Particulate air pollution, with emphasis on traffic generated aerosols

Fauser, Patrik

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Particulate Air Pollution with Emphasis on Traffic Generated Aerosols

Patrik Fauser

Risø National Laboratory, Roskilde, Denmark
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Abstract

Experimental methods for identifying particles generated from the wear of automobile tires and roadway asphalts have been developed. The methods have been employed on aerosols, collected with Berner low pressure cascade impactors, in Copenhagen and Risø and aerosols collected with medium volume samplers on two locations in Copenhagen. Furthermore the deposited particulate matter has been measured in soil near highways and at remote sites, and finally the ad- and absorbed particulate matter has been measured on plant leaves sampled in Copenhagen and at remote sites.

Tire and bitumen particles constitute each about 5 wt-% of the collected suspended particulate matter in inner city air. The particle size distribution shows that 92 % of the mass of airborne particulate tire debris have aerodynamic diameters smaller than 1 µm. The mean aerodynamic diameter is about 1 µm for the bitumen particles.

Soil concentrations in the vicinity of a highway indicate an approximate exponential decrease with increasing distance from the road. Constant values are reached after about 5 m for the tire particles and 10 m for the bitumen particles. This implies a presence of larger particles, typically larger than 20 µm, that deposit immediately and that are not collected by the aerosol samplers. Concentrations in soil that has not been touched for at least 30 years show a decrease in tire concentration by a factor of 30 when moving from the top soil to a depth of 3 cm. The bitumen concentration is approximately constant to a depth of 10 cm.

The leaf samples indicate a slightly higher tire particle concentration on the adaxial side compared to the abaxial side and an increased surface retention for pubescent leaves. About 0.5 µg tire pr. cm² leaf is found near a highway, and about 65 % of this concentration derives from adsorbed particles on both leaf sides. The remainder is either respired through stomata or incorporated in the epicuticular wax layer.

The fact that a substantial amount of the airborne tire and bitumen particles occur in the submicron range permits long range transportation and uptake and assimilation in the human respiratory system as well as absorption in plant tissue.
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Accepted and submitted papers

2 Quantification of Bitumen Particles in Aerosol and Soil Samples using HP-GPC. *Petroleum Science and Technology International*, accepted November 1998. 120

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3 Tire-Tread and Bitumen Particle Concentrations in Aerosol and Soil Samples, *Environmental Science and Technology*, 1998-1999. 136
Preface

The present thesis “Particulate Airpollution, with Emphasis on Traffic Generated Aerosols” has been submitted in partial fulfilment of the requirements for obtaining the Ph.D. degree from the Technical University of Denmark (DTU).

Associate Professor Jens Christian Tjell, Department of Environmental Science and Engineering, DTU, acted as responsible supervisor, Associate Professor Hans Mosbæk, Department of Environmental Science and Engineering, DTU, and Senior Scientist Kim Pilegaard, Plant Biology and Biogeochemistry Department, Risø National Laboratory, acted as supervisors.

At the final examination Associate Professor Mats Bohgard, Department of Industrial Engineering, Lund Institute of Technology, Sweden, Professor Jan Erik Johnsson, Department of Chemical Engineering, DTU, and Associate Professor Ib Johnsen, Botanical Institute, Copenhagen University, participated as external censors.

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Patrik Fauser
Risø National Laboratory and
Technical University of Denmark

August 1998
1 Introduction

The purpose of the present Ph.D. project is to determine the concentrations of airborne particulate matter from tire and bitumen abrasion in the environment, and to investigate whether the particles are small enough to be transported over long distances, be inhaled by man or absorbed by vegetation. Tire tread and bitumen constitute a number of toxic compounds, e.g. polyaromatic hydrocarbons (PAH’s), and the determination of tire and bitumen concentrations may help to enlighten the understanding of the origin of these compounds.

The existing work concerning atmospheric transport in the gas phase is extensive. The gases are homogeneously mixed with the surrounding air and are thus very mobile. Many investigations have dealt with the SO$_2$ and NO$_x$ emissions from power plants among others, with the aim to explain forest decline and reduced agricultural production. This has led to the assumption that the gaseous emissions are the main sources of these environmental problems even though the concentrations in many cases are not sufficiently high to cause the observed effects.

However, other investigations show that activities such as waste incineration, burning of coal and straw, diesel combustion and the wear of automobile tires and roadway asphalts contribute with extensive amounts of organic as well as inorganic particulate pollution. Among the chemical compounds that are identified in the particles are the polyaromatic hydrocarbons (PAH’s) and other high molecular organic compounds. Also heavy metals are known to have a high affinity to particles. Many PAH’s are carcinogenic and the heavy metals are harmful to man, animals and vegetation.

More than 95% of the fine fraction particulate matter, diameter < 2 µm, in Denmark is originating from anthropogenic activities and especially the traffic related particulate pollution is increasing at present.

Both gases and particles are contributors to air pollution and in some cases the effects may even be synergistic. It is therefore of decisive importance to raise the scientific insight to particulate emission, transport, deposition and effects. To describe the cycle of airborne particles in the environment the following topics must be investigated:

- The transportation and deposition properties for different particle sizes as a function of meteorology and deposition surface morphology.
- The main sources of particulate organic- and inorganic pollution.
- The characteristic sizes of the particles from these sources.
- The concentration levels in air, soil, plants etc.
- Whether the deposited particulate material is “available” to the organism or if it is removed by e.g. rainfall or wind.
- The effects on man, animals and vegetation.
This work emphasises the determination of the sizes of airborne tire tread and bitumen particles and the measurement of the concentration levels in air, soil and on plant surfaces. The obtained data enables an evaluation of the extent of the pollution on the environment from these sources.

This thesis consists of a report describing important factors concerning airborne particulate pollution derived from tire and bitumen abrasion and from particles in general. The characteristic aerodynamic diameter vs. mass-distribution is discussed and the sources of the different size groups are stated. The chemical compositions of tires and bitumen and the employed sampling and experimental analysis techniques are described followed by a summary of the determined concentrations of these two sources in aerosols, soil and in plant samples. Finally the possibility for inhalation is commented and the potential PAH-concentration levels in human lungs are calculated.

In the appendix more detailed studies of physical and chemical aspects of atmospheric particles are discussed. Calculations of lower detection limits and evaluations of reproducibility of the developed analytical methods are also performed.

Finally three scientific papers are presented:


In this paper the experimental method developed with the purpose to identify and quantify tire particles is described. A second previously used method based on other chemical characteristics of the rubber is used in parallel and the possible interferences from other particulate sources are evaluated with respect to these two methods. The tire concentrations in aerosols and soil samples determined with the two methods are in agreement, but the developed method is faster and yields a detection limit that is lower by a factor of 2. It is less sensitive with respect to extraction time, and furthermore the existing method is more applicable to private car tires, which gives an underestimation of the total tire particle load in the environment.


A new experimental method for identification and quantification of bitumen particles in the environment is described. A second method, not previously employed for submilligram determination, is used in parallel and the possible interferences from other particulate sources are evaluated with respect to these two methods. The bitumen concentrations in aerosols and soil samples determined with the two methods are in agreement. The developed method is fast and robust and yields a detection limit that is a factor of 3.5 lower than the other method. Previously very few investigations have been performed with the purpose to quantify bitumen particles, but the new method permits fast and reliable determination of submilligram amounts of bitumen in the environment.
In this paper the two methods developed in paper 1 and 2 are employed to determine the tire and bitumen concentrations in aerosols and soil samples in the vicinity of highways and at remote sites. The particle size distribution profiles are measured with low pressure cascade impactors and they show that approximately 92 wt-% of the collected airborne particulate tire mass has aerodynamic diameters smaller than 1 µm and that the mean aerodynamic diameter for collected airborne particulate bitumen particles is approximately 1 µm. Tire and bitumen particles each comprise approximately 5.5 wt-% of the total suspended particulate mass in air sampled in Copenhagen. An important result from this work is the considerable concentration of submicron particles which have the potential to spread far from the sources of emission and also to enter the human respiratory system and be absorbed by vegetation.
2 Particle size fractionation

Many properties are of importance when one has to evaluate the extent of particulate pollution. For the particles to be able to spread over long distances they have to be small, since large particles to a great extent are subject to gravitational settling. When dealing with human health, submicron size particles can be inhaled and transported to the alveoli where accumulation and release of harmful compounds may take place. Furthermore submicron particles can be absorbed in plants by entering the stomata. The particle size is therefore of great interest when the effects of airborne particulate pollution are concerned.

Aerosol particles cover a size range roughly between 0.003 \( \mu m \) and 100 \( \mu m \). The lower limit approximates the point where the transition from molecule to particle takes place and particles with diameters larger than 100 \( \mu m \) do not stay suspended in the air long enough to be of interest in aerosol science.

How do one define the size of a particle? There is only one shape that can be described by one unique number and that is the sphere. When the diameter is known the size is described exactly. For an irregular particle there are a number of properties that can be described by one number, such as the weight, volume or surface area. By measuring one of these properties, say the weight of the particle, it is possible to convert this weight to the weight of a sphere hence deriving an equivalent sphere diameter to describe the particle.

It is commonly used to define a particle diameter in terms of particle settling velocity. All particles having similar settling velocities are considered to be of the same size, regardless of their actual size, composition or shape. In ambient particulate sampling the most appropriate definition is the aerodynamic diameter, \( d_a \), which is defined as the diameter of a smooth, unit density (\( \rho_0 = 1 \text{ kg pr. l} \)) sphere which has the same settling velocity, \( v_s \), as the original particle. The settling velocity is the terminal velocity reached by a particle in air falling under the influence of gravity. According to this definition particles of varying shape or density will have the same aerodynamic diameter if the settling velocity is the same.

The particle Stokes diameter, \( d_s \), is defined as the diameter of a sphere which has the same density and settling velocity as the particle. The relationships between the physical particle size and the Stokes and aerodynamic diameters are illustrated in figure 1 (Air Sampling Instruments, 1989).

![Figure 1 Stokes and aerodynamic diameters for an irregularly shaped particle](Air Sampling Instruments, 1989).
Particles with the same physical size and shape but different densities will have the same Stokes diameter but different aerodynamic diameters. For the same Stokes diameter, particles of larger density will have the larger aerodynamic diameters.

When particle diameter is mentioned in the following it always refers to the aerodynamic diameter, unless otherwise stated. The expression for the aerodynamic diameter, $d_a$, is derived in appendix A, where correction for irregular shapes is also mentioned. $d_a$ is defined as

$$d_a = \sqrt{\frac{\rho_p \cdot C_p}{\rho_0 \cdot C_a}} \cdot d_p$$

(1)

where:

$C_a$ = Cunningham slip factor evaluated for $d_a$.
$C_p$ = Cunningham slip factor evaluated for $d_p$.
$d_p$ = physical diameter for spherical particles and Stokes diameter for non spherical particles [cm].
$\rho_0 = 1$ g pr. cm$^{-3}$.
$\rho_p$ = density of the particle [g pr. cm$^{-3}$].

The slip factor, C, represents the mechanism for transition from the continuum to the molecular case and should always be included when particles are less than 1 µm in diameter. The factor is always equal to or greater than one.

Figure 2 shows a plot of C as a function of particle diameter for air at normal conditions of temperature and pressure.

For atmospheric aerosols a wide range of sizes may be present in numbers which can vary by several orders of magnitude. Aerosols containing one single particle size are very rare in nature and when they do appear they generally have short life-times.

There are different ways of plotting particle frequency versus size. If the ordinate is the particle number the smaller particles may completely overwhelm the display of larger particles. The opposite is the case when mass or volume is used as ordinate. To visualise a broad size range the logarithms of the diameters are plotted on the abscissa. In appendix B the variations in distribution profiles are shown as a function of ordinate parameter.
In figure 3 a schematic particle size distribution found in urban air, presented as aerodynamic diameter vs. particulate weight, shows the typical trimodal size model, comprising of three log-normal distributions. The main sources of mass for each mode are stated together with principal processes involved in mass transfer and removal.

Figure 3 Schematic curve of aerosol aerodynamic diameter vs. mass (Whitby, 1977).

It is commonly accepted to divide aerosol particles into two size groups, based on their aerodynamic diameter, $d_a$:

Fine particles: $d_a < 2 \, \mu m$.
Coarse particles: $d_a > 2 \, \mu m$.

This fractionation is appropriate because the two fractions typically originate from different sources and there is negligible mass transport from one fraction to the other. That is, they originate, transform and deposit separately. As a consequence the chemical composition will also be different. The fine fraction is primarily originating from combustion whereas the coarse fraction is generated from mechanical processes. The fine and coarse fraction are also referred to as soot and flyash respectively.

The fine fraction consists of two log-normal distributed size ranges:

**Nucleation range:**
Characteristic diameter: $0.003 - 0.07 \, \mu m$.
Concentrations in remote sea areas: $0.0005 \, \mu m^3$ pr. $cm^3$.
Concentrations near heavily trafficked roads: $9 \, \mu m^3$ pr. $cm^3$.
Mean residence time in the atmosphere: a few hours.

Nuclei range particles are formed by combustion of fossil fuels etc. when the volatile compounds condense at decreasing temperatures and the gases convert to less volatile compounds in the atmosphere. These primary particles soon coagulate to form larger particles in accumulation range.
Experiments show that nuclei range particles formed by condensation in an initially particle free smog chamber will grow within tens of seconds from 15 - 20 Å to sizes on the order of 75 Å. Subsequent growth is slower. In the real atmosphere the presence of larger particles in accumulation range will change the coagulation pattern of the fine fraction since the coagulation velocity between nuclei range particles and accumulation range particles exceeds the coagulation velocity between nuclei range particles alone, (Whitby, 1977). Particles in nuclei range will therefore quickly be transferred to the following group.

**Accumulation range:**
Characteristic diameter: 0.07 - 2 µm.
Concentrations in “clean” marine and continental areas: 1 µm$^3$ pr. cm$^3$.
Concentrations in heavily polluted cities: 300 µm$^3$ pr. cm$^3$.
Mean residence time in the atmosphere: 15 - 22 days.

These particles are generated in the same way as the nuclei range particles, by condensation of gasses and subsequent coagulation to other particles. A further growth is very slow for this group and processes like dry deposition and scavenging are reduced, consequently the accumulation range contains the prominent part of the aerosol mass.

The **coarse range** is defined as:
Characteristic diameter: 2 - 50 µm.
Concentration range: 2 - 1000 µm$^3$ pr. cm$^3$.
Mean residence time in the atmosphere: a few hours to a couple of days.

These particles are mainly generated by mechanical wear processes such as abrasion of automobile tires, roadway asphalts and resuspension of soil. Furthermore salt particles from sea spray and combustion products are found in this range.

The reason for the physical separation of the fine and coarse fraction arise from the fact, that the coagulation velocity, by which mass is transferred from a smaller particle size to a larger, is decreasing drastically for particle sizes larger than 0.5 µm. By using the concentrations that occur in accumulation mode and a coagulation velocity of 10$^{-9}$ µm$^3$ pr. cm$^3$, it is found that the time needed to transfer mass to the coarse range exceeds the residence time in accumulation mode (Whitby, 1977).

Recent investigations indicate a further differentiation into more narrow size subranges, but with respect to this work where the main objective is to identify the "fine" and "coarse" particles, the above stated characterisation is adequate.
3 Sources and chemical compositions

Aerosol sources can be classified as primary or secondary. Primary aerosols are those emitted directly into the atmosphere in particulate form from sources such as power stations, motor vehicles, soil dust, sea salt, soot etc. These particles can undergo chemical and physical transformations once emitted into the atmosphere resulting in a continuously changing chemical composition and particle size distribution. Secondary particles are those formed during chemical and physical conversions such as photo oxidation of the various pollutants and during formation of new particles in the atmosphere by nucleation.

The major elements in the primary particles, are the crustal elements (Si, Al, Ca, Fe, K, Ti, Mn, Sr etc.), elemental carbon and a series of organic compounds. The secondary aerosols typically constitute inorganic compounds, mainly sulphates, nitrates, chlorides, ammonium and water or carbonaceous material. The diagram in figure 4 outlines the relationship between size and composition for important primary and secondary particles.

![Diagram of aerosol composition and mass distribution vs. size range.](image)

*Figure 4 Composition and mass distribution vs. size range. Fine particles < 2.5 µm, coarse particles 2.5-15 µm. For each source the % of mass with diameter < 2.5 µm can be read on the abscissa at the vertical line (Colbeck, 1995).*

Primary and secondary sources to the fine fraction are:

- Exhaust products from automobiles (especially diesel engines).
- Industrial- and domestic waste incineration.
- Soot from oil-, straw- and coal combustion.
- Long-range transported aerosols.
Primary and secondary sources to the coarse fraction are:

- Soil dust.
- Bioaerosols: plant parts, pollen, insect parts etc.
- Sea aerosols.

In this work traffic related particles generated from the wear of roadway asphalts and automobile tires are emphasised. These particles are in this work and previous investigations found to exist both in the fine and the coarse fraction. The results presented in paper 3 reveal a surprisingly large fraction of submicron airborne tire and bitumen particles.

In appendices C, D and E the formation and growth, chemical constituents in aerosols and morphology of particles respectively are mentioned.
4 Sampling

The purpose of sampling has been to determine the chemical compositions and concentration levels that exist in aerosols, soil etc. (for different particle sizes if possible) on a specific site. The sample has to be representative, that is, it must reflect the typical fingerprint that the surrounding sources produce at the specific site and time.

Deviations from the normal values can be caused by contributions from not normally occurring sources such as paving of roads or atypical wind conditions that carry a smoke plume across the sampling site. Crop and dust will contribute considerably to the airborne particulate mass in the harvesting season like soil dust will when the fields are barren.

In this work four different types of samples are collected and analysed:

Homogeneous samples: This category comprises tire or tire powder for rerubbering, bitumen, soot from diesel and petrol engines, engine oil, dust from disc and drum brakes, flyash from private woodburners (beech and birch), flyash from power stations and waste incineration plants. Some samples are more homogeneous than others and for flyash from private woodburners there will obviously be a varying degree of carbonisation of the particles and woodparts.

Apart from the power plant flyash, the samples were collected with cleansed tools and kept in paper bags. To remove adsorbed, sorbed and occluded water the samples are dried at 60°C for 24 hours after which approximately 1 g of sample is weighed for further analysis. If the sample is solid it is granulated and mixed to obtain a maximum surface area and to achieve a homogeneous mixture. Tire samples cut from used tires are put in plastic bags, dipped in liquid nitrogen (-197°C) for about 5 minutes and pounded to small bits with a clean hammer. The plastic bags are not destroyed by this treatment.

Aerosol samples: Two types of aerosol samplers are used in this work. In Copenhagen a medium volume sampler, with an airflow of 2.5 m$^3$ pr. hour, with celluloseacetate/cellulosenitrate filters (Millipore RA, diameter: 50 mm, pore size: 1.2 µm) is used. Each day one filter is exposed (sampled air volume = 60 m$^3$) which gives a typical concentration of total suspended particulate matter (TSP) of 90 µg pr. m$^3$ (5.4 mg pr. filter) in inner city air. The filter has a nominal retention efficiency (98 % efficiency level) of 0.5 µm.

In Copenhagen and at Risø two Berner 11-stage low pressure cascade impactors (BLPI) are used in conjunction with a pump that provides a flow of 25.7 l pr. minute. The concentration of suspended particulate matter ranges from 0.5 to 16 µg pr. m$^3$ (0.2 to 7 mg) in the various size stages. The characteristics of the impactors are described in section 4.1.

As impactor collector medium Teflon discs are used. These are circular discs with an inner and outer diameter of 34 and 70 mm respectively, see figure 5. Each filter is cleaned by rinsing it 1 minute succeedingly in four beakers with ½ litre of 1 M nitric acid solution, as shown in figure 5. After rinsing five filters solution 1 is renewed and placed in position 4 thus keeping a decreasing impurity gradient from beaker 1 through 4.
The aerosol filters are stored in petri dishes and prior to weighing they are dried in a silicagel exiccator for 24 hours.

**Soil samples:** Soil samples are taken on different locations mostly from the top soil, which in this work is defined as the top 0.5 cm. They are taken with a clean knife and put in paper bags. On some locations samples are taken in varying depths down to 10 cm, and here a circular aluminium cylinder with an inside cross-sectional area of 2.5 cm² is used. The soil cylinder is then pressed out and cut into 0.5 cm thick sections at the desired depths.

Soil samples are clearly inhomogeneous and larger pebbles, roots, twigs etc. are avoided. The sample is dried at 60°C for 24 hours after which the entire sample, typically 10 g, is granulated and mixed and from this mixture 1 g is weighed and used for further analysis.

**Plant samples:** Sampling and preparation is described separately in section 8.

### 4.1 Methods for aerosol sampling

The normal technique for sampling airborne particulates is by pumping a known air volume through a filter or past a collection surface whereupon particles that meet given aerodynamic requirements are withheld. The size ranges of different aerosol sampling devices are shown in figure 6.

![Size ranges of different aerosol samplers](image)

*Figure 6 Size ranges of different aerosol samplers (American Industrial Hygiene Association, 1986).*
Sampling methods are prone to errors because the concentrations, size distributions etc. of the true particles in the undisturbed environment from which the sample is taken must be extrapolated from the sampled volume. There are many situations where the actual sampling conditions may bias the process, such as when the aerosol flow vector and the sampling flow vector do not coincide or when the average mass velocity, $v_{ae}$, is different from the average carrier gas velocity, $v_{sam}$. In general the two velocities are not identical in outdoor sampling so that inertial particulate losses, see figure 7, can be expected.

Figure 7 Isoaxial sampling regimes: a isokinetic sampling ($v_{sam} = v_{ae}$); b hyperkinetic sampling ($v_{sam} > v_{ae}$) with depletion of large particles; c subkinetic sampling ($v_{sam} < v_{ae}$) with enrichment of large particles, (Holländer, 1995).

Depending on the particulate sizes and total mass one needs to collect, hi-or medium-volume samplers can be employed. The hi-volume sampler carries a “roof” that prevents dust from falling directly onto the horizontally placed filter, but there is nevertheless a possibility for collection of wind blown particles which can lead to substantial overestimation. Medium-volume samplers are equipped with a downward pointing nozzle that minimises the afore mentioned problem but only smaller samples can be collected on account of the lower air flow. Typical flow values for hi- and medium-flow samplers are 60 and 2.5 m$^3$ pr. hour respectively.
The medium volume samplers do not separate the particles according to size. To do this cascade impactors can be used. These are based on the principle of inertia, where particles are removed from the air stream by impaction on a collector medium, caused by the bending of streamlines as the air flow bypasses a solid object such as a collection plate. In figure 8 a five stage cascade impactor is depicted. By using smaller diameter jets and by decreasing the spacing between the collection plate and the jet exit, continuously smaller particles are removed from the air stream on its way through the impactor.

![Figure 8 Five-stage cascade impactor and principle of particle impaction](image)

Impactor theory does not account for non ideal effects such as particle bounce-off from the collection surface, which probably is the greatest limitation in the use of impactors. It assumes that all particles striking the collection surface adhere to it. In practice this criterion is not always met as dry particles may bounce from the surface and be re-entrained in the air flow and pass on to subsequent stages, which will result in distortions of the size distributions.

Particle bouncing is significant for dry and compact particles while moist and sticky particles will adhere to a greater extent. To obtain uniform adhesion the use of a adhesive coating such as oil can be employed. The disadvantage is interference in chemical analysis and the possibility of reaction with particle bound compounds.
As particles adhere to the collector platform they will accumulate and form piles that continuously decrease the distance between the jet exit and the collection plate and consequently collect particles with diameters smaller than desired. With a flow of 25.5 l pr. min a sampling period of about 7 days must not be exceeded if the this problem is to be minimised.

It is thus important to find the collection surface material with the optimum adhesive properties combined with minimum chemical interferences. Lange (1995) found that Teflon filters proved to fulfil these requirements most satisfactorily.

Impactor theory combines the processes of drag force upon the particle, particle momentum and the effective transit time across the collection plate into the dimensionless Stokes number (Reist, 1984)

$$\text{St} = \frac{\rho \cdot d_p^2 \cdot C \cdot v}{9 \cdot \mu \cdot W} \quad (2)$$

where:
- $$\rho$$ = particle density.
- $$d_p$$ = particle Stokes diameter.
- $$C$$ = Cunningham slip factor.
- $$v$$ = mean velocity in the jet.
- $$\mu$$ = air viscosity.
- $$W$$ = jet diameter or width.

Every stage has a 50 % cut-point diameter, $$d_{50}$$, that indicates the aerodynamic diameter with a 50 % collection efficiency. In theory it is assumed that all particles above the cut-point diameter are collected and all particles below pass on to the next stage, but in practice a crossover in particle sizes between stages occurs.

$$d_{50}$$ corresponds to a single Stokes number, $$St_{50}$$. The value of $$St_{50}$$ is approximately constant for different impactor stages and even for different impactors. Its value lies between 0.22 and 0.25 for most round jet impactors (American Industrial Hygiene Association, 1986).

For round jet impactors $$d_{50}$$ can be expressed as

$$d_{50} = \sqrt[3]{\frac{9 \cdot \mu \cdot \pi \cdot n \cdot W^3 \cdot St_{50}}{4 \cdot \rho \cdot Q \cdot C}} \quad [\mu m] \quad (3)$$

where
- $$n$$ = the number of jets pr. stage.
- $$Q$$ = sampler flow rate.

The Berner 11-stage low pressure cascade impactor (BLPI) that is used in this project is designed to cover particle aerodynamic diameters ranging from 0.021 µm to approximately 16 µm. Larger particles are lost by collision with the coat around the impactor inlet.

$$d_{50}$$ has been found by Hauke in 1993 for each stage for a volumetric flow rate, $$Q$$, of 25.7 l pr. min., at 20 °C and atmospheric pressure. The exhaust pressure is 40 mbar. $$d_{50}$$, mean
aerodynamic diameter, number of jets and nozzle diameter for the Berner 11-stage low pressure cascade impactor are stated in table 1.

Table 1 Berner low-pressure cascade impactor data (Hauke, 1993).

<table>
<thead>
<tr>
<th>Stage no.</th>
<th>d_{50} [µm]</th>
<th>Mean aerodynamic diameter [µm]</th>
<th>Number of jets</th>
<th>Nozzle diameter [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>16</td>
<td>-</td>
<td>1</td>
<td>16.0</td>
</tr>
<tr>
<td>10</td>
<td>8.0</td>
<td>11.3</td>
<td>12</td>
<td>4.10</td>
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<td>4.0</td>
<td>5.7</td>
<td>24</td>
<td>2.10</td>
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<td>2.0</td>
<td>2.8</td>
<td>44</td>
<td>1.10</td>
</tr>
<tr>
<td>7</td>
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<td>0.18</td>
<td>25</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>0.06</td>
<td>0.087</td>
<td>125</td>
<td>0.25</td>
</tr>
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<td>0.03</td>
<td>0.042</td>
<td>125</td>
<td>0.30</td>
</tr>
<tr>
<td>1</td>
<td>0.015</td>
<td>0.021</td>
<td>250</td>
<td>0.30</td>
</tr>
</tbody>
</table>

It is important to underline that the term "total suspended particulate matter (TSP)", that is used in the following, refers to the particles that are collected with the described impactor or the medium volume sampler respectively. The sampling limitations primarily result in a deficiency in the larger particles (> 10 µm) for both devices and in the submicron particles for the medium volume sampler.
5 Tires

5.1 Composition

A rubber tire consists of:

- Rubber mixture (85 %)
- Steel (12 %)
- Textile (3 %)

The composition of the rubber mixture in wt-% is typically, (Ahlbom et al., 1994):

- Rubber polymer, elastomer (40 - 60 %)
- Fillers, reinforcing (25 - 35 %)
  , softening (15 - 20 %)
- Vulcanisers (1 - 2 %)
- Accelerators (0.5 - 2 %)
- Activators (2 - 5 %)
- Antioxidants (1 - 2 %)
- Additives (1 - 2 %)

Elastomers are polymers that exhibit characteristic rheological properties. They must be amorphous under unstrained conditions and must be above their glass transition temperature to exhibit elastic deformations under strain.

For private cars a mixture of rubber polymers such as the below stated is often used (Korsbæk, personal communication, 1996):

- Natural rubber, NR (~ 40 wt-%)
- Styrene butadiene rubber, SBR (~ 30 wt-%)
- Butadiene rubber, BR (~ 20 wt-%)
- Butyl and halogenated butyl rubber, CIIR (~ 10 wt-%)

The copolymer SBR is one of the most commonly used polymers in tires and it typically consists of 75 wt-% 1,3-butadiene and 25 wt-% styrene

\[
\text{CH}_2=\text{CH} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow -\text{CH}_2-\text{CH}-\text{CH}=\text{CH}-\text{CH}_2- \\
\text{Ph} \quad \text{Ph} \quad \text{Styrene} \quad 1,3-\text{Butadiene} \quad \text{SBR-copolymer}
\]

\textit{Figure 9 SBR copolymer.}

In truck tires a mixture with about 90 wt-% natural rubber, which is a polymer of conjugated 2-methyl-1,3-butadiene (isoprene), is used
The elastomer itself is a weak thermoplastic substance that is readily soluble in hydrocarbons and that do not possess useful mechanical properties. To achieve the desired properties regarding tensile strength, stiffness, resistance towards solvents, abrasion and tear resistance and durability it is necessary to join the polymer chains in a mesh of cross bonds. This process is called vulcanisation. The chemical reactions associated with vulcanisation are varied and involve only a few atoms in each polymer molecule.

Sulphur is mainly used as vulcaniser but also non sulphur compounds such as selenium, tellurium, organic peroxides, nitro and azo compounds can be applied. Only a few percent of the rubber products are formed in non sulphur vulcanisation since they are only applied for high temperature use. They have relatively mediocre properties and are expensive compared to sulphur vulcanised rubber products (Korsbæk, personal communication, 1998).

In appendix F the principles in non sulphur vulcanisation are depicted.

In sulphur vulcanisation the sulphur can undergo a variety of reactions. Some of it is used in the formation of sulphide and disulphide bonds between the rubber polymers

\[
\text{CH}_3 \quad -\text{CH}-\text{C}=\text{CH}-\text{CH}_2^- \quad \text{S} \quad \text{S} \quad -\text{CH}-\text{C}=\text{CH}-\text{CH}_2^- \quad \text{CH}_3
\]

*Figure 11 Disulphide bond in sulphur vulcanisation.*

Sulphur is a strong proton acceptor and this can lead to saturation of double bonds and formation of hydrogen sulphide, which is a known product of sulphur vulcanisation. The sulphur that is bonded within the elastomer matrix can only be released by degradation or combustion as oxidised inorganic sulphur. The result of sulphur vulcanisation is optimised when 0.5 - 5 parts by weight of sulphur is combined with 100 parts of rubber. If the reaction is allowed to continue until considerably more sulphur has combined, say 30 - 50 parts pr. 100 parts rubber, a rigid, non elastic plastic known as hard rubber or ebonite is formed (Textbook of polymer science, 1962).

The process of vulcanisation is slow without the presence of accelerators. Most accelerators are free radical formers or strong electron acceptors but little is known about their specific action in
speeding up the process. Accelerators can be inorganic such as lead, calcium, magnesium or zinc oxides but especially organic sulphur containing compounds such as thioureas, thiophenols, mercaptans, dithiocarbamates, xanthes, trithiocarbamates, dithio acids, mercaptobenzothiazoles, mercaptobenzothiazoles and thuram sulphides plus a few nonsulphur compounds such as ureas, guanidines and aldehydeamines have proven to be efficient accelerators. Two or three different organic accelerators, mostly sulphur containing, are used in practically all rubber stocks in amounts of 0.5 – 2 wt-% of the total mixture. Some dissociate thermally at vulcanisation temperatures and the sulphur is consumed in promoting vulcanisation.

Almost all organic accelerators must be used with an activator to obtain the full effect. These can be basic metallic oxides or salts of lead, calcium, magnesium or zinc. As a rule of thumb 5 parts of zinc oxide is added to 100 parts of rubber polymer, and gives zinc concentrations of about 1 % in the final rubber product. The zinc forms chelates with the accelerators (e.g. figure 12) which in turn initiate free radical formation of the rubber polymers resulting in carbon-carbon crosslinks.

![Figure 12 Formation of disulphide bonds through intermediate zinkmercaptide complex, (Hofmann, 1965).](image)

In figure 12 the reaction pathway between zinkoxide and mercaptobenzthiazole with formation of a disulphide bond and zincoxide is shown. Hofmann (1965) states that the formation of the disulphide bond is unlikely to occur without the presence of zincoxide.

Vulcanised rubber products containing double bonds, such as NR and SBR, are sensitive to sunlight, heat and oxygen. The rubber can get soft and brittle and lose the necessary tensile properties unless antioxidants are added. They do not participate in vulcanisation and must be able to translocate in the rubber structure. The most commonly used antioxidants are phenyl α- and β-naphtylamines.

Ozone is an effective oxidant, that can cause considerable damage to tires especially under strain and to prevent this anti ozonants such as diamines and waxes are added. Waxes are added in amounts from 0.5 to 1.0 % of the rubber stock and act as softeners as well as UV and ozone
protectors, which resembles the effect obtained by natural waxes on plant surfaces. The waxes are extracted from the paraffin fraction of the crude oil and consists of high molecular n-alkanes (sunproof waxes). (Rogge et al., 1993) has found that n-alkanes in the molecular size range from C\textsubscript{19} to C\textsubscript{41} are the largest organic groups in tire particles.

The rubber stock is made workable by the aid of softening fillers such as mineral oils. They are cheap and 50 to 60 parts of oil is added to 100 parts of rubber polymer which corresponds to approximately 25 wt-% of the finished rubber product. Oils and carbon black (see below) are added in equal amounts to obtain combined optimum strength and workability. The tire tread surface contains the oil amount stated above to acquire elasticity and stickiness, whereas the rest of the tire has a lower concentration. The mean concentration in a tire is about 15 wt-% (Korsbæk, personal communication, 1996).

For many purposes the required strength and resistance is achieved by addition of a reinforcing filler with a primary purpose to establish a mesh connecting the weak fixpoints to the stronger surrounding polymer structure. The vulcanisation reduces the ability for larger extensions whereas the mobility on a smaller scale is retained. The reinforcing filler is increasing the stability of the structure by decreasing the smaller scale mobility. The most common reinforcing filler is carbon black which constitutes approximately one third of the tire. Carbon black consists of hexagonal carbonatoms with a crystal structure similar to graphite. They form chain like non porous particles in the size range 10 to 500 nm with large specific surface areas. The reinforcing effect is enhanced by reducing the particle size down to a diameter of about 100 Å, which is the lower production limit (Textbook of polymer science, 1962).

The carbon layers are placed randomly on top of each other resulting in unsaturated bonds which explain the large adsorption potential to rubber polymers. The adsorbed amount is proportional to the surface area of the carbon black particles (Textbook of polymer science, 1962).

### 5.2 Tire indicators

Zinc has been used as a tire indicator by many investigators. Pierson et al. (1974) found that there is a clear correlation between traffic activity and zinc concentrations in particles in the air and in the soil. Still one must be careful in assigning all the zinc to tire wear since the sources of particulate zinc are many. According to Ahlbom (1994) the particulate zinc contribution via tire wear amounts only to about 10 % of the total particulate zinc load in cities in Sweden. The zinc concentration levels in the environment are generally low (the zinc content in "clean" soil in Denmark is typically around 50 µg Zn pr. g soil).

The major part of the zinc in tires is present as excess ZnO and ZnS, where the latter is produced by reaction of zinc ions with the vulcaniser (sulphur). In this work the extractable organic zinc, defined as zinc-accelerator complexes, is used as tire indicator. As is shown in paper 1 tires are, with the exception of motor oils, the only significant contributor to extractable organic zinc in airborne particles.

The different zinc compounds are probably not incorporated in the rubber matrix but act as fillers after the vulcanisation has taken place (Korsbæk, personal communication, 1998).
As a second indicator styrene butadiene rubber (SBR) is used, which is appropriate since SBR is the most commonly used rubber polymer in tires. About 30% of the rubber polymer used for private automobile tires is SBR, truck and bus tires however consist of 90% natural rubber. It is stated that 65% of the SBR production in the United States is used for tire manufacturing and furthermore that the particulate SBR contributions from other sources are small (Pierson et al., 1974).

5.3 Experimental methods for tire identification

5.3.1 Zinc

It is the total amount of extractable organic zinc that is of interest in this work and not a specific compound. When this zinc is brought into an aqueous solution it is readily analysed by absorption spectroscopy (AAS) and depending on the actual concentration levels either flame atomic absorption spectroscopy (FAAS) or heated graphite atomiser (HGA) can be employed. The characteristics of these two techniques are described below.

A number of other techniques are described in the literature for quantifying a diversity of elements, including zinc, in aerosol samples, namely proton induced X-ray emission (PIXE), X-ray fluorescence (XRF), neutron activation analysis (NAA), inductive coupled plasma mass spectroscopy (ICP-MS) and X-ray diffraction (XRD). In PIXE, NAA and XRF concentrations of a number of elements can be achieved directly from the unprepared sample, it is however the total concentrations that are quantified and there is no differentiation between organic and inorganic compounds.

In this work the samples are analysed by FAAS and HGA at the Department of Environmental Science and Engineering at the Technical University of Denmark and FAAS and ICP-MS at the Plant Biology and Biochemistry Department, Risø. Aerosol samples are analysed with PIXE at the Niels Bohr Institute in Copenhagen and NAA at the Nuclear Safety Department, Risø. Two aerosol samples have been examined with a scanning electron microscope (SEM) in combination with X-ray fluorescence at the Materials Research Department, Risø.

The developed experimental procedure regarding sample preparation and AAS analysis is thoroughly described in paper 1. The paper also discusses the possible interferences from other sources. In paper 3 the method is employed on aerosol and soil samples and in section 8 the tire concentrations found on plant leaves are presented.

In the following paragraphs the experimental procedures are discussed with respect to detection limits and reproducibility. In appendix G and H the main experimental principles, calibration curves and calculations of detection limits are presented for HGA and FAAS respectively.

Atomic absorption spectroscopy

Once the organic constituents are oxidised and the metal is brought into an aqueous solution the concentrations are measured by either Flame Atomic Absorption Spectroscopy (FAAS) or a heated graphite atomiser (HGA) depending on the concentration levels in the samples. In atomic absorption spectroscopy the metal can be quantified regardless of its bonding to other atoms.
since the molecular structures are degraded at the high temperatures that are required to evaporate the metal.

**Flame Atomic Absorption Spectroscopy (FAAS)**

The used apparati are Perkin-Elmer laminar-flow burners with atmospheric air as oxidant and acetylene as fuel. FAAS can be used in concentrations ranging from 0.1 to 1 mg Zn pr. l (ppm).

It was not possible to analyse directly on the organic extract containing the extractable organic zinc, since the flame was quenched and furthermore the ventilation was not adequate to remove the toxic gases.

To ensure that there was no loss of analyte in the extraction procedure a sample spiked with zinc nitrate, to reach a concentration of 0.5 mg Zn pr. l was analysed. The mean recovery was 107 % for 5 determinations.

Even though the samples are boiled in concentrated nitric acid, organic material can be found especially in the plant samples. Presence of organic material in the samples requires adjustment of the fuel flow (temperature) from the standard settings. Control measurements regarding the samples containing the largest amount of organic material were performed at standard and adjusted settings. The results were approximately identical (COV = 7 %), and the standard settings were used henceforth.

Mean values, coefficients of variation and number of analysis are presented in appendix H for 0-, blank and soil samples. Duplicate determination can not be performed for aerosol samples as the entire samples are used in one analysis. The extractable organic zinc concentrations in plant samples are too low to be detected with FAAS.

The detection limit, or minimum detectable quantity, subtracted the blank value, is calculated in appendix H to be

\[ \Delta x_{\text{min}} > 0.0165 \text{ mg Zn pr. l (ppm)}. \]

Each sample is diluted in 10 ml solvent. The mean concentration of extractable organic zinc, for all investigated tire types, is in paper 1 found to be 1290 µg org. Zn pr. g tire (COV = 5 %), which leads to a tire detection limit of

\[ \Delta x_{\text{min}} \text{(tire)} > \frac{16.5 \mu g \text{ Zn pr. l} \cdot 0.011}{1290 \mu g \text{ Zn pr. g tire}} = 0.13 \text{ mg tire pr. sample.} \]

**HGA**

The detection limit can be enhanced considerably by employing a heated graphite furnace atomiser. For zinc the typical concentration working range is from 2 to 30 µg Zn pr. l (ppb) (2 to 100 ppb in solubilised aerosol samples) and it is thus very important to wash the glass equipment in 0.1 M nitric acid and rinse it in ion exchanged distilled water to minimise contamination.
To prevent anions to interfere and to separate the metal from other cations an automatic extraction procedure is executed in connection with the HGA: Sodium diethyl dithiocarbamate trihydrate (NaDDC) and isobutylmethylketone are added to form complexes with the metal and to extract it into the organic phase which is then analysed.

The reference values for soil and plant samples have been calculated in the determination of extractable organic zinc and can be seen in appendix G. The detection limit for HGA is calculated in appendix G to be

$$\Delta x_{\text{min}} > 1.6 \, \mu g \, Zn \, pr. \, l \, (ppb).$$

leading to the following tire detection limit

$$\Delta x_{\text{min}} \, (\text{tire}) = \frac{1.6 \, \mu g \, Zn \, pr. \, l \cdot 0.011}{1290 \, \mu g \, Zn \, pr. \, g \, \text{tire}} = 12.4 \, \mu g \, \text{pr. sample.}$$

5.3.2 SBR

Infra red analysis (IR)

A second independent and reliable method is used in parallel to confirm the results found by AAS. The methods are based on different chemical characteristics of the samples to minimise the possibility of a common factor having the same effect on both methods.

The method has previously been described by Brachaczek et al. (1974). In paper 1 the experimental procedure adapted to the present work is described. From the flow sheet in figure 1 in paper 1 it is seen, that the initial sample preparation is similar in the two methods, which does not lead to an elimination of all of the method and personal errors, but at least the instrument errors are not related.

The IR analysis is performed on a Perkin-Elmer 1760 X Infra Red Fourier Transform Spectrometer with a resolution of 4 cm\(^{-1}\) and 200 scans are used to minimise the background noise. It is important to obtain a homogeneous mixture of the sample in the ground KBr powder to enable maximum quantification reliability.

In figure 13 a 1.9 mg tire spectrum (total tire mass prior to extraction) ranging from 400 to 4000 cm\(^{-1}\) is shown. Moving from the left to the right the characteristic absorption lines are

Water or intermolecular hydrogen bonds (O-H vibrations):

$$\nu_{O-H} = 3400 \, \text{cm}^{-1}$$

Paraffins (C-H vibrations):

$$\nu_{\text{as,CH}_3} = 2962 \, \text{cm}^{-1}$$
$$\nu_{\text{s,CH}_3} = 2872 \, \text{cm}^{-1}$$
$$\nu_{\text{as,CH}_2} = 2924 \, \text{cm}^{-1}$$
$$\nu_{\text{s,CH}_2} = 2853 \, \text{cm}^{-1}$$
$$\delta_{\text{s,CH}_2} = 1467 \, \text{cm}^{-1}$$
$$\delta_{\text{as,CH}_3} = 1450 \, \text{cm}^{-1}$$
$$\delta_{\text{s,CH}_3} = 1378 \, \text{cm}^{-1}$$
\[ \rho_{\text{CH}_2} = 721 \, \text{cm}^{-1} \]

*Carbonyl (C=O vibrations):*  
\[ \nu_{\text{C}=\text{O}} = 1700 \, \text{cm}^{-1} \, \text{(normal)} \]  
\[ \nu_{\text{C}=\text{O}} = 1685 \, \text{cm}^{-1} \, \text{(aromats)} \]

*Alcohols and phenols (C-O vibrations):*  
\[ \nu_{\text{C}-\text{O}} = 1170 \, \text{cm}^{-1} \]  
\[ \nu_{\text{C}-\text{O}} = 1040 \, \text{cm}^{-1} \]

*Aromats (C-H vibrations):*  
\[ \delta_{\text{C-H}} = 966 \, \text{cm}^{-1} \, \text{(disubstituted transalkenes)} \]  
\[ \delta_{\text{C-H}} = 910 \, \text{cm}^{-1} \, \text{(monosubstituted alkenes)} \]  
\[ \delta_{\text{C-H}} = 760 \, \text{cm}^{-1} \]  
\[ \delta_{\text{C-H}} = 700 \, \text{cm}^{-1} \, \text{(styrene)} \]

Where \( \nu, \delta \) and \( \rho \) denote stretching, bending and rocking respectively and the subscripts \( s \) and \( as \) are symmetrical and asymmetrical vibrations.

![Figure 13 IR-spectrum (400 to 4000 cm\(^{-1}\)) of 1.9 mg tire sample.](image)

By comparing with IR spectra of other sources to airborne particulate matter it is found that tires have a unique combination of absorption lines in the interval ranging from 600 to 1000 cm\(^{-1}\), see figure 14.
The simultaneous occurrence of the 700 and the 966 cm\(^{-1}\) lines are used as tire indication in the aerosol and soil samples. The tire spectrum in figure 14 is used as standard and the tire concentration in a sample can be calculated by using the following equation

\[
\text{Conc.}(\text{tire}) = \left( \frac{\text{abs} \ (700 \text{ cm}\,^{-1})_{\text{sample}}}{\text{abs} \ (700 \text{ cm}\,^{-1})_{\text{tire}}} + \frac{\text{abs} \ (966 \text{ cm}\,^{-1})_{\text{sample}}}{\text{abs} \ (966 \text{ cm}\,^{-1})_{\text{tire}}} \right)^{\frac{1}{2}} \cdot \text{mass}_{\text{tire}},
\]

where

\[
\text{abs} \ (700 \text{ cm}\,^{-1})_{\text{tire}} = \log_{10} \left( \frac{I_0}{I} \right) = \log_{10} \left( \frac{66.20}{64.30} \right) = 0.0126 \text{ Abs.}
\]

\[
\text{abs} \ (966 \text{ cm}\,^{-1})_{\text{tire}} = \log_{10} \left( \frac{65.95}{63.14} \right) = 0.0189 \text{ Abs.}
\]

From figure 14 it is seen that transmissions below about 0.02 % are not discernible in an IR spectrum, which corresponds to a minimum absorption of

\[
\Delta \text{Abs}_{\text{min}} = \log_{10} \left( \frac{63.78}{63.76} \right) = 0.1362 \text{ mAbs.}
\]

Leading to a tire detection limit of

\[
\text{Conc.}_{\text{min}} (\text{tire}) = \left( \frac{0.1362 \cdot 10^{-3} \text{ Abs}}{0.0126 \text{ Abs}} + \frac{0.1362 \cdot 10^{-3} \text{ Abs}}{0.0189 \text{ Abs}} \right) \cdot 0.5 \cdot 1.9 \text{ mg tire}
\]

\[
= 0.0171 \text{ mg tire pr. sample or pill}
\]

This is a factor of 1.5 higher than the detection limit for HGA. If the solvent volume is decreased, the detection limit for HGA decreases proportionally whereas the detection limit for IR remains unchanged as the entire sample is applied to the KBr pill.
A comparison of the results found by IR and HGA is done in paper 1 as well as an evaluation of the interferences of selected sources to the analytical methods.

5.4 Results, tires and zinc

In this section the main results concerning measurements of tire particles and zinc in aerosol, soil and some selected samples, found by AAS, NAA and PIXE, are presented. The entire work concerning organic zinc and tire concentrations can be found in papers 1 and 3.

5.4.1 Determination of indicator zinc

In the outset of this work it was soon realised that zinc was an obvious choice as a tire indicator, and the crucial point was to establish a procedure that enabled the identification of zinc compounds that are unique to tire particles.

Initially it was tried to identify the tire zinc on basis of zinc oxide. The samples were first boiled in a weak acid solution thus removing zinc compounds originating from other sources than tires, as zinc oxide is insoluble in weak acid. Second the remains were boiled in concentrated acid giving primarily zinc oxide. As each sample was also analysed for bitumen, an organic dichloromethane extract of the samples was produced as a first step, and to achieve a distribution profile of the total tire zinc pool this extract was also analysed for zinc.

A suitable acid concentration that dissolved zinc compounds other than zinc oxide was sought. 0.1 M and 0.5 M nitric acid were used on a number of tire samples and to evaluate the effect of the acid strength on another main zinc source flyash from a waste incineration plant, containing a high concentration of inorganic zinc, was included in the measurements, see table 2. The organic extracts were boiled in concentrated nitric acid and all fractions were redissolved in 0.01 M nitric acid prior to analysis. Approximately 1 g of sample was analysed.

By comparing the results in table 2 and 3 it is seen that 16.9 % more tire zinc is dissolved in the 0.5 M fraction than in the 0.1 M fraction. An increase of only 1.8 % is seen in the flyash sample. The conclusion from this limited experiment is that 0.1 M nitric acid is more suitable than 0.5 M for separating tire zinc from other zinc sources.

The procedure for these introductory experiments can be summarised as follows: The organic zinc chelates can be extracted in an organic solvent such as dichloromethane (CH$_2$Cl$_2$) and by boiling the organic extract in concentrated nitric acid the organic material is oxidised and the zinc can be brought into an aqueous solution. After boiling a tire sample in 0.1 M or 0.5 M nitric acid a larger amount of the tire zinc is obtained as ZnS is dissolved, and when boiling in concentrated nitric acid ZnO is dissolved and all of the organic constituents in the rubber material are destroyed.

In table 4 the different zinc fractions, now using 0.1 M nitric acid, are given for a number of sources related to particulate pollution. The concentrated HNO$_3$ zinc fraction, that should be characteristic to tires, is also found in considerable amounts in diesel exhaust, drum brake dust and especially in flyash from waste incineration. However the surprising point is that only tires
and engine oils (containing anti wear additives such as zinc dithiophosphate) contribute to the organic zinc fraction. Unfortunately the concentration levels are approximately the same in tires and engine oils, about 1 mg org Zn pr. g, but since the exhaust samples show no extractable organic zinc, organic engine oil zinc will probably only spread in the environment through dripping on the road surface where it may adsorb onto soil particles. These are typically larger than 2 µm which reduces the tendency toward resuspension. The main part will however be washed into the gutters during rainfall and thus never be airborne.

These introductory findings lead to the assumption that extractable organic zinc is the most suitable tire zinc indicator since tires are the main source to extractable organic zinc in aerosols with 1394 µg Zn pr. g tire (COV = 17.8 %), from table 2 and 3, or 1290 µg Zn pr. g tire as found in paper 1. When boiling an aerosol or soil sample in acid the abundant inorganic zinc that is present in other sources such as flyash, will concurrently be dissolved and thus drown the zinc contribution from tires.

In the following only the extractable organic zinc, for quantifying tire particles, and the total remaining zinc, from ashing at 500 °C, is determined (see figure 25 and figure 1 paper 1).
Table 2 Zinc distribution in tire and flyash samples, using 0.1 M nitric acid [µg Zn pr. g d.w.].

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Extracted in CH₂Cl₂ [µg Zn pr. g d.w.]</th>
<th>Boiled in 0.1 M HNO₃ [µg Zn pr. g d.w.]</th>
<th>Boiled in concentrated HNO₃ [µg Zn pr. g d.w.]</th>
<th>Ashed at 500 °C [µg Zn pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tire (used), XT 165/70-R14</td>
<td>1720 (20.5 %)</td>
<td>2820 (33.7 %)</td>
<td>3520 (42.1 %)</td>
<td>320 (3.8 %)</td>
</tr>
<tr>
<td>Tire (used), 185/60-R14 Radial 82T</td>
<td>1190 (11.9 %)</td>
<td>3000 (30.1 %)</td>
<td>5530 (55.3 %)</td>
<td>270 (2.7 %)</td>
</tr>
<tr>
<td>Tire (used), 145 SR 14 Radial 76S</td>
<td>1220 (12.5 %)</td>
<td>3850 (39.4 %)</td>
<td>4520 (46.2 %)</td>
<td>190 (1.9 %)</td>
</tr>
<tr>
<td>Truck tire (used), ?</td>
<td>1400 (14.5 %)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Truck tire (unused), Bridgestone 385/65-R22.5</td>
<td>1900 (13.0 %)</td>
<td>3670 (25.1 %)</td>
<td>8760 (59.9 %)</td>
<td>300 (2.0 %)</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>1390 (16.3 %)</td>
<td>2990 (35.0 %)</td>
<td>4010 (47.0 %)</td>
<td>140 (1.7 %)</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>1240 (15.7 %)</td>
<td>2820 (35.6 %)</td>
<td>3620 (45.8 %)</td>
<td>230 (2.8 %)</td>
</tr>
<tr>
<td>Flyash from waste incineration plant</td>
<td>b.d.</td>
<td>20140 (91.2 %)</td>
<td>1440 (6.5 %)</td>
<td>500 (2.3 %)</td>
</tr>
<tr>
<td>Flyash from waste incineration plant</td>
<td>b.d.</td>
<td>18500 (90.2 %)</td>
<td>1550 (7.6 %)</td>
<td>470 (2.3 %)</td>
</tr>
</tbody>
</table>

Table 3 Zinc distribution in tire and flyash samples, using 0.5 M nitric acid [µg Zn pr. g d.w.].

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Extracted in CH₂Cl₂ [µg Zn pr. g d.w.]</th>
<th>Boiled in 0.5 M HNO₃ [µg Zn pr. g d.w.]</th>
<th>Boiled in concentrated HNO₃ [µg Zn pr. g d.w.]</th>
<th>Ashed at 500 °C [µg Zn pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tire (used), XT 165/70-R14</td>
<td>1420 (13.5 %)</td>
<td>5290 (50.2 %)</td>
<td>3560 (33.8 %)</td>
<td>270 (2.6 %)</td>
</tr>
<tr>
<td>Tire (used), 185/60-R14 Radial 82T</td>
<td>1150 (11.2 %)</td>
<td>5750 (56.3 %)</td>
<td>2990 (29.3 %)</td>
<td>320 (3.1 %)</td>
</tr>
<tr>
<td>Tire (used), 145 SR 14 Radial 76S</td>
<td>1230 (12.4 %)</td>
<td>4980 (50.3 %)</td>
<td>3420 (34.5 %)</td>
<td>270 (2.7 %)</td>
</tr>
<tr>
<td>Truck tire (used), ?</td>
<td>1220 (9.8 %)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Truck tire (unused), Bridgestone 385/65-R22.5</td>
<td>1850 (12.8 %)</td>
<td>6930 (48.0 %)</td>
<td>5410 (37.5 %)</td>
<td>240 (1.6 %)</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>1280 (11.8 %)</td>
<td>5190 (48.1 %)</td>
<td>4140 (38.3 %)</td>
<td>190 (1.7 %)</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>1300 (11.9 %)</td>
<td>5190 (47.4 %)</td>
<td>4310 (39.4 %)</td>
<td>140 (1.3 %)</td>
</tr>
<tr>
<td>Flyash from waste incineration plant</td>
<td>b.d.</td>
<td>21030 (92.3 %)</td>
<td>1340 (5.9 %)</td>
<td>410 (1.8 %)</td>
</tr>
<tr>
<td>Flyash from waste incineration plant</td>
<td>b.d.</td>
<td>21220 (92.6 %)</td>
<td>1310 (5.7 %)</td>
<td>400 (1.7 %)</td>
</tr>
</tbody>
</table>
Table 4 Zinc distribution in various samples. Zn is measured with FAA unless otherwise stated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extracted in CH$_2$Cl$_2$ [µg Zn pr. g d.w.]</th>
<th>Boiled in 0.1 M HNO$_3$ [µg Zn pr. g d.w.]</th>
<th>Boiled in conc. HNO$_3$ [µg Zn pr. g d.w.]</th>
<th>Ashed at 500 °C [µg Zn pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt, Svaleholm</td>
<td>3.85* (4.0 %)</td>
<td>60 (62.3 %)</td>
<td>36 (37.7 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Asphalt, Jagtvej</td>
<td>1.77* (4.1 %)</td>
<td>30 (69.9 %)</td>
<td>13 (30.1 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Asphalt, Newly laid</td>
<td>1.50* (3.9 %)</td>
<td>25 (65.5 %)</td>
<td>13 (34.5 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Diesel exhaust on quartzfilter: Pallflex 2500 qat-up</td>
<td>b.d.</td>
<td>944 (63.5 %)</td>
<td>411 (27.7 %)</td>
<td>130 (8.8 %)</td>
</tr>
<tr>
<td>Quartzfilter: Pallflex 2500 qat-up</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Soot from exhaust pipe, gasoline car</td>
<td>b.d.</td>
<td>104 (13.5 %)</td>
<td>666 (86.5 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Soot from exhaust pipe, diesel car</td>
<td>b.d.</td>
<td>188 (23.2 %)</td>
<td>624 (76.8 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Engine oil (unused), Shell standard, Helix 10W-40</td>
<td>1085 (99.0 %)</td>
<td>11 (1.0 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Engine oil (after 1000 km), Shell standard, Helix</td>
<td>967 (89.5 %)</td>
<td>113 (10.5 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Engine oil (after 1500 km), Diesel car</td>
<td>947 (98.0 %)</td>
<td>19 (2.0 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Engine oil (after 1700 km), gasoline car</td>
<td>650 (97.6 %)</td>
<td>16 (2.4 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Dust from disc brakes, scratched from blocks</td>
<td>b.d.</td>
<td>117 (79.5 %)</td>
<td>30 (20.5 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Dust from drum brakes (dirty)</td>
<td>b.d.</td>
<td>335 (63.5 %)</td>
<td>111 (21.2 %)</td>
<td>81 (15.4 %)</td>
</tr>
<tr>
<td>Flyash from private woodburner (beech)</td>
<td>b.d.</td>
<td>b.d.</td>
<td>21 (100 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Flyash from private woodburner (birch)</td>
<td>b.d.</td>
<td>b.d.</td>
<td>26 (100 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Flyash from coalfired power station 1)</td>
<td>b.d.</td>
<td>15 (33.6 %)</td>
<td>30 (66.4 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Flyash from coalfired power station 2)</td>
<td>b.d.</td>
<td>16 (37.9 %)</td>
<td>26 (62.1 %)</td>
<td>b.d.</td>
</tr>
<tr>
<td>Flyash from waste incineration plant 3)</td>
<td>b.d.</td>
<td>20138 (91.2 %)</td>
<td>1438 (6.5 %)</td>
<td>498 (2.3 %)</td>
</tr>
<tr>
<td>Flyash from crematorium</td>
<td>b.d.</td>
<td>10 (13.7 %)</td>
<td>64 (86.3 %)</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

*1) Measured with HGA.

b.d. = below detection limit for FAA (< 0.2 µg Zn pr. g d.w.).

1) With electrostatic filter. Less than 50 mg/m$^3$ left in the exhaust.

2) With electrostatic filter, filterbag and scrubber. No more than 10 mg/m$^3$ left in the exhaust.

3) Semi dry and filterbag and scrubber.
If a source contributes to the total suspended particulate matter (TSP) with 1.0 wt-% of TSP or more, and TSP has a typical value of 5 mg, the lower detectable concentration limit in terms of extractable organic zinc is

$$\text{Conc.}(\text{Zn})_{\text{min,FAAS}} = \frac{0.0165 \cdot 10^3 \mu g \text{ Zn pr.} 1 \cdot 0.011}{0.01 \cdot 5 \cdot 10^{-3} g} = 3300 \mu g \text{ Zn pr. g source.}$$

$$\text{Conc.}(\text{Zn})_{\text{min,HGA}} = \frac{1.6 \mu g \text{ Zn pr.} 1 \cdot 0.011}{0.01 \cdot 5 \cdot 10^{-3} g} = 320 \mu g \text{ Zn pr. g source.}$$

for FAAS and HGA respectively.

Or in other words; if a source is to be quantified in an aerosol sample down to a concentration of 1.0 wt-% of TSP, the extractable organic zinc concentration in the source must not be lower than 3300 \( \mu g \) Zn pr. g or 320 \( \mu g \) Zn pr. g, as measured with FAAS and HGA respectively. From table 2, 3 and 4 it can be concluded that only tire and engine oil contain extractable organic zinc in concentrations sufficiently high to be quantified in aerosol samples.

### 5.4.2 Aerosol samples

The principal result that has been obtained from the aerosol measurements, is the characteristic size distribution of the airborne tire tread particles found with impactors in Copenhagen and at Risø. Figure 15 shows a representative distribution profile sampled in Copenhagen during cold and dry weather in January 1996.

The following mean airborne particulate tire mass distribution has been found

- Tire particles with \( d_a > 10 \mu m \): 7.8 wt-% (COV = 53.1 %, \( N = 4 \)).
- Tire particles with \( d_a < 1 \mu m \): 92.2 wt-% (COV = 4.5 %, \( N = 4 \)).

The tire particles comprise between 2.2 and 5.8 wt-% of the TSP, where the larger value is from Copenhagen in dry weather.
From another impactor set taken in Copenhagen, the results in figures 16 to 18 are produced. The TSP size-mass distribution in figure 16 shows the predominance of accumulation mode particles. A nuclei stage can be distinguished whereas a distinct coarse fraction is absent.

![Figure 16 TSP distribution in impactor sample.](image1)

The total zinc and the extractable organic zinc distributions, found with HGA, are shown in figure 17.

![Figure 17 Total and extractable organic zinc (x 10) in impactor sample, measured with HGA.](image2)

The tire concentration is proportional to the organic zinc concentration and again there are two peaks or groups of tire particles, one large fraction comprising of 87% of the total airborne tire mass for aerodynamic diameters below 1 µm, and a small fraction, 13% of the total tire mass, for diameters larger than 10 µm. The tire particles constitute about 20% of the total zinc in TSP.
Blank readings found with HGA for the Teflon filters are below the detection limits both for the organic and the total zinc fraction.

In figure 18 the total zinc distribution is found with NAA and it can be seen that it is in accordance with the HGA measurements. The total amount of zinc is however a factor of 1.6 lower than the HGA results.

To illustrate that the aerosol particles in the different size fractions have different origin and elemental compositions a series of elements in the same impactor set as above are shown appendix I.

Seven medium volume filters sampled during one week in May 1995 in Copenhagen have been analysed with PIXE as well as with HGA. The total zinc and organic zinc results are shown in figure 19.
The daily mean tire mass contribution is 6.6 wt-% of the TSP.

The blank results for one cellulose acetate/cellulose nitrate filter are below the detection limit and 4.8 ng Zn pr. m$^3$ (60 m$^3$ pr. day) for organic zinc and total zinc respectively, as found with HGA. PIXE yields a blank value of 2.47 ng total zinc pr. m$^3$.

### 5.4.3 Soil samples

Tire concentrations have been measured in top soil in different distances from highways and in different depths in the soil. The total and organic zinc distributions in soil from Utterslev Mose are shown in figure 20. The organic zinc approximately constitute 0.2 % of the total zinc. The tire constitutes from 0.05 to 0.63 mg tire pr. g soil at 30 m and 0 m from the highway respectively.

It is assumed that close to the road the large particles (> 20 µm) deposit. The small particles (< 1 µm) remain airborne and spread by turbulence and diffusion and contribute to a background concentration that can be found far from traffic activities. Pierson et al. (1974) found that only between 2 and 7 % of the SBR derived from tire wear is recovered as aerosols and that the predominant fraction deposits immediately in the roadside.

Vertical tire concentration profiles show that the concentrations in depths of 3 cm are only 20 % of the top soil concentrations, which indicate that the extractable organic zinc is originating from airborne sources and not from the soil.

![Total and organic zinc concentrations in top soil samples near highway.](image)
5.5 Discussion, tires

The size distribution found in this study is similar to that of previous investigations which show that airborne particles generated from the wear of tires are divided into two size groups, namely particles with aerodynamic diameters larger than 7 µm and a smaller group about 1 µm (Cardina, 1974, Dannis, 1974, Pierson et al., 1974 and Cadle et al., 1978).

This remarkable bimodal airborne tire size distribution has been explained by Cadle et al. (1978) suggesting, that part of the tire wear derives from local hot spots on the tire surface, where the temperature exceeds 180 ºC and particulate material is produced by polymer degradation and volatilisation of extender oils. This thermoparticulation could account for the submicron particles. By mechanical abrasion particles larger than 10 µm are generated and give rise to the dominant part of the tire wear.

In contrast to this Pierson et al. (1974) state that thermal degradation during use is negligible since experiments show that the necessary temperature in the contact zone between the tire and asphalt is about 380 ºC when the induction time for thermal degradation is equal to the actual contact time, which is about 10⁻² sec.

Increasing driving velocities increase the amount of tire debris and lower the mean particulate size (Dannis, 1974). Both the amount and distribution of the tire dust particles are dependant on the roughness of the road surface and the driving pattern (Dannis, 1974). Wear rates of 0.006-0.09 gₜire pr. km are stated in the literature.

Assuming that the tire wear rate is 30 mg pr. km pr. tire and the traffic density for the highway near Utterslev Mose is 37900 vehicles pr. day the tire mass emission rate is 4.5 kg tire pr. km pr. day. According to figures 3, 4 and 5 in paper 3 the predominant amount of airborne tire debris deposits within 5 m beside the highway and mixes with the upper 1 cm of the soil. If the deposited rubber does not decompose, is distributed evenly and is not removed from the soil, the annual tire concentration in this soil (ρ = 2.4 kg pr. l) would be 7 mg tire pr. g soil, which is a factor of 10 higher compared to the measured concentrations. Factors like degradation or physical removal under heavy rainfall or maintenance will reduce the concentrations.

The breakdown of SBR on account of photochemical decomposition (UV-light) and oxidation by oxygen and ozone will undoubtedly have an influence on both the airborne and the deposited particulate SBR. The rate of degradation will nevertheless be slow for aerosols because of the low temperature and the presence of antioxidants in the rubber material (Dannis, 1974).

According to Dannis (1974) there is no evidence of biodegradation of the rubber polymers, while others have found that SBR and natural rubber (NR) slowly will be attacked by fungi and bacteria which will result in considerable breakdown.

Resuspension of settled material will also contribute to removal and reentrainment of particulate matter. Resuspension is more easily achieved on a smooth surface than on a dirt road where the particles as a function of time can attach to soil particles and mix with the top layer or be washed away.
Bearing in mind that motoroils contain an equivalent amount of extractable organic zinc as tires do, it is important to include the interference from the oil coated soil particles in the immediate vicinity of the roads. These particles are also subject to further spreading by resuspension but it is assumed that they will not spread further than about 10 m from the road. In zinc profiles such as in figure 20 the analytical procedure does not permit differentiation between oil and tire organic zinc.
6 Bitumen

6.1 Composition

About 90 wt-% of asphalt is fillers such as sand and stone and to stabilise this mineral matrix lime or flyash is used. To bind and strengthen the material bitumen is added. Bitumen is a dark brown to black viscous, non-volatile residue from oil distillation with a highly complex composition that varies according to the origin and refining procedures of the oil. To improve the adherence fatty amines are added and additional fillers like cork and rubber are often used. The organic compounds used in asphalt materials generally have low vapour pressures and consequently high particulate affinity as air pollutants.

A model of bitumen can be as described by Branthaver et al. (1992): Polar and aromatic compounds are dispersed in a less aromatic non polar solution. The polar fraction contains the largest percentage of heteroatoms, e.g. N, O, S and metals, and has the higher molecular weight and viscosity.

Hagen et al. (1989) use the following model: Bitumen is a residuum composed of a colloidal dispersion of solid particles known as asphaltenes in an oily medium of saturated and aromatic hydrocarbons known as oils and resins respectively. The viscosity and strength of the asphalt depend on the quantity and size of the asphaltene particles and on the relative amounts of oils and resins that solubilise them.

Hagen et al. (1989) defines the different fractions as follows: The oils function as the dispersion medium for the asphaltenes which are solubilised by the resins. They represent the lowest molecular weight component of the asphaltic system with a molecular weight range of 200 to 600. They are composed of a single fused naphthenic ring substituted with linear and branched aliphatic side chains of varying lengths as well as alkylated aromatic ring systems.

The resins have higher molecular weights and are predominantly comprised of saturated polyaromatics (6 to 16 condensed rings) containing heteroatoms. The resins are more polar than the oils. The aromatic properties and the presence of heteromolecules control the solubility of the asphaltenes in the oils fraction. Chemically speaking the resins are a mixture of oils and asphaltenes.

The asphaltenes contain the largest organic compounds in the bitumen product, with molecular weights ranging up to about 1000 corresponding to about 80 carbon atoms. The asphaltenes are the only hydrocarbons that are not soluble in n-heptane. It has been suggested that the asphaltenes are a maturing product of the resins and therefore are quite similar in structure. There is however a higher degree of aromacity and polar substituent groups and heterocyclic content than in the resins. The aromatic structure of the asphaltenes contain free radical sites with reactive unpaired electrons that are liable to form complexes with metals such as Ni and V.

Hagen et al. (1989) have stated the following compositions (wt-% carbon)

Table 5 Bitumen classification according to Hagen et al. (1989).
Oils Resins Asphaltenes Total (bitumen)

<table>
<thead>
<tr>
<th></th>
<th>Oils</th>
<th>Resins</th>
<th>Asphaltenes</th>
<th>Total (bitumen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic compounds</td>
<td>20</td>
<td>30</td>
<td>52</td>
<td>32</td>
</tr>
<tr>
<td>Saturated ring systems and other aliphatics</td>
<td>60</td>
<td>55</td>
<td>35</td>
<td>47</td>
</tr>
<tr>
<td>Linear aliphatics</td>
<td>17</td>
<td>13</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Branched aliphatics</td>
<td>8</td>
<td>4</td>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>

Others have used a similar classification criteria (wt-% carbon)

Table 6 Bitumen classification.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>68</td>
<td>42</td>
<td>32</td>
<td>35</td>
<td>24</td>
</tr>
<tr>
<td>Saturates</td>
<td>26</td>
<td>29</td>
<td>34</td>
<td>64</td>
<td>19</td>
</tr>
<tr>
<td>Polars</td>
<td>6^1</td>
<td>16</td>
<td>12</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>-</td>
<td>13</td>
<td>22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27</td>
</tr>
</tbody>
</table>

^1) All molecules contain heteroatoms like N, O, S and possibly heavy metals.

6.2 Bitumen indicator

Very few investigations have been done with the aim to identify bitumen particles in the environment, but rather to characterise the bitumen in terms of maximum strength and ductility properties.

At the Danish Technical University in Lyngby two separate investigations have nevertheless been performed with the purpose to measure bitumen concentrations in aerosols, soil and in plant samples.

Elvebakken (1991) used PAH's as indicators although previous measurements showed that particulate PAH’s originated from a number of sources other than bitumen. More than 300 different PAH’s are present in bitumen but each compound only occurs in concentrations below about 0.1 % and there is no PAH that is unique for bitumen. The advantage of identifications based on PAH’s are the standardised measurement techniques that exist, but the lacking specificity to bitumen were estimated to render the methods unfitted for the desired purpose in this work.

He et al. (1993) and Rosenmejer (1993) used the polar, aromatic and saturated fractions, achieved by high performance liquid chromatography (HPLC) with a reversed phase C-18 column, as indicators. In this way the polarity of the solubilised organic compounds is determining for the affinity to the stationary phase or the liquid (mobile) phase respectively. The stationary phase in a C-18 column comprises unbranched aliphatic molecules with 18 carbon atoms, i.e. the relatively large and non polar compounds will have larger affinity to the stationary phase than to the more polar solvents like e.g. dichloromethane. The groups will elute in the following order: polar, aromatic and saturated compounds. This approach was tried with a variety of solvents, but did not reveal a usable fingerprint profile for bitumen.
The HPLC analysis did however lead to the assumption that relatively large organic molecules could be used as indicators. This was confirmed by articles dealing with the molecular weight distributions in bitumen and other particulate sources such as brake lining and tires (Rogge, 1993).

Jennings et al. (1992) found a mean molecular weight for bitumen around 800. Dark et al. (1978) state an empirical mean molecular formula determined by GPC in the interval: \( \text{C}_{33}\text{H}_{51}\text{N}_{0.1}\text{O}_{1.6} \) to \( \text{C}_{78}\text{H}_{133}\text{N}_{0.5}\text{O}_{0.3} \). Barbour et al. (1992) have found carbon numbers between 30 and 110 in different bitumens. Waxes and oils from e.g. bitumens and plants and the soluble fraction of soot and flyash from the burning of fossil fuels have molecular weights below 200. In the interval above 1000 one will find complex aromatic compounds, originating mainly from bitumens. Plants and bacteria can contribute with polysaccharides, starch, cellulose, proteins and nucleic acids where some are water soluble. Some enzymes like the nitrogenases can be separated into two protein parts with molecular weights around \( 260 \times 10^3 \) and \( 240 \times 10^3 \) (Cotton et al., 1995).

These investigations combined with the performed HPLC analysis indicated that the larger airborne organic molecules predominantly originated from asphalts.

### 6.3 Experimental methods for bitumen identification

The molecular size separation is performed with high performance gel permeation chromatography (HP-GPC) with fluorescence detection and the instrumental setup is illustrated in figure 21. Again IR is used as a second method.

The experimental methods are described in detail in paper 2 where the interferences from other sources to particulate airborne pollution are also evaluated. In the following sections the detection limits, specific molecular sizes and infra red characteristics are presented for HP-GPC and IR.

#### 6.3.1 HP-GPC

In appendix J the calibration curve, lower detection limit and reference values are shown. The lower detection limit is 17 µg bitumen pr. sample (dissolved in 10 ml solvent).
Figure 21 Schematic outline of HP-GPC setup with fluorescence detection.

6.3.2 IR

As for the tire analysis a second independent method is employed to verify the results found with HP-GPC. The instrument is described previously in the text.

In figure 22 an IR-spectrum, showing the interval between 400 and 4000 cm\(^{-1}\), of a 2.2 mg bitumen sample is shown. The characteristic absorption lines in bitumen are identical to the lines in tires in the high energy part of the spectrum.

The important differences lie in the low energy region, ranging from 600 to 950 cm\(^{-1}\) where the lines that are specific to bitumen are (see figure 23)

\textit{Aromats (C-H vibrations):} \[ \begin{align*} \delta_{\text{C-H}} &= 875 \text{ cm}^{-1} \\ \delta_{\text{C-H}} &= 814 \text{ cm}^{-1} \\ \delta_{\text{C-H}} &= 765 \text{ cm}^{-1} \\ \delta_{\text{C-H}} &= 748 \text{ cm}^{-1} \end{align*} \]
The simultaneous occurrence of the 748 and the 875 cm\(^{-1}\) lines are used as bitumen indication in the aerosol and soil samples. The bitumen spectrum in figure 23 is used as standard and the bitumen concentration in a sample can be calculated by using the following equation

\[
\text{Conc.}(\text{tire}) = \left( \frac{\text{abs}(748 \text{ cm}^{-1})_{\text{sample}}}{\text{abs}(748 \text{ cm}^{-1})_{\text{bitumen}}} + \frac{\text{abs}(875 \text{ cm}^{-1})_{\text{sample}}}{\text{abs}(875 \text{ cm}^{-1})_{\text{bitumen}}} \right)^{1/2} \cdot \text{mass}_{\text{bitumen}}.
\]

where

\[
\text{abs}(748 \text{ cm}^{-1})_{\text{bitumen}} = \log_{10} \left( \frac{10}{T} \right) = \log_{10} \left( \frac{46.30}{45.64} \right) = 0.00624 \text{ Abs.}
\]

\[
\text{abs}(875 \text{ cm}^{-1})_{\text{bitumen}} = \log_{10} \left( \frac{46.74}{45.77} \right) = 0.00911 \text{ Abs.}
\]

From figure 23 it is seen that transmissions below about 0.02 % are not discernible in an IR spectrum, which corresponds to a minimum absorption of

\[
\Delta \text{abs}_{\text{min}} = \log_{10} \left( \frac{42.28}{42.26} \right) = 0.2055 \text{ mAbs.}
\]

Leading to a bitumen detection limit of

\[
\text{Conc.}(\text{bitumen})_{\text{min}} = \left( \frac{0.2055 \cdot 10^{-3} \text{ Abs}}{0.00624 \text{ Abs}} + \frac{0.2055 \cdot 10^{-3} \text{ Abs}}{0.00911 \text{ Abs}} \right) \cdot 0.5 \cdot 2.2 \text{ mg bitumen}
\]

\[
= 0.061 \text{ mg bitumen pr. sample or pill}
\]
which is approximately 60 µg tire pr. KBr pill and a factor of 3.5 higher than the detection limit for HP-GPC. If the solvent volume is decreased the detection limit for HP-GPC decreases proportionally while the detection limit for IR remains unchanged as the entire sample is applied to the KBr pill.

A comparison of the results found by the two methods is done in paper 2 as well as an evaluation of the interferences of selected sources to the analytical methods.

### 6.4 Results and discussion, bitumen

#### 6.4.1 Indicator molecules

The composition of the examined asphalts is found to be

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% of Bitumen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen</td>
<td>12.7 (COV = 21.0 %, N = 7)</td>
</tr>
<tr>
<td>Maltenes (n-heptane solubles)</td>
<td>80.2 (COV = 7.2 %, N = 7)</td>
</tr>
<tr>
<td>Asphaltene (n-heptane insolubles)</td>
<td>23.2 (COV = 30.6 %, N = 7)</td>
</tr>
</tbody>
</table>

In figure 3a in paper 2 the chromatograms of bitumen, maltenes and asphaltene samples from a newly laid asphalt are shown. The bitumen size distribution is bimodal with \( M_p \) around 1500 and 400. The n-heptane soluble fraction (maltenes) has a \( M_p \) around 400. The asphaltene distribution is broad with two discernible peaks around 1600 and 400. Assuming that the fluorescence is identical for the molecules larger than 2000 g pr. mol, it can be calculated from figure 3a, that 74 % of the bitumen molecules larger than 2000 g pr. mol are asphaltenes.

By comparing with the chromatograms of other sources, see table 2 in paper 2, it is found that bitumen is the main contributor to organic molecules larger than 2000 g pr. mol in aerosol samples, since the interferences are insignificant from tire (oils and waxes), exhaust soot, brake lining and flyash samples, whereas the diesel exhaust and engine oil samples, especially the fresher oils, can cause some problems. 1 g of engine oil yields an equivalent bitumen content of about 100 mg.

#### 6.4.2 Aerosol samples

In figure 24 the airborne bitumen particle profile in Copenhagen air is shown. The bitumen distribution follows the TSP distribution and has an approximately normally distributed mass peak around 0.71 µm.

71 wt-% (COV = 8.8 %, N = 4) of the bitumen debris occurs in the interval between 0.35 µm and 2.8 µm.
With the medium volume sampler it is found that the daily mean mass contributions of bitumen particles are 10.1 wt-% of the TSP. The daily mean gravimetrically determined organic matter comprises 17.3 wt-% of the TSP.

### 6.4.3 Oxidation of bitumen

An experiment was performed to verify the fact that the molecular weights of the bitumen fractions increase under the influence of photo oxidation and oxidising gases that are present under normal weathering conditions.

Bitumen, maltene and asphaltene fractions that were placed between two quartz discs and were exposed to sunlight for three months during the summer showed a slightly different molecular size distribution than the unexposed fractions. The gravimetrically determined asphaltene content (extracted from the oxidised bitumen fraction) increased from 18.2 to 22.0 wt-% of the bitumen, and correspondingly the maltene fraction decreased from 86.4 to 80.8 wt-%. The oxidised maltene chromatogram now showed a bimodal structure with $M_p$ around 1400 and 300.

The increase of larger and more polar molecules can be accounted for by the oxidation by UV-light and atmospheric oxygen, resulting in an increased polymerisation of saturates and introduction of oxygen containing functional groups (Huang et al., 1995 and 1997).

This is confirmed by Bech-Jacobsen et al. (1989) where ageing of bitumens by storing tablets in incubators at 60 to 80 °C for up to 93 days show that additional or increased absorption lines arise at carbonyl (C=O) 1700 cm$^{-1}$, sulphur dioxide (SO$_2$) 1130 cm$^{-1}$ and sulphur monoxide (S=O) 1034 cm$^{-1}$.

Brûlé et al. (1986) investigated the changes in molecular sizes by blowing the asphalt cement. By blowing the asphalt an artificial weathering is performed and the complex colloidal equilibrium:

$\text{Molecules} \leftrightarrow \text{Micelles} \leftrightarrow \text{Aggregates}$
is shifted to the right. The same phenomenon was observed by low temperature oxidation during in-situ weathering. The shift is accompanied by an increase in the asphaltene content at the expense of the oils and resins as well as an increase in the amount of micelles interacting to form aggregates that give the material an intermediate sol-gel structure with a viscoelastic behaviour. In the extreme case, for oxidised cements, the perfect gel structure is reached in which the asphaltenes are organised in a three dimensional network, giving the medium its elasticity.

The oxidation of asphalt is the major factor contributing to the age hardening and is believed to result primarily from the introduction of oxygen containing chemical functionalities such as carbonyl groups which, because of their polar nature, greatly increase molecular interaction forces, thus increasing viscosity. Jennings et al. (1989) suggest that the large molecular size portion of a bitumen is a measure of the relative tendency of asphalts to undergo transverse cracking.

The consequence of bitumen particles being exposed to oxidising conditions is thus a change in the molecular size distribution yielding larger molecules and a change in molar absorptivity with respect to absorption of UV-light and accordingly an alteration in the concentration of the remaining fluorophoric materials (Mitchell et al., 1992). This implies that the quantification of bitumen in airborne or deposited particles is dependant on the exposure time and size of the bitumen particles. When using large molecules as indicators smaller particles combined with long residence times in the atmosphere yield an overestimation of bitumen when a newly laid bitumen is used as standard.

Finally the relevance in using fluorescence detection is briefly commented. The aromatic compounds are highly fluorescent whereas saturated organics are not and these require other detection techniques such as differential refractive index detection which is capable of detecting virtually all material, but suffers from drifting baseline, low sensitivity and lack of reproducibility. Saturated compounds which constitute about 30% of the bitumen will not absorb UV-light, and the problem concerning varying molar absorptivity in the UV-region is of great importance. The types of functional groups that potentially yield fluorescence emissions are those containing π-electrons (most aromatic compounds and conjugated aliphatic polyenes), those containing heteroatoms of oxygen and nitrogen and carbonyl groups associated with ketones and aldehydes. Since these groups are abundant especially in the larger fraction of bitumen fluorescence is believed to be the most fitted detection method in these investigations.

The combined experimental procedure for samples that are to be analysed for tire and bitumen is outlined in the flowsheet in figure 25.
7 Combined flow-sheet for tire and bitumen analysis

Figure 25 Flow sheet of chemical analysis method for tire and bitumen.

1) 3 ml when bitumen IR-analysis is performed.
8 Deposition and absorption of tire particles on plants

8.1 Introduction

The majority of agricultural areas are situated well away from polluting sources, but appreciable concentrations of trace metals are nevertheless found in the atmosphere on rural sites (Harrison et al., 1982 cited by Harrison et al., 1989). The accumulation is found to decrease rapidly with increasing distance from the source and the contamination of crops in rural areas that actually take place, is believed to be a consequence of long range transportation of submicron particles.

There are several pathways where aerial contaminants may enter a plant. The root system has for a long time been accepted as the principal nutrient absorbing organ, but numerous studies have shown that the aboveground parts of the plant like the leaves, the bark and the fruits may act as deposition platforms for airborne particulates. The crucial point is to determine whether harmful deposited pollutants will be absorbed, enter the plant and be translocated throughout the plant to cause adverse effects on the plants physiological processes, or if they simply will adsorb to the surface and be removed by rainfall and wind.

The purpose of this work is to measure the concentrations of particulate tire debris that is ad-, and absorbed in plant leaves. Identification of tire material is described in paper 1. Airborne tire debris is predominantly found in the aerodynamic diameter range 0.042 - 1 \( \mu \text{m} \) (paper 3) and thus have the potential to spread to remote areas.

8.2 Deposition on plants

For particles larger than 0.1 \( \mu \text{m} \) in diameter the pubescence of the leaves are highly determinant for the retention on leaf surfaces. Wedding et al. (1975) found a ten times greater collection efficiency of PbCl\(_2\) particles with aerodynamic diameter 3.4 \( \mu \text{m} \) for the pubescent leaves of *Helianthus anuus* (sunflower) than for the glabrous leaves of *Liriodendron tulipifera* (tulip poplar). This enhanced capturing ability is essentially due to an increased deposition area caused by greater roughness or hairiness.

The roughness profile appears most prominently to the particles when the leaf is parallel to the direction of particle trajectory (Wedding et al., 1975). The removal can be caused simply by capturing by roughness elements or by impaction where particles from a turbulent airstream are projected across the viscous sublayer by transverse eddy velocities. Deposition will only occur if the stopping distance of the particle in question exceeds the boundary layer thickness (Wells et al., 1967).

For submicron particles the dominant transfer process is eddy diffusion and the pubescence becomes less important, however Impens et al. (1972) (cited by Little et al., 1977) and Keller (1974) showed that the filtration effect for exhaust Pb, that are mainly in the submicron range, of hedges along a motorway varied with different plant species, which implies that the surface morphology is of importance. Little et al. (1977) found that leaves possessing micro surface
roughness elements in the form of hairiness or other surface discontinuities demonstrated significantly higher Pb collecting efficiencies. As the leaf becomes smaller the turbulence around the edges reduces the laminar boundary layer and the resistance toward deposition by eddy diffusion. Sectioning of whole leaves demonstrated that Pb deposition was largest at the leaf tips and around the leaf margins (Chamberlain, 1960 cited by Little et al., 1977).

According to Little et al. (1977) the nature of surface wax deposits do not appear to affect Pb deposition markedly since the heavy crystalline incrustations of wax on the abaxial surface of oak leaves collected similar quantities as the smoother abaxial surface of willow leaves. Furthermore no results showed that the deposition velocities of Pb were consistently greater on the adaxial leaf surfaces compared to the abaxial surfaces. A study investigating the influence of leaf senescence showed no consistent results as to suggesting that the breakdown of the leaf surface in autumn would result in a more efficient collection of airborne particulates. For some species e.g. sycamore and elm it was true but for others such as aspen it was not (Little et al., 1977).

Once having reached the surface there are again a number of circumstances that will influence the adsorption and the velocity of possible uptake by the plant. For the particles to enter the plant via the foliage they have to penetrate the epicuticular waxes and the cuticle (see figure 27). The cuticle is a non cellular structure covering the epidermal layers of leaves, stems and fruits and is composed primarily of cutin, which is an hydrophobic insoluble lipid polymer and an important structural component of many plant cell walls. The major function of this polymer is to form a matrix in which waxes, that are long chain lipid compounds, are embedded. The waxes in particular, constitute a barrier that helps prevent the loss of water and other molecules from the aerial, or aboveground parts of the plant.

![Figure 26 Stoma of the privet (Ligustrum ovalifolium) (Baron, 1979).](image)

The cuticle can be interrupted by stomata through which the predominant part of the water and gaseous exchanges to the interior of the leaf take place, see figure 26. Some leaves possess stomata only on their lower surface, while others have them on both surfaces. Their numbers vary from 50 to 500 mm$^{-2}$ and the pore diameter is typically about 10 µm. Even if the gaseous or particulate compound enters the stoma, a substomatal, albeit delicate, cuticular barrier is
present (Franke, 1967 cited by Arvik et al., 1974). In spite of the barriers to foliar absorption sites are available on the plant surface that binds ions and pathways exist for the penetration of both lipid and water soluble substances (Franke 1967 cited by Arvik et al., 1974).

Many plant structures have a layer of wax on the outside of the cuticle called epicuticular wax, see figure 27.

![Figure 27 Cross section of leaf (Jeffree et al., 1976).](image)

This is usually secreted in the form of tubes, rods, granules or plates giving rise to a distinctive wax pattern. Arvik et al. (1974) found that removal of the epicuticular wax, by washing in chloroform, permitted passage of a significantly greater amount of particulate PbBrCl compared to when wax was present. Martin et al. (1957) (cited by Cutter, 1976) have shown that when grapes are dried water passes from the cells to inside the cuticle and thence by diffusion through the cuticle until it evaporates on reaching the exterior. The rate of drying was inversely proportional to the amount of cuticle present.

From this short review of previous investigations dealing with particulate deposition on leaves it is seen that there are many morphological factors that influence particle deposition and uptake in plants.

### 8.3 Sampling

The factors that are considered in the present work are pubescence, distance from the source (road) and precipitation. When possible, similar leaf species were collected on the different sites. It was emphasised to collect the samples from the same height, approximately 1.5 m above ground, so as to eliminate the varying degree of soil resuspension.

In table 7 the different leaf species are mentioned with respect to texture and leaf area. All species have an epicuticular wax layer.
Table 7 Sampled species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Texture Adaxial side</th>
<th>Texture Abaxial side</th>
<th>Approximate leaf area [cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wych elm <em>Ulmus glabra</em></td>
<td>highly pubescent</td>
<td>pubescent</td>
<td>69</td>
</tr>
<tr>
<td>Park elm <em>Ulmus carpinifolia</em></td>
<td>highly pubescent</td>
<td>pubescent</td>
<td>32</td>
</tr>
<tr>
<td>Cherry plum <em>Prunus cerasifera</em></td>
<td>slightly pubescent</td>
<td>slightly pubescent</td>
<td>13</td>
</tr>
<tr>
<td>Spindle tree <em>Euonymus europaeus</em></td>
<td>smooth</td>
<td>slightly pubescent</td>
<td>49</td>
</tr>
<tr>
<td>Laurel <em>Laurus nobilis</em></td>
<td>smooth</td>
<td>smooth</td>
<td>14</td>
</tr>
<tr>
<td>Cornelian cherry <em>Cornus mas</em></td>
<td>slightly pubescent</td>
<td>slightly pubescent</td>
<td>41</td>
</tr>
<tr>
<td>Willow <em>Salix aurita</em></td>
<td>slightly pubescent</td>
<td>slightly pubescent</td>
<td>33</td>
</tr>
<tr>
<td>Privet <em>Ligustrum vulgare</em></td>
<td>smooth</td>
<td>smooth</td>
<td>26</td>
</tr>
<tr>
<td>Beech <em>Fagus sylvatica</em></td>
<td>smooth</td>
<td>smooth</td>
<td>16</td>
</tr>
</tbody>
</table>

Leaf samples were taken on the locations stated below. The environmental conditions with respect to precipitation and distance from the roads are stated.

*Risø, by Roskilde Fjord:* The site is well away from main traffic activities and situated near a path in an overgrown area. It was attempted to sample three different leaf species of varying pubescence, namely wych elm, cherry plum and spindle tree, from the beginning of the growth season in May and then every month until the beginning of October, but due to shortness of time a sample series was performed from July to October 1997. Samples were taken from marked twigs to ensure similar age and exposure of the leaves. The varying precipitation is stated for each month in table 8.

Table 8 Weather conditions prior to leaf sampling, 1997.

<table>
<thead>
<tr>
<th>Weather conditions</th>
<th>July</th>
<th>August</th>
<th>September</th>
<th>October</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>warm and dry</td>
<td>warm and dry</td>
<td>rainy and windy</td>
<td>rainy and windy</td>
</tr>
</tbody>
</table>

*Hillerød highway:* Cherry plum and park elm samples were collected at two different distances in the brim of a forest, from the east and west side of the highway during dry and warm weather in August 1996.

*Lyngby highway:* Park elm leaves were collected 5 m from a highway in dry and warm weather in August 1996.
Åboulevarden: Åboulevarden is a heavily trafficked road in the centre of Copenhagen. Samples of wych elm from a single bush were collected 2 m from the road and 2 m above ground during dry weather and after rain in September 1996.

DTU, Lyngby: DTU is situated 10 km north of Copenhagen. Wych elm leaves were sampled approximately 200 m away from a highway during dry weather in September 1996.

Lyngby park cemetery: Laurel and cornelian cherry leaves were collected in the park area during rainy weather in November 1996.

Dyrehaven: Is a forest 10 km north of Copenhagen. Beech leaves were collected in dry weather in August 1996.

Botanical Garden: Is situated in the middle of Copenhagen. Willow and privet leaves were collected in October 1996 after a heavy rainfall.

Moss and millfoil samples were taken on the below stated locations. The surface textures of mosses and millfoil are highly complex and they are efficient filtrators of aerosols. Furthermore the mosses posses no epicuticular wax layer.

Svaleholm, Risø: Svaleholm is situated near Risø and lies adjacent to a main road. Moss and millfoil samples were taken from a garden surrounded by trees 5 m from the road during wet weather in October 1995.

Dannemare: Dannemare is a small village on Lolland. Moss samples were collected in a garden far from traffic in April 1996.

Utterslev Mose: Simultaneously with the soil samples, mosses were collected on the west side in three distances from a highway just outside Copenhagen in a park area in May 1996 during dry weather.

### 8.4 Sample treatment

#### 8.4.1 Removal of adsorbed particles

Particulate material that is deposited on the plant surface or that has been enclosed by the epicuticular wax layer can be removed from the remaining plant material by means of a procedure described by Rentschler (1982), where the sample is coated with a thin plastic film that successively is removed together with particles and epicuticular wax. This enables differentiation of absorbed or assimilated matter and particles that are merely adsorbed on the surface or that has been filtrated by hairiness on the surface. Rentschler mentions that the method is also usable when no wax layer is present and that hairs and other surface irregularities remain intact after the treatment. Furthermore it is possible to distinguish between ab and adaxial deposition.

Initially the sample is weighed and the dry/wet ratio is found for each plant type. The leaves are photocopied and the surface area is calculated.
Pioloform B (polyvinyl butyrals) type BL 16, from Wacker-Chemie, with the following composition and technical data, is used:

- Vinyl alcohol: 15 - 18 wt-%.
- Vinyl acetate: 80 - 84 wt-%.
- Vinyl acetate: 1 - 3 wt-%.
- K-value, DIN 53726: 44.
- Softening temperature, DIN 53460 Vicat A: 75 °C.
- Viscosity, DIN 53015: 24.5 mPa⋅s.

One wt-part of Pioloform is dissolved and mixed in 4 wt-parts of 96 % ethanol and put aside for approximately one hour in a glass beaker covered with Parafilm. The solution is dripped on the sample with a plastic pipette and the layer is spread to cover the entire surface by tilting the sample. It is important that the solution does not run off the sample and that the pipette is not used to spread the solution as particulate matter may be removed from the sample.

After drying the plastic film for approximately one hour until it is hardened but still soft, it is removed with plastic tweezers. It contains all the particulate matter deposited on the leaf surface and the epicuticular wax layer with enclosed particles. The plant surface remains intact as shown by scanning electron microscopical examination (Rentschler, 1982).

The leaf or plant samples that are to be treated with the plastic film must be fresh since the removal of the film is hindered when the sample is dry due to cracking and adherence of small plant fragments onto the film. Pubescence will enhance the adhering effect which makes the removal from fresh samples even more important.

### 8.4.2 Experimental procedures

#### Bitumen identification

Haas et al. (1984) found that approximately 90 % of the total cuticular wax on blackberry leaves was in the epicuticular layer and about 10 % were present as intracuticular wax. The total cuticular wax on the adaxial side was present in amounts of 14.4 µg pr. cm$^2$. Table 9 summarises the results from this work.

<table>
<thead>
<tr>
<th>Component</th>
<th>Total cuticular</th>
<th>Epicuticular</th>
<th>Intracuticular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free fatty acids</td>
<td>8</td>
<td>7 (C$<em>{16}$-C$</em>{20}$ + C$<em>{26}$-C$</em>{30}$)</td>
<td>20 (C$<em>{16}$-C$</em>{18}$ + C$<em>{28}$-C$</em>{32}$)</td>
</tr>
<tr>
<td>Triterpenoid acids</td>
<td>1</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Free alcohols</td>
<td>36</td>
<td>30 (C$<em>{26}$-C$</em>{30}$)</td>
<td>44 (C$<em>{26}$-C$</em>{32}$)</td>
</tr>
<tr>
<td>Alcohol acetates</td>
<td>32</td>
<td>36 (C$<em>{28}$-C$</em>{30}$)</td>
<td>28 (C$<em>{28}$-C$</em>{32}$)</td>
</tr>
<tr>
<td>Esters</td>
<td>21</td>
<td>25 (C$<em>{46}$-C$</em>{48}$)</td>
<td>2 (C$<em>{44}$-C$</em>{46}$)</td>
</tr>
<tr>
<td>Alkanes</td>
<td>2</td>
<td>2 (C$<em>{29}$-C$</em>{31}$)</td>
<td>2 (C$<em>{29}$-C$</em>{31}$)</td>
</tr>
<tr>
<td>Total yield [µg/cm$^2$]</td>
<td>14.4</td>
<td>12.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The constituents of the epicuticular wax are stated together with chain length maxima for the individual compounds. The main groups are free alcohols, alcohol acetates and esters which...
account for approximately 90 wt-% of the total wax amount. The maximum chain length lies around 40 carbon molecules yielding a molecular weight of 480 g pr. mol.

In paper 2 describing bitumen quantification it is found that organic molecules with molecular weights above 2000 g pr. mol can be used as bitumen indicators, and with this in mind there should be no problem in including the epicuticular wax in the analysis, as they are well below this limit, provided that the above stated wax composition is valid for the used plant species.

HP-GPC nevertheless shows that there is a crucial interference from the waxes in the large molecular interval of the chromatograms, which makes the method inapplicable to plant samples, since the bitumen concentrations are several orders of magnitude smaller than the wax concentrations.

It was tried to boil the plant samples in 2 M potassium hydroxide for half an hour to hydrolyse the esters and other -O- containing compounds, but the resulting chromatograms showed no improvements in shortening the wax molecule chains sufficiently for bitumen identification, and it is not known whether the aerosol analysis are influenced by this treatment or not.

Unfortunately bitumen can not be identified in plant samples possessing epicuticular wax.

**Tire identification**

When the film is removed from the plant sample it is dried and weighed and the procedure for determining tire material, described in paper 1, is employed. Dichloromethane dissolves the film and epicuticular wax layer rapidly.

The samples are treated in three different ways to achieve a differentiation of the particulate matter, as illustrated in figure 28.

---

**Figure 28 Schematic illustration of cross-section of leaf with ad- and absorbed particles.**

*Untreated leaf:* The entire sample is ground in a mortar and treated as described in paper 1. All of the particulate material (1. + 2. + 3.) is sampled.
Film on ad- and abaxial side: The adsorbed (1.) and enclosed (2.) particulate material is sampled together with the film layer for the ad- and abaxial side and treated as described in paper 1.

Leaf washed in water: The adsorbed (1.) particles are removed and the enclosed (2.) and absorbed (3.) are sampled together with the plant sample which is ground and treated as described in paper 1.

For each sample treatment three leaves are analysed which yields 1 - 2 g of sample and approximately 100 cm$^2$ of surface area.

8.5 Results, plant samples

In the following the tire concentrations found in leaves, moss and milfoil samples are presented. Missing data points represent tire concentrations that are below the detection limit.

![Graph showing tire concentrations in Park elm leaves across different locations and distances from the Hillerød highway.](graph.png)
By subtracting the ad- and abaxial tire concentrations from the untreated concentrations an estimate of the respired or absorbed tire concentration is found. This mean value is 0.17 µg pr. cm² (COV = 57 %, N = 4) for the smooth cherry plum leaves and 0.18 µg pr. cm² (COV = 32 %, N = 4) for the pubescent park elm leaves. These concentrations comprise 35 % of the total tire concentrations from the untreated leaves for both species.

As expected the concentrations of absorbed particles (small particles) are identical for both species. It was anticipated that the adsorbed amount would be larger for the pubescent elm leaves, especially close to the road where the concentrations of large particles are at a maximum, but equal concentrations are found.

Except for the measuring point at west 0 m, the concentrations of deposited particles on the adaxial side are larger than on the abaxial side, which correspond to a relatively high concentration of large particles that deposit as a consequence of gravitation.

\[ \text{Tire concentrations in leaf samples near Hillerød highway.} \]

![Graph showing tire concentrations for cherry plum leaves near Hillerød highway](graph.png)
Figure 30 Tire concentrations in leaves sampled on different locations.

In figure 30 tire particle concentrations on the pubescent wych and park elm leaves, the slightly pubescent cornelian cherry and willow and the glabrous beech, laurel and privet are shown. The highest concentrations are found in Copenhagen (Åboulevarden and the Botanical Garden) and near highways (Lyngbyvej).

The willow and privet samples from the Botanical Garden indicate that increasing pubescence implies larger concentrations with respect to adsorbed as well as absorbed tire particles. The absorbed tire concentration ranges from practically zero for the leaves grown in Lyngby cemetery and Dyrehaven to approximately 0.9 µg pr. cm$^2$ for the willow and privet leaves from the Botanical Garden. No distinct pattern can be seen with respect to ad- vs. abaxial deposition.

Figure 31 Tire concentrations in untreated and washed leaves from Risø.

In figure 31 tire particle concentrations in untreated and washed leaves from Risø are shown. The untreated leaves show a general increase in concentration over time, with a peak in August. The washed leaves show a reduction in concentration, with the exception of the cherry plum leaves, which remain relatively constant. The concentrations are given in µg pr. cm$^2$. The leaves are classified by species and location.
It is not possible to differentiate between ad- and abaxial deposition for the samples taken near Risø in figure 31, since the concentration levels in the Piaoform films, allowing for blank values, are below the detection limit. This value is calculated and commented in section 8.6. Instead the leaves are washed and brushed gently with the fingers in ion exchanged distilled water thus removing adsorbed particles on both surfaces.

For all three species the tire concentrations in the untreated leaves increase with a mean percentage of 89 % in the period from July to August, where the weather was dry and warm. Between the next two samplings there were periods with rain and wind that result in a decrease, and the concentrations remain on a constant level from September to October.

For the pubescent wych elm leaves the washed leaves comprise an average of 63 % of the unwashed leaves. For the slightly pubescent cherry plum and the smooth spindle tree this value is 84 % and 82 % respectively, indicating that a higher percentage can be washed of a hairy surface as a consequence of increased deposition.

![Moss and millfoil](image)

**Figure 32 Tire concentrations in untreated and washed Moss and Millfoil.**

The moss samples from the west side of the highway near Utterslev Mose show an increase in tire particle concentrations when moving from 0 to 3 m from the road, and then an decrease from 3 to 10 m from the road.

The Utterslev Mose concentrations are lower than at Svalholm near Risø, even though this is a smaller road. The reason could be that the grass is cut more often in Utterslev Mose than in Svalholm leading to a shorter exposition time.

The millfoil concentrations are a factor of 3.8 higher than the moss samples in Svalholm.
8.6 Discussion, plant samples

8.6.1 Blank and reference samples

Analytical methods with very sensitive detection techniques are required since the amount of deposited particles is small. Furthermore the trace element concentration of zinc in the plastic film and the contamination in the sample treatment must be low.

The lower detection limit has been found to be 12.4 µg tire pr. sample for the HGA analysis. A typical leaf sample has a surface area of approximately 150 cm², leading to a lower detection limit of

\[ \Delta x_{\text{min}} \text{ (tire)} = \frac{12.4 \text{ µg tire}}{150 \text{ cm}^2} = 0.08 \text{ µg tire cm}^2. \]

A blank Pioloform sample was analysed for extractable organic zinc on the HGA during each plant session. For 8 blank samples the following mean organic zinc concentration was found to be

\[ x_{\text{Pioloform (zinc)}} = 0.54873 \text{ µg Zn pr. g d.w. (COV = 11.6 %)}. \]

Approximately 1 g of Pioloform is used pr. plant sample, resulting in a blank concentration of

\[ x_{\text{Pioloform (zinc)}} = \frac{0.54873 \text{ µg Zn pr. g d.w.} \cdot 1 \text{ g}}{0.011} = 55 \text{ ppm.} \]

This is a factor of five larger than the typical extractable organic zinc concentration found in leaf samples and as a consequence the precision of the zinc measurements are reduced by this large bulk zinc concentration.

Duplicate determination has only been performed on two different leaf samples, yielding the results in table 10.

<table>
<thead>
<tr>
<th></th>
<th>( \bar{x} ) [µg tire pr. cm²]</th>
<th>COV [%]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Park elm, adaxial</td>
<td>0.17</td>
<td>35.2</td>
<td>4</td>
</tr>
<tr>
<td>Hillerød highway, east 0 m</td>
<td>0.28</td>
<td>44.8</td>
<td>4</td>
</tr>
</tbody>
</table>

The coefficients of variation suggest that the reliability of the method for quantifying tire particles in plant samples by organic zinc is reasonable allowing for blank contributions.

Cercasov (1985) has found the following trace element concentrations in a blank sample of Pioloform BL 16 powder dissolved in chloroform by means of neutron activation analysis.
Table 11 Elemental content of Pioloform BL 16 blank found by NAA (Cercasov, 1985).

<table>
<thead>
<tr>
<th>Film mass [mg pr. cm$^2$]</th>
<th>Na [ng pr. cm$^2$]</th>
<th>K [ng pr. cm$^2$]</th>
<th>Fe [ng pr. cm$^2$]</th>
<th>Zn [ng pr. cm$^2$]</th>
<th>Sc [ng pr. cm$^2$]</th>
<th>Sb [ng pr. cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pioloform BL16</td>
<td>7.2</td>
<td>118</td>
<td>33</td>
<td>180</td>
<td>3.7</td>
<td>0.003</td>
</tr>
</tbody>
</table>

The total zinc concentration is thus

$$x_{\text{Pioloform}} (\text{zinc}) = \frac{3.7 \cdot 10^{-3} \frac{\mu g \text{ Zn}}{cm^2}}{7.2 \cdot 10^{-3} \frac{g \text{ d.w.}}{cm^2}} = 0.51388 \frac{\mu g \text{ Zn}}{pr. \text{ g d.w.}}.$$

This is the same order of magnitude as the extractable organic zinc concentration.

**8.6.2 Deposition rates**

In this section different numbers for the deposited zinc, tire and bitumen concentrations on plant leaves found by estimates and other investigators are presented and compared.

Hovmand (personal communications, 1996) informed that the mean annual deposition (dry + wet) of total zinc in Denmark is about 10 mg Zn pr. m$^2$, or

$$\frac{10 \cdot \frac{mg \text{ Zn}}{m^2 \cdot \text{year}} \cdot 10^{-4} \cdot \frac{1}{12}}{83 \cdot \frac{ng \text{ Zn}}{cm^2 \cdot \text{month}}} = \frac{\mu g \text{ Zn}}{pr. \text{ g d.w.}}.$$

From the medium volume filters and impactor measurements the organic zinc amounts to approximately 4% of the total particulate zinc, and using the factor 1290 $\mu g$ org. Zn pr. g tire, the deposited tire concentration pr. cm$^2$ leaf is

$$\frac{83 \cdot 10^{-3} \cdot 0.04 \cdot \frac{\mu g \text{ org. Zn}}{cm^2 \cdot \text{month}} \cdot 10^6}{1290 \frac{\mu g \text{ org. Zn}}{g \text{ tire}}} = 2.58 \frac{\mu g \text{ tire}}{cm^2 \cdot \text{month}}.$$

Another estimate based on the dry deposition velocity can be done

Tire concentration: 2.90 $\mu g$ tire pr. m$^3$ (from impactor).
Dry deposition velocity: 0.20 cm pr. s (mean value for the size interval 0.065 - 0.90 $\mu m$ diameter (Hummelshøj, personal communication, 1997).

In one month the deposited tire material on a leaf surface is
m_{tire} = 2.90 \cdot 10^{-5} \frac{\mu g \text{ tire}}{cm^3} \cdot 0.20 \frac{cm}{s} \cdot (60 \cdot 60 \cdot 24 \cdot 30) = 1.50 \frac{\mu g \text{ tire}}{cm^2 \cdot \text{month}}.

These two numbers are in agreement. For an elm leaf in Copenhagen the deposited (dry + wet) tire concentration is found from figure 30 to be approximately 0.5 µg tire pr. cm$^2$ after heavy rainfall in September. The reason for the low measured concentration compared to the estimates could be that the particles are washed off or that the collected leaves are younger than one month.

Cercasov (1985) has measured the elemental content of particles deposited on single blackberry and beech leaves in the vicinity of a highway by the Pioloform film method. The total zinc concentrations found by NAA corrected for blank values and stated as averages for a group of leaves was found to be

*Table 12  Zinc concentration of deposited particles on blackberry and beech leaves (Cercasov, 1985).*

<table>
<thead>
<tr>
<th></th>
<th>Blackberry</th>
<th>Beech</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Near highway</td>
<td>Distance 200 m</td>
</tr>
<tr>
<td>Adaxial</td>
<td>Adaxial</td>
<td>Adaxial</td>
</tr>
<tr>
<td><strong>Total zinc</strong></td>
<td><strong>[ng pr. cm$^2$]</strong></td>
<td><strong>[ng pr. cm$^2$]</strong></td>
</tr>
<tr>
<td></td>
<td>78.9</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Assuming that the leaves have been exposed for more than a month the zinc concentrations are lower than anticipated.

The only work that deals with bitumen depositions on leaves has been performed by Elvebakken (1991). The found bitumen concentrations in hawthorne (*Crataegus*) leaves near a highway and 100 m away are 1.5 and 0.4 µg bitumen pr. cm$^2$ respectively (for untreated samples).

The aerosol samples in this work (paper 3) show that the tire and bitumen concentrations are approximately identical. Neglecting the differences in particulate sizes and assuming that the deposited bitumen concentration is equal to the deposited tire concentration, which is approximately 0.5 µg pr. cm$^2$, the deposited bitumen concentration corresponds well with the results from Elvebakken (1991).

The present work has confirmed that tire particles can spread over long distances and that the deposited concentrations can be measured with the developed method. The detection limit for HGA is found to be 12.4 µg tire pr. sample and to obtain this amount a plant sample of 100 cm$^2$ (approximately 3 leaves) that have been exposed for 2 days will suffice, when the dry deposition rate is 2 µg tire pr. cm$^2$ pr. month.

The particles are small enough to enter the stomata and it has been found that approximately one third of the total tire concentration in leaves is absorbed in the leaves.
9 Inhalability

The most serious environmental problems in city areas today are gaseous and particulate air pollution which constitute a still increasing effect on human health. Formerly problems such as sulphur and soot pollution from private burners, local power plants and the industry in general were the main concern but “cleaner” fuels combined with improved combustion techniques and the introduction of district heating from central power plants with gas and particle removal have to a great extent minimised these problems.

The dominating source in cities is without a doubt the emissions from automobile traffic and looking on the 12 % increase in the number of private cars in Copenhagen during the last 3 years, the problem will probably continue to increase in the years to come. Some important approaches such as the removal of lead additives in gasoline and the introduction of catalysators and the regular check of older cars have proven to have an effect on particulate lead and gases such as hydrocarbons and nitrous oxide in the environment. It is nevertheless very difficult to change the tendency as the main concern is the drastic increase in the number of private cars on a global scale.

Particles, nitrogen dioxide, ozone, PAH’s, benzene, 1,3-butadiene, ethene, propene, formaldehyde, acroleine and acetaldehyde are topping the list of airpolluting substances derived from traffic activities. The effects of the single compounds are known and include infections in the respiratory systems, allergies and cancer. Some investigations have shown that the combined effect of particles and gasses may even be synergistic.

Out of each 100000 residents in Copenhagen 140 die each year of lung cancer. In Frederiks Borg and Roskilde the number is approximately 100. Lung cancer is a very important factor when the effects of airpollution is evaluated but also somewhat critical as the main source to this illness is smoking.

The most critical component in the traffic produced airpollution is particles. 1.8 to 2.9 million people in Denmark living in cities are probably exposed to particulate pollution leading to long term health effects such as heart diseases but also acute illnesses such as bronchial infection are frequently observed. The health problem concerning airborne particles is increasing for decreasing diameters. The following connection between inhalability and particle aerodynamic diameters can be used (e.g. Cardina, 1974)

> 7 µm: not inhalable.
3.3 - 7.0 µm: to trachea and bronchi principalis.
2.0 - 3.3 µm: to bronchioli.
1.1 - 2.0 µm: to bronchioli respiratrii.
< 1.1 µm: to alveoli.
Once the particles have entered the lungs they can be removed from the air and deposit on the lung tissue. In appendix K, figures K1 and K2, the deposition rate as a function of particle diameter is shown. It is interesting to see that for particles with diameters around 0.5 µm, which is the size range for the collected fine tire particles, there is a minimum in deposition rates and the possibility for removal by exhalation is thus considerable. It is beyond the scope of this work to determine the actual concentrations of deposited tire and bitumen particles in the lungs.

The submicron particles can be harmful to the organism even if the particles are not harmful themselves, since the mere presence in the lungs can suffice to cause health problems in the form of irritation of the lung tissue.

Whether the organism will be exposed to the particle bound compounds or not is dependant on the particle size and the solubility of the compounds of interest, as a water soluble compound will be easier removed from the lungs than a hydrophilic compound.

If a person is inhaling 14 litre inner city air per minute, where the submicron tire concentration is 2.6 µg pr. m$^3$, and 50 % is adsorbed in the alveoli 1.09 µg tire dust or about 0.14 µg of PAH’s are deposited in the respiratory system pr. hour. The PAH’s may not all be available to the tissue as the tire matrix must first be destroyed, but due to the low solubility in water it can remain in the lungs long enough for the matter to accumulate and reach health hazardous concentrations.

The corresponding number for bitumen is 0.62 µg bitumen or 0.19 µg of PAH’s.

The PAH’s in tires derive from carbon black and softening fillers where 40 to 50 wt-% are PAH’s (Korsbæk, personal communication, 1998). Ahlbom et al. (1994) emphasises that the
particulate PAH supply to the environment via tire wear exceeds the contributions from asphalt abrasion and even diesel exhaust.

Apart from particulate emissions Cadle et al. (1978) found that gaseous hydrocarbons were emitted continuously during use. These are 1,3-butadiene, isoprene, vinylycloclohexene, p- and m-dipentene and styrene, that are all monomers and dimers of the SBR copolymer, and precursors of photochemically produced eye irritants including formaldehyde, PAN, acrolein and PBzN. PAH's comprising of four rings or less have large gas affinity whereas the larger are bound to particles.
10 Summary and conclusions

Methods for identifying and quantifying debris generated from the wear of automobile tires and roadway asphalts have been developed. The main objective has been to establish chemical procedures that facilitates the quantification of trace amounts of debris in the environment without reducing the sensitivity or reproducibility of the methods.

Tire method

The method for identifying tire-tread particles is based on the measurement of extractable organic zinc, that is present in concentrations of about 1290 µg org. Zn pr. g tire. The high sensitivity of atomic absorption spectrometry with a heated graphite atomiser (HGA) permits assessment of submilligram amounts of tire debris collected from the atmosphere. To validate the findings a basically different method previously developed by Brachaczek et al. (1974) is employed. This is based on the measurement of the rubber polymer styrene butadiene rubber (SBR) by infra red spectrometry (IR).

The tire concentrations found by the two methods differ by a factor of maximum 2.2. The lower detection limits are 12.4 and 17.1 µg tire pr. sample for HGA and IR respectively. It is found that the HGA method is less time consuming and more sensitive, and that the IR method is highly dependable on the extraction efficiency of the organic materials. Considerable uncertainties are furthermore connected with the measurement of the peak height in an IR spectrum, and when many peaks are overlapping the identification of the baseline is questionable.

The only other examined source that contribute with organic zinc is engine oil, but with respect to aerosol samples the oil concentration is believed to be insignificant.

Bitumen method

Bitumen is found to be the only contributor to airborne particles containing organic molecules with molecular weights larger than 2000 g pr. mol. These are separated and identified by using High Performance Gel Permeation Chromatography (HP-GPC) with fluorescence detection. As an additional detection method Infra Red spectrometry (IR) is employed for selected samples.

The bitumen concentrations differ by a factor of maximum 6.5. Taking sample preparation and analysis time into consideration HP-GPC is a fast and reproducible method. The detection limits are 17 and 61 µg bitumen for HP-GPC and IR respectively.

Environmental samples

The methods have been employed on aerosol samples, collected with 11-stage Berner low pressure cascade impactors, in Copenhagen and Risø and aerosols collected with medium volume samplers on two locations in Copenhagen. Furthermore the deposited particulate matter have been measured in soil near highways and on remote sites, and finally the ad- and absorbed
particulate matter has been measured on plant leaves sampled in Copenhagen and on remote sites.

Tire and bitumen particles constitute each about 5 wt-% of the total suspended particulate matter (TSP) in inner city air. The airborne particle size distribution obtained with a Berner low pressure impactor shows that 92 wt-% of the tire debris have aerodynamic diameters smaller than 1 µm. The mean aerodynamic diameter is about 1 µm for the bitumen particles.

Soil concentrations in the vicinity of a highway indicate an approximate exponential decrease with increasing distance from the road. Constant values are reached after about 5 m for the tire particles and 10 m for the bitumen particles. Concentrations in soil that has not been touched for at least 30 years show a decrease in tire concentrations by a factor of 30 when moving from the top soil to a depth of 3 cm. The bitumen concentrations are approximately constant to a depth of 10 cm.

The leaf samples indicate a slightly higher tire particle concentration on the adaxial side compared to the abaxial side and an increased surface retention for pubescent leaves. About 0.5 µg tire pr. cm² leaf is found near a highway, and about 65 % of this concentration derives from adsorbed particles on both leaf sides. The remainder is either respired through stomata or incorporated in the epicuticular wax layer.

The important result that has been found or confirmed in this work is the presence of submicron tire and bitumen particles. They have the potential for long range transportation and uptake in the human respiratory system. Polyaromatic hydrocarbons (PAH’s) comprise about 10 % of the rubber material and even more of bitumens, and considering the carcinogenic properties of these compounds and the relatively high aerosol concentrations that have been found, tire and bitumen abrasions are important factors that must be considered when dealing with the health effects of airborne pollution.
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Appendix A

Derivation of aerodynamic diameter

The atmosphere around us constitute the carrier gas in which the aerosol particles are suspended. To describe the interactions between particle and carrier gas, different regimes for large and small particles must be discerned. For large particles the primary source of resistance is the viscosity of the medium which can be regarded as a continuum, whereas for smaller particles viscosity is no longer important and the predominant resisting mechanism is due to the inertia of the gas molecules that the particles encounter. For this purpose the Cunningham slip factor, $C_p$, is applied which accounts for the reduction in the drag force on smaller particles caused by the slip of the gas molecules at the particle surface. The presence of small particles does not significantly disturb the velocity distribution of the molecules of the carrier gas whereas collisions between the surface of large particles and gas molecules will modify it markedly and consequently increase the drag force between particle and carrier gas.

The resisting force, or drag force $F_D$, offered by a medium upon a particle can be expressed by Stokes law, and introducing the reduction factor, $C_p$, it can be written as:

$$F_D = \frac{3 \cdot \pi \cdot \mu \cdot v \cdot d_p}{C_p} \left[ \frac{g \cdot \text{cm}}{s^2} \right]$$  \hspace{1cm} (A1)

where:

- $\mu$ = medium viscosity [g·cm$^{-1}$·s$^{-1}$].
- $v$ = particle velocity relative to the medium [cm·s$^{-1}$].
- $d_p$ = physical diameter for spherical particle and Stokes diameter for nonspherical particle [cm].
- $C_p$ = Cunningham slip factor evaluated for $d_p$.

As mentioned before the settling velocity is the terminal velocity of a particle reached under the influence of gravity, $F_G$, and friction, $F_D$, alone. In this state the two forces are equal and opposite directed:

$$F_D = F_G \iff \frac{3 \cdot \pi \cdot \mu \cdot v_s \cdot d_p}{C_p} = \rho_p \cdot \frac{4}{3} \cdot \pi \cdot \frac{1}{8} \cdot d_p^3 \cdot g \iff$$

$$d_p = \sqrt[3]{\frac{18 \cdot \mu \cdot v_s}{C_p \cdot \rho_p \cdot g}}$$  \hspace{1cm} (A2)

where:

- $\rho_p$ = density of the particle [g·cm$^{-3}$].
- $g$ = gravitational acceleration [cm·s$^{-2}$].

To derive an expression for the aerodynamic diameter, $d_a$, for a smooth unit density sphere, $\rho_0 = 1$ g·cm$^{-3}$, having the same flow properties as the particle above, a relationship fundamental to fluid mechanics, saying that the forces acting on either body must bear the same ratio at any instant, is employed. This is equivalent to saying:
\[ \frac{F_{D,d}}{F_{G,d}} = \frac{F_{D,0}}{F_{G,0}} \Rightarrow d_a = \frac{d_p}{d_a} \left( \frac{18 \cdot \mu \cdot v_s}{C_a \cdot \rho_0 \cdot g} \right) \]

\[ d_a = \sqrt{\frac{\rho_p \cdot C_p}{\rho_0 \cdot C_a}} \cdot d_p \quad \text{(A3)} \]

where \( C_a \) = Cunningham slip factor evaluated for \( d_a \).

The Cunningham slip factor can be expressed as:

\[ C_p = 1 + \frac{\lambda}{d_p} \left( \alpha + \beta \cdot \exp \left( -\frac{\gamma \cdot d_p}{\lambda} \right) \right) \quad \text{(A4)} \]

Where \( \lambda \) = mean free path of the gas molecules (0.066 \( \mu \)m at normal atmospheric conditions).

The empirical factors are by Holländer (1995) stated to be

\[ \alpha = 2.2284. \]
\[ \beta = 1.116. \]
\[ \gamma = 0.500. \]

By insertion of these factors in equation (A4) the following slip factors and aerodynamic diameters can be derived for large and small particles respectively.

For large particles (\( d_p >> \lambda, d_p > 5 \mu m \)):

\[ C_p = 1 \]
\[ d_a = \sqrt{\frac{\rho_d}{\rho_0}} \cdot d_p. \]

For small particles (\( d_p << \lambda \)):

\[ C_p > 1 \]
\[ d_a = \frac{\rho_d}{\rho_0} \cdot d_p. \]

The correction factor represents the mechanism for transition from the continuum to the molecular case and should always be included in Stokes law when particles are less than 1 \( \mu \)m in diameter. The factor is always equal to or greater than one.
In the derivation of Stokes’ law it is assumed that the particles are spherical in shape. Particles have in many cases irregular shapes, depending on the formation mechanisms and the amount of agglomeration that have taken place. Liquid aerosols are however always spherical in shape and isometric particles deviate only slightly to this assumption. For long chains or flocculated particles a correction factor, $\kappa$ known as the dynamic shape factor, is introduced in Stokes’ law:

$$F_D = 3 \cdot \pi \cdot \mu \cdot v \cdot d_e \cdot \kappa$$  \hspace{1cm} (A5)

Where $d_e$ is the diameter of a sphere having the same volume as the chain or fiber. $\kappa$ is varying according to the number of agglomerated particles and their configuration. The factor is 1.27 for three equivalent spherical particles in a straight line and 1.73 for 8 spherical particles in a straight line. For equal particle numbers $\kappa$ is decreasing when the formation is deviating from linearity (Stöber et al., 1969 cited by Reist, 1984). For small aggregate particulate sizes the Cunningham slip factor should also be used.

Reist (1984) mentions that the aerodynamic diameter of a rod or fiber is influenced very little by its length but much more by the cross-sectional diameter, which implies that fibres of different lengths but similar cross-sections will have similar aerodynamic properties, despite possibly large differences in mass.
Appendix B

Size distribution

To visualise a broad particle size range the logarithms of the diameters are plotted on the abscissa. To maintain the relationship that the area between two particle size intervals is proportional to the total number, mass or volume of particles, the ordinate scale is depicted as follows

\[
\text{Ordinate} = \frac{\Delta n}{n_{\text{total}} \Delta \log_{10} d} \quad (B1)
\]

The number, mass etc. in each interval is divided by the total number, mass etc. multiplied the difference in the logarithms of the largest and the smallest particle diameters of that interval. This is calculated for each interval. If this plot resembles a normal distribution it is said to be log-normally distributed and the geometric mean and geometric standard deviation are found by (Reist, 1984)

\[
\log_{10} \bar{d}_g = \frac{\sum n_i \cdot \log_{10} d_i}{\sum n_i} \quad (B2)
\]

\[
\log_{10} \sigma_g = \sqrt{\frac{\sum n_i \cdot (\log_{10} d_g - \log_{10} d_i)^2}{\sum (n_i) - 1}} \quad (B3)
\]

where \( i \) is the number of intervals.

Figure B1 shows a typical urban aerosol size distribution presented in five different ways. From figure B1(a) and B1(c) it is seen that the number size distribution is dominated by the nucleation range particles and can be fitted by a power function of the form

\[
\frac{d n}{d \log d} = a \cdot d^k \quad (B4)
\]

In figure B1(d) the surface area size distribution is dominated by the accumulation range particles and the volume size distribution in figure B1(e) is dominated by particles in accumulation and coarse range. For further details see Whitby (1977).
Figure B1 Average urban aerosol plotted in five different ways (Whitby, 1977).
Appendix C

Formation and growth

Condensation

The formation and growth of aerosol particles by vapor condensation is the most important pathway for material transfer between the gas and aerosol phase in the atmosphere. Natural phenomena such as the condensation of water to form clouds and anthropogenic combustion of fossil fuels which form soot are examples of aerosol formations that have effects on global and local scales.

The formation of aerosols by condensation requires the presence of a surface of condensation such as a cluster of vapor molecules, an ionic cluster or particles of some other material. When condensation takes place solely on a cluster of similar vapor molecules without the assistance of other nuclei or ions it is called homogeneous nucleation or self-nucleation, and when condensation occurs on a dissimilar material it is called heterogeneous nucleation.

Homogeneous nucleation takes place in three steps. First the vapor must be supersaturated to an extent that condensation will take place. Second, small clusters of molecules must form and finally, the vapor must condense on these clusters so that they are permitted to grow into nuclei that subsequently become droplets. For heterogeneous nucleation only the first and the last steps take place.

In the case of homogeneous nucleation supercooling below the freezing point is necessary and supersaturation to prevent the droplets from evaporating even when the surrounding gas is saturated is equally necessary to maintain the drops in equilibrium. To produce droplets with decreasing particle diameters an increasing degree of supersaturation is demanded since the probability of net loss from a surface increases with the extent of convexity. By considering the change in free energy, $\Delta G$, in droplet formation it is shown (e.g. Reist, 1984) that there exist an energy barrier that acts to prevent the growth of droplets smaller than a critical size. Droplets smaller than this size will reduce their free energy by evaporation. Drops larger than the critical size will continue to grow and in this way decrease the free energy of the system, see figure C1.

Under normal atmospheric conditions there will be an abundance of small particles acting as condensation nuclei (heterogeneous nucleation) that facilitate the process of condensation without supersaturation. This class of particles range from near molecular size to particles larger than 1 µm and they originate from a variety of sources such as photo oxidation of natural organic materials, windblown soil particles, sodium chloride nuclei from sae salt spray and particles from volcanic eruptions etc.

Only a small fraction of the total number of airborne particles act as condensation nuclei. Virtually all types of particles can enter the process; organic, inorganic, soluble, insoluble or insoluble with a soluble coating. Due to the relatively small concentration of aerosols, approximately 1 mg pr. m$^3$ air in cities, and the complex mixture of particles it is difficult to determine the predominant condensation pathway.
Generally it can be said that the largest and most soluble particles are activated first followed by particles of smaller sizes. With soluble nuclei, such as a sodium chloride sea spray particle, the condensing vapor dissolves the nuclei and succeeding condensation dilutes the solution more and more finally leaving a drop of pure liquid. Insoluble nuclei that are easily wetted rapidly take on the appearance of a droplet and subsequently behave like one. If the particle surface is not easily wetted the condensation proceeds much slower as the condensing liquid tends to pull into small spheres on the particle surface and only when the entire surface is covered with spheres a liquid coating is formed. Experiments by Fletcher (1958) (cited by Reist, 1984) support these considerations as it is found that high supersaturation is required before condensation on non-wettable particles takes place.

Aggregation and coagulation

When solid airborne particles collide they can coalesce to form larger chains or flocs made up of many particles. This process can be initiated simply by random motion and subsequent collision of particles (thermal coagulation) but a number of external physical factors such as turbulence, electrical or gravitational effects or sonic agglomeration can act to enhance or retard the coagulation efficiency. Kuhlman (1982) (cited by Reist, 1984) has shown that the coagulation rate reaches a minimum when monodisperse (equal-sized) particles are involved. However, coagulation of monodisperse particles increases polydispersity, so that for any coagulating aerosol the coagulation rate is not constant.

A coagulating aerosol should with time reach the same steady-state size distribution regardless of the aerosols initial size distribution. When this state is reached gains by coagulation in the number of particles of a given size are equalled by losses from that size either by coagulation or deposition. For very small particles deposition losses are unimportant and for very large ones coagulation losses can be neglected. As can be seen from figure 3 on page 11 this implies three distinct distribution functions over the entire size spectrum.
Appendix D

Important elements and organic compounds in aerosols

In the following selected elements are commented with respect to their particulate origins together with concentration levels and important reaction pathways. In appendix I impactor samples analysed with neutron activation analysis (NAA) show the particle size distribution for selected elements.

The schematic description in figure D1 shows the main pathways for production of atmospheric aerosols, some of which are mentioned in the text below.

![Figure D1 Reaction pathways in the formation of aerosols (Pandis et al., 1995)](image)

*Lead*, Pb, is mainly originating from the combustion of petrol containing anti-knock additives such as tetra-alkyl lead, and from foundries. In rural areas in England concentrations in the range 300 - 1300 ng pr. m$^3$ has been found by Lee et al. (1994). The lead is present both in the fine fraction from automobile exhaust and in the coarse fraction from road dust (Johansson, 1994).

*Brom*, Br, is equally added in petrol and is furthermore derived from the combustion of fossil fuels. Smaller sources are volcanic activities and sea spray although marine aerosols rapidly lose the particulate Brom to the vapour phase. Lee et al. (1994) state concentration levels in urban areas in England between 110 and 230 ng pr. m$^3$. Brom is found in the fine fraction. Samples containing Brom must not be stored for longer periods on account of the high vapour pressure.

*Sodium*, Na, and *Chloride*, Cl, are predominantly of marine origin and are found in the coarse fraction. The chloride and sodium concentrations in urban areas are 2.6 - 4.5 µg pr. m$^3$ and 1.2 -
1.5 µg pr. m³ respectively (Johansson, 1994). Sodium is also originating from road salt and chloride from coal combustion and industrial- and domestic waste incineration.

The particulate Sulphur emissions originate from anthropogenic as well as natural sources. Coal combustion accounts for roughly 60 % of all SO₂ emitted. Petroleum refining and combustion of other fuels contribute around 30 % and smelting of metallic ores and other industrial processes around 10 % of the global anthropogenic SO₂ emission. Sulphur is predominantly connected to the accumulation range disregarded if the gaseous sulphur is forming separate condensation nuclei or if it condenses on existing aerosol particles. Sulphur is in great extent found in long-range transported aerosols such as NH₄SO₄.

More than 90 % of the Sulphur, deriving from the combustion of fossil fuels, is emitted as SO₂, (Johansson, 1994). 1 - 4 wt-% per hour is oxidised to SO₄²⁻ and sulphuric acid. The gas phase oxidation of SO₂ is dominated by the reaction with the OH radical whereas the major aqueous phase oxidation routes include reactions with H₂O₂, O₃, O₂, OH and HO₂.

In contrast to anthropogenic emissions the natural emissions are primarily in the form of reduced sulphur such as hydrogen sulphide (H₂S) that is generated biogenically and through volcanic production, dimethyl sulphide (DMS, CH₃SCH₃) produced by bacteria and freshwater green and blue algae, carbon disulphide (CS₂) from biogenic production, dimethyl disulphide (CH₃SSCH₃), carbonyl sulphide (COS) from biogenic production and methyl mercaptan (CH₃SH).

Nitrogen, N. Nitrate (NO₃⁻) is a major constituent in atmospheric aerosols. The most important nitrate forming oxides are NO₂, NO, N₂O₅ together with NH₃. NO is formed from combustion processes by oxidation of the atmospheric N₂. NO₂ is produced both naturally and anthropogenically through a variety of mechanisms including oxidation of ammonia, lightning, combustion and oxidation of NO. It is estimated that half of the NOₓ is oxidised to nitric acid which is present both in the gas phase and the condensed phase such as aerosols and droplets. The natural emissions of nitrogen containing gases are greater than anthropogenic emissions.

NH₃, HNO₃, HCl, H₂SO₄ and H₂O are the major inorganic gas phase species involved in the formation and growth of aerosol species in the atmosphere. Most of the elements found in coarse aerosol particles over land or sea are involatile and chemically inert with the exception of a few elements such as chloride. Chloride is mainly emitted as NaCl in sea salt particles and these particles can react with sulphuric and nitric acid to produce gaseous hydrochloric acid and the following inorganic compounds of the solid aerosol phase: NaNO₃, Na₂SO₄ and NaHSO₄.

Both nitric acid and hydrochloric acid vapour react reversibly with ammonia gas, largely arising as a product of decomposition of animal urine, to form ammonium salts:

\[ \text{NH}_₄\text{NO}_₃ \text{ (aerosol)} \leftrightarrow \text{NH}_₃ \text{ (gas)} + \text{HNO}_₃ \text{ (gas)} \]
\[ \text{NH}_₄\text{Cl} \text{ (aerosol)} \leftrightarrow \text{NH}_₃ \text{ (gas)} + \text{HCl} \text{ (gas)} \]

The salts are appreciably volatile and may release their parent acids under conditions of low ammonia, high temperature or reduced humidity. Particles formed by gaseous reactions are initially small (< 0.2 µm) but grow rapidly by either coagulation or by surface accumulation of material from the gas.
Gas phase ammonia can furthermore react with sulphuric acid to produce an equilibrium with the following inorganic solid aerosol components: \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{HSO}_4\), and \((\text{NH}_4)_3\text{H(SO}_4)_2\) (Colbeck, 1995).

*Nickel,* \(\text{Ni}\), and *Vanadium,* \(\text{V}\), derive mainly from oil burning. The concentration levels in cities are approximately equal for the two elements: 10 - 30 ng pr. m\(^3\) (Lee et al., 1994). *Cadmium,* \(\text{Cd}\), is emitted from foundries, waste incineration and paint- and plastic manufacturing. The concentrations in cities are 3 - 10 ng pr. m\(^3\) (Lee et al., 1994). *Chromium,* \(\text{Cr}\), comes from burning of coal. *Mercury,* \(\text{Hg}\), posses large gasaffinity and the use is decreasing. *Scandium,* *Cerium,* *Samarium,* *Iron* and *Aluminium* are predominantly originating from the soil.

*Zinc* can be divided into in two size groups, a fine fraction from the burning of coal and waste, and a coarse fraction from mechanical processes such as the wear of tires and soil. “Clean” soil in Denmark contains around 50 ppm-wt Zinc.

*Carbon.* Carbonaceous material contributes 10 - 20 wt-% of the total suspended particulate mass. Of the total carbon mass the organic carbon contributes 60 - 80 %, and the remaining part is elemental carbon, often referred to as soot. Between 50 and 85 % of the measured concentrations of elemental carbon are attached to aerosols with diameter smaller than 1 µm, (Pacyna, 1995).

The ocean is a dominant natural source to *organic carbon* due to the injection of naturally derived marine surfactants from bubble bursting processes. Terrestrial sources include natural products emitted from vegetation such as terpenes, isoprene, plant waxes, macromolecular plant fragments such as pollen, spores together with fungi and algae which may be significant where the biosphere experiences a seasonal cycle. The global emission of natural non-methane hydrocarbons (NMHC) is estimated to be approximately 700 Tg pr. year out of which about 10 % may be converted to aerosols (Colbeck, 1995).

Anthropogenically emitted NMHC’s contribute about 10 % of the total NMHC pool and comprises mainly of alkanes (waxes and oils), aromats and polyaromatic hydrocarbons, PAH’s. Contrary to the naturally emitted NMHC’s which are mainly alkenes like terpenes and isoprene, only a few percent of the anthropogenic NMHC’s are alkenes. This is an important fact since alkanes contrary to alkenes are far less reactive and therefore react slower with the most important oxidising agents that occur in the troposphere: ozone, nitrate and the hydroxyl radical.

It is only the hydroxyl radical that will contribute noticeably to the conversion of anthropogenically emitted NMHC’s. The OH-group will break a C-H bond in the alkane by abstracting the hydrogen atom, which demands an activating energy between 385 and 410 kJ pr. mol, depending on the location of the hydrogen atom in the molecule. The same applies for aromats and PAH’s. OH-addition to a double bond in e.g. alkenes demands close to 0 kJ pr. mol (Morrison et al., 1992).

An important example on the oxidation of anthropogenically emitted NMHC’s caused by OH is the conversion of propane to peroxyacetyl nitrate, PAN, which is toxic to especially vegetation but also to man and animals.

Of the organic carbonaceous material the *PAH’s* are of special interest due to their toxic and mutagenic effects on man and animals. *PAH* is a generic term covering a number of two or more ringed aromatic carbohydrates. They represent the oldest known group of chemical carcinogens.
and combined with the fact that they are difficultly degradable and easily accumulative, special interest has been drawn to this group of carbohydrates through a number of years.

The PAH’s are highly non-polar which gives them high affinity to the suspended phase in marine environments. In soils the compounds are immobile and especially in soil rich on organic substances the PAH’s will adsorb to the surface of the soil particles, which is frequently occurring in the upper layers. It is only the more hydrophile compounds such as naphthalene that are leached to the groundwater. In the air the low molecular PAH compounds, with less than 4 rings, are present in the gasphase while the larger, more than 4 rings, are bound to particles in the fine as well as the coarse fraction.

Aromatic compounds and especially benzene is naturally present in small amounts in petrol. Alkanes and cycloalkanes that are abundant in crude oil is converted to aromatic compounds by catalytic reforming (dehydrogenation at high temperatures). Investigations show that PAH’s can be synthesised by plants as well.

The main anthropogenic sources to airborne PAH’s are waste incineration, combustion of fossil fuels together with field burning. On a local scale automobile exhaust and power plants yield a large contribution. The main source to soil and plant pollution is atmospheric particulate deposition, only a smaller amount is brought the plants from the surrounding soil.

As a rule of thumb the toxicity increases with increasing molecular weight, which is valid for compounds smaller than 6 rings. Furthermore the toxicity increases with increasing substitution and PAH’s with angular placed rings are potentially more carcinogenic than linear or condensed systems.

PAH’s with two or three rings, especially naphthalenes and phenanthrenes, are easily degradable under aerobic conditions, whereas PAH’s with four or more rings are more or less persistent. Some PAH’s can be converted/decomposed by plants and organisms or by photo oxidation.
Appendix E

Morphology of particles

A source identification of airborne particles based alone on the chemical compositions can give erroneous results. According to (Xie et al., 1994) the x-ray fluorescence spectra of a clay mineral and a flyash particle produced by coal combustion are identical with predominant aluminium and silicon peaks together with smaller potassium and iron peaks. The shapes are however differing markedly since the clay mineral particle has a rough porous surface and the flyash particle presents a smooth sphere.

This shows how important it is to combine a chemical identification with a visual interpretation of the aerosol particles. A powerful tool for this purpose is the combination of a scanning electron microscope, SEM, and an x-ray fluorescence spectrometer, XRF.

An alternative procedure can be to first identify the particles visually by using light microscopy where particles larger than about 1 µm normally can be identified, followed by dissolving the sample and performing extraction and analysing procedures. The disadvantages are that an exact correlation between morphology and chemistry, other than based on optical properties, is not feasible and that the sample is destroyed.

The shape of a particle is a result of the internal and external forces acting on the structure. There are different ways of classifying particle morphology. Reist (1984) mentions the following based exclusively on the shape:

- **Isometric particles**: All three dimensions are approximately the same. Spherical and regular polyhedral particles belong in this class. Most extensive knowledge regarding aerosol behaviour pertains to isometric particles.

- **Platelets**: Two dimensions are long and the third is small. Examples are leaves or leaf fragments, scales and discs.

- **Fibres**: Two small dimensions and one large. Prisms, needles, threads and mineral fibres such as asbestos fall into this class.

When one studies the origin of the particles it is more convenient to divide the particles into the following three categories:

- **Crystals**.
- **Bioaerosols**.
- **Source specific particles**.

The crystals are characterised by their symmetrical structure, this can be either axial-, planar- or point symmetry describing the internal order in the crystal. The crystal lattice may be a result of its molecular crystalline structure in two general ways. The first and most characteristic is crystal growth, such as NH$_4$NO$_3$ formed on glass fibre after being immersed in mounting fluid.

The second way is through the arrangement of the cleavage planes in the material. Cleavage planes reflect the relative bonding energies through the lattice and are generally less
characteristic of specific compounds. Cleavage is the tendency of a crystal to part along specific lattice planes in response to stress, and if the forces are nearly identical in all directions, such as in quartz, no cleavage fragments will be formed. Mica has weak bonds between the hydroxyl ions along one plane in the lattice which account for a single evident cleavage plane that can be found in all mica fragments. Feldspars exhibits two and calcite has three and often one additional less perfect plane diagonal to the others (Hopke, 1985).

The morphology of biological materials is considerably more varied and complex than that of the crystals, as they exhibit texture, internal structure, wall patterning, functional subunits, characteristic terminus and so on. Typical biologicals encountered during an analysis of airborne particles include insect parts or fibres, herbaceous plant parts or hairs, charred herbaceous plant parts, cereal plants, wood parts, charred wood, pollens, spores, conidia, bacteria, algae and animal hairs. The contribution of these biologicals to the total airborne burden can amount to 25 wt-% (Jaenicke, personal communication, 1996).

The source specific particles are, as the name indicates, characteristic of the different sources. Combustion related particles and weathered soil particles are two typical examples. Oil cenospheres are formed when liquid materials are burned. They are carbonised small droplets of the original liquid fuel, typically oil but also plastics, resins in coal, tars and similar materials with melting points well below the boiling points will form oil cenospheres when combusted.

Oil cenospheres are all roughly spherical with a highly carbonised surface structure. One extreme is a black solid sphere that still contain a high proportion of volatile organics. These are formed during quick passage of the fuel in the combustion chamber. If the particle remains exposed to high heat in an oxygen deprived atmosphere, the volatile organics bake out leaving a lacy, hollow sphere (Hopke, 1985).

The predominant part of the carbonaceous particles produced by the combustion of liquid fuels consist of submicron soot particles. The coarse fraction of oil fly ash particles account for less than 10 %. Oil cenospheres have a trimodal distribution of composition and morphology vs. size. Large particles (> 3 µm, geometric diameter) have a spongy or lacy appearance and are rich in carbonaceous material and sulphur. Particles in the middle mode (0.7 - 3 µm) occur mainly as mineral rich spheres. The small mode (0.7 µm) consists mainly of nonspherical sulphate particles, (Mamane, 1986).

The combustion of solid fuels such as coal produces another set of characteristic particles consisting of fusion products of mineral impurities in the fuel that reflect the conditions in the firing chamber. The flyash can be identified as having a calcite, clay, feldspars, pyrite or quartz origin. Calcite (CaCO₃) changes to CaC + CO₂. The carbon dioxide is trapped in the CaO matrix producing a frothy glass sphere. Clays are coloured brown to yellow with a few small gas inclusions from released water. The feldspars and quartz tend to form spheres of glass without inclusions. Pyrite becomes a hematite sphere, (Hopke, 1985).

The coarse fraction of coal flyash accounts for about 90 % of the total mass. The particles are mainly alumino-silicate spheres that are somewhat variable in composition and are coated with a surface layer of sulphate, (Mamane, 1986). Other investigators have reported the occurrence of cenospheres as a distinctive feature of very large coal fly ash particles.
Other sources to the source specific particle group are numerous. Of special interest are the products derived from traffic activities. Mechanical abrasion of tires, asphalts and brake lining contribute up to 25 wt-% of the total suspended particulate mass in heavily trafficked areas. The aerodynamic diameters are typically larger than 1 µm.
Appendix F

Main reaction pathways in non sulphur vulcanisation

A free radical is formed by decomposition or oxidation of the vulcaniser and this radical abstracts a hydrogen atom on a methylene group α to the polymer double bond.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{R}^• + \text{~CH-CH}_2^- & \rightarrow \text{RH} + \text{~CH-C-CH}_2^- \\
\text{H} & \\
\end{align*}
\]

*Figure F1 Initial free radical attack in non sulphur vulcanisation* (Textbook of polymer science, 1962).

The hereby formed rubber polymer radical successively attacks a double bond in an adjacent rubber polymer resulting in a formation of a crosslink and a radical on the primary carbon, as illustrated in figure F2.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{~CH-C-CH}_2^- + \text{~CH}_2-C-\text{CH}_2^- & \rightarrow \text{~CH-C-CH}_2^- \\
\text{~CH}_2-C^- & \quad \text{CH-CH}_2^- \\
\text{•} & \\
\end{align*}
\]

*Figure F2 Formation of a crosslink in non sulphur vulcanisation* (Textbook of polymer science, 1962).

The vulcanisation may continue by several such propagation steps and termination is probably achieved by reaction of the rubber radical with a radical of the vulcaniser. Termination by reaction between two polymer radicals is considered unlikely because of the low probability of two such radicals coming into position to react.
Appendix G

Heated graphite atomiser (HGA)

The detection limit can be enhanced considerably by employing a heated graphite furnace atomiser. For zinc the typical concentration working range is from 2 to 30 µg zn pr. l (ppb). The sensitivity is enhanced due to the fact that the entire sample is atomised and the residence time of the atoms in the optical path is approximately 1 sec.

20 µl of sample is placed on a platform in a 5 cm long graphite tube that is attached to a water cooled electrical contact in either end. By electrothermal heating the solvent is initially evaporated at approximately 150 °C after which the sample is ashed at approximately 350 °C and finally it is atomised at approximately 1900 °C. An external stream of argon prevents the mixture of surrounding air and an internal stream of argon removes gasses from the measuring area during the two first steps (Skoog et al., 1992).

Calibration curves and detection limits

Standards and 0-samples were made from a 0.01 M HNO₃ solution (pH = 2) where 70 µl of concentrated nitric acid (65 %) was added to every 100 ml of ion exchanged distilled water. Zinc chloride (ZnCl₂, 136.456 g pr. mol) was used for the zinc standards.

The following standard solutions were used: 5, 10, 15, 20 and 25 µg Zn pr. l (ppb). Nine separate experimental series, each comprising between 16 and 69 samples, were analysed for extractable organic zinc during a period of one and a half years, and after every third series the standards were renewed.

Every series started and ended with a 0 and a blank sample followed by the standards (only one standard was analysed at the end).

One specific soil and plant sample was stored as reference and was extracted and analysed every time the respective sample type was included in a series to ensure the reproducibility of the procedure in terms of determinate errors, i.e. instrument, method and personal errors. This could not be done for the aerosol samples as the entire samples were used in an extraction procedure.

The reference values in the determination of extractable organic zinc, are presented as

\[ \bar{x} = \text{mean value for the nine series [Abs].} \]
\[ \text{COV}_{\text{pooled}} = \text{pooled coefficient of variation, see below [\%].} \]
\[ N = \text{total number of analyses.} \]

The pooled coefficient of variation (\( s_{\text{pooled}} \) divided by \( \bar{x} \)) is an estimate of the standard deviation that is superior to the value for any individual subseries or the overall standard deviation. The sources of indeterminate errors are assumed to be the same in all samples which is valid if the samples have similar composition and have been analysed in exactly the same way (Skoog et al., 1992).

The pooled standard deviation can be calculated from equation G1 (Skoog et al., 1992).
\[
S_{\text{pooled}} = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i - \bar{x}_1)^2 + \sum_{j=1}^{N_2}(x_j - \bar{x}_2)^2 + \sum_{k=1}^{N_3}(x_k - \bar{x}_3)^2 + \ldots}{N_1 + N_2 + N_3 + \ldots - N_s}}
\]  
\text{(G1)}

where \(N_1\) is the number of data sets in series 1, \(\bar{x}_1\) is the mean value for series 1 and \(N_s\) is the number of subseries being pooled (\(N_s = 9\)).

The blank samples have been subtracted the 0-samples and the soil and plant samples have been subtracted the blank samples for the series in question.

*Table G1 Extractable organic zinc reference values for HGA.*

<table>
<thead>
<tr>
<th></th>
<th>(\bar{x}) [Abs]</th>
<th>COV(_{\text{pooled}}) [%]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-sample</td>
<td>0.0323</td>
<td>16.1</td>
<td>50</td>
</tr>
<tr>
<td>Blank sample</td>
<td>0.0557</td>
<td>20.8</td>
<td>18</td>
</tr>
<tr>
<td>Soil sample</td>
<td>0.4405(^1)</td>
<td>11.1</td>
<td>8</td>
</tr>
<tr>
<td>(Utterslev Mose, east 0 m):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant sample</td>
<td>0.2155(^2)</td>
<td>12.1</td>
<td>8</td>
</tr>
<tr>
<td>(Moss, Utterslev Mose)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Abs pr. g d.w.
\(^2\) Abs pr. 100 mg d.w.

In figure G1 the standard calibration curve for the nine series, subtracted the respective 0-sample values, is shown. A pooled standard deviation is again calculated.

*Figure G1 Standard calibration curve for HGA, allowing for blank values.*
The detection limit, or minimum detectable quantity, for HGA can be estimated by (Skoog et al., 1992)

\[
\Delta x_{\text{min}} = \bar{x}_{\text{sample}} - \bar{x}_{\text{blank}} > t \cdot s_{\text{blank}} \cdot \sqrt{\frac{N_{\text{sample}} + N_{\text{blank}}}{N_{\text{sample}} \cdot N_{\text{blank}}}}
\]  

where:

- \( \bar{x}_{\text{blank}} \) = mean blank value of \( N_{\text{blank}} \) analyses.
- \( \bar{x}_{\text{sample}} \) = mean sample value of \( N_{\text{sample}} \) analyses.
- \( s_{\text{blank}} \) = standard deviation of blank measurements.
- \( t \) = statistical factor accounting for the number of degrees of freedom in the calculation of \( s \), and for the desired confidence level.

For a typical sample the mean value is found of two analyses, \( N_{\text{sample}} = 2 \). The number of blank samples are \( N_{\text{blank}} = 18 \) and the standard deviation is \( s_{\text{blank, pooled}} = 0.0116 \) Abs. For a 99 \% confidence level and a number of degrees of freedom equal to \( 2 + 18 - 2 = 18 \), the statistical factor is found from table 3-2 in Skoog et al., 1992 to be \( t = 2.58 \), giving a detection limit, subtracted the blank value, of

\[
\Delta x_{\text{min}} > 2.58 \cdot 0.0116 \cdot \sqrt{\frac{2 + 18}{2 \cdot 18}} = 0.0223 \text{ Abs.}
\]

From linear regression of the standard calibration curve in figure G1 the detection limit corresponds to a zinc concentration of

\[
\Delta x_{\text{min}} > 1.6 \mu g \text{ Zn pr. l (ppb)}.
\]

According to the experimental procedure described in paper 1 each sample is diluted in 10 ml solvent. The amount of extractable organic zinc in a tire sample is found to be 1290 \( \mu g \) org. Zn pr. g tire (coefficient of variation = 5 \%) which leads to a tire detection limit of

\[
\Delta x_{\text{min}}(\text{tire}) = \frac{1.6 \mu g \text{ Zn pr.g tire} \cdot 0.011}{1290 \mu g \text{ Zn pr.g tire}} = 12.4 \mu g \text{ tire pr.sample}
\]
Appendix H

Flame atomic absorption spectrometer (FAAS)

Spectroscopic analysis of atoms or elementary ions by means of ultra violet (UV) or visible (VIS) radiation is performed in the gaseous state, where the atoms and ions are efficiently separated. The used apparatus are Perkin-Elmer laminar-flow burners with atmospheric air as oxidant and acetylene as fuel. This combination produces a flame that have temperatures in the 2200 to 2400 °C range. Since all elements ionise to some degree in a flame, the equilibrium

\[ \text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e^- \quad (H1) \]

is established in the inner cone of the flame and the position of this equilibrium depends on the temperature and the Zn concentration as well as on the total concentration of electrons in the sample. The spectra of Zn and Zn\(^{2+}\) differ totally and it is therefore of decisive importance to control the flame temperature (Skoog et al., 1992).

The typical setting for the oxidant is: pressure = 2.1 kg pr. cm\(^2\) and flow = 55. For the fuel the pressure is set at 0.5 kg pr. cm\(^2\) and the flow is 25. The wavelength for zinc analysis is set at 213.9 nm and adjusted to obtain maximum radiation intensity, and the slit is 0.7 nm.

The aqueous sample is nebulised by the flow of oxidant and is mixed with fuel. The resulting aerosol then flows past a series of baffles that removes all but the finest droplets resulting in a large loss of sample which is drained into a waste container. The mixture is then fed into a slotted burner that provides a flame that is approximately 10 cm in length. In the base region of the flame the solvent is evaporated and the finely divided particles are then carried to the inner cone, which is the hottest part of the flame (approximately 2300 °C), where the particles are split into gaseous atoms or ions. It is here that the analyte is radiated by a hollow cathode lamp with a radiation wavelength corresponding to the absorption wavelength characteristic for the metal in question. Finally the sample is oxidised in the outer cone and is removed by the ventilation system (Skoog et al., 1992).

The disadvantage with FAAS is the poor utilisation of the analyte since it is only a fraction of the metal atoms that pass through all of the processes in the flame and because the residence time in the optical beam is short (approximately 10\(^{-4}\) sec.).

Some metals such as titanium, zirconium and tungsten form oxides that are not totally oxidised at the relatively low temperatures that are present in an air/acetylene burner. When the diameter of the metal oxide particles are larger than the wavelength of the incoming radiation they will scatter the incoming beam.

Chemical interferences in the form of anions forming low volatile compounds with the metal can also occur. This problem can be solved by adding a releasing agent comprised of cations that bind the interfering anions or by addition of a protective agent that form stable volatile compounds with the metal (Skoog et al., 1992).
Calibration curves and detection limits

The following standard solutions were used: 0.2, 0.4, 0.6, 0.8 and 1.0 mg Zn pr. l (ppm). Eight separate experimental series, each comprising 20 to 42 samples, were analysed during a period of two years and after every third series the standards were renewed.

The extractable organic zinc concentrations in plant samples were too low to be detected with FAAS, therefore only a soil sample was stored as reference as shown in table H1. The blank samples have been subtracted the 0-samples and the soil samples have been subtracted the blank samples.

Table H1 Extractable organic zinc reference values for FAAS.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{x}$ [Abs]</th>
<th>COV$_{pooled}$ [%]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-sample</td>
<td>0.006</td>
<td>65.5</td>
<td>39</td>
</tr>
<tr>
<td>Blank sample</td>
<td>0.013</td>
<td>24.6</td>
<td>15</td>
</tr>
<tr>
<td>Soil sample (Utterslev Mose, west 1 m):</td>
<td>0.012$^*$</td>
<td>21.6</td>
<td>3</td>
</tr>
</tbody>
</table>

$^*$ Abs pr. g d.w.

In figure H1 the standard calibration curve, subtracted the blank values, is shown.

![Figure H1 Standard calibration curve for FAAS, allowing for blank values.](image)

The detection limit for FAAS, subtracted the blank value, is

$$\Delta x_{min} > 2.58 \cdot 0.0032 \cdot \sqrt{\frac{2 + 15}{2 \cdot 15}} = 0.0062 \text{ Abs.}$$
From linear regression of the standard calibration curve the detection limit corresponds to a zinc concentration of

$$\Delta x_{\text{min}} > 0.0165 \text{ mg Zn pr. l (ppm)}$$

leading to the following tire detection limit

$$\Delta x_{\text{min}} (\text{tire}) > \frac{16.5 \mu g \text{ Zn pr. l} \cdot 0.011}{1290 \mu g \text{ Zn pr. g tire}} = 0.13 \text{ mg tire pr. sample.}$$
Appendix I

Elemental composition in impactor samples as measured with NAA

In figures I1 through I3 three elemental distribution profiles are shown for an impactor set sampled in Copenhagen in January 1996 during cold and dry weather. Sodium and Scandium are examples of typical coarse fraction elements and Brom is an example of an element predominantly found in the accumulation mode.

Figure I1 Sodium distribution in impactor sample.

\[ \text{Na} = 1039 \text{ ng pr. m}^3 \]

Figure I2 Scandium distribution in impactor sample.

\[ \text{Sc} = 0.0731 \text{ ng pr. m}^3 \]

Scandium is an earth crust element that occurs in concentrations around 22 mg Sc pr. kg soil and sodium is originating from sea spray \(1.08 \cdot 10^4\) mg pr. l and in trafficked areas from road salt. Concentrations about \(2.36 \cdot 10^4\) mg Na pr. kg soil is found in the continental crust.
Figure I3 Brom distribution in impactor sample.

Br = 4.03 ng pr. m³
Appendix J

High performance gel permeation chromatography (HP-GPC)

Standards were made from a newly laid asphalt sample that was dissolved in dichloromethane, centrifuged, dried and the bitumen was weighed. From this five different standards were made in 10 ml of dichloromethane giving the following concentrations 86.2, 43.1, 21.6, 10.8 and 5.8 mg pr. l (ppm). Duplicate determination yielded the calibration curve shown in figure J1.

![Figure J1 Standard calibration curve for HP-GPC.](image)

Blank samples gave negligible contributions to the chromatograms.

The minimum detectable quantity can be derived from the fact that peaks smaller than 0.2 cm are not discernible with the used amplification factor. The lower detection limit can extrapolated from the peak heights to be 17 µg bitumen pr. sample (dissolved in 10 ml solvent).

The areas of the bitumen chromatograms, for molecules larger than 2000 g pr. mol have a mean value of 1.32 cm², which gives the calibration factor 35.6 mg bitumen pr. l pr. cm². The mean factor for all analysed bitumen samples is 33.2 mg bitumen pr. l pr. cm² (coefficient of variation = 8 %).

Table J1 Peak height reference values for HP-GPC.

<table>
<thead>
<tr>
<th></th>
<th>( \bar{x} ) [cm]</th>
<th>COV&lt;sub&gt;pooled&lt;/sub&gt; [%]</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-sample</td>
<td>-0</td>
<td>-0</td>
<td>32</td>
</tr>
<tr>
<td>Blank sample</td>
<td>-0</td>
<td>-0</td>
<td>20</td>
</tr>
<tr>
<td>Soil sample</td>
<td>5.8&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>8.9</td>
<td>10</td>
</tr>
<tr>
<td>(Utterslev Mose, east 0 m)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>1)</sup> cm pr. 100 mg d.w.
Appendix K

Deposition

The deposition of airborne particulate matter can be described as either wet or dry deposition. Wet deposition is occurring in saturated air e.g. clouds, mist or fog that is in direct contact with the deposition surface. Dry deposition is different when gasses and particles are concerned and depends on several factors such as micrometeorology (temperature, humidity, wind etc.), deposition surface (structure, material, growth etc.) and depositing material (size, morphology, density, diffusion characteristics, water content etc.). The particulate dry deposition from the atmosphere to say a leaf surface can be described by combining three different mechanisms: turbulent transport, diffusion and gravitational settling.

Diffusion, where particles migrate as a consequence of collisions with moving gas molecules, is important for particles with diameters smaller than approximately 0.1 \( \mu \text{m} \). It tends to move particles from high concentrations to areas of lower concentrations such as to walls and other surfaces where the concentrations are essentially zero due to deposition. This molecular motion, known as Brownian motion, can be described by Fick’s law

\[
F = -D \cdot \frac{dC}{dy} \left[ \frac{g}{m^2 \cdot s} \right]
\]

(K1)

where: 
- \( D \) = molecular diffusion coefficient \([m^2 \cdot s^{-1}]\).
- \( \frac{dC}{dy} \) = concentration gradient \([g \cdot m^{-3} \cdot m^{-1}]\).

Molecular diffusion is important where the concentration gradient is large and the velocity gradients are small or in other words the flow is laminar and governed by viscous forces and not by turbulence. It is only in the immediate vicinity of a surface, typically one tenth of a millimetre, that this is the case. Factors that increase this laminar boundary layer are lower wind speed together with smoother and larger surfaces. As the flow trajectories are parallel to the surface in laminar flow, the movement of matter across this layer can only occur by diffusion, impaction or gravitational settling. Turbulence will increase the movement considerably.

In principle the immediate atmosphere over a given surface contains two boundary layers of interest. A laminar boundary layer resulting from the concentration gradient near the surface and an aerodynamic boundary layer resulting from the velocity gradient established at the boundary. For turbulence the particle flux can be described in terms of an eddy diffusion coefficient, \( \varepsilon \), similar to \( D \) in equation K1.

A one-dimensional steady-state continuity equation to predict the particle deposition flux in terms of effective eddy diffusion, Brownian diffusion, gravity settling and a constant particle concentration above a reference height has been set up by Sehmel (1971):

\[
F = -(\varepsilon + D) \cdot \frac{dC}{dy} - v_t \cdot C \left[ \frac{g}{m^2 \cdot s} \right]
\]

(K2)

where: 
- \( v_t \) = terminal settling velocity \([m \cdot s^{-1}]\).
C = airborne particle concentration \([\text{g} \cdot \text{m}^{-3}]\).

The deposition velocity can now be defined as, (Sehmel, 1971):

\[
K = -\frac{F}{C_0} \frac{m}{s}
\]

(K3)

where: \(C_0 = \text{constant particle concentration above reference height [g} \cdot \text{m}^{-3}]\).

The reference height can reasonably be chosen as 1 cm, as the principal resistance toward particle mass transfer takes place in the region below 1 cm, (Sehmel, 1971).

Turbulence causes the particles to fluctuate to and from a surface establishing an approximately constant aerosol concentration in the turbulent layer. As the particles move closer to the surface these fluctuations diminish to such a level where molecular diffusion takes over as the predominant mass transferring process. Increasing turbulence increases particle motion and as a consequence particles can deposit by being projected across the laminar boundary layer (impaction). Particle sizes may be so large (> 10 \(\mu\text{m}\)) that they are influenced only slightly or not at all by turbulence and in these cases the enhanced gravitational influence will govern the deposition tendency. Smaller particles follow to a greater extent the turbulence and the deposition of particles in the size range 2 to 10 \(\mu\text{m}\) is greatly enhanced by impaction.

The inertia of particles below 2 \(\mu\text{m}\) in diameter is not adequate to thrust them across the laminar layer by impaction. For these particles the Brownian motion in the laminar layer plays an important role and it is found that the diffusion increases with decreasing particulate size leading to only particles with aerodynamic diameters smaller than 0.1 \(\mu\text{m}\) can diffuse through the laminar boundary layer. According to this there are reduced settling properties for the particulate sizes ranging from 0.1 \(\mu\text{m}\) to 2 \(\mu\text{m}\) which is visualised in figure K1.

\[\text{Figure K1 Deposition velocity as a function of particle size (Sehmel, 1973).}\]
Clough (1973) measured the deposition properties for different particle sizes, namely *Lycopodium* spores (diameter 30 µm), polystyrene spheres (ca. 5 µm), oleic acid droplets (0.5 µm) and Aitken nuclei (ca. 0.08 µm). The particles were tagged with radioactivity and were sprayed in a wind tunnel where the floor was completely covered with parallel strips of copper foil and filter paper. The velocity of deposition, $v_g$, as a function of particle size is presented in figure K2.

![Figure K2 The effect of particle size on dry deposition to extended surfaces of copper (+) and filter paper (O) (Clough, 1973).](image)

The relationship between particle size and deposition efficiency resembles the theoretical line for a smooth surface calculated by Sehmel (1971). The results for the filter paper are consistently slightly higher, probably due to the roughness of the paper (Clough, 1973).
QUANTIFICATION OF TIRE-TREAD PARTICLES USING EXTRACTABLE ORGANIC ZINC AS TRACER

Patrik Fauser
Plant Biology and Biogeochemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark and
Department of Environmental Science and Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

Jens Christian Tjell, Hans Mosbaek
Department of Environmental Science and Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

and

Kim Pilegaard
Plant Biology and Biogeochemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

Abstract - A method for identifying and quantifying tire-tread particles in the environment has been developed. It is based on the measurement of extractable organic zinc. The high sensitivity of atomic absorption spectrometry (AAS) with a heated graphite atomiser (HGA) permits assessment of submilligram amounts of tire debris in environmental samples. To validate the findings a basically different method previously developed by ¹ is employed. This is based on the measurement of the rubber polymer styrene butadiene rubber (SBR) by infra red spectrometry (IR). The analysis are among others performed on aerosol and soil samples.

INTRODUCTION

The purpose of this work is to develop a method which enables the identification and quantification of debris generated from the wear of automobile tires. The main objective has been to establish a chemical procedure that facilitates the quantification of trace amounts of tire debris without reducing the sensitivity or reproducibility of the method.

Infrared spectrometry (IR) is widely known and used for the identification of polymers. The choice of styrene butadiene rubber (SBR) as a tire indicator is appropriate since SBR is the most commonly used rubber polymer in tires. About 30 % of the rubber polymer used for private automobile tires is SBR, truck and bus tires however consist of 90 % natural rubber. It is stated that 65 % of the SBR production in the United States is used for tire manufacturing and furthermore that the particulate SBR contributions from other sources are small².

The IR procedure based on SBR, developed by ¹ suffers from high dependence on the initial removal of organic material as well as on the efficiency of the solubilisation of the vulcanised rubber. After proper extraction one faces the problem in measuring the peak heights in the spectrum as considerable uncertainties are encountered in determining the base line. Other IR techniques that are standard in the rubber industry require large
amounts of rubber and are thus inapplicable to the present situation. Other investigators that have used SBR identification by IR are 2 and 3.

Another obvious tire indicator is zinc which has been used by many investigators. 2 found that there is a clear correlation between traffic activity and zinc concentrations in particles in the air and in the soil. Still one must be careful in assigning all the zinc to tire wear. According to 4 the particulate zinc contribution via tire wear amounts only to about 10 % of the total particulate zinc load in cities in Sweden.

Zinc oxide is added as activator to the vulcanising process and gives zinc concentrations of about 1 % in the final rubber product. To speed the vulcanisation two or three different organic accelerators, mostly sulphur containing, are added in practically all rubber stocks in amounts of 0.5 – 2 wt-% of the total mixture. The zinc forms chelates with the accelerators which in turn initiate free radical formation of the rubber polymers resulting in carbon-carbon crosslinks5,6. The major part of the zinc in tires is present as excess ZnO and ZnS. The extractable organic zinc, that is of interest in this project, is defined as zinc-accelerator complexes. As will be shown tires are, with the exception of engine oil, the only significant contributor to extractable organic zinc in airborne particles.

In the following two chemical analytical procedures are described, based on the measurements of extractable organic zinc by AAS and SBR by IR. The procedures are employed on a few aerosol and soil samples and possible interferences from other particulate sources are examined and discussed. A more thorough discussion of the IR method can be found in 1.

**ANALYTICAL METHOD**

The methods are briefly outlined in Figure 1. Prior to the chemical analysis the aerosol samples are dried in a silicagel exiccator for 24 hours and weighed. The other samples are dried at 60 °C for 24 hours.

1: About 1.0 g of the sample is extracted in 10 ml dichloromethane (DCM), CH₂Cl₂ Merck 6044 (b.p. 40 °C), in a 250 ml flask with reflux condenser for about 8 hours. In aerosol samples the total particulate weight is approximately 5 mg.

Bitumen, oils, waxes etc. are dissolved in DCM. Only non vulcanised or degraded rubber molecules (about 2 percent of the total polymer amount) are dissolved. Put together with the oils, waxes and accelerators that are present in the tire material a total of about 16 % of the rubber material can be extracted.

The tire extract from step 1 is brownish with tire particles floating on top. The colour is probably originating from carbon black and oils. For practical reasons and to overcome the volumetric problems in storing DCM solutions the zinc is brought into an aqueous solution in step 2.
2: The extract is centrifuged and 8 ml is evaporated, boiled with concentrated nitric acid and finally redissolved in 0.01 M nitric acid. In this way the dissolved organic material is oxidised and the extractable organic zinc is dissolved as inorganic zinc.

3: Once the degraded organic zinc is brought into an aqueous solution the concentrations can be measured with a heated graphite atomiser (HGA).

Due to the low concentration levels which are about 2 - 100 ppb in the solubilised aerosol samples it is very important to use clean glass equipment to minimise contamination. This is achieved by washing it in 0.1 M nitric acid and rinsing it in ion exchanged distilled water.

To prevent anions to interfere and to separate the metal from other cations an automatic extraction procedure is executed in connection with the HGA: Sodium diethyl dithiocarbamate trihydrate (NaDDC) and isobutylmethylketone is added to form complexes with the metal and to extract it into the organic phase which is then analysed. Samples that contain larger amounts of zinc, e.g. tire samples, can be analysed with a flame atomiser (FAA).

4: The zinc in the extracted remains is determined by drying 1/3 of the non-soluble fraction at 105 °C for 8 hours, reducing it to ashes at 500 °C for 4 hours and dissolving it in 0.01 M nitric acid.

500 °C is used since the zinc will evaporate at higher temperatures and at lower temperatures the organic material will not be totally degraded.

5: Once having removed the organic substances, in step 1, that could interfere with the IR measurements of SBR, two thirds of the non-soluble matter from the DCM extract is extracted in about 80 ml o-dichlorobenzene (o-DCB) (b.p. 179 °C) in a Soxhlet apparatus for 8 hours.

This extraction leads to partial polymer chain rupture and since the boiling point is well below the pyrolysis temperature of the rubber there are only minor changes in the polymer structure which justifies the application of IR spectrometry. To obtain an optimum IR-spectrum with respect to detectable absorption lines a base line with a minimum of 50 % transmission and about 2 mg of organic matter in the sample is required. In this way Beer’s law is valid and quantification is possible. The amount of dissolved SBR is about 0.01 mg in a solubilised aerosol sample.

6: Depending on the amount of organic matter in the sample, the entire o-DCB extract or part of it is evaporated to one tenth of a millilitre, ground in 300 mg of Kbr to a homogeneous mixture, pressed into a 0.7 mm thick pellet and dried. The analysis is carried out on a Perkin-Elmer 1760 X Infra Red Fourier Transform Spectrometer with a resolution of 4 cm⁻¹. Since the SBR concentration is low, each sample is scanned 200 times to minimise the background noise.

**Organic zinc**
In Table I zinc and SBR concentrations in tires and other particulate samples are shown. The zinc measurements are carried out using FAA, except for the bitumen samples, and concentrations below about 0.2 µg Zn pr. g d.w. are therefore not quantified.

The tire samples that are taken from private cars and trucks are cut from the outer 0.5 cm. The samples are placed in a plastic bag and dipped in liquid nitrogen (-197 °C) for about 5 minutes whereupon they are pounded to small bits with a hammer. The plastic bag is not destroyed by this procedure. The characteristic diameters span from a couple of mm and downward. The shape and size differ considerably compared to the tire aerosols occurring in the atmosphere as they are sharper edged and more spherical.

The outer layer of a used tire will contain substances like sand, stone and bitumen. To minimise these contributions tire powder for rerubbering of private car tires, received from Scanrub A/S, is analysed. This powder originates from used tires but here more than the outer layer is used so contamination is considerably smaller.

According to Table I the only examined source apart from tires that contribute to the extractable organic zinc is engine oils. The zinc in engine oils originates from anti wear additives such as zinc dithiophosphate, which is added in concentrations of 0.11 wt-% zinc. It is important to note that the extractable organic zinc concentration in engine oil equals the concentration found in tires. Since the exhaust samples show no extractable organic zinc, organic engine oil zinc can only spread in the environment through dripping on the road surface where it may adsorb onto soil particles. These are typically larger than 2 µm which reduces the tendency toward resuspension. The main part will however be washed into the gutters during rainfall and thus never be airborne.

Assuming that tire wear is the sole contributor to airborne particulate extractable organic zinc, the tire particle concentrations can be determined in any sample, e.g. an aerosol or a soil sample, by use of the factor \(1290 \mu g \text{ org. Zn pr. g tire} \) (standard deviation = 5 %). This factor is the mean value of the four analysed tire powder samples received from Scanrub A/S, see Table I.

**SBR**

IR-absorption lines below about 1200 cm\(^{-1}\) (above about 9 µm) involve other groups than C-H, C=H, C≡H and C-C. These can be carbon-heteroatom bonds like C-N or C-S, but most important are the absorptions due to monosubstituted alkenes (vinyls) 915 - 905 cm\(^{-1}\), disubstituted transalkenes 980 - 960 cm\(^{-1}\) and styrene about 700 cm\(^{-1}\) which are the characteristic lines in the IR-spectrum of SBR. All of the stated lines arise from the out of plane C-H bending.

The two lines at 700 cm\(^{-1}\) and 966 cm\(^{-1}\) are found to be the most representative of SBR rubber and are therefore used in the SBR identification. Interfering absorption lines due
to transolefinic and monosubstituted aromatic compounds may naturally occur at 966 cm\(^{-1}\) and 700 cm\(^{-1}\) respectively.

In Figure 2a segments of the absorption spectra around these two wave numbers are shown pr. mg of three selected samples. The equivalent tire concentrations, quantified on basis of the tire spectrum in Figure 2a, are determined by calculating the mean ratio between the absorptions of the 700 cm\(^{-1}\) and 966 cm\(^{-1}\) peaks in a given sample and the tire sample:

\[
\text{Conc.}(\text{tire}) = \left( \frac{\text{abs}(700\text{ cm}^{-1})_{\text{sample}}}{\text{abs}(700\text{ cm}^{-1})_{\text{tire}}} + \frac{\text{abs}(966\text{ cm}^{-1})_{\text{sample}}}{\text{abs}(966\text{ cm}^{-1})_{\text{tire}}} \right)^{\frac{1}{2}} \cdot \text{mass}_{\text{tire}}.
\]

The results are shown in Table I.

The 700 cm\(^{-1}\) peak is more reproducible than the 966 cm\(^{-1}\) peak, and the interferences on the 966 cm\(^{-1}\) peak are more prominent. The 966 cm\(^{-1}\)/700 cm\(^{-1}\) ratio is 1.59 for the tire sample in Figure 2a. As a guideline the ratio is about 1.72 for the standard tread vulcanizate described in “Standard Specification for Standard Tire for Pavement Tests” ASTM Designation E249-66, 1970 Annual book of ASTM standards, pp. 896-899.

It is only in the tire samples that the two peaks are occurring simultaneously which implies that the results obtained with IR are consistent with the organic zinc measurements, except for the engine oils. The IR-spectra of asphalt and engine oil give no absorption peaks that are coinciding with the two stated wavelengths, as these are soluble in DCM and are removed in step 1.

Thus having shown that some important particulate sources are not interfering with the analysis, the methods are employed on aerosol (Table II and Figure 2b) and soil samples (Table III and Figure 2c).

**AEROSOL SAMPLES**

Aerosol samples were collected in the inner city of Copenhagen at two sites.

With a medium volume sampler, airvolume = 60 m\(^3\) pr. day, aerosols were collected on celluloseacetate/cellulosenitrate filters, with 50 mm diameter and 1.2 \(\mu\)m pore size, on 5. May 1995 at Jagtvejen which carries 19700 vehicles pr. day.

On Blegdamsvej, 8000 vehicles pr. day, samples were collected with a Berner low pressure impactor, total airvolume = 368.81 m\(^3\), during ten days in January 1996. The particles are divided into 11 size fractions and collected on Teflon discs.

In Table II the zinc and SBR measurements are presented for the medium volume filter and the two impactor fractions 5 and 8 with mean aerodynamic diameters \(d_a = 0.35 \mu\)m.
and $d_a = 2.8 \, \mu m$ respectively. Particles with $d_a$ smaller than 2 $\mu m$ are normally defined as the fine fraction and particles with $d_a$ larger than 2 $\mu m$ as the coarse fraction. In Figure 2b the IR-absorptions pr. 150 m$^3$ sampled air are shown.

The IR-spectrum for the filter collected in May 1995 yields a tire concentration of 5.4 $\mu g$ tire pr. m$^3$ which is 93 % of the concentration found by AAS. The 966 cm$^{-1}$ peak is nearly 4 times smaller than the 700 cm$^{-1}$ peak, but still discernible. A base peak at about 805 cm$^{-1}$ derives from the remains of the cellulose filter.

The total amount of tire zinc in the same sample amounts to 48 % of the total particulate zinc when it is assumed that the extractable organic zinc fraction comprises 16 % of the total zinc in tires, see Table I.

Impactor stage 5 yields 0.45 $\mu g$ tire/m$^3$ and stage 8 approximately 0 as the 966 cm$^{-1}$ peak is absent. The corresponding tire concentrations based on the organic zinc are 0.71 and 0 $\mu g$ tire pr. m$^3$ respectively.

SOIL SAMPLES

Soil samples from three different sites are analysed. The results are presented in Table III and in Figure 2c the IR-spectra are shown pr. 200 mg soil.

From Blegdamsvej in Copenhagen road dust was collected in May 1996. From a highway near Utterslev Mose just outside Copenhagen samples were taken from the top soil adjacent to the highway. From a park area 10 km north of Copenhagen soil was collected at a depth of 3.0 cm in the ground in November 1996.

The IR-spectrum from Blegdamsvej gives 0.67 mg tire pr. g soil. A prominent peak can be seen about 875 cm$^{-1}$ which also can be found in the disc brake spectrum. The AAS method gives a mean value of 0.40 mg tire pr. g soil.

The soil sample from Utterslev Mose gives 0.65 mg tire pr. g soil with the IR method and 0.30 with the AAS method.

The soil sample 3.0 cm in the ground is approximately zero due to the missing 966 cm$^{-1}$ line. There is however an overall resemblance with the Utterslev Mose soil sample. The AAS method gives 0.008 mg tire pr. g soil as a mean value.

DISCUSSION

Approximately two thirds of the abraded tire material in Denmark is originating from private automobiles and one third from trucks and busses. The SBR content in private car tires is about three times higher than in truck and bus tires\textsuperscript{5}. This fact makes the IR
method more applicable to private car tires and the determination of the total tire particle load is underestimated when private car tires are used as reference.

The organic zinc concentration is approximately constant for the different tire types and although the method for extracting organic zinc is very procedure specific it is found to be robust.

An important point is to determine the organic solvent with which to dissolve the SBR. By extracting a fresh tire sample in benzene only a few percent of the SBR content is dissolved, whereas a considerably larger fraction can be extracted from an aerosol sample\(^1\). About 10% of the rubber polymer is dissolved from a fresh tire sample in o-DCB, and as with benzene the percentage is higher in an aerosol sample. This indicates a breakdown of the vulcanised network when the material is exposed in particulate form to oxidising conditions.

In contrast\(^1\) have shown that when aerosols are present in the sample, the SBR adheres to the residual aerosol material resulting in a gross reduction of dissolved SBR. This factor is minimised in Soxhlet extraction, but it could nevertheless be the explanation to the fact that the tire concentrations in aerosol samples found by IR are consistently lower compared to the organic zinc measurements, see Table II.

Another explanation could be that the presence of engine oil in the aerosol could be the source to the excess organic zinc although it is unlikely to find such amounts of airborne particulate bound oil droplets. The oil can not be detected in IR as it is removed in DCM prior to the analysis.

In soil samples the tire concentrations based on extractable organic zinc are lower than based on SBR. The probability of finding oil substances on non airborne soil particles should be larger than on aerosols and this should enhance the overestimation of organic zinc in soil samples. The results show that the opposite is the case. Furthermore the amount of tire material in the aerosol and soil samples are around 0.3 mg but the amount of residual material is approximately 5 mg in an aerosol sample and 1000 mg in a soil sample. The latter fact should increase the adhesion effect of the SBR to the residual matter in soil samples and thus lower the solubilisation of SBR in a soil sample, but again this is not the case.

Absorptions below 0.1 mAbs are not discernible in an IR spectrum and this leads to a detection limit of approximately 20 µg tire in a KBr pill. The detection limit in HGA is approximately 10 µg tire pr. 10 ml solvent.

Other solvents have been tried in the present work e.g. acetone, toluene and ethanol, and it is found that o-DCB is the most efficient solvent (the rubber swells in o-DCB\(^3\)) and that the interference in the IR-spectrum is low.

\(^2\) state that particulate samples from gasoline exhaust extracted in benzene show an equivalent absorption at 966 cm\(^{-1}\) of 0.2 % SBR and in o-DCB less than 0.1 % SBR.
Similar experiments with diesel exhaust showed negligible absorptions at these wavelengths. Asphalt does not absorb at the same wavelengths. Air samples far from traffic activities also showed no absorption\(^2\).

**CONCLUSION**

An experimental procedure for assessing submilligram amounts of tire tread particles in aerosol and soil samples has been developed and tested on aerosol, soil and other particulate samples. The procedure is based on measuring extractable organic zinc which is present in concentrations of about 1290 µg org. Zn pr. g tire. The only other examined source that contribute with organic zinc is engine oil, but with respect to aerosol samples the oil concentration is believed to be insignificant.

The results obtained with this procedure have been compared with the results obtained with an already existing method where the SBR concentration in tires is found with IR. The results differ by a factor of maximum 2.2. It was found that the AAS method is less time consuming and more sensitive and that the IR method is highly dependable on the extraction efficiency of the organic materials. Considerable uncertainties are furthermore connected with the measurement of the peak height in an IR spectrum. Since the IR method is based on SBR, tires from trucks and buses are underestimated as the SBR concentrations are smaller by a factor of approximately 3 compared to private car tires.

**ACKNOWLEDGEMENTS**

We would like to thank Senior Scientist Kaare Kemp, National Environmental Research Institute, for supplying aerosol filters. Scanrub A/S, KARA and the Department of Energy Engineering, DTU, for supplying rubber powder, flyash and diesel exhaust particles respectively.

**REFERENCES**


Fig. 1 Flow sheet of chemical analysis method for tire tread.
Fig. 2 IR-spectra for 2a: tire, diesel exhaust and disc brake, 2b: aerosol and 2c: soil samples.
<table>
<thead>
<tr>
<th>Sampled mass</th>
<th>Total zinc FAA</th>
<th>Organic zinc FAA</th>
<th>Equivalent tire conc. IR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[µg Zn/g d.w.]</td>
<td>[µg Zn/g d.w.]</td>
<td>[mg “tire”/g d.w.]</td>
</tr>
<tr>
<td>Tire (used), XT 165/70-R14</td>
<td>8353 (100 %)</td>
<td>1716 (20.5 %)</td>
<td>1042</td>
</tr>
<tr>
<td>Truck tire (unused), Bridgestone 385/65-R22.5</td>
<td>14587 (100 %)</td>
<td>1902 (13.0 %)</td>
<td>1035</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>8554 (100 %)</td>
<td>1391 (16.3 %)</td>
<td>981</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>7916 (100 %)</td>
<td>1241 (15.7 %)</td>
<td>1019</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>8062 (100 %)</td>
<td>1256 (15.5 %)</td>
<td>-</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>7582 (100 %)</td>
<td>1270 (16.8 %)</td>
<td>-</td>
</tr>
<tr>
<td>Bitumen, Svaeholm</td>
<td>948 (100 %)</td>
<td>37.7* (4.0 %)</td>
<td>-</td>
</tr>
<tr>
<td>Bitumen, Jagtvej</td>
<td>309 (100 %)</td>
<td>12.6* (4.1 %)</td>
<td>≈ 0</td>
</tr>
<tr>
<td>Bitumen, Newly laid</td>
<td>381 (100 %)</td>
<td>14.9* (3.9 %)</td>
<td>-</td>
</tr>
<tr>
<td>Diesel exhaust on quartzfilter: Pallflex 2500 qat-up</td>
<td>1486 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Quartzfilter: Pallflex 2500 qat-up</td>
<td>24763</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Soot from exhaust pipe, gasoline car</td>
<td>771 (100 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Soot from exhaust pipe, diesel car</td>
<td>812 (100 %)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Engine oil (unused), Shell standard, Helix 10W-40</td>
<td>1096 (100 %)</td>
<td>1085 (99.0 %)</td>
<td>967 (89.5 %)</td>
</tr>
<tr>
<td>Engine oil (after 1000 km), Shell standard, Helix</td>
<td>1080 (100 %)</td>
<td>967 (89.5 %)</td>
<td>947 (98.0 %)</td>
</tr>
<tr>
<td>Engine oil (after 1500 km), Diesel car</td>
<td>966 (100 %)</td>
<td>650 (97.6 %)</td>
<td>-</td>
</tr>
<tr>
<td>Engine oil (after 1700 km), gasoline car</td>
<td>666 (100 %)</td>
<td>b.d.</td>
<td>≈ 0</td>
</tr>
<tr>
<td>Dust from disc brakes, scratched from blocks</td>
<td>147.8 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Dust from drum brakes (dirty)</td>
<td>528.2 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Flyash from private woodburner (beech)</td>
<td>21.1 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Flyash from private woodburner (birch)</td>
<td>26.9 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Flyash from coalfired power station</td>
<td>45.6 (100 %)</td>
<td>b.d.</td>
<td>≈ 0</td>
</tr>
<tr>
<td>Flyash from coalfired power station</td>
<td>43.1 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
<tr>
<td>Flyash from waste incineration plant</td>
<td>22095 (100 %)</td>
<td>b.d.</td>
<td>≈ 0</td>
</tr>
<tr>
<td>Flyash from crematorium</td>
<td>74.4 (100 %)</td>
<td>b.d.</td>
<td>-</td>
</tr>
</tbody>
</table>

* Measured with HGA.

b.d. = below detection limit for FAA (< 0.2 µg Zn pr. g d.w.).

1) With electrostatic filter. Less than 50 mg/m³ left in the exhaust.

2) With electrostatic filter, filterbag and scrubber. No more than 10 mg/m³ left in the exhaust.

3) Semi dry and filterbag and scrubber.
### Table II
**Zinc and tire concentrations in aerosol samples, Zn is measured with HGA.**

<table>
<thead>
<tr>
<th>Medium volume filter. 60 m³, Copenhagen.</th>
<th>Total suspended particulate matter [µg pr. m³]</th>
<th>Total zinc HGA [ng Zn pr. m³]</th>
<th>Organic zinc HGA [ng Zn pr. m³]</th>
<th>Tire concentration HGA [µg tire pr. m³]</th>
<th>Tire concentration IR (SBR) [µg tire pr. m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impactor fraction, dₐ=0.35 µm. 368.81 m³, Copenhagen.</td>
<td>105.0 (100 %)</td>
<td>100.5</td>
<td>7.7 (7.7 %)</td>
<td>5.84</td>
<td>5.4</td>
</tr>
<tr>
<td>Impactor fraction, dₐ=2.8 µm. 368.81 m³, Copenhagen.</td>
<td>4.53</td>
<td>10.10 (100 %)</td>
<td>0.93 (9.2 %)</td>
<td>0.71</td>
<td>0.45</td>
</tr>
</tbody>
</table>

### Table III
**Zinc and tire concentrations in soil samples, Zn is measured with HGA.**

<table>
<thead>
<tr>
<th>Sampled mass d.w. [g]</th>
<th>Total zinc HGA [µg Zn pr. g d.w.]</th>
<th>Organic zinc HGA [µg Zn pr. g d.w.]</th>
<th>Tire concentration HGA [mg tire pr. g d.w.]</th>
<th>Tire concentration IR (SBR) [mg tire pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utterslev Mose, top soil. Copenhagen. As above</td>
<td>1.51359</td>
<td>178.05 (100 %)</td>
<td>0.30 (0.2 %)</td>
<td>0.23</td>
</tr>
<tr>
<td>Blegdamsvej, road dust. Copenhagen. As above</td>
<td>2.35008</td>
<td>193.04 (100 %)</td>
<td>0.58 (0.3 %)</td>
<td>0.44</td>
</tr>
<tr>
<td>Park, 3.0 cm in ground. Lyngby. As above</td>
<td>1.1762</td>
<td>57.34 (100 %)</td>
<td>0.013 (0.02 %)</td>
<td>0.010</td>
</tr>
<tr>
<td>Park, 3.0 cm in ground. Lyngby. As above</td>
<td>1.1689</td>
<td>34.63 (100 %)</td>
<td>0.007 (0.02 %)</td>
<td>0.005</td>
</tr>
</tbody>
</table>
QUANTIFICATION OF BITUMEN PARTICLES IN AEROSOL AND SOIL SAMPLES USING HP-GPC
(Accepted for publication in Petroleum Science and Technology, November 1998)

Patrik Fauser
Risø National Laboratory, DK-4000 Roskilde, Denmark and
Technical University of Denmark, DK-2800 Lyngby, Denmark

Jens Christian Tjell, Hans Mosbaek
Technical University of Denmark, DK-2800 Lyngby, Denmark

and

Kim Pilegaard
Risø National Laboratory, DK-4000 Roskilde, Denmark

ABSTRACT

A method for identifying and quantifying bitumen particles, generated from the wear of roadway asphalts, in aerosol and soil samples has been developed. Bitumen is found to be the only contributor to airborne particles containing organic molecules with molecular weights larger than 2000 g pr. mol. These are separated and identified using High Performance Gel Permeation Chromatography (HP-GPC) with fluorescence detection. As an additional detection method Infra Red spectrometry (IR) is employed for selected samples. The methods have been used on aerosol, soil and other samples.

INTRODUCTION

The main perspective of these investigations has been to determine the influence of the chemical composition on field performance. That is, the resistance toward the mechanical, thermal and oxidative effects provided by the traffic and the surrounding atmosphere. Asphalt is worn off the roads in rates of 13 tonnes asphalt $\cdot$ km$^{-1}$ $\cdot$ year$^{-1}$ for main roads and 17 tonnes asphalt $\cdot$ km$^{-1}$ $\cdot$ year$^{-1}$ for highways (Muschack, 1990) and despite these large numbers very few investigations have been performed with the aim to determine the fate and the concentration levels of the abraded bitumen material in the environment.

Bitumen is a dark brown to black viscous, non-volatile residue from oil distillation that is used to strengthen and bind the sand and stone matrix in asphalt. The large number of organic compounds in bitumen are varying according to the origin and refining procedures of the oil. They generally have low vapour pressures and consequently high particulate affinity as air pollutants. They are slowly biodegradable and among the numerous compounds is a high percentage of the carcinogenic poly aromatic hydrocarbons (PAH's).

The main objective of this work has been to establish a chemical procedure that enables a fingerprint identification of bitumen. By employing this procedure on aerosol and soil samples bitumen concentrations are found for a few samples. Finally interfering sources to particulate air pollution are investigated. To verify the results a method based on Infra Red (IR) spectrometry is used.

**EXPERIMENTAL METHOD FOR BITUMEN**

To be able to perform a fingerprint identification it is necessary to have a compound or groups of compounds that are characteristic for bitumen and are known not to originate from other sources or at least not in considerable amounts. Due to high concentration of large organic molecules in bitumen the identification is here based on a separation of the molecules according to their molecular size by using High Performance Gel Permeation Chromatography (HP-GPC) with fluorescence detection.

The left side of the flow-sheet in Fig. 1 briefly outlines the analytical method described below to separate bitumen.

1: The samples are initially dried at 60 °C for 24 hours and weighed.

2a-2c: 1 to 5 g of sample is dissolved in 20 ml of dichloromethane (DCM). The solution is filtered and evaporated after which the asphaltenes are separated as the insoluble phase when 20 ml of n-heptane is added and settled overnight at room temperature. The asphaltenes are separated by filtering the solution through Munktell 00K filtering paper and subsequently redissolved in 20 ml of DCM to reach a concentration of about 0.1 g pr. l. Bitumen and the n-heptane solubles, known as maltenes, are also redissolved in DCM to a concentration of about 0.1 g pr. l.
Bitumen is readily dissolved in DCM. DCM (CH₂Cl₂, Merck 6044, b.p. 40 °C) is used both in the extraction and as eluent in HP-GPC. Ethanol 99.9 % and 96 %, n-heptane, methanol, acetonitrile and isopropanol have been tried as solvents but DCM turned out to have the best overall viscous, solubility and optical properties.

The separation of the organic size groups is performed with HP-GPC. Three columns are used in series: a NucleoGel GPC 10 P guard column followed by a NucleoGel GPC 50-10 and a NucleoGel 500-10 column. They consist of porous gel particles with 10 µm diameter. The two analytical columns have dimensions 30 cm × 7.8 mm ID and are used for size fractionation in the intervals 0-2000 g pr. mol and 0-25000 g pr. mol respectively. The pore sizes are 50 Å and 500 Å respectively. Smaller molecules are more liable to enter the gel matrix which results in longer retention times. The maximum retention time (for the smallest molecules) is about 20 minutes for the three columns in series. The total volume from the injection valve to the detector is about 2 ml.

3: 100 µl of the bitumen, maltene and asphaltene samples are injected into a 6 port rotation injection valve. 1.0 ml of DCM is pumped pr. minute by a LKB 2150 HPLC pulse free pump. The solvent and sample are lead through a LKB 11360-1 1.0 ml mixer driver with a rotating magnet. Finally the elution is lead through a Perkin Elmer LC 240 fluorescence detector with excitation wavelength set at 280 nm and emission wavelength set at 330 nm.

The excitation wavelength should not be any lower due to the increasing absorption by DCM. Higher excitation wavelengths (lower energy), e.g. in the interval 400 - 500 nm, can be used more specifically in the assessment of polyaromatics with more than 6 rings.

4: Depending on the amount of organic matter in the sample, the remaining DCM extract or part of it is evaporated to one tenth of a millilitre, ground in 300 mg of Kbr to a homogeneous mixture, pressed into a 0.7 mm thick pill and dried. The IR analysis is carried out on a Perkin-Elmer 1760 X Infra Red Fourier Transform Spectrometer with a resolution of 4 cm⁻¹ and 200 scans to minimise the background noise.

To obtain an optimum IR-spectrum with respect to detectable absorption lines a base line with a minimum of 50 % transmission and about 2 mg of organic matter in the sample is required. In this way Beer’s law is valid and quantification is possible. The amount of bitumen is about 0.3 mg in an aerosol sample.

**HP-GPC**

In Fig. 2 the calibration curve of peak molecular weight, $M_p$, versus elution time is produced by using ten polystyrene standards with molecular masses of 162, 580, 925,
1350, 2100, 2850, 4950, 7000, 10850, 20650 g pr. mol respectively (Polymer Laboratories, 1998). When using the graph the molecular size of the eluted compounds can be read as a function of the eluent volume (1 ml = 60 sec.).

In Fig. 3a the chromatograms of bitumen, maltene and asphaltene samples from a newly laid asphalt are shown. The bitumen size distribution is bimodal with $M_p$ around 1500 and 400. The n-heptane soluble fraction (maltenes) has a $M_p$ around 400. The asphaltene distribution is broad with two discernible peaks around 1600 and 400. By gravimetry it is found that the maltene and the asphaltene fractions comprise 86.4 and 18.2 wt-% of the bitumen respectively, see Table I. Assuming that the fluorescence is identical for the molecules larger than 2000 g pr. mol, it can be calculated from Fig. 3a, that 74 % of the bitumen molecules larger than 2000 g pr. mol are asphaltenes.

It is assumed that fluorescence intensity, and hence the area of a chromatogram is proportional to the concentration of organic compounds in bitumen. Obviously the fluorescence is not identical for different compounds, but with respect to different bitumens the concentration-area ratio is approximately constant (coefficient of variation = 8 % for 6 samples) under the given experimental conditions. By comparing with the chromatograms of other sources it is found that bitumen is the main contributor to organic molecules larger than 2000 g pr. mol (~ 930 sec.), see Table II. The concentration-area ratio for this size group can be used to determine the bitumen concentration in e.g. an aerosol or soil sample when corrections are made with respect to solvent volumes and the amplification factors on the detector.

**IR**

To be able to identify bitumen by means of IR-spectrometry it is necessary to use absorption lines that are present in bitumen spectra and that are not found in other typically occurring airborne particulate matter. By comparing with IR-spectra of other sources it is found that the simultaneous presence of the aromatic C-H bending lines at 748 cm$^{-1}$ and 875 cm$^{-1}$ respectively, with a few exceptions, are specific to bitumen.

In Fig. 4a the IR-spectrum of a bitumen sample around 748 and 875 cm$^{-1}$ is shown as absorption pr. 10 mg d.w. By using this spectrum as a standard, the bitumen concentration in any sample can be found by calculating the mean ratio between the absorptions in the sample and the bitumen sample:

$$\text{Conc. (bitumen)} = \left( \frac{\text{abs} (748 \text{ cm}^{-1})_{\text{sample}}}{\text{abs} (748 \text{ cm}^{-1})_{\text{bitumen}}} + \frac{\text{abs} (875 \text{ cm}^{-1})_{\text{sample}}}{\text{abs} (875 \text{ cm}^{-1})_{\text{bitumen}}} \right) \cdot \frac{1}{2} \cdot \frac{\text{mass}_{\text{bitumen}}}{\text{mass}_{\text{sample}} \text{ or volume}_{\text{sample}}}$$
EXPERIMENTAL METHOD FOR AEROSOL AND SOIL SAMPLES

The experimental procedure described above is now employed for aerosol and soil samples. The extraction in n-heptane in step 2b was done with the purpose to determine the molecular size distribution of the different bitumen fractions and this is not performed for the aerosol and soil samples for practical reasons. The general procedure includes the below stated alteration to step 2 and is outlined at the right hand side of Fig. 1.

Aerosol samples are dried in a silicagel exiccator for 24 hours.

2: About 1.0 g of a soil sample (about 5 mg of an aerosol sample) is extracted in 10 ml DCM in a 250 ml flask with reflux condenser for about 8 hours. The solvent is evaporated and the sample is redissolved in 10 ml DCM. The solution is then centrifuged and 5 ml is either evaporated or diluted to reach a concentration of about 0.1 g pr. l. If the amount of soluble organic matter is to be measured 20 ml is used and 10 ml of this solution is evaporated and weighed.

RESULTS AEROSOL SAMPLES

Aerosol samples were collected in the inner city of Copenhagen at two sites.

With a medium volume sampler, airvolume = 60 m$^3$ pr. day, particles were collected on celluloseacetate/cellulosenitrate filters, with 50 mm diameter and 1.2 µm pore size, on 5. May 1995 at Jagtvejen which carries 19700 vehicles pr. day.

On Blegdamsvej, 8000 vehicles pr. day, samples were collected with a Berner low pressure impactor, total airvolume = 368.81 m$^3$, during ten days in January 1996. The particles are divided into 11 size fractions and collected on Teflon discs.

In Table III and Figs. 3b and 4b the HP-GPC and IR measurements are presented for the medium volume filter and impactor fractions 5 and 8 with mean aerodynamic diameter $d_a = 0.35$ µm and $d_a = 2.8$ µm respectively. Particles with $d_a$ smaller than 2 µm are normally defined as the fine fraction and particles with $d_a$ larger than 2 µm as the coarse fraction. In Fig. 4b the ordinate is mAbs pr. 450 m$^3$ sampled air.

The filter from 5. May 1995 subtracted the blind spectrum gives a bitumen concentrations of 7.8 and 8.1 µg pr. m$^3$ found by HP-GPC and IR respectively. The peak at about 3200 g pr. mol in the chromatogram derives from the cellulose filter, and by comparison with a tire chromatogram the peak at about 420 g pr. mol could be tire tread. Corresponding tire peaks can however not be identified in the aerosol IR-spectrum, as the 700 cm$^{-1}$ (styrene) and the 966 cm$^{-1}$ (disubstituted transalkenes) peaks are not detectable.
The bitumen concentrations in impactor stages 5 and 8 are determined on the basis of the 875 cm\(^{-1}\) peak alone since the 748 cm\(^{-1}\) peak is enveloped in the predominant 755 cm\(^{-1}\) peak in both spectra. Stage 5 yields 3.3 and stage 8 yields 0.6 µg bitumen pr. m\(^3\). In both spectra there is a peak at about 700 cm\(^{-1}\) that also is present in the tire spectrum. It is possibly the out of plane C-H bending in the styrene polymer originating either from tire particles or from styrene butadiene polymer modified bitumens.

RESULTS SOIL SAMPLES

Soil samples from three different sites are analysed. From Blegdamsvej in Copenhagen road dust was collected in May 1996. From a highway near Utterslev Mose just outside Copenhagen samples were collected from the top soil adjacent to the highway. From a park area 10 km north of Copenhagen soil was collected at a depth of 3.0 cm in the ground in November 1996.

The results are presented in Table IV and Figs. 3c and 4c. In Fig. 4c the ordinate is mAbs pr. g d.w. The possibility for recovering bitumen particles when collecting road dust is obviously high and accordingly the spectrum from Blegdamsvej shows a high resemblance with the bitumen spectrum. The sample from Lyngby 3.0 cm in the ground, show small peaks in Figs. 3c and 4c, which is an indication that the possible natural interferences from the soil are small. Both IR-lines are present for all of the soil samples which enhances the reliability of the method.

DISCUSSION

One of the reasons for the many detection techniques that are used is the obvious problem in identifying all of the organic material leaving the separating columns. The highly complex chemical composition of bitumen causes the eluent at any given point to be a mixture of many compounds and consequently the detection response relative to the eluted mass is continuously changing. The choice of fluorescence detection constitutes a problem in the detection of saturated compounds. When using the larger molecules as tracers the influence of the saturates however diminishes since the larger compounds are predominantly aromats that are highly fluorophoric. In previous works concerning HPLC it has been a common routine not to inject the asphaltenes to prevent clogging of the columns (e.g. Dark et al., 1978 and Bollet et al., 1981).

HP-GPC is commonly used in the polymer industry and is particularly useful in the study of complex mixtures. However in the determination of molecular weights of bitumen several factors including eluting solvent, compatible calibration standards, concentration of sample and interaction of sample molecules to form molecular aggregates have been reported to affect the measurements (e.g. Jennings et al., 1992). It is important that the concentrations are not raised above 0.1 g pr. l (100 ppm) since the degree of molecular self association, giving larger aggregates, increases at increasing concentrations resulting in a shift to higher molecular sizes. Furthermore at higher
concentrations quenching becomes significant which gives smaller apparent concentrations.

In the bitumen quantification it is assumed that the tracer molecules are approximately chemically identical irrespective of the occurrence of the particles, i.e. if it is an aerosol, soil or an asphalt sample. However aerosols are to a greater extent exposed to oxidising conditions which will result in a transformation to the larger and more polar asphaltenes (Huang et al., 1997). This effect should result in an overestimation of aerosol bitumen particles by HP-GPC whereas the soil concentrations should be less affected. IR is not sensible to this effect. It is thus expected that bitumen concentrations in aerosols should be higher by HP-GPC than IR. The results in Table III show that the opposite is the case.

From a HP-GPC bitumen calibration curve it is found that the detection limit is 17 µg bitumen pr. 10 ml solvent. In IR-spectra bitumen peaks are discernible for absorptions larger than 0.2 mAbs corresponding to 61 µg bitumen in a KBr pill. When the amount of bitumen in a pill decreases below about 0.3 mg, as found by HP-GPC in Table III, the discrepancy between the two methods increases rapidly. One explanation could be the increasing difficulties in distinguishing the peaks and baselines in the IR spectra.

To ensure that the procedure described above is specific to bitumen, a number of other sources that are contributors to aerosols and in particular traffic related aerosols are analysed to evaluate the possible interferences.

The interferences in HP-GPC are low from tire (oils and waxes), exhaust soot, brake lining and flyash samples, whereas the diesel exhaust and engine oil samples, especially the fresher oils, can cause some problems. 1 g of engine oil yields an equivalent bitumen content of about 100 mg, see Table II. Oil spill can adsorb onto soil particles. These are predominantly in the coarse mode (> 2 µm) which reduces the tendency toward resuspension. The main part will probably be washed into the gutters during rainfall and thus never be airborne.

With respect to IR the 748 cm⁻¹ line is present in the tire sample and the 875 cm⁻¹ line is detectable in the tire and the disc brake sample. The absorption lines in tire powder are derived from the extender oils and waxes and additional lines at 966, 915 and 700 cm⁻¹ are disubstituted transalkenens, monosubstituted alkenes and styrene respectively, originating from the unvulcanised styrene butadiene rubber mono- and polymers and possibly from rubber particles. These lines can also be found in styrene butadiene polymer modified bitumens. None of the other examined samples absorb notably at the used frequencies.

CONCLUSION

A method has been developed with the purpose to identify and quantify bitumen particles in aerosol and soil samples. The assessments are based on High Performance
Gel Permeation Chromatography (HP-GPC) with fluorescence detection. IR-spectrometry has been employed to verify the findings. Taking sample preparation and analysis time into consideration HP-GPC is a fast and reproducible method with a detection limit that is about a factor of 3 lower than IR. IR is based on measuring peak heights and when many peaks are overlapping the identification of the baseline is questionable.

By using fluorescence with UV-excitation one must be aware of the varying fluorescence intensities that exist for the numerous organic constituents in bitumens. Bitumen molecules larger than 2000 g pr. mol are used as tracers, and previous investigations show that these molecules are fluorophoric on account of a high degree of aromacity or presence of heteroatoms or carbonyl groups. The saturated compounds (about 30 wt-% of bitumen) do not absorb UV-radiation and therefore are not accounted for in the chromatograms. For aerosol samples the bitumen concentrations found by IR are consistently higher than those found by HP-GPC. For soil samples there are no such systematic observations.

ACKNOWLEDGEMENTS

We would like to thank Senior Scientist Kaare Kemp, National Environmental Research Institute, for supplying aerosol filters. Scanrub A/S, KARA and the Department of Energy Engineering, DTU, for supplying rubber powder, flyash and diesel exhaust particles respectively.

REFERENCES


# TABLE I

<table>
<thead>
<tr>
<th>Sampled mass</th>
<th>Bitumen [g (wt-% of asphalt)]</th>
<th>Maltenes [g (wt-% of bitumen)]</th>
<th>Asphaltenes [g (wt-% of bitumen)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt, Newly laid</td>
<td>4.9643 0.5014 (10.1 %)</td>
<td>0.4332 (86.4 %)</td>
<td>0.0903 (18.2 %)</td>
</tr>
<tr>
<td>Asphalt, Newly laid, Exposed to sunlight for 3 months</td>
<td>2.0522 0.2134 (10.4 %)</td>
<td>0.1724 (80.8 %)</td>
<td>0.0470 (22.0 %)</td>
</tr>
<tr>
<td>Asphalt, Jagtvej, Copenhagen</td>
<td>1.0068 0.1421 (14.1 %)</td>
<td>0.1122 (79.0 %)</td>
<td>0.0359 (24.9 %)</td>
</tr>
<tr>
<td>Asphalt, Svalholm, Risø</td>
<td>0.60345 0.06204 (10.2 %)</td>
<td>0.04418 (71.2 %)</td>
<td>0.02358 (37.6 %)</td>
</tr>
<tr>
<td>Asphalt, Blegdamsvej, Copenhagen</td>
<td>1.09787 0.13067 (11.9 %)</td>
<td>0.10075 (77.1 %)</td>
<td>0.03136 (24.2 %)</td>
</tr>
<tr>
<td>Asphalt, Utterslev Mose, Copenhagen</td>
<td>1.23649 0.20150 (16.3 %)</td>
<td>0.15835 (78.6 %)</td>
<td>0.04030 (19.9 %)</td>
</tr>
<tr>
<td>Asphalt, DTU, Lyngby</td>
<td>1.55836 0.24315 (15.6 %)</td>
<td>0.21446 (88.2 %)</td>
<td>0.03890 (15.8 %)</td>
</tr>
</tbody>
</table>
### TABLE II

**“Bitumen” concentrations.**

<table>
<thead>
<tr>
<th>Sampled mass [g]</th>
<th>Organic mass [g] (wt-%)</th>
<th>Equivalent bitumen conc. HP-GPC [mg “bitumen” pr. g d.w.]</th>
<th>Equivalent bitumen conc. IR [mg “bitumen” pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tire (used), XT 165/70-R14</td>
<td>0.11157</td>
<td>0.02233 (20.0 %)</td>
<td>35</td>
</tr>
<tr>
<td>Truck tire (unused), Bridgestone 385/65-R22.5</td>
<td>0.080</td>
<td>0.0075 (9.4 %)</td>
<td>-</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>0.9427</td>
<td>0.1091 (11.6 %)</td>
<td>30</td>
</tr>
<tr>
<td>Genan rubber powder, 0.4-0.7 mm, Scanrub A/S</td>
<td>0.9799</td>
<td>0.1269 (12.9 %)</td>
<td>-</td>
</tr>
<tr>
<td>Diesel exhaust on quartzfilter: Pallflex 2500 qat-up</td>
<td>0.00141</td>
<td>-</td>
<td>118</td>
</tr>
<tr>
<td>Quartzfilter: Pallflex 2500 qat-up</td>
<td>0.24763</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Soot from exhaust pipe, gasoline car</td>
<td>0.54890</td>
<td>0.09325 (17.0 %)</td>
<td>-</td>
</tr>
<tr>
<td>Soot from exhaust pipe, diesel car</td>
<td>0.79080</td>
<td>0.11310 (14.3 %)</td>
<td>-</td>
</tr>
<tr>
<td>Engine oil (unused), Shell standard, Helix 10W-40</td>
<td>1.54778</td>
<td>1.48946 (96.2 %)</td>
<td>101</td>
</tr>
<tr>
<td>Engine oil (after 1000 km), Shell standard, Helix</td>
<td>0.1010</td>
<td>0.0991 (98.1 %)</td>
<td>-</td>
</tr>
<tr>
<td>Engine oil (after 1500 km), Diesel car</td>
<td>0.1561</td>
<td>0.1491 (95.5 %)</td>
<td>-</td>
</tr>
<tr>
<td>Engine oil (after 1700 km), gasoline car</td>
<td>0.0914</td>
<td>0.0893 (97.7 %)</td>
<td>-</td>
</tr>
<tr>
<td>Dust from disc brakes, scratched from blocks</td>
<td>0.09929</td>
<td>0.00181 (1.8 %)</td>
<td>0.6</td>
</tr>
<tr>
<td>Dust from drum brakes (dirty)</td>
<td>0.21406</td>
<td>0.01435 (6.7 %)</td>
<td>-</td>
</tr>
<tr>
<td>Flyash from private woodburner (beech)</td>
<td>1.0149</td>
<td>0.0006 (0.1 %)</td>
<td>0</td>
</tr>
<tr>
<td>Flyash from private woodburner (birch)</td>
<td>1.0459</td>
<td>0.0006 (0.1 %)</td>
<td>0</td>
</tr>
<tr>
<td>Flyash from coalfired power station(^1)</td>
<td>1.09016</td>
<td>0.00227 (0.2 %)</td>
<td>0</td>
</tr>
<tr>
<td>Flyash from coalfired power station(^2)</td>
<td>1.01970</td>
<td>0.00067 (0.1 %)</td>
<td>0</td>
</tr>
<tr>
<td>Flyash from waste incineration plant(^3)</td>
<td>0.99485</td>
<td>0.00040 (≈ 0 %)</td>
<td>0</td>
</tr>
<tr>
<td>Ashes from crematorium</td>
<td>0.984</td>
<td>0.002 (0.2 %)</td>
<td>0</td>
</tr>
</tbody>
</table>

---

- : No measurements.

1) With electrostatic filter. Less than 50 mg/m\(^3\) left in the exhaust.

2) With electrostatic filter, filterbag and scrubber. No more than 10 mg/m\(^3\) left in the exhaust.

3) Semi dry and filterbag and scrubber.
### TABLE III
Bitumen concentrations in aerosol samples.

<table>
<thead>
<tr>
<th>TSP [µg pr. m³]</th>
<th>Organic mass [µg pr. m³]</th>
<th>Bitumen concentration HP-GPC [µg bitumen pr. m³]</th>
<th>Bitumen concentration IR [µg bitumen pr. m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium volume filter. 60 m³, Copenhagen.</td>
<td>105.0</td>
<td>15.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Impactor fraction 5, dₐ=0.35 µm. 368.81 m³, Copenhagen.</td>
<td>4.53</td>
<td>-</td>
<td>0.51</td>
</tr>
<tr>
<td>Impactor fraction 8, dₐ=2.8 µm. 368.81 m³, Copenhagen.</td>
<td>6.48</td>
<td>-</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### TABLE IV
Bitumen concentrations in soil samples.

<table>
<thead>
<tr>
<th>Sampled mass d.w. [g]</th>
<th>Organic mass [g]</th>
<th>Bitumen concentration HP-GPC [mg bitumen pr. g d.w.]</th>
<th>Bitumen concentration IR [mg bitumen pr. g d.w.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utterslev Mose, top soil. Copenhagen.</td>
<td>1.51359</td>
<td>0.00203</td>
<td>4.17</td>
</tr>
<tr>
<td>As above</td>
<td>1.51822</td>
<td>0.00252</td>
<td>6.08</td>
</tr>
<tr>
<td>Blegdamsvej, road dust. Copenhagen.</td>
<td>2.35008</td>
<td>0.02363</td>
<td>16.47</td>
</tr>
<tr>
<td>As above</td>
<td>1.87011</td>
<td>0.02480</td>
<td>10.24</td>
</tr>
<tr>
<td>Park, 3.0 cm in ground. Lyngby.</td>
<td>1.1762</td>
<td>0.0014</td>
<td>0.61</td>
</tr>
<tr>
<td>As above</td>
<td>1.1689</td>
<td>0.0019</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Fig. 1. Flow-sheet of chemical analysis method.
Fig. 2. Molecular polystyrene weight as a function of eluted volume.
Fig. 3. HP-GPC, a: bitumen, maltene and asphaltene samples, b: aerosol samples, c: soil samples.
Fig. 4. IR-spectra of a: bitumen, tire and flyash samples, b: aerosol samples, c: soil samples.
TIRE-TREAD AND BITUMEN PARTICLE CONCENTRATIONS IN AEROSOL AND SOIL SAMPLES

Patrik Fauser
Risø National Laboratory, Roskilde, Denmark and
Technical University of Denmark, DK-2800 Lyngby, Denmark

Jens Christian Tjell, Hans Mosbaek
Technical University of Denmark, DK-2800 Lyngby, Denmark

and

Kim Pilegaard
Risø National Laboratory, DK-4000 Roskilde, Denmark

Abstract - Tire and bitumen particle concentrations are determined in aerosol and soil samples. They each constitute about 5 wt-% of the total suspended particulate matter (TSP) in inner city air, collected with a Berner low pressure impactor, 5 m from a road. The particle size distribution shows that 92 % of the mass of airborne particulate tire debris have aerodynamic diameters smaller than 1 µm. The mean aerodynamic diameter is about 1 µm for the bitumen particles. Soil concentrations in the vicinity of a highway indicate an approximate exponential decrease with increasing distance from the road. Constant values are reached after about 5 m for the tire particles and 10 m for the bitumen particles. Concentrations in soil that has not been touched for at least 30 years show a decrease in tire concentration by a factor of 30 when moving from the top soil to a depth of 3 cm. The bitumen concentration is approximately constant to a depth of 10 cm.

INTRODUCTION

The purpose of this work is to evaluate the contribution of tire-tread and bitumen abrasion to particulate air pollution. Particulate samples along highways have previously shown to give tire concentrations of about 5 µg pr. m³ corresponding to about 5 wt-% of the total suspended particulate matter (TSP) (Pierson et al., 1974). It is known that it can contribute up to 10 wt-% of the TSP in heavily trafficked areas. Polyaromatic hydrocarbons (PAH’s) amount to about 10 % of the rubber material. Considering the carcinogenic properties and the slow biodegradability of the PAH’s, tire debris must be taken into account when dealing with particulate air pollution.

Rubber is used for various products and tire production makes up the largest amount. In Sweden in 1992, 90 % of the tire production was used for private automobiles (4 million tires) and trucks and busses (500.000 tires each). A total of 1 million rerubbered tires are sold in Sweden each year of which about 800.000 are used for private cars. 60.000 tonnes of tire material is used each year and of this about 10.000 tonnes are worn off of the roads (Ahlbom, 1994). In Denmark 1.9⋅10⁶ private car tires are worn out per year with each tire losing 2.4 kg of rubber by abrasion. The corresponding numbers for larger vehicles are 2.5⋅10⁵ tires per year and 11 kg rubber per tire. The total annual loss of tire rubber in the environment in Denmark is thus 7300 tonnes (Elvebakken, 1991).
Previous investigations have shown that airborne bitumen particles amount up to 11 wt-
% of the total suspended particulate matter sampled near a highway (He et al., 1993).
Wear rates of 13 tonnes asphalt \( \cdot \text{km}^{-1} \cdot \text{year}^{-1} \) for main roads and 17 tonnes asphalt \( \cdot \text{km}^{-1} \cdot \text{year}^{-1} \) for highways (Muschack, 1990) indicate that it is of great interest to
determine the fate of the asphalt debris.

It is estimated that 25 % of the abraded asphalt is disposed via sewers, 25 % is
 deposited within 150 meters on each side of the roads and the remaining 50 % is
removed by long range transportation (Elvebakken, 1991). Various investigators state
that asphalt or bitumen particles occur in the coarse fraction, defined as particles with
aerodynamic diameter larger than 2 \( \mu \text{m} \), which suggests that the possibility for inhaling
and far range transportation is reduced.

The information on whether the particles deposit near the roadside as lumps that are
indisposed to resuspension or whether they are sufficiently small to spread over long
distances and possibly enter the human and animal respiratory systems is not adequate.
To gain further knowledge it is essential to determine the size of the airborne particles
and measure the concentrations levels in aerosol and soil.

In order to identify and quantify the amount of tire and bitumen particles experimental
analysis methods that have been developed in paper 1 and 2 are employed in this work.
Organic zinc extracted in dichloromethane and measured with a Heated Graphite
Atomiser (HGA), is used as tire tracer (paper 1) and molecules larger than 2000 g pr.
mol, measured by High Performance Gel Permeation Chromatography (HP-GPC) with
fluorescence detection, are used as bitumen tracers (paper 2).

The results from aerosol and soil samples are presented followed by a summary of
earlier findings stated in the literature.

**AEROSOL SAMPLES**

**Sampling**

With a medium volume sampler, flow = 60 m\(^3\) pr. day, aerosol samples were collected
on celluloseacetate/cellulosenitrate filters with diameters = 50 mm and pore size = 1.2
\( \mu \text{m} \). During May 1995 one filter was exposed per day on Jagtvejen (19700 vehicles per
day), a closed road carrying heavy traffic in the inner city of Copenhagen. The sampling
inlet was placed 3 m above the ground and 2 m from the road.

Aerosol samples were collected with a Berner low pressure impactor (BLPI) with an
air flow of 25.4 l pr. min. The particles are divided into eleven size fractions based on a
50 % cut off diameter. In each stage the particles are collected on a cleansed Teflon
disc which is then dried and weighed to determine the total suspended particulate
matter (TSP). Four impactor sets were collected.
Risø: During three weeks in September 1995 one impactor was placed 3 m from a paved road near Risø 1 m above the ground, and another impactor was placed 15 from the first impactor perpendicular to the road, 1 m above the ground. There was no vegetation between the impactors and the road. The weather was overcast and rainy and the soil was wet so the contribution from resuspension of soil was minimal. The total airflow through each impactor was 763.52 m$^3$.

Copenhagen: During twelve days in January 1996 impactor samples were taken on a shed roof 3 m above the ground and 5 m from Blegdamsvej (8000 vehicles per day) which is an open road in the inner city of Copenhagen. The weather was moist and foggy and part of the time the temperature was below the freezing point. The total air flow was 432.82 m$^3$.

Copenhagen: During ten days in January and February 1996 impactor samples were taken at the same place as above. But this time the weather was dry and the temperature was below zero all the time. Total air flow: 368.81 m$^3$.

Some of the impactor samples have been exposed to neutron activation analysis (NAA) and analysed with a scanning electron microscope (SEM) at Risø. The medium volume filters are measured with proton induced x-ray emission (PIXE) at the Niels Bohr Institute in Copenhagen. NAA and PIXE give concentrations of elements with molecular weights larger than 13.

Results

Medium volume filters

Figure 1 shows the total suspended particulate matter and the airborne tire and bitumen debris in the air in Copenhagen during one week in May 1995. A weekly pattern for TSP, tire and bitumen particles can be observed. The daily mean mass contributions of tire and bitumen particles are 6.6 and 10.1 wt-% respectively of the TSP. The daily mean gravimetrically determined organic matter comprises 17.3 wt-% of the TSP. Since the road is closed on both sides there is a possibility for circulation of the abraded material and an accumulation of the airborne pollutants.

Impactor samples

Risø, 3 m’s from road (figure 2a): The TSP, tire and bitumen concentration profiles are shown. The bitumen distribution follows the TSP distribution and can be described as bimodal with peaks around 0.042 µm and 0.71 µm. 69 wt-% of the bitumen debris occur in the interval between 0.35 µm and 2.8 µm. The tire distribution is also bimodal with 93 wt-% of the mass below 1 µm and a small fraction larger than 10 µm.
Risø, 18 m’s from road (figure 2b): It was expected that the amount of submicron particles would be the same at the two distances and the amount of particles larger than about 10 µm would be larger closer to the road. The former is found not to be the fact as the TSP and the tire debris smaller than 1 µm both have increased 40-50 % when moving from 3 to 18 meters from the road. Both the TSP and the tire particles larger than 10 µm decrease with about 35 %.

The bitumen concentration in the interval from 0.35 µm to 2.8 µm has increased with 148 %. The bitumen particles larger than 10 µm have increased 250 %.

Copenhagen, wet weather (figure 2c): The TSP and the tire particle distribution are again bimodal though not coincident. The smaller tire particles are with good agreement normally distributed. The sampling inlet is 5 m above the ground compared to 1 m at Risø which should lead to a drop in particles larger than 10 µm. The amount of larger tire particles compared to the total tire concentration is however the same. The amount of larger bitumen particles compared to the total bitumen concentration has decreased about 80 %. Note there is no tire mass in stage 10 and an additional particle fraction (stage 11: > 16 µm) is collected in figures 2c and 2d.

5.8 wt-% of the TSP is bitumen particles. This is a factor of 4 larger than at Risø. Unlike Risø the TSP and the bitumen distributions are not coincident, as the bitumen has a single peak at 0.71 µm and TSP is bimodal with peaks at 0.087 µm and 1.4 µm. 68 wt-% of the bitumen aerosols are found in the interval between 0.35 µm and 2.8 µm. The particles are with good agreement normally distributed. 5.0 wt-% are tire particles and this is a factor of 2 larger than at Risø.

Copenhagen, dry weather (figure 2d): Here the weather was dry compared to figure 2c where it was wet or moist during the whole sampling period. 5.8 wt-% of the TSP is tire particles which is 14 % more compared to figure 2c. 5.1 wt-% of the TSP is bitumen particles which is 26 % less compared to figure 2c.

The TSP is larger in figure 2c where it is expected that the airborne particles will deposit as a consequence of the enhanced scavenging effect. The bi- or even trimodal TSP distribution is more evident in dry weather, where the drop in particulate mass at about 2 µm is seen as well as an increase in submicron particles. In wet weather the agglomeration of particles will cause them to gain larger diameters and thus shift the impactor profile to the right. The possibility for water droplets to enter the impactor are small since rain drops generally are larger than 0.5 mm. In connection with fog they can decrease below 0.2 mm. Ice and snow crystal have larger variability and can even enter the submicron range. Water accumulations on the Teflon discs were nevertheless observed at the stages around 1 µm predominantly during the wet and foggy sampling periods.

A scanning electron microscopy picture (SEM) of an assumed tire particle found in the > 16 µm fraction from figure 4d resembles the oblong sausage shape described in earlier
experiments and the x-ray fluorescence spectrum (XRF) shows dominant Cl, S, Si and Na peaks. No considerable zinc peak is found but it is doubtful whether the ZnO, ZnS and organic zinc complexes are homogeneously distributed within the tire matrix. The S peak could originate from the added vulcaniser. It looks like smaller particles are adsorbed onto the tire particle and these could be road salt and soil particles accounting for the Cl, Si and the Na peaks.

No tire particles could be identified either on basis of structure (SEM) or zinc (XRF) in the other stages. Particles smaller than 1 µm are difficult to characterise on structural basis due to the higher degree of agglomeration and the subsequent less differentiated picture.

SOIL SAMPLES

Sampling

Blegdamsvej is a busy road in Copenhagen (8000 vehicles per day). Road dust was collected from the gutter by brushing it into a paper bag. Plantparts, twigs and other larger objects were avoided. It was collected in May 1996 during dry and cold weather.

Risø is a fenced area east of Roskilde fjord. The soil sample was collected with a clean knife from the top 0.5 cm, about 5 m from one of the smaller roads that pass through the area. The roads are asphalted every three years. Collected in October 1995 during wet conditions.

Utterslev Mose is a park and bog area situated immediately outside Copenhagen. The soil samples were collected from the top 0.5 cm in different distances from a highway (37900 vehicles per day) on both sides of the northeast-southwest going highway near a crossing. The area is a public park and the soil had probably not been touched in the last three years. Collected in May 1996 during hot and dry weather.

Lyngby park cemetery. Samples were taken from the top soil and in depths of 0.5, 1.0, 3.0 and 10.0 cm with an aluminium tube with an inside sectional area of 2.5 cm² on a spot 10 m from a road in Lyngby about 10 km north of Copenhagen during wet and cold weather in November 1996. The soil had not been touched for at least 30 years.

Highway 2 km south of Køge. Soil samples were taken during dry weather in September 1996 from the top 0.5 cm in different distances from the highway on the east side. In the immediate vicinity to the road and 10 m from the road additional samples were taken in 2 depths: 1.0, 3.0 and 10.0 cm.
Results

Highway near Utterslev Mose

In figure 3 the tire and bitumen concentrations in the upper 0.5 cm of the soil are shown in different distances from the highway. It is believed that the soil has not been worked on for the last three years, but it is not known whether the whole area has been treated in the same way or not.

The measurements indicate that the deposited particles are predominantly found within the first 5 m’s and 10 m’s from the road side for tire and bitumen particles respectively. These deposited particles probably have diameters larger than 20 µm according to deposition properties and to earlier findings by e.g. Brachaczek et al. (1974) and Cadle et al. (1978). The high bitumen concentration close to the road probably arises from spill during road paving and from the spreading of asphalt lumps. Further away from the road the concentrations are approximately constant. The decrease in concentrations with increasing distance from the road can be described by an exponential or a power function. Since the movement of submicron particles is governed by molecular diffusion they can spread over long distances and result in a constant “background” concentration.

The particles may adsorb to the soil particles and reduce the disposition towards resuspension as a consequence of the enhanced effect of gravitational settling. During paving of the roads, bitumen is spilled and spread in the near surroundings. This probably accounts for the major part of the bitumen concentration in the immediate vicinity of the road. From figure 3 it can be seen that there was a prevailing easterly wind direction before the sampling. This fact was confirmed by The Danish Meteorology Institute (DMI).

The gutter sample from Blegdamsvej in Copenhagen gives a tire concentration of 0.4 mg pr. g corresponding to the concentrations found close to the highway in figure 3. A soil sample from the top 0.5 cm taken in the Risø area 5 m from a smaller road gives 0.11 mg tire pr. g which approximately equals the background concentrations in figure 3 and 4. The sample from Blegdamsvej gives a bitumen concentration of 13.35 mg pr. g which is about a factor of 2.5 larger than found close to the highway in figure 3. The Risø sample gives 0.25 mg bitumen pr. g and this approximately equals the background concentrations in figure 3.

Highway 2 km south of Køge

Again the concentrations in figure 4 are decreasing with increasing distance from the road, and the orders of magnitude are approximately the same as in figure 3. The decreases are not as steep as in figure 3, probably because the driving velocities are generally higher in figure 4. Higher velocities increase the turbulence and the resuspension of settled material and consequently increase the movement of the coarser particles in the air.
Lyngby park cemetery and highway near Køge

In figure 5 the tire and bitumen concentrations in different depth are shown at distances 0 m and 10 m from the highway near Køge and 10 m from the road in Lyngby Park Cemetery.

The tire tread is kept in the upper 1 cm of the soil and there is evidently negligible movement downward even by submicron particles. The tire concentrations from Lyngby decrease by a factor of 30 when moving from the top soil to a depth of 3.0 cm. In the immediate vicinity to the highway near Utterslev Mose the decrease is a factor of 15.

0 m from the highway near Køge there is a 35 % increase in the bitumen concentration when moving from the top 0.5 cm to a depth of 1.0 cm. Subsequently the concentration decreases to about 2 mg bitumen pr. g soil at a depth of 10 cm. Farther from the road and at Lyngby Park Cemetery the vertical bitumen concentration profile is approximately constant.

DISCUSSION

Aerosol samples that are stored for longer periods will lose some of the volatile compounds due to evaporation. Oxidation can also be considerable for the more unstable or reactive compounds, so the maximum yield of airborne substances are obtained immediately after the collection. The cellulose filters comprise a substantial amount of the extracted organic material, and it has therefore been tried to expose filters rinsed in dichloromethane simultaneously with unrinsed filters. The rinsed filter shrivel and shrink but the same amount of TSP is collected and the organic fractions allowing for filter contributions are approximately the same.

In the impactor samplings the collection of particles larger than about 20 µm is not satisfactory due to the flow characteristics around the impactor coat, which could explain that the occurrence of larger airborne tire particles is lower than anticipated. The density of tire rubber lies around 1.18 kg pr. l and bitumen range from 1.1 to 1.2 kg pr. l, while silica rich particles have densities over 2.4 kg pr. l. The generally lower density of the rubber and bitumen particles causes the aerodynamic diameters found by e.g. impactors to be relatively smaller.

The organic mass is not measured for the impactor samples since the organic part of TSP is the same order of magnitude as the uncertainties connected to gravimetric determinations (~ 0.05 mg). Organic matter calculated on basis of the chromatograms in HP-GPC, see paper 2 is not performed due to the missing fluorescence detection of aliphatic compounds.
Previous investigations show that airborne particles generated from the wear of tires are black oblong or sausage shaped with aerodynamic diameters predominantly larger than 7 µm and a smaller amount about 1 µm (Cardina, 1974). Dannis (1974) has found aerodynamic diameters between 5 and 100 µm with a mean value of 25 µm, it is important to mention that particles smaller than 2 µm were not collected. Pierson et al. (1974) found tire particles larger than 7 µm and smaller than 1.1 µm, the latter group is however determined with considerable uncertainty due to low recovery. According to Cadle et al. (1978) about 80% of the tire debris is larger than 11 µm and the rest is below 0.43 µm.

The findings from this work support the presence of submicron tire particles. Even bitumen particles have a large fraction smaller than 1 µm and this enables uptake in human and animal respiratory systems which can cause health problems when exposing the system to e.g. PAH’s.

As concluded by Cadle et al. (1978) part of the tire wear derives from local hot spots on the tire surface, with temperatures greater than 180 °C, where polymer degradation and volatilisation of extender oils produce particulate material. This thermoparticulation could account for the submicron particles. By mechanical abrasion particles larger than 10 µm are generated and give rise to the predominant part of the tire wear.

About 20% of the total zinc found in aerosol samples in inner city air originates from tire particles. For the soil samples in figure 5 the tire zinc comprises approximately 1% of the total zinc. The distribution of total zinc in the soil follows the same pattern at different distances from the road as the distribution of organic zinc. Close to the highway the concentrations are 435 and 249 µg total Zn pr. g soil on the west and east side respectively and at a distance of 10 m the concentrations have dropped to about 80 and 90 µg Zn pr. g soil. This considerable drop in total zinc with increasing distances is mainly caused by tire debris but also other zinc containing coarse particles related to traffic activities, such as engine oils adsorbed onto soil particles, may contribute. “Clean” soil in Denmark contains about 50 µg Zn pr. g soil.

There is a possibility for transportation of organic zinc from deeper soil layers to the top soil by plant root uptake and wilting. But the soil results shown in figures 3, 4 and 5 indicate that the traffic is the dominating zinc source and that the organic zinc concentration in deeper layers are only about 20% of the top layers so there is a good indication that the organic zinc is originating from airborne pollution and not from the soil.

Since the extractable organic zinc is chelated to organic accelerator molecules in the tire rubber matrix it is questionable whether these complexes as aerosols will remain intact or if they will be oxidised by solar radiation and gasses such as oxygen and ozone. If this conversion takes place the found results are an underestimation of the actual airborne tire particle concentration.
CONCLUSION

The concentrations of tire and bitumen particles in aerosol and soil samples have been determined.

5.0 - 5.8 wt-% (about 2.8 µg tire pr. m$^3$) of the total suspended particulate matter collected in Copenhagen air is tire debris, where the higher value was found in dry weather. About 95 % of the airborne tire particles have diameters smaller than 1.0 µm and the remaining part is larger than 10 µm. Measurements at a rural site give concentrations of about 1.4 µg tire pr. m$^3$ (2.4 wt-% of the TSP).

The bitumen aerosol concentration in Copenhagen is about 5 wt-% of TSP (3 µg bitumen pr. m$^3$). The mean aerodynamic bitumen particle size is around 1 µm. The presence of submicron particles enables long range transportation and human uptake both by tire and bitumen debris.

0.3 - 0.5 mg tire pr. g soil was found in the top 0.5 cm soil in the immediate vicinity of a highway. After 3 - 5 m the concentrations dropped to about 0.15 mg tire pr. g soil. The same concentration levels were found in road dust in Copenhagen (0.4 mg tire pr. g soil) and at a rural site in Risø (0.11 mg tire pr. g soil). The tire concentrations at Lyngby Parkkirkegård decrease with a factor of 3 when moving from the top 0.5 cm soil to a depth of 1.0 cm, and a factor of 30 at 3.0 cm.

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Figure 1 TSP, tire and bitumen concentrations in medium volume filters from Copenhagen. Allowing for blindfilter contributions.
Figure 2 TSP, bitumen and tire concentrations in impactor samples.

2a: Risø, 3 m's from road; 2b: Risø, 18 m's from road;
Figure 3 Bitumen and tire concentrations in top soil near Utterslev Mose. Where duplicate
determination is performed the coefficient of variation (COV) is calculated as

\[
\text{COV} = 100 \% \cdot \sqrt{\frac{\sum (\log(x_1) - \log(x_2))^2}{2 \cdot N}}, \text{ where } N \text{ is the number of sample sets.}
\]

Figure 4 Bitumen and tire concentrations in top soil near Køge.
Figure 5 Vertical tire and bitumen concentration profiles in soil.
Particulate Air Pollution with Emphasis on Traffic Generated Aerosols

Patrik Fauser

Abstract (max. 2000 characters)

Experimental methods for identifying particles generated from the wear of automobile tires and roadway asphalts have been developed. The methods have been employed on aerosols, collected with Berner low pressure cascade impactors, in Copenhagen and Risø and aerosols collected with medium volume samplers on two locations in Copenhagen. Furthermore the deposited particulate matter has been measured in soil near highways and at remote sites, and finally the ad- and absorbed particulate matter has been measured on plant leaves sampled in Copenhagen and at remote sites.

Tire and bitumen particles constitute each about 5 wt-% of the collected suspended particulate matter in inner city air. The particle size distribution shows that 92 % of the mass of airborne particulate tire debris have aerodynamic diameters smaller than 1 µm. The mean aerodynamic diameter is about 1 µm for the bitumen particles.

Soil concentrations in the vicinity of a highway indicate an approximate exponential decrease with increasing distance from the road. Constant values are reached after about 5 m for the tire particles and 10 m for the bitumen particles. This implies a presence of larger particles, typically larger than 20 µm, that deposit immediately and that are not collected by the aerosol samplers. Concentrations in soil that has not been touched for at least 30 years show a decrease in tire concentration by a factor of 30 when moving from the top soil to a depth of 3 cm. The bitumen concentration is approximately constant to a depth of 10 cm.

The leaf samples indicate a slightly higher tire particle concentration on the adaxial side compared to the abaxial side and an increased surface retention for pubescent leaves. About 0.5 µg tire pr. cm² leaf is found near a highway, and about 65 % of this concentration derives from adsorbed particles on both leaf sides. The remainder is either respired through stomata or incorporated in the epicuticular wax layer.

The fact that a substantial amount of the airborne tire and bitumen particles occur in the submicron range permits long range transportation and uptake and assimilation in the human respiratory system as well as absorption in plant tissue.

Descriptors INIS/EDB

Available on request from Information Service Department, Risø National Laboratory, (Afdelinger for Informationservice, Forskningscenter Risø), P.O.Box 49, DK-4000 Roskilde, Denmark.
Telephone +45 4677 4004, Telefax +45 4677 4013