Particles with $d_{ae} > 30\ \mu\text{m}$ are giant particles. Artifacts observed in sampling atmospheric trace components employing filter techniques were originated in the development of the clearcut separation between gases and particulate matter with *demuder* systems. In its most elementary form a denuder is a cylindrical tube coated with a reagent which selectively samples a specific gaseous or volatile component from an aerosol. The concept is schematically shown in Figure 7. Thermal denuders rely on heated tubes in which specific aerosol particles are evaporated and decomposed. Methods for monitoring or studying air pollution consist in general of several stages : sample collection, analysis and finally data interpretation. These distinct stages in the entire problem solving process are interdependent. They also depend on the overall area of concern (ambient, source, or exposure monitoring, ...), then on the analytical entities under scrutiny (trace elements, speciated

elements, organic compounds, specific crystallographic structures, ...), and finally on the aim of the study (human toxicology, pollution abatement, meteorology, climatology, ...).

Table II : Mass median diameter of iron, lead and benzo[a]pyrene of typical urban aerosol and percentage deposited in respiratory tract (F. Adams, 1983).

	mass median diameter	nasopharyngeal	tracheo-bronchial	pulmonary
iron	2.7	48	7	22
lead	0.56	17	6	32
benzo[a]pyrene	0.15	5	7	39

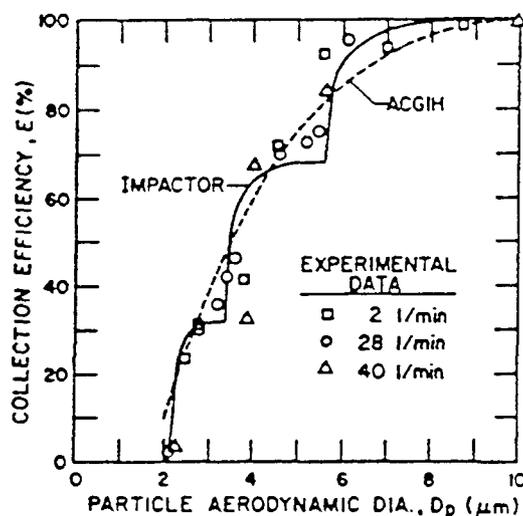


Figure 6 : comparison of the ACGIH respirable curve to theoretical and experimental collection efficiencies of impactors (Maple V.A., 1982).

4. ANALYTICAL CHEMISTRY OF BULK AND SIZE FRACTIONATED PARTICULATE MATTER

Analytical chemistry of the bulk aerosol and size fractionated atmospheric particles have in the past been performed with many different inorganic and organic analytical techniques. Emphasis needs to be placed on rapid, sensitive, *multi-element* (or for organic analysis *multi-component*) methods. Not only is rapid and panoramic analysis necessary to handle the large sample loads often encountered, but also these characteristics help to reveal significant correlations between different pollution components and different pollution sources. In addition, the ability to measure more elements or components than just a few ones, often does not significantly raise analytical costs, but greatly increases the usefulness of the results. Another important factor is *specificity*. There is a growing interest in analytical methods capable of identifying the actual chemical compounds in which potentially toxic trace elements exist in the aerosol. This is the area of *speciation* analysis performed often with hyphenated analytical methods (combinations of a separation based on

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

chromatography e.g. gas chromatography, with a specific spectroscopical detection method e.g. atomic absorption spectrometry). Another area of quick advance is in the *microscopical* or *surface sensitive* detection of elemental and organic impurities.

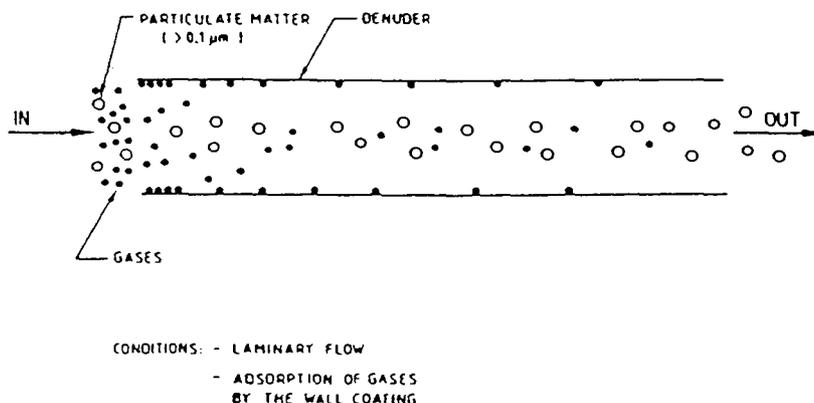


Figure 7 : Diffusional separation of gases and particulate matter in a denuder tube (Slanina, 1992).

Some of the most successful analytical techniques derive their advantages from the absence of the need for chemical separations or of dissolution of the solid material. For inorganic analysis dissolution of the particulate matter for analysis is not always a trivial task. It is, moreover, often quite time consuming. Hence, direct non destructive methods of analysis have a definite advantage.

4.1 Inorganic analysis

The elemental analysis of air pollution particulate samples is a unique problem. The total amount of material sample is usually small (down to mg amounts); it becomes much smaller still for size fractionated material (a few tens of μg per size). This small sample contains a broad range of potentially interesting elements (and compounds) at variable concentration levels. Several methods are in routine use.

We will present here 6 of them, the most important in routine air particulate analysis: neutron activation analysis (NAA), X-ray fluorescence analysis (XRF), particle induced X-ray emission (PIXE), atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP-AES) and ditto mass spectrometry (ICP-MS). The basic principles are explained in Table III. Three of these methods (XRF, PIXE and instrumental NAA or INAA) allow non-destructive multielement analysis of solid samples and can be applied on the aerosol particles as they are sampled on a filter or an impactor surface. 30 to 40 elements are typically observed by INAA (but not all of them can be considered as relevant data) versus only 15-20 by XRF or PIXE. The latter two methods offer high speed and the advantage of low cost (in the case of XRF) or small sample size requirements (in the case of PIXE), so that they are often preferred in programs, where large sample loads are encountered. INAA also suffers from the limited (and declining) availability of research reactors. AAS although a single element technique and suffering from the fact that the analyte element has to be brought in solution before analysis, is perhaps the most widely applied method for aerosol analysis, especially in the graphite furnace electrothermal (ET-AAS) variety instead of the technologically simpler flame atomization. It thanks this status to its modest cost, the simplicity of operation, and its high sensitivity for a number of toxicologically important elements (e.g. Cd, Hg and Pb). ICP-AES and ICP-MS are now considered as attractive all round methods despite the fact that the particulate matter needs to be dissolved (or extracted) before analysis. Their advantage is derived from the panoramic analytical potential and the high sensitivity

(especially for ICP-MS). Detection limits as ppm in the particulate material for 16 elements are given in Table IV for the six analytical methods. They are compared with average concentrations in urban aerosols. For AAS ICP-AES and ICP-MS the detection limits assume that solutions were obtained with a concentration of 0.1 % particulate matter. As a few ml of solution are required in the ICP methods, this implies that several mg of sample are available for analysis. In ETA-AAS only 10-100 μl of sample solution is required for a single analysis, but as the determinations are mono-elemental, mg amounts of sample are necessary. In INAA the sample size required for analysis depends on the neutron flux available for irradiation, but is typically of the order of a few mg of sample. The 100 $\mu\text{g}/\text{cm}^2$ particulate loading on the filter substrate are samples sizes that can be readily achieved for filter sampling. For size fractionated sampling with cascade impactors such loading cannot be achieved. Detection limits of PIXE can be optimised to about a factor of 10 better than in XRF. Detection limits in XRF assume the measurement with an energy dispersive (ED) system. With wavelength dispersive (WD) systems considerably lower detection limits are achieved at the expense of a more cumbersome analytical procedure. It is apparent from Table IV that none of the three non-destructive techniques (INAA, XRF and PIXE) is sensitive enough to determine all relevant elements in urban particulate matter. Besides all methods considered here are only suitable for metallic elements; non-metals such as H,C,N,O,P,S and the halogens exhibit high detection limits or cannot be determined at all. Hence, the *mass balance* cannot be readily obtained.

Table III : Characteristics of inorganic methods of analysis.

NAA	Sample with filter are irradiated with thermal neutrons in reactor; Induced radioactivity is measured after separation (radiochemical NAA) with gamma-ray spectrometry (instrumental NAA/INAA) requires reactor ; multi-element, time consuming, easy calibration, accurate
XRF	Sample on filter are irradiated with X-ray tube (usually with monochromatic radiation) Fluorescent (characteristic) X-rays are measure with energy dispersive detector (ED) or (exceptionally for aerosols) with a wavelength dispersive (WD) spectrometer easy to apply for filters (more difficult for cascade impactors) quantitation difficult (absorption effects of radiation)
PIXE	Sample on filter is excited with MeV particle beam Characteristic X-radiation is measured with ED detector. requires accelerator, more sensitive than XRF, same general characteristics
AAS	Sample is brought in solution and is atomised in flame (FAAS) or in graphite (electrothermal) furnace (ETAAS). Absorption of characteristic radiation of analyte is measured and related to concentration widely available and cheap instrument, time consuming and difficult to apply for many elements (mono-element);
ICPAES	Same preparation as in AAS but solution is aspirated in inductively coupled plasma and analyte elements are excited Characteristic emission lines are measured with optical spectrometer moderately sensitive, large elemental range
ICPMS	same as in ICPAES but ions formed in plasma are detected with quadrupole mass filter or exceptionally magnetic mass spectrometers; more sensitive than ICPAES and AAS; widely panoramic (all elements), interferences

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES

Table IV : Detection limits in $\mu\text{g/g}$ particulate material for 6 analytical techniques. Comparison with average concentrations in urban aerosol (W. Maenhaut, 1989).

Element	Detection limits						Conc. in urban aerosols
	INAA	ED-XRF ^a	PIXE ^a	ETA-AAS ^b	ICP-AES ^b	ICP-MS ^b	
As	40	40	4	0.2	35	0.04	62
Cd	100	60	100	0.003	1.7	0.06	46
Cr	10	160	8	0.01	4	0.06	150
Cu	1000	60	3	0.02	3.5	0.32	2000
Hg	5	70	10	2	17	0.02	15
In	1		140		40	0.07	2.5
Mn	6	120	6	0.01	0.95	0.10	750
Mo	2000	50	19	0.02	5.5	0.04	32
Ni	500	50	4	0.2	6.5	0.10	200
Pb		80	11	0.05	30	0.05	12000
Sb	10	80	140	0.1	20	0.05	93
Se	10	20	4	0.5	50	0.79	25
Sn		80	160	0.1	17	0.06	200
Tl			11	0.1	25		0.5
V	10	200	13	0.2	3.5	0.03	500
Zn	50	50	3	0.001	1.2	0.21	5200

^a A particulate loading of $100 \mu\text{g}/\text{cm}^2$ on the filter was assumed

^b For solutions, containing 0.1 % dissolved particulate material

The foregoing remarks pertain for routinely determined impurities in pollution aerosols. Other methods are often applied in specific situations e.g. anodic stripping voltammetry (ASV) and various forms of isotope dilution mass spectrometry (IDMS). Laser excited atomic fluorescence spectrometry (AFS) has an extreme sensitivity as compare with the other spectrometric techniques e.g. for Pb determinations in the remote environment where femtogram detection limits have been demonstrated (Bolshov et al., 1989).

4.2 Organic Analysis

Organic compounds reach the atmosphere from widely differing anthropogenic and natural sources. Estimates of the direct particulate organic carbon emission range up to 50 Mtons/year; gas-to particle conversion adds another 60 Mtons/year to this number. With an average particle life time of 4-10 days this implies a total organic carbon burden of 1-6 Mton. The variety of organic compounds present in the aerosol must be enormous, and it is an hopeless task to try to devise methods of analysis for all the individual compounds assumed to be present. The measurement of low concentrations of organic compounds in the atmosphere has been a subject of research for many years. Measurement methods are now well established for relatively non-polar volatile organic compounds (VOCs) such as chlorinated and aromatic hydrocarbons. These compounds are routinely sampled from the gas phase of the air with stainless steel canisters followed by cryogenic sample preconcentration, gas chromatographic (GC) separation and measurement with a sensitive

detector. Fully automated equipment is now available designed to meet standard procedures such as the U.S. Environmental Protection Agency's (EPA) TO14 compendium method. Detection is based on flame ionization or mass spectrometry (MS) in GC/MS instruments. GC/MS is the method of choice for analysis but fails for the analysis of about 50 % of extractable organic matter : only relatively volatile, non-polar and thermally stable compounds can be subjected to GC separation. More complex separations by liquid chromatography (LC) are necessary for the other compounds. The less-volatile organic compounds such as those emitted as primary emissions from gasoline- and diesel powered vehicles are present in inhalable fine particles. They are called collectively polar VOCs (PVOCs) and their measurement is more difficult than that of the VOCs. Research to date is guided by the mutagenic and genotoxic potential of certain compounds in this particulate phase e.g. polycyclic aromatic hydrocarbons (PAH), oxygenated PAH (oxy-PAH) and nitroarenes.

GC/MS is used for analysis after high volume sampling or size-fractionation. Methods of sampling and analysis should take into account partitioning of these compounds between the air and the particulate phase. We cannot go in detail on the extremely complex subject of the sampling and analysis of the organic compounds.

4.3 Speciation Analysis

Each of the many physico-chemical forms (or species) of a given trace element has its own characteristic environmental distribution and interactive effects -beneficial or toxic- with living organisms. An increasing awareness of this species-specific behaviour over the course of the past two decades has triggered the development of new analytical opportunities -commonly referred to as speciation analysis- and stimulated the creation of techniques combining separation and specific detection which are now approaching maturity (Broekaert et al., 1990). These methods which combine a chromatographic technique for separation with a spectrometric technique for detection are termed *hyphenated* methods. Thus speciation, in its generally accepted sense, may be defined as the qualitative (identification) and quantitative determination of the individual forms that together comprise the total concentration of a particular trace element.

Lead was the first trace metal on which attempts to apply speciation analysis were focused in atmospheric analysis. This was due to the importance of obtaining information on the fate of organolead compounds in the environment. Tetraalkyllead (TAL, with alkyl- either methyl or ethyl) was produced and used in huge quantities (up to $3.5 \cdot 10^5$ tons annually in the 1970's) as gasoline additives to prevent premature ignition of the air-fuel mixture in internal combustion engines. Despite the fact that the specific form in which the compounds entered the atmosphere is largely inorganic (TALs are unstable compounds which decompose to inorganic lead in the biosphere), emissions were since long suspected to modify the "total lead" burden considerably.

The use of gas chromatography coupled to atomic absorption spectrometry or atomic emission spectrometry (GC-AAS and GC-AES) have contributed considerably in elucidating the biogeochemical cycle of organolead compounds in environmental air and the pathway of its breakdown products in the environment. Analytical methods for analysing these compounds are now sensitive enough to detect the organolead at concentrations of a few picogram per gram in snow and ice in central Greenland, thus providing a proof for the long range transport of these compounds (Łobinski R. and Adams F., 1992).

4.4 Isotopic analysis

The measurement of stable isotope ratios can provide information on the aerosol e.g. it can help in tracing the origin of particulate emissions. Applications are few in the literature and concern either

source tracing of volcanic emissions, through the accurate measurement of various isotope ratios, or the characterization of sources of lead using stable lead isotopes. In this case the isotope ratios of source related materials such as coal and leaded gasoline are measured and compared with the ratios in airborne lead. Tracer experiments based on the use of lead ores from Broken Hill and Mt. Isa in Australia were used to investigate the importance of organolead emissions as a predominant lead source in the environment.

5. CHARACTERIZATION OF INDIVIDUAL ENVIRONMENTAL PARTICLES

Bulk analytical methods suffer from a major limitation caused by the fact that even after size classification environmental particles are morphologically and chemically quite heterogeneous. Thus, in such studies it is impossible to differentiate between a high concentration of a given component present in only a few particles or alternatively a low concentration present in all or most of the particles. Several microanalytical techniques can be applied to the analysis of particulate environmental samples. Such microanalyses can reveal whether a specific element or compound is uniformly distributed over all the particles of a population or whether it is a component only of a specific group of particles. Sometimes even the element distribution within a single particle can be inferred. In this way it becomes more straightforward to assign particles to specific emission sources (by analyzing particles with a specific composition or shape), while also more refined information about source mechanisms and heterogeneous surface reactions can often be derived.

This section is concerned with the techniques that are suited for the analysis of individual particles by means of characteristic physical interactions between electrons, ions or photons and the specimen.

Table V gives an overview of the main analytical features of the methods considered.

5.1 Electron beam methods

The more conventional analytical electron microscope (AEM) evolved into specialised instruments such as the scanning electron microscope with x-ray analysis (SEM), the scanning transmission electron microscope (STEM) and the electron microprobe microanalyser incorporating wavelength dispersive (WD) and/or energy dispersive (ED) X-ray analysis. In addition there exist the possibilities of measuring transmitted electrons in the transmission electron microscope (TEM), now with a lateral resolution at the atomic level. Selected area electron diffraction (SAED) provides structural information on the microscopical level. In electron energy loss spectrometers (EELS) possibilities exist for obtaining chemical information through the measurement of the electron energy spectrum as well as its imaging in electron energy loss imaging (ESI). Auger and photoelectrons provide surface sensitive information in scanning Auger microscopes (SAM) and X ray photon spectrometers (XPS, or ESCA, electron spectroscopy for chemical analysis). The phenomena which arise on electron bombardment are shown in Figure 8.

Four techniques will be briefly reviewed as far as their microscopical potential is concerned (Fig. 8) : electron probe X-ray microanalysis (EPXMA), scanning Auger microscopy (SAM), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectrometry (EELS). EELS studies the primary electrons which have impinged and interacted with the sample through the excitation between a core level and an unoccupied state. EPXMA, SAM and XPS involve de-excitation processes in which a higher lying electron fills the hole produced by primary electron interactions

giving rise to the ejection of characteristic X-rays (EPXMA), Auger electrons (SAM) or secondary electrons (XPS).

Table V: *Methods for surface analysis used in studies of microparticulate solids.*

Probe	Analytical signal	Technique	Acronym	Resolution	
				Lateral	Surface
Electrons	Electrons	Auger electron spectroscopy	AES	50 nm	1-2 nm
	Electrons	Electron energy loss spectroscopy	EELS	10 nm	thin sample
	X-rays	Energy dispersive x-ray spectrometry	EDXRS	0.2 μm	2 μm
X-ray photons	Electrons	X-ray photoelectron spectroscopy	XPS	10 μm (tube)	nm
	Electrons	X-ray absorption near edge spectroscopy	XANES	1 μm (synchrotron)	nm
Low energy ions	Ions	Ion scattering spectrometry	ISS	none	nm
keV ions	Ions	Secondary ion mass spectroscopy (dynamic)	SIMS	0.1 μm	3 nm
	Ions	Secondary ion mass spectroscopy (static)	SSIMS	1 μm	nm
IR photons	Photons	Fourier transform infrared spectroscopy	FTIR	20 μm	μm
UV photons (laser)	Ions	Laser microprobe mass analysis / Fourier transform laser microprobe mass spectrometry	LAMMA / FT-LMMS	1-5 μm	50 nm
X-rays (synchrotron)	X-rays	Fluorescence X-rays	SRXRF	1 μm	none
Protons	X-rays	Micro-Proton induced X-ray micro-analysis	micro-PIXE	1-10 μm	thin sample

The methods with electron excitation give rise to high spatial resolution as the exciting electron beam can be focused to a 10 nm diameter probe and then be scanned over the specimen.

EPXMA has been used for many years now for the analysis of micrometer sized particles. Due to the development of computer controlled analysis, a large population of individual environmental particles can be analysed chemically and morphologically in a fast and efficient way. Lateral resolution is limited to about 1 μm determined by the x-ray emission volume.

AES combines a higher spatial resolution (the analytical volume is several orders of magnitude less than in EPXMA as only surface generated electrons escape the sample) with a favourable surface sensitivity of 50 to 200 nm. The strong surface predominance of carbon and sulfur on fly ash particles was first demonstrated with this method.

XPS is a powerful tool for the investigation of the chemical state at the particle surface exploiting the photoelectron binding energy shifts, while in-depth information can be obtained by ion beam sputtering. The spatial resolution of XPS has increased (through the progress in X-ray optics) to lateral resolutions nowadays of 5-20 μm .

EELS and ESI allow the identification of extremely small specific particles e.g. individual asbestos fibers. Electron microscopes require reasonably high vacuum conditions. It is not at all guaranteed that composition and shape is retained in vacuum and under intense irradiation. In order to be able to observe objects in a wet state or in a controlled gaseous environment the environmental electron microscope (ESEM) was developed.

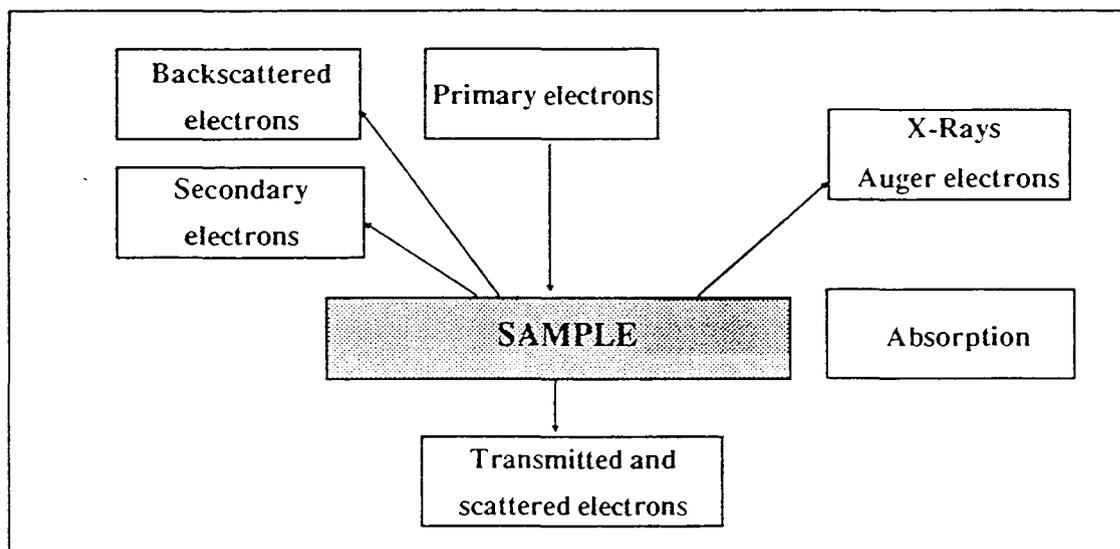


Figure 8 : Electron-matter interactions in an electron microscope.

Electron optical instruments of the various types have many advantages in the study of atmospheric particles (Adams and De Waele, 1988; Van Grieken and Xhoffer, 1992; Berghmans et al., 1993).

5.2 Ion beam methods

Several methods can be used for microscopical particle analysis. They can be divided according to the energy of the interacting projectile. In the scanning particle (proton) microprobe (SPM), a focused beam (0.5 to 10 μm , current up to 100pA) of high energy (1 to 3 MeV from an accelerator source) is scanned over the sample. A wide variety of signals can be collected and processed to obtain unique information on the sample. When the generated X-rays are measured one obtains particle induced X-ray analysis (PIXE) and elements heavier than sodium can be detected with detection limits well in excess of those in EPXMA (1-10 ppm). Backscattered particles provide information on the light elements (carbon, nitrogen and oxygen) through the Rutherford backscattering (RBS) analysis. The proton beam interaction also generates gamma-rays from nuclear interactions which can be used in particle induced gamma emission (PIGE).

Low energy primary ions (e.g. A or Cs^+ in the keV range) give rise to sputtering of secondary ions from the target which can be separated in a mass spectrometer in a technique called secondary ion mass spectrometry (SIMS). Ion microscopes and ion microprobes extend the technique to the microscopical analytical level with now a submicron lateral resolution. Applications for individual atmospheric particle analysis are few but will certainly increase in the near future. As a function of time erosion progresses and deeper inside layers of the material are analysed. The three dimensional image of a particle can be reconstructed with suitably automated systems.

In static SIMS (SSIMS) the primary ion beam current density is lowered to values corresponding with a sputtering rate as long as several hours for one monolayer. In such conditions SIMS

becomes a true surface sensitive technique of the top surface layer with high (sub-monolayer) detection sensitivity for organic as well as inorganic components.

5.3 Light beam methods

Laser microprobe mass analysis (LAMMS) is based on the mass spectrometric analysis of ions formed by the interaction of a high power density pulsed laser beam with the sample. LAMMS has several interesting features as it allows the detection of all elements and in addition organic material with quite good detection limits in samples as small as a few μm . The method has been intensively applied in single particle analysis. Drawbacks are the fact that the technique is rather irreproducible and difficult to apply in more or less routine way.

Raman scattering is applied in the micro Raman spectrometer and the potential for single microparticle analysis was demonstrated for fingerprint identification of species and the determination of crystal structure. Fourier transform infrared spectroscopy (FTIR) can be exploited as a microscope. FTIR microscopy can be used for the rapid analysis of particles especially asbestos fibers.

New possibilities for the sensitive analysis of elementary composition and structure of microscopical environmental particles are coming to the fore with intense X-ray beams in microscopical (synchrotron) storage rings.

6. CONCLUSIONS

The analysis of atmospheric particulate matter can be regarded at several levels of complexity. Present standards for toxic metals in air are mostly based upon measurements of the total ambient concentration of the metals regardless of the size of the particles which contain them. Bulk filter samplers which collect all airborne particulates up to a large, rather undefined size are used to collect material which is analysed with one of the following of analytical techniques, neutron activation analysis, X-ray fluorescence, particle induced X-ray emission, flame or furnace atomic absorption spectrometry, inductively coupled plasma with emission spectrometry or with mass spectrometry. Such methods have proven their utility in many local and regional studies of the polluted urban and industrial environment.

Air particulate matter is, however, a complex and heterogeneous system and there are many reasons to study the system in a more detailed way. If one is interested in particle size dependent measurements the same methods as in bulk analysis are often applied after sampling of the particles in several aerodynamic size fractions. This separation of the particulates according to size can be done with cascade impactors for collection in a number of different sizes or with dichotomous samplers or virtual impactors for a separation in two sizes of specific interest. For such work the analytical problems become a lot more complex but the reward is undoubtedly a more profound understanding of the system studied. Generally speaking these methods are too complicated in their application to analyse large particle collections on a routine basis but analytical methods are rapidly becoming available. Individual particle analysis is essential, however, in the study of the earth's atmosphere on a global level e.g. in relation to the issue of global change.

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