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Nanoparticles - Chemical Facts and Artefacts: 1. Effect of Sampling Procedures on Chemical parameters of Soot Particles

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The chemical properties of soot particles are probably crucial in determining the adverse effects of soot particles to human health, the reactivity of soot particles in the atmosphere, and their influence on our climate.

In the health related issues, the soot particles are discussed as carrier of potentially mutagenic or phytotoxic material coming from the primary exhaust emissions but also being formed via secondary reactions of other exhaust constituents in the atmosphere. For instance, polycyclic aromatic hydrocarbons (PAH), their nitroderivatives, or other metabolites of primary aromatic and phenolic compounds are associated with soot particles in the atmosphere or are partitioned to cloud and fog droplets (Allan et al., 1997).

Soot particles absorb light and may therefore affect the earth's radiation balance directly. In addition, ageing of the initially hydrophobic soot particles in the oxidising atmosphere increases the amount of water soluble material on the particle surface and thereby increases its capability to act as cloud condensation nuclei (Weingartner, et al., 1997). Knowledge of soluble organic and inorganic ions associated with soot particles is therefore important in an assessment of the effect of soot particles on our climate.

The presence of reactive species on the soot surface determines the interaction of soot particles with gaseous atmospheric trace constituents. For instance, NO_2 can react with soot particles to form nitrous acid (HONO) (Ammann et al., 1998). HONO is rapidly photolysed by sunlight leading to OH radicals and NO. OH is one of the main ingredients driving ozone formation in polluted air. On the other hand, soot particles may absorb and eventually destroy radical species such as HO_2, RO_2, NO_3 from the gas phase. These examples show how soot particles in a complex way interact with atmospheric chemistry.

One of the main problems associated with soot particles is the chemical complexity involved. A large fraction of soot has not yet been identified (e.g., Rogge et al., 1998). Even among the identified fraction it is virtually impossible to adequately address the different topics mentioned above. Most analysis tools available are able to detect some specific compounds but the degree of specialisation is such that sampling and analysis procedures for different compound classes exclude each other. One way out of these problems is to use chemical indicators which are not specific but give a hint of

overall reactivity. As an example, the reaction of NO_2 with soot is used in the following to discuss the chemical properties of soot particles under various conditions. NO_2 is an ubiquitous oxidant of the atmosphere and is a secondary product of combustion like soot itself. NO_2 is involved in ozone formation and in the formation of nitroaromatic compounds. NO_2 is a radical exposing an unpaired electron; however, it is much less reactive than NO_3 or OH, but more reactive than O_2. In the context considered here, the rate of reaction of NO_2 with the surface of soot particles reflects the ability of the soot surface (including the outer surface as well as the inner surface of agglomerate particles) to interact with mild oxidants. If a type of soot does not interact with NO_2 to a measurable extent, it is likely that its constituents are relatively stable. The reactivity with NO_2 also indicates the speed with which secondary, potentially toxic products are formed from the primary soot particles. Compared on a mole basis, the sensitivity with which NO_2 can be detected is orders of magnitudes better than can nowadays be reached for the organic species under question, thus allowing rapid and efficient screening of soot samples.

The aim of the experimental work presented below was to exploit sampling procedures for soot particles which conserve their chemical properties which may be relevant for health, ozone formation, and climate related studies. Figure 1 shows a soot aerosol extraction scheme which was used to sample soot particles from the exhaust of a 4kW diesel engine for studying their reactivity with NO_2 as a function of sampling and engine conditions.

Part of the hot exhaust gas is fed to the dilution unit with a short metal line kept at 70°C, i.e. well above the water dew point (ca. 45°C). This excludes water condensation, but does not exclude nucleation or condensation of sulphuric acid or organic compounds. Nevertheless, the residence time before dilution (< 1s) keeps the influence of these effects as low as possible. The dilution unit allows a variable dilution ratio (10 to 2000) to be adjusted and operates at 70°C. A large fraction of the particles in the exhaust gas are charged, reflecting equilibrium charging conditions at the end of combustion. Because part of the particles may have nucleated after this point, the charge distribution may be non-homogeneous over chemically different particles, so that charge induced losses in the sampling lines after dilution may lead to an unrepresentative sample. Therefore, the neutraliser immediately after the dilution unit re-establishes a charge equilibrium, and the subsequent electrostatic precipitator removes all charged particles. This set-up, however, has the disadvantage, that the electrofilter has to be cleaned regularly to avoid new artefacts due to soot deposition. Because the exhaust gas itself contains reactive species in the gas-phase, which can react with sampled particles on the filter, water, volatile organic compounds (VOC) and NOx have to be separated from the aerosol in a series of diffusion denuders containing silica gel, activated carbon, and cobalt oxide, respectively. The separation time (about 2s at 1 l air per min) is limited by diffusion and constrained by the technical possibilities to design these denuders. This set-up effectively reduces the mixing ratio of these species below the ppb level, but conserves the physical properties of the aerosol as shown in Figure 2 giving an example

of size distributions of soot particles collected after the dilution unit and at the end of the denuder line, respectively, using a scanning mobility particle sizer.

Reactivity studies were performed by exposing soot particles collected on glass fibre filters at the end of the sampling system shown in Figure 1 to NO_2 and humidity. After sampling and storage at 4°C, a humidified gas stream containing NO_2 in synthetic air was passed through the filter, and the amount of nitrous acid (HONO) formed on the soot was measured downstream of the filter. HONO formation is always normalised to the total surface area of all collected soot particles using the mobility diameter to calculate a proxy for the surface area of the agglomerate particles. Figure 3 depicts, as an example, HONO formation as a function of the engine load, clearly showing an increase in reactivity for higher loads in parallel with a decreasing air fuel ratio. Further investigations will address the details of the reaction and its dependence of humidity and NO_2 concentration.

An important question raised with these samples is whether they really represent diesel soot particles emitted from the tailpipe of real diesel cars, trucks or stationary sources. In reality the process of dilution at the point of emission is very complex and also highly variable. Under most conditions, it will be faster than in our set-up, and the surface to volume ratio of the air parcel outside the tailpipe will be much lower than within our sampling lines. In the atmosphere, an equilibrium partitioning of various semivolatile species is established between the gas and the condensed phase, i.e., aerosol particles, droplets, and possibly ground surfaces. In a sampling scheme as ours, however, semivolatile species may be retained on the tube walls and, of course, in the activated carbon denuder, effectively stripping these species from the particles. For comparison, Figure 4 shows the large difference in reactivity between samples taken upstream and downstream of the denuder series (see Figure 1), respectively. On the one hand, this example shows that an important fraction of reactive species is semivolatile. On the other hand, it also shows how the choice of sampling conditions may greatly affect chemical parameters of soot particles even if the physical parameters such as size, number and mass indicate 'correct' sampling.

References

Ammann M; Kalberer M.; Jost D.T.; Tobler L.; Rössler E.; Piguet D.; Gäggeler H.W.; Baltensperger U. Heterogeneous production of nitrous acid on soot in polluted air masses. Nature 395:157-160; 1998.

Allan, J.O.; Dookeran, N.M.; Taghizadeh, K.; Lafleur, A.L.; Smith, K.A.; Sarofim, A.F. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environ. Sci. Technol. 31:2064-2070, 1997.

Weingartner, E.; Burtscher, H.; Baltensperger, U. Hygroscopic properties of carbon and diesel soot particles. Atmos. Environ. 31: 2311-2327; 1997.

Rogge, W.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol. 9. Pine, Oak, and synthetic log combustion in residential fireplaces. Environ. Sci. Technol. 32: 13-22; 1998.

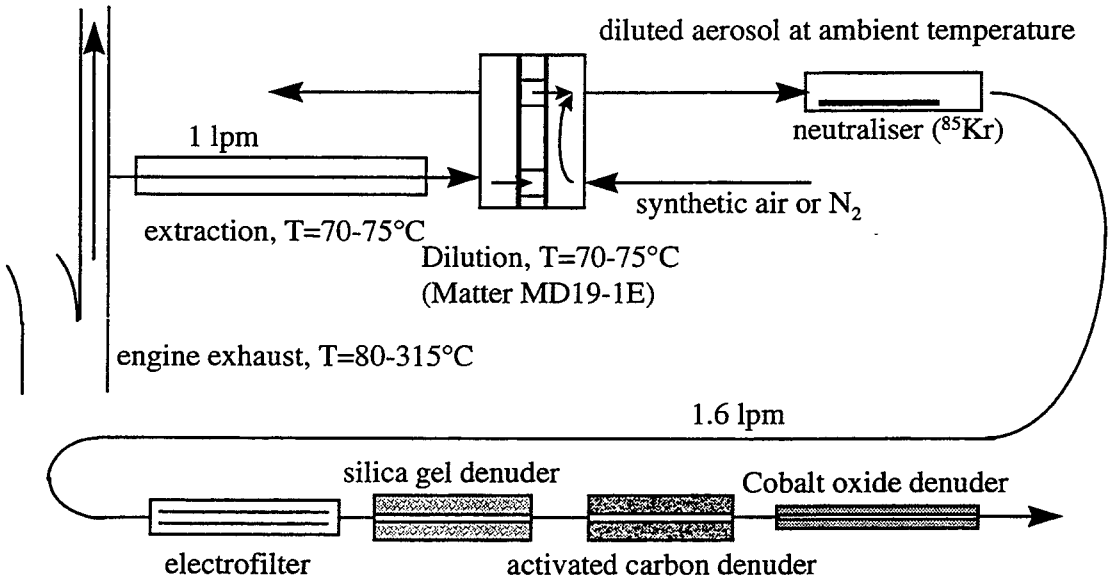

Figure 1. Extraction scheme to collect aerosol samples from the exhaust of a diesel engine.

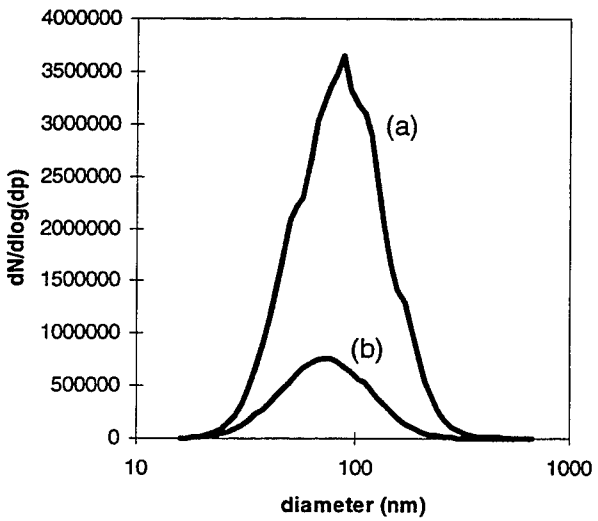

Figure 2. Size distribution of soot aerosol immediately after dilution (a) and after the denuder series (b), respectively, obtained by a differential mobility analyser coupled to a condensation particle counter. The main part of the loss is due to the removal of all charged particles in the electrostatic precipitator ('electrofilter', see Figure 1).

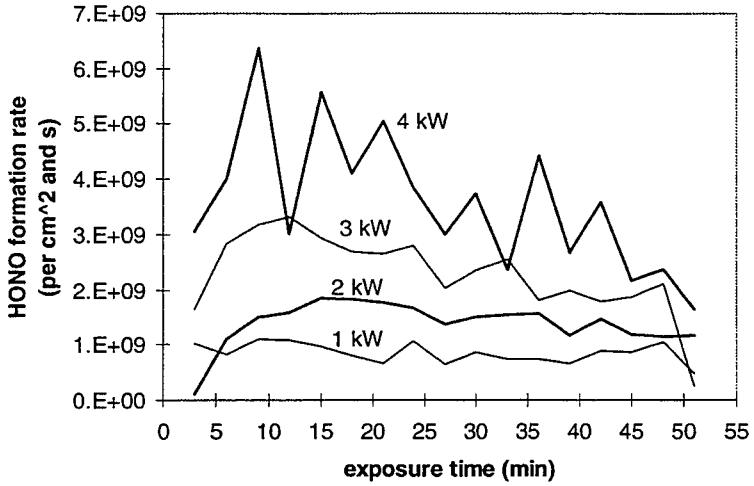

Figure 3. Rate of reaction of NO_2 to HONO per unit particle surface area for soot samples collected using the scheme shown in Figure 1. The four curves show the variation of the reactivity of the soot particles with the load of the diesel engine. The NO_2 concentration was 6ppb and the relative humidity 30%.

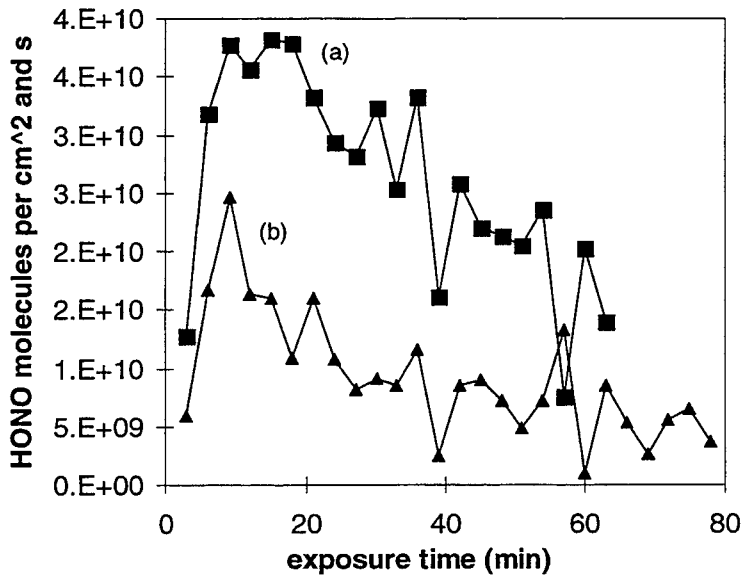

Figure 4. Rate of the reaction of NO_2 to HONO per unit particle surface area for soot samples collected upstream (a) and downstream (b) of the denuder series, respectively. The NO_2 concentration was 85ppb and the relative humidity 30%.