

## SAMPLING AND ANALYSIS OF AEROSOLS

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Abstract - Assessment of the potential environmental hazard and toxic effects of aerosols emitted into the atmosphere requires their detailed physical and chemical characterisation. A number of instrumental, mostly multi-element or multicomponent, analytical methods are used for the sensitive bulk characterisation of particulate matter sampled from the atmosphere. Information on an individual particle basis can also be obtained with a number of microanalytical techniques. Surface analysis is used to gain insight into the heterogeneous distribution and the surface predominance of elements or organic compounds. Some methods allow chemical speciation.

### INTRODUCTION

Most metallic elements and a considerable number of organic compounds are emitted into the atmosphere in association with solid or liquid particles. Certain more volatile elements and species are emitted as vapors and the surface of finely divided particles may act as sites for adsorption or condensation. On the particle surface catalytically or photochemically induced reactions may further occur. The airborne particulate matter which is hence formed directly or through secondary reactions has a widely varying composition, aerodynamic dimension, shape and degree of uniformity. The aerosol thus consists of a complex interacting dynamic system. Particulate matter amounts to more than 50 % of all air pollutants.

The assessment of the potential environmental and toxic effects of particulate matter in the atmosphere requires their detailed physical and chemical characterisation. Of prime importance is the size of the particles, their overall and microscopical chemical composition and finally their chemical reactivity and physical characteristics.

Methods for monitoring or studying particulate 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, organic compounds or specific crystallographic structures) and finally on the aim of the study (human toxicity, pollution abatement, meteorology or climatology).

In what follows I will review some recent advances in the field from the (biased) experience of someone involved with environmental analytical chemistry; examples will be selected

predominantly from my own laboratory's experience in bulk aerosol characterisation and the analysis of individual particles and particle surface regions.

### SAMPLING

Few methods allow a direct measurement of particulate matter in the air. Different methods of separation use sedimentation, electrostatic or inertial collection, centrifugation or filtration. Filter sampling is often used and is still prescribed in most official standard procedures as it is easy, straightforward and cheap. 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. Any discussion of environmental standards and measurements implies the use of terms such as total dust or total suspended material. There are not strictly definable as the falling velocity of particulate matter depends on the air velocity. The only practical upper limit to particle size is that beyond a certain size particles become so rare that they make a negligible contribution to the total airborne mass. 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. It is hence surprising that the bulk aerosol sampled is still to this date so often referred to with little specification of the actual sampling conditions.

Filter sampling is easily affected by various sources of errors : direct errors in air volume or flow rate, air leaks in the sampling train, wrong calibrations, sample losses during or after sample collection and wrong estimates of filter blanks or contamination. Lack of agreement between identical high volume aerosol samplers to the extent of 10 % are common (Ref. 1), thus making sampling errors often more important than those in subsequent analytical procedures.

Filter collection systems have no capability of resolving the particle size distribution. This precludes measurements in terms of the "inhalable particulate matter" i.e. the fraction of the size population likely to penetrate in the human respiratory system. Technological advances towards an increased burning efficiency of fossil fuel and better control techniques for stack emissions of particles decrease large particle emissions considerably and hence increase the relative importance of particles in the respirable range.

Of the collection systems with a capability of size classification, inertial impactors are the most popular. Though there are many different types the underlying principle is simple and the same for all : an aerosol jet is forced to change its direction rapidly 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 partial streams where they remain airborne and can be separated e.g. by filtration. Cascade impactor arrangements use this principle repeatedly to collect particles in several (typically 6-8) size fractions. An overview of commercially available instruments is given by Maple and Willeke (2).

The cut-off sizes of any single impactor stage can be calculated accurately from the geometric, fluid and particle parameters. Theory shows that properly designed impactor stages will provide sharp classification between particles above a certain aerodynamic diameter collected and smaller particles which are not. Special precautions must, however, be taken to insure reliable and accurate data. Disturbing effects may be due to inter-stage losses (particles deposited on surfaces other than the impactor plates), particle reentrainment (bounce-off and blow-off in the air stream) and inlet losses dependent on the air velocity at the sampling location. A practical example of the importance of particle size classification is given in Table 1, where the mass median diameter for iron, lead and benzo[a]pyrene for a typical ambient aerosol is used to calculate the fraction deposited in several respiratory regions of the lung (ref. 3).

TABLE 1. Mass median diameter of iron, lead and benzo[a]pyrene of typical urban aerosol and percentage deposited in respiratory tract

	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

Whereas normal impactors are designed to provide a sharp cut-off, in some cases it may be desirable for the cut-off to be a specific function of particle size. Such a design for a cut-off efficiency simulating lung retention allows the collection of respirable dust. The direct advantage of such a system is that only two distinct particulate fractions need to be analysed to provide a measure of human exposure to certain air pollutants. One practical design (Ref. 4) simulates the respirable dust curve proposed by the U.S. Conference of Governmental Industrial Hygienists and is shown in Fig. 1, as an example.

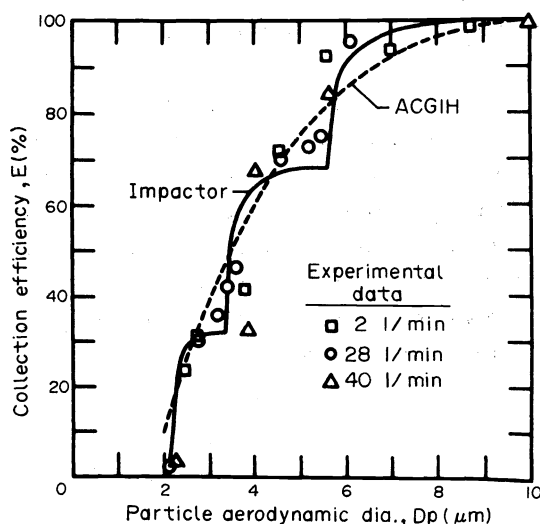


Fig. 1. Comparison of the ACGIH respirable curve to theoretical and experimental collection efficiencies of impactors (Ref. 4).

The technical difficulties in designing systems for aerosol sampling are compounded by lack of international agreement on what is understood by respirable dust. In fact, the standardisation needs to reconcile different national practices and philosophies, sometimes backed by decades of practical use. Through its Technical Committee Nr. 146 (ISO TC 146), the International Standards Organisation attempts specifications that can be applied uniformly in the workplace and in the general environment.

The measurement of particle emissions in industrial process streams e.g. in stacks, is made with filter samplers, cascade impactors or cyclones. Problems arise from the generally high velocity of the gas stream, the high temperature and the moisture content. All this makes representative particle sampling from the often very hostile environment of stacks a complicated task, requiring extensive manpower and resources. Test methods for stationary and mobile emissions tend to be specific for each industry and have a limited application. Also, the measurements are taken over short periods of time and because pollutant concentrations normally fluctuate temporarily and spatially, sequential samples cannot often be considered as representative.

#### AEROSOL ANALYSIS

Bulk aerosols and size fractionated particulates have in the past been performed with many different inorganic and organic analytical techniques. Emphasis has to be placed on rapid, sensitive, multi-element (or for organic compounds 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 pollutant components. In addition, the ability to measure more elements or components than just a few pollutants, often does not significantly raise analytical costs, but greatly increases the usefulness of the results. Another important general 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.

Some of the more successful analytical techniques derive their advantage from the absence of chemical separation. For instance for inorganic analysis dissolution of the sample is not a trivial task. Hence direct methods of analysis - that is without dissolution - have a net advantage.

#### Inorganic analysis

The elemental analysis of air pollution particulate samples is a unique problem. The total amount of material is ordinarily small but the sample may contain a large number of elements over a broad atomic number range and at widely differing concentrations. An effective analytical scheme must measure a considerable number of elements of interest; it must have good detectability in order to provide reliable results at low concentrations even in the presence of large amounts of other elements. Several methods have been widely used :

- X-ray spectrometry is attractive because it meets most of the requirements for some 20 elements. The methodology applied for air pollution analysis utilises mostly energy-dispersive detectors and excitation with X-ray tubes (EDXRF) or protons (or other elementary ions (PIXE)). Especially in the latter excitation mode sample weight can be

extremely small which allows short term sampling within a reasonably short analysis time. The difficulties inherent in X-ray spectrometry namely the data analysis of the energy dispersive spectra, and matrix absorption of the fluorescent X-rays have gradually been solved by computer analysis.

- Instrumental neutron activation analysis has been extensively used. A recent literature survey lists 225 references (Ref. 5). A drawback is that toxicologically very important elements such as lead or cadmium are insensitive.
- Spectrometric methods of analysis suffer from the need to dissolve the particulate matter (atomic absorption spectrometry or inductively coupled plasma emission spectrometry) or from limitations in sensitivity or precision (d.c. arc emission spectrometry).

There is evidence that the Zeeman background correction could be useful for the direct atomic absorption determination of a number of elements (Ref. 6).

### Organic analysis

Organic compounds reach the atmosphere from widely differing anthropogenic and natural sources. Estimates of the direct particulate organic carbon emission range between 23 and 50 M tons  $g^{-1}$ ; gas-to-particle conversion adds another 60 Mtons  $g^{-1}$  to this number (Ref. 7). With an average particle life time of 4-10 days this implies a total organic carbon burden of between 1 and 6 Mton (Ref. 8). Perhaps more important is the wide variety of organic compounds. Nevertheless the number of compounds presently determined is rather limited : in 1977 only ca. 450 had been identified in the particulate phase of the atmosphere (Ref. 9). It is an almost hopeless task to attempt to devise methods for all of the individual organic compounds which can be assumed to be present.

Major interest has been devoted till now to the determination of polycyclic aromatic hydrocarbons (PAH) because this class of compounds is related to the combustion of fossil fuels and because several of its members exhibit carcinogenic properties. Current analytical methods are based on the separation of individual compounds by thin-layer or high performance liquid chromatography (TLC and HPLC) with luminescence detection, or gas chromatography with flame ionisation detection or mass spectrometry. Gas chromatography-mass spectrometry (GC-MS) is the method of choice. It requires first the isolation of the PAH as a compound class followed by their specific determination. This procedure is not only time consuming but also isomeric pairs such as benzo[a]pyrene and benzo[e]pyrene are difficult to separate. There is a continuing interest in alternatives that would eliminate or at least simplify the concentration steps in the procedure.

Recently alternatives have appeared : luminescence using the Shpol'skii effect (Ref. 10), matrix isolation (Ref. 11) or fluorescence line narrowing (Ref. 12) spectroscopy combined with site selective laser excitation. Also the improved mass spectrometric identification based on mass spectrometry-mass spectrometry (MS-MS, also called MIKES, mass analysed kinetic energy spectrometry) has been applied (Ref. 13).

An important problem in the organic analysis with GC-MS is the lack of a reasonable mass balance. Indeed, the method only permits the determination of relatively volatile, non-polar and thermally stable compounds, which only account for about 50 % of the extractable organic matter. It has been demonstrated that PAH-derivates such a oxidised, nitrated or sulfonated compounds are important toxicologically. Such compounds are directly formed in car exhausts, emission stacks and plumes but especially during transport of PAH through the atmosphere. Analysis for PAH-derivates is presently still in a qualitative stage. Complex separations by off-line HPLC are usually required. Direct LC-MS coupling or MS-MS hold promise for future work into this area.

Another group of environmentally important compounds is the chlorinated dibenzodioxins and dibenzofurans. The different isomers of these compounds exhibit markedly different stabilities and toxicities, the hexa-, penta- and octa-chloroisomers being relatively stable and the tetra chloroisomers tetrachlorobenzodioxin (TCDD) and tetra-chlorodibenzofuran (TCDF) extremely toxic. The dioxine isomer 2,3,7,8 TCDD is considered the most toxic with an acute lethality (LD 50) in guinea pigs of  $1 \mu\text{g kg}^{-1}$  body weight (Ref. 15).

In 1977 the first reports on significant amounts of dioxins adsorbed on precipitated fly ash samples from municipal incinerators appeared. Even then, the analytical methodology needed to deal with such complex isomeric mixtures at such trace levels is still evolving and being perfected. The method of choice for the determination is GC-MS, but radio-immunoassay may be used for a preliminary screening of a large number of samples for the presence or absence of the compounds. Extraction procedures, purification steps and column packings have improved since Buser and Rappe (Ref. 16) first separated 2,3,7,8 TCDD from environmental material (and from its isomers). Results obtained at different locations agree now sufficiently to give confidence in the results (Ref. 15).

Recent reviews on the analysis of air particulate matter for organic compounds are published (Ref. 5, 14).

#### Data treatment

In the past decade multivariate data analysis methods such as e.g. principal component analysis, factor analysis and cluster analysis have become valuable tools for data treatment. Many applications of these methods for the evaluation of pollution aerosol analyses exist in the literature. These types of data sets have in general a very complicated structure as many natural and anthropogenic sources contribute to the aerosol load and composition. In contrast with this situation, at remote locations the aerosol is often made up of only a few major contributing sources. The data hence become more easily understandable. Table 2 shows the results obtained by principal component analysis on a 34 sample set of trace elemental data from the air particulate matter in the altiplano in Bolivia. Samples were taken with a 5 stage cascade impactor and 23 elements were systematically determined with PIXE and XRF. The complexity of the data set prevented the elucidation without resorting to artificial intelligence. Five distinct components explain the variability of trace elemental concentrations : a soil derived component, a component related to biological processes possibly forest fires and/or agricultural burning activities, and three components of unknown origin labeled here as sulfur, lead and calcium because of the predominance of these elements.

TABLE 2. Percentage variance in the data of the different size fractions of remote aerosol explained by the identified components.

Fraction $\mu\text{m}$	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

### Microscopical analysis

The majority of methods for the analysis of airborne particulate matter require at least microgram or milligram amounts of material. Consequently, the analytical information obtained is statistically representative of a large number of airborne particles collected. In principle, the most definitive information can only be extracted from a collection of particles by the analysis of a large number of carefully selected individual particles. Indeed, with such data it is possible to obtain information about the sources of pollution and their relative contributions to an ambient aerosol. Also, it is possible to investigate changes in the aerosol as it travels from its source. Finally, the potential effects of individual particles can be estimated in a direct and straightforward way.

Microscopical methods which have been used for the characterisation of micrometer sized particles are based on the application of light microscopy (LM), electron probe microanalysis (EPMA) or scanning electron microscopy (SEM), ion microanalysis (IPMA) and transmission or scanning transmission electron microscopy (TEM or STEM).

Light microscopy is a powerful yet simple tool which by simple observation allows the characterisation of a number of particles, their size distribution, shape and morphology down to a size limit of 0.5 - 1  $\mu\text{m}$ . Chemical identification is indirect and relies on a plethora of properties more or less characteristic of a given chemical compound. These include transparency, colour, refractive index, birefringence, size, shape and morphology. Direct chemical information is attainable by utilising microchemical reactions. These can, however, hardly be used in routine applications and they often merely indicate the presence of a particular cation or anion rather than providing information about the overall chemical composition. Besides, not many people have the intensive background in mineralogical LM required for the full exploitation of the method. Consequently, there is a tendency to replace LM by other microscopical methods which enable chemical information to be obtained from some associated spectroscopic measurement.

Analytical tools which are well suited for the analysis of individual particles include the electron beam instruments: EPMA, SEM and TEM/STEM. The X-rays induced under electron bombardment can be measured with an energy dispersive or wavelength dispersive X-ray spectrometer which forms the basis of a powerful, non-destructive multi-element analytical

capability. Size and morphology can be examined using the backscattered or secondary electrons generated by electron impact on the sample (in EPMA or SEM) or by using the primary electrons transmitted through the specimen in TEM or STEM. All these instruments provide similar data, the electron probe being optimized for analytical work and the other instruments for morphological studies. TEM produces the least intense X-ray spectra but is well adapted for the analysis of the smallest particles below  $0.1 \mu\text{m}$ , and for the exploitation of selected area electron diffraction (SAED) to derive crystallographic information about selected particles or regions thereof. Routine studies in air particulate research have been based on all of these methodologies (e.g. Ref. 18-21).

The manual analysis of particles with electron microscopes may be a very time consuming process. Minicomputer based automatic image analysis methods for analytical electron microscopy are now available (Ref. 22). They allow unaided rapid analysis of size, shape and composition of a number of particles in sequence. Particles can also be automatically classified. Fig. 2 shows one possible representation of part of the results of the analysis in less than 1 hr of 450 particles sampled near a metallurgical factory (Ref. 23). The number of particles containing more than 5 % of an element is plotted as a function of X-ray energy. The presence of a few particles which contain e.g. Ni become clearly identifiable within the collection and can be selected for a closer study. It is clear that such measurements collect large amounts of information which can only be fully processed with computer data reduction.

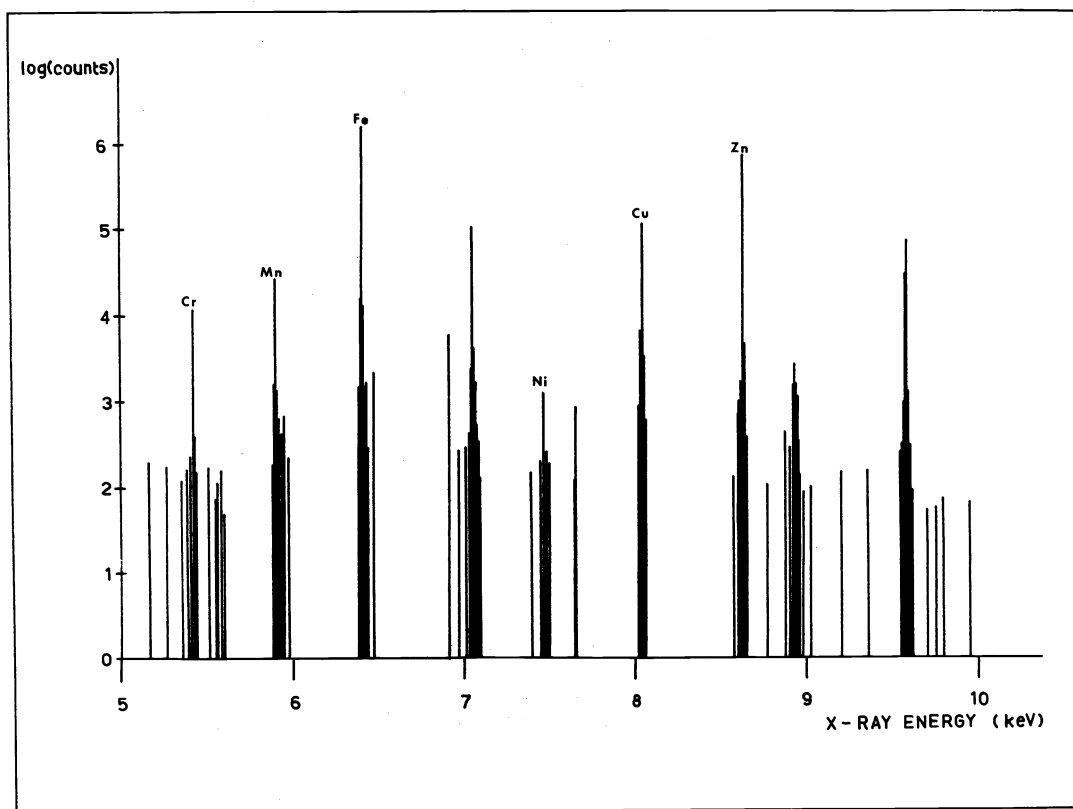


Fig. 2. Cumulative intensities of X-rays between 5 and 10 keV in 450 airborne particles collected near metal refining plant.



More recently two new instruments which utilise laser irradiation have been developed for the analysis of microscopical objects. The first is the laser microprobe mass analyser (LAMMA) which vaporises and partly ionises a selected particle with dimension down to  $\sim 1 \mu\text{m}$ . Mass analysis is performed in a time of flight mass spectrometer. The second is the laser Raman microprobe of which two types of instruments are available, the Raman microprobe developed at the National Bureau of Standards (Ref. 24) specifically for the analysis of micrometer sized particles and the now commercially available Raman microprobe-microscope MOLE (molecular optical laser examiner). Details on critical aspects of instrument design and performance and on measurement criteria have been reported. (Ref. 25, 26).

The applications of LAMMA lie in the following areas:

- qualitative and semiquantitative analysis for identifying and estimating both matrix and trace level constituents
- as a means of establishing a fingerprint to recognise sources of particulates. Fig. 3 shows as an example the positive mass spectrum of an unknown atmospheric particle present in the remote background aerosol in the Atacama desert (Chile) and the fingerprint spectrum of  $\text{NaNO}_3$  (Ref. 27). The negative mass spectra provide further evidence for the similarity in composition
- as a means for detecting inorganic and organic molecular constituents (see Fig. 5).

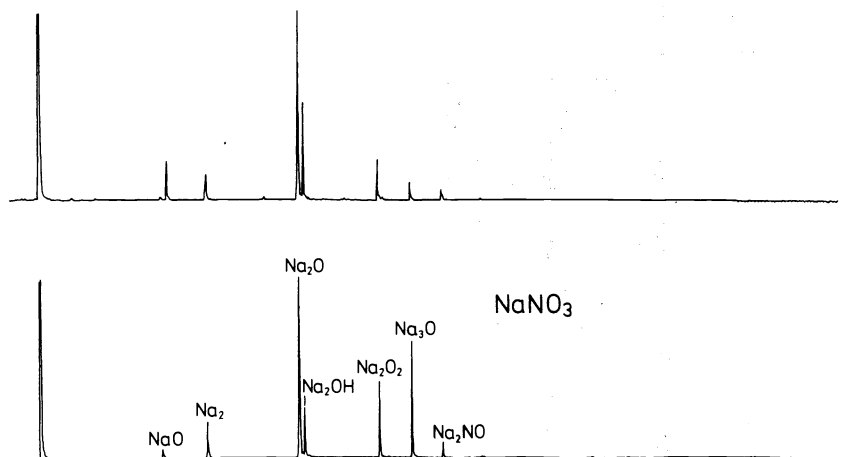


Fig. 3. Positive mass spectrum of a typical particle from Chapiquina (top) and positive fingerprint mass spectrum of  $\text{NaNO}_3$  crystals (bottom).

The Raman microprobe also has unique capabilities for particle analysis. Examples of its use are given by Etz and Blaha (28). They include the characterisation of inorganic species, microparticulate organics, the characterisation of fly ash from oil-fired combustion and the South Pole aerosol.

Single particle investigation is also possible by Auger electron spectroscopy and secondary ion mass spectrometry with an ion microprobe or microscope. These methods will be described later. Some characteristics of microanalytical techniques are summarised in Table 3.

TABLE 3. Analytical characteristics of a number of microanalytical techniques.

Method	EPMA	ion micro- cope/probe	Auger micro analysis	Laser micro Raman	LAMMA
Resolution					
lateral, $\mu\text{m}$	1	1	0.3	0.5-1	0.5
depth, $\mu\text{m}$	1	$5 \cdot 10^{-4}$	$10^{-3}$	?	0.1-0.3
Elements detected	B-U	all	Li-U	-	all
Isotopes	no	yes	no	no	yes
Molecular information	some	yes	some	yes	yes
Abs. sensitivity, g	$10^{-14}$ - $10^{-16}$	$10^{-19}$	$10^{-15}$	$10^{-8}$	$10^{-18}$ - $10^{-20}$
Rel. sensitivity (ppm)	100	1	1000	$10^4$ - $10^5$	1

### Surface analysis

The inverse dependence of trace constituents on particle size (Table 1) is due to condensation onto the particle surfaces from the vapor phase. One can thus expect to find a number of more volatile elements and compounds on particle surfaces.

The techniques which have been utilised for the analysis of surface regions are X-ray photoelectron spectroscopy, XPS (or ESCA), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). A more limited form of surface information is also available with electron probe microanalysis (EPMA) although here the depth resolution obtained is limited ( $\sim 1 \mu\text{m}$ ). Of these techniques AES and SIMS are most useful, owing to the high sensitivity and the good depth resolution resulting from etching (sputtering) with an energetic ion beam. Both methods also possess microprobe capabilities with incident beam diameters of the order of  $1 \mu\text{m}$  or below. SIMS has an extremely high sensitivity ranging from 100 ppm to  $10^{-2}$  ppm depending on the element and the primary beam used, enabling determinations at trace levels. XPS and AES provide information on molecular species and are hence useful for speciation and for the study of heterogeneous reactions on particle surfaces (Ref. 29).

For the most part applications have involved qualitative analyses since quantitative work, although possible in principle, is far from straightforward. I shall now consider microscopical SIMS as an example and consider some of the difficulties involved.

- difficulties are encountered in establishing even semi-quantitative depth scales. Depth calibration is normally obtained by calibrating the rate of removal of surface material. If this is more or less readily done with simple standard materials, with environmental particles there are considerable difficulties in matching the surface composition of a standard with that of a poorly defined aerosol or fly ash.
- the method is subject to several types of interferences and artifacts e.g. spectral interferences from multiply charged and molecular ions which may obscure measurements

even at high mass resolution.

- volatilisation losses and migration of sample species may occur under the influence of the primary ion beam. Also, the poor electrical conductivity of the samples gives rise to problems.

Applications of SIMS to the study of air particulates have been few. The method has been applied to semi-quantitative studies of the surface of coal fly ash (Ref. 29) and automobile exhaust particles in conjunction with several other microanalytical and surface sensitive techniques including EPMA, AES and ESCA. The results have proven to be of considerable importance from the standpoint of environmental chemistry and demonstrated the need for more quantitative determinations both of particle surface concentrations and of elemental depth profiles.

Van Craen et al. (Ref. 30) achieved quantitative results by applying a matrix correction procedure which corrects changes of composition with depth. Fig. 4 shows the variation of concentration with erosion time for Na and Co in a typical steel dust sample. Comparison of the interior regions of the sample with SIMS and X-ray fluorescence proved the accuracy of the depth profiles as shown in Table 4 (Ref. 31).

TABLE 4. Comparison of bulk concentrations obtained by XRF and SIMS.

element	concentration, wt %	
	XRF	SIMS
Al	0.8 ± 0.15	0.6 ± 0.15
K	1.0 ± 0.2	0.34 ± 0.12
Ca	4.0 ± 0.6	5.0 ± 0.3
Pb	1.4 ± 0.2	1.8 ± 0.4
V	0.037 ± 0.0075	0.0410 ± 0.0145
Ti	0.037 ± 0.011	0.027 ± 0.006

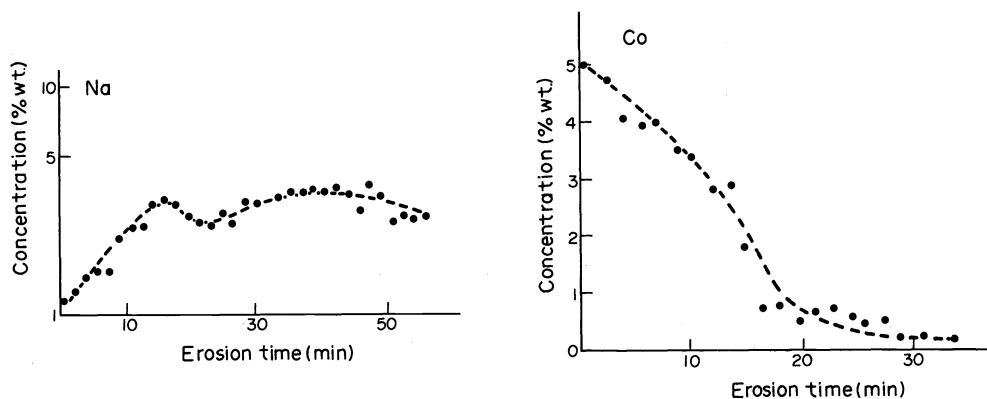


Fig. 4. Concentration vs. erosion time depth profiles for  $\text{Na}^+$  and  $\text{Co}^+$  (Ref. 30).

Solvent leaching can also provide insight into the surface predominance and even the association of elements in the surface region. Moreover it provides information on the solubility of compounds present. For example although AES and SIMS indicate little surface enrichment of iron in coal fly ash, aqueous leaching rapidly removes this element indicating its presence in a readily soluble form.

There are few examples in the literature on the detection of the surface predominance of organic material e.g. the polycyclic aromatic compounds. Laser microprobe mass analysis used under laser desorption conditions appears to readily be able to detect organic impurities on single particles (Ref. 31). Fig. 5 shows the LAMMA laser desorption spectrum of a Diesel exhaust particle. Several molecular ions which can be attributed to polycyclic aromatic compounds are present.

Contamination of asbestos fibers with organic products e.g. polycyclic aromatic compounds, or plasticisers can equally be studied with laser desorption LAMMA. Fig. 6 shows on characteristic example.

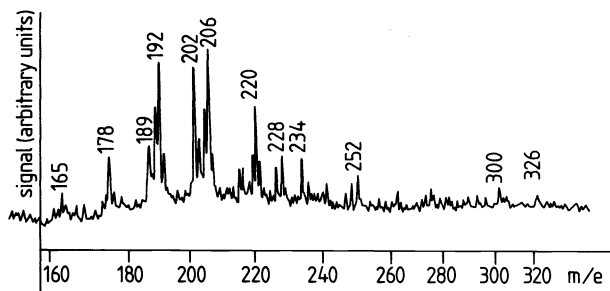


Fig. 5. Positive laser desorption LAMMA spectrum of a Diesel exhaust particle.

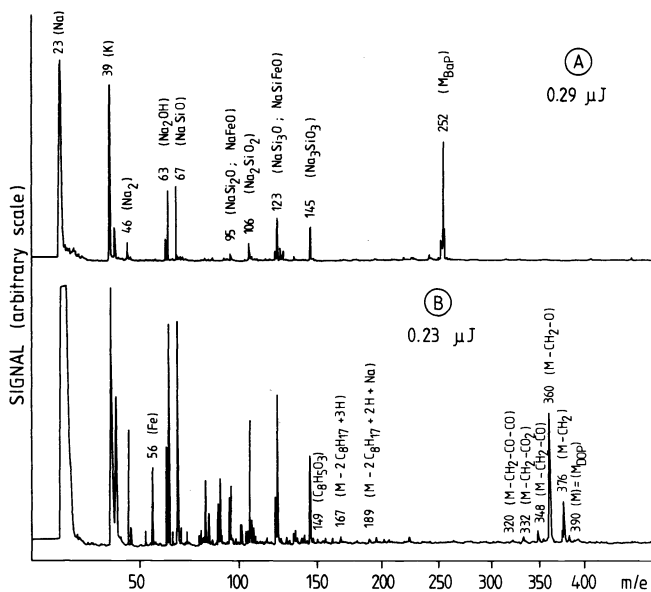


Fig. 6. Positive laser mass spectra of benzo[a]pyrene doped crocidolite (580 ppm) (A) and of di-(2-ethylhexyl) phtalate ( $\sim 1000$  ppm) (B) as surface contaminants on crocidolite.

### Determination of chemical form and crystallographical structure

There is a wealth of information available regarding the concentration of elements in atmospheric particles. However, most of the element related problems facing environmental and toxicological scientists remain unsolved because mostly the chemical form in which the elements are present remains unknown. Also the toxicity of some air pollutants such as asbestos is related to their particular crystallographical structure.

We have seen in a preceding paragraph that microanalytical methods provide compound related information. These methodologies however, are in general hampered by inadequate detection limits. The following examples give further information on species selective determinations in a few important areas.

1. The assessment of asbestos pollution requires analytical methods which provide an accurate identification of fibers and a determination of fiber concentration. The problem is compounded by the existence of different varieties (chrysotile, crocidolite, amosite, tremolite, anthophyllite) and also by the occurrence of non-asbestos fibers (e.g. glass fibers). Asbestos is present in the respirable fraction of the urban aerosol in concentrations of the order of a few  $\text{ng m}^{-3}$ , although they may be present at much higher concentration levels in or near factories or mines. Diameters range between about 20 nm and several hundred nm and lengths from ca. 100 nm to several  $\mu\text{m}$ . Presently the only successful approach for their measurements in the particulate fraction of the air or water samples consists in their identification with TEM or STEM. Single particle quantitative X-ray analysis or at least the measurement of the ratios of elemental intensities is required for a more or less safe identification. There is an uncertainty of identification and a non-negligible possibility for a confusion between asbestos minerals and others which happen to have a similar (silicate) composition. Therefore, morphological characterisation and crystal structure as obtained by SAED are often considered mandatory (Ref. 33, 34).

Such a procedure is very time consuming and it has been stated that asbestos is the only of the 129 priority pollutants selected by the Environmental Protection Agency for which a recommended procedure is not available (Ref. 35). As a result of systematic measurements on some 30 different asbestos samples of widely differing origin, I believe that LAMMA could provide a fast and cost effective alternative. The characteristic positive and negative fingerprint mass spectra provide enough information on elemental constituents but also the molecular ions are of considerable help. Fig. 7 shows schematically the relative intensities and variation coefficients as obtained for the 5 standard compounds prepared by the International Union against Cancer (UICC) (Ref. 36). Compound specific bulk methods of analysis such as X-ray diffraction (XRD) are not in general suitable as the concentration of asbestos in nearly all practical situations is too small.

2. The characterisation and classification of atmospheric sulfates is also a topic of concern, arising from the possible association of sulfates with adverse health effects and from their importance in the acid rain problem. Biggins and Harrison (37) have reviewed the current state of knowledge and identified the sulfate species summarised in Table 5. The dominant species  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  are omitted from the table. The tertiary nature of some compounds results from the reaction of secondary sulfate (formed from  $\text{SO}_2$  in the atmosphere) with other compounds. The lead containing species given in the table, result from vehicle exhausted lead halides. All these compounds were identified by XRD.

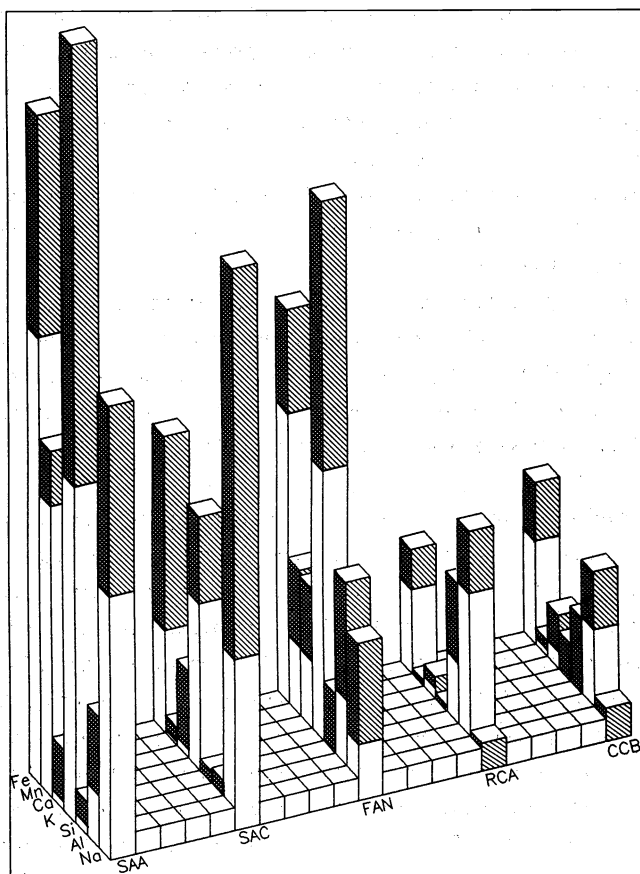


Fig. 7. Relative intensity ratio to  $^{24}\text{Mg}$  for a number of elemental constituents in positive LAMMA spectra. SAA and SAC : South African amosite and crocidolite (SAC : scale divided by 10), RCA and CCB : Rhodesian (Zimbabwe) and Canadian crocidolite, FAN : Finnish anthophyllite. One standard deviation is indicated for repeated analysis of different fibers (Ref. 27).

TABLE 5. Sulfate species identified in the atmosphere.

Classification	Compound
Primary	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Primary	$\text{Na}_2\text{SO}_4$
Primary	$\text{PbSO}_4$
Primary	$\text{PbO} \cdot \text{PbSO}_4$
Secondary	$\text{PbSO}_4$
Secondary	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{HSO}_4$
Secondary	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
Tertiary	$\text{PbSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$
Tertiary	$2\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$
Tertiary	$\text{Fe}_2(\text{SO}_4)_3 \cdot 3(\text{NH}_4)_2\text{SO}_4$
Tertiary	$\text{ZnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

There are many inherent difficulties in speciation of atmospheric strong acids because they must be detected apart from the simultaneously present precursors ( $\text{NO}_x$ ,  $\text{SO}_2$ ). Therefore it is in general necessary to combine a chosen detection system with an appropriate sampling and sample pretreatment procedure. A few in-situ techniques are available such as nephelometry for  $\text{H}_2\text{SO}_4$  (Ref. 38).

3. The speciation of metals is a difficult task. Nevertheless, pollution incidents involving mercury have shown that the total metal data are insufficient and often misleading in assessing the potential hazards.

Until recently most metal speciation was performed with electrochemistry, especially anodic stripping voltammetry, or chromatography with conventional detectors. Gas liquid chromatography is suitable for the separation of volatile compounds but recently it has been supplemented with more metal-specific detectors such as atomic absorption spectrometry (AAS) (Ref. 39) or microwave plasma detection (MWDP) (Ref. 40).

My laboratory has been involved during the last 6 years with GC-AAS for the determination of selenium and lead compounds in the atmosphere. Chromatography combined with AAS proved to be an extremely versatile and specific methodology. Detection limits down to ca. 100 pg absolute or  $100 \text{ pg m}^{-3}$  relative could be reached for organolead species (Ref. 41). Three methylated selenium compounds could be detected in environmental air and biomethylation of selenium could be proven (Ref. 42). Organic lead compounds on the other hand derive their significance from the huge amounts of tetraalkyllead (TAL) compounds consumed in leaded gasoline. TAL and especially its degradation product trialkyllead halides (TriAL) are much more toxic than inorganic lead. TAL's are volatile and hence present in the gaseous fraction of the aerosol, the TAL content of the particulate fraction being extremely small. They can be collected on adsorbents or trapped cryogenically for analysis (Ref. 43). The TriAL compounds and their further degradation products the dialkyllead salts are considerably less volatile and hence cannot be determined readily by GC/AAS (Ref. 44).

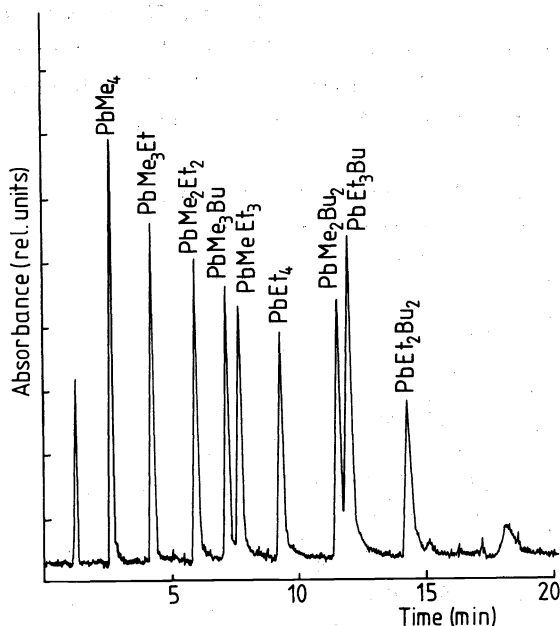


Fig. 8. Gas chromatogram with graphite furnace AAS detection of standard mixture of TAL's and butylated TriAL and DiAL compounds.

A breakthrough in the direct speciation of alkyllead compounds in environmental samples was recently published by Chau et al. (Ref. 45). Di- and trialkyllead compounds and inorganic lead are quantitatively extracted from aqueous solutions by chelation/extraction with dithiocarbamate and benzene. The alkyllead compounds are butylated by Grignard reagent to the tetraalkyl form,  $R_nPbBu_{4-n}$  (R = methyl or ethyl, Bu = butyl) and inorganic lead to  $Bu_4Pb$ , all of which are determined together with GC/AAS. TAL compounds in the sample are also extracted and determined simultaneously. A detection limit of  $0.1 \mu\text{g l}^{-1}$  was obtained in water samples. Figure 8 shows a characteristic chromatogram obtained with graphite furnace AAS detector. All individual species are clearly identifiable. Up to now this method was not applied in air pollution research.

A less elegant procedure based on successive extractions and AAS was applied in our laboratory for the specific determination of TriAL compounds (Ref. 46). It appeared that rain water samples obtained in our near cities contains a concentration of these toxic compounds at a level of  $\sim 150 \text{ ng l}^{-1}$ , a concentration about 1000 times lower than that of inorganic lead (Ref. 47). In view of the toxicity of these compounds (the LD is roughly an order of magnitude higher than that of  $Pb^{2+}$  in rats) and the possibility that they become accumulated in the biosphere, this is significant. In one earlier study by Nielsen et al. (Ref. 48) a considerably higher concentration of organic lead was found in the brain tissue of city dwellers than in that of village people. Similar chemical speciation needs exist for mercury, selenium, arsenic, chromium and perhaps several other elements.

Most of the TAL compounds in gasoline reacts during combustion with ethylene dihalide 'scavengers' with the consequent emission of the lead in an inorganic particulate form, predominantly  $PbBrCl$ . The association of the halogens especially Br with lead has been used for tracing automotive lead:  $PbBrCl$  should give a Br/Pb mass ratio of 0.38. It has been reported, however, that the lead halide is not stable in the atmosphere with a progressive loss of the halogens in a volatile form (Ref. 49). Three compounds identified by XRD as components of vehicle exhaust are  $PbBrCl$ ,  $PbBrCl \cdot 2NH_4Cl$ ,  $\alpha\text{-}2PbBrCl \cdot NH_4Cl \cdot PbSO_4$  and  $PbSO_4 \cdot (NH_4)_2SO_4$  (Ref. 50). Since lead represents only of the order of 1 % of the total particulate matter in air, enrichment either by density separation or by preferential sampling of the smallest particles which contain most of the lead was necessary.

Street dusts and roadside soils become enriched with lead with concentrations ranging between the  $1000\text{-}4000 \text{ mg kg}^{-1}$  near busy streets. Speciation of lead in dusts have been carried out by Olson and Skogerboe (Ref. 51) and Biggins and Harrison (Ref. 52). Only a minor proportion of lead appears to be in a crystalline form susceptible to XRD analysis.

#### CONCLUSION

The aerosol is a complex interacting system which requires the most sophisticated instrumental analytical techniques for its chemical and physical characterisation. Its complexity implicates that it is an exciting topic of investigation in environmental analytical chemistry. For routine control of the environment - a topic which was deliberately not covered in this survey - other factors prevail especially the enormous complexity of data sets generated.



### Acknowledgment

The author is indebted to Eric Denoyer, Johan De Waele, Bert Raeymaekers and Marc Van Craen for the use of experimental data. Our experimental work was carried out under research grant 80/85-10 of the Interministerial Commission for Science Policy, Belgium.

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