Optical properties of atmospheric fog and cloud droplets
collected in the Po Valley, Italy

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The optical properties of fog samples, collected in the Po Valley at three different days during the winter 1998-1999, are reported. In the infrared region the specular reflectance was measured and the complex index of refraction was derived by the Kramers-Kronig transformation. In the UV/Visible region the transmission was measured and the absorption index was derived. Significant daily variations in the optical properties of the fog samples are observed in the UV/Visible spectral region.

This paper is dedicated to Professor Thorvald Pedersen who has just retired from his position at the Institute of Chemistry, University of Copenhagen. Through the years we have benefited from his genuine interest and knowledge in molecular spectroscopy and atmospheric chemistry.

1 Introduction

Atmospheric aerosols interact with both solar and terrestrial radiation; the scattering and absorption of incoming solar radiation is known as the direct aerosol effect. In addition, aerosols have an indirect effect on climate through their influence on clouds. The actual impact of aerosols on climate is associated with a large uncertainty. First, observations and characterisations of aerosols on a global scale are scarce. Second, the optical properties of aerosols are not well characterised. The radiative properties of aerosols are usually modelled by Mie theory in which the complex index of refraction, \( N(\lambda) = n(\lambda) + ik(\lambda) \), enters as a necessary parameter; \( n(\lambda) \) is the refractive index and \( k(\lambda) \) is the absorption index. The situation is often complicated as real aerosols occur as both internal and external mixtures, and the optical properties of mixtures can deviate much from those derived from a model assuming a linear relationship with the concentrations of the components present. There is also a large uncertainty in the cloud-radiative interaction, described by the Mie theory, and important parameters are droplet size, phase, and extend of cloud cover.1-3

The indirect effect of aerosols on the climate is due to their function as cloud condensation nuclei (CCN) whereby they affect the cloud microphysics and the albedo. Aircraft measurements show that in polluted regions a sixfold increase in CCN leads to a three to five fold increase in the droplet concentration in clouds.3 The increase in droplet concentration results in 10-25 % smaller droplets and a correspondingly larger total surface area: the net effect is an increase in the albedo.3,4 Another consequence of smaller cloud droplets is longer atmospheric residence time and hence suppressed precipitation.2,3,5

In this work we report the first experimental results of optical properties of samples of fog and cloud droplets. These samples are collected in the Po Valley, Italy and the compositions of the samples are highly influenced by the anthropogenic emissions in this region through absorption of trace gases, scavenging of aerosols and the CCN themselves.6,7 The content of organic components in fog water exhibits a clear similarity with that observed for the water-soluble fraction of the fine aerosol collected in polluted areas.9

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2 Experimental section

Samples. We have investigated fog samples collected at the field station of S. Pietro Capofiume in the Po Valley.\textsuperscript{6,9} The station is located in an area characterised by intensive industrial trading and agricultural activities. High levels of pollution are reported and the pollution appears to be relatively homogeneously distributed throughout the Po Valley during the fall and winter.\textsuperscript{7} The samples were collected at different days during the winter 1998-99; the sampling procedure and the fog and droplet characterisation is described elsewhere.\textsuperscript{6,8,9} The chemical analysis of the investigated samples is summarised in Table 1. In this analysis the concentration of elemental carbon, EC, defined as the difference between total carbon and total organic carbon, TOC, is not specified. Reported values of EC in aerosols for this geographical region is 0.5–1 µg m\(^{-1}\) or ~5–10 % of the total carbon content.\textsuperscript{8}

<table>
<thead>
<tr>
<th>Table 1. Chemical analysis of fog water samples collected in the Po Valley. Concentrations given in ppm.</th>
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<tbody>
<tr>
<td>LWC(^b), g m(^3)</td>
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<tr>
<td>pH</td>
</tr>
<tr>
<td>Conductivity</td>
</tr>
<tr>
<td>Na(^+)</td>
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<tr>
<td>NH(_4)(^+)</td>
</tr>
<tr>
<td>K(^+)</td>
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<tr>
<td>Mg(^2+)</td>
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<tr>
<td>Ca(^2+)</td>
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<td>Cl(^-)</td>
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<td>NO(_2)</td>
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<tr>
<td>NO(_3)</td>
</tr>
<tr>
<td>SO(_4)(^2-)</td>
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<tr>
<td>TOC(^b)</td>
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\(^a\)LWC, Liquid water content. \(^b\)TOC, total organic carbon.

Refractive and absorption index in the infrared region. The experimental method applied in the infrared region has previously been described in detail.\textsuperscript{10,11} Specular reflectance spectra at near normal incident were obtained with a Perkin-Elmer System 2000 FTIR spectrometer equipped with a room temperature DTGS detector and averaging 64 scans at a nominal resolution of 4 cm\(^{-1}\). A simple modification of the optical beam path allows the surface of the sample support to be oriented horizontally, which makes liquid surface studies feasible.

The experimental specular reflectance spectra, \(R(\lambda)\), were obtained as a ratio of two single-beam spectra \(I(\lambda)\) and \(I_0(\lambda)\), where \(I(\lambda)\) is the intensity of the radiant flux reflected from the sample surface, and \(I_0(\lambda)\), is the intensity of the radiant flux reflected from blank aluminised or gold plated mirrors which exhibits constant reflectivity close to unity over the IR region under investigation. The complex index of refraction was derived by the use of the Kramers-Kronig analysis of the specular reflectance spectra, \(R(\lambda)\). The algorithm assumes that the spectral cut-off must fall in a moderately flat unstructured region. In the low wave number region this requirement is not strictly fulfilled, and this can lead to large errors in the derived refractive and absorption index.\textsuperscript{10} To obtain reliable results we have calculated the specular reflectance spectra of water from the refractive and absorption index given by Bertie and Lan.\textsuperscript{12} We have then extended our observed \(R(\lambda)\) spectra (6500–400 cm\(^{-1}\)) by the synthetic water reflectance spectrum in the 400 – 1 cm\(^{-1}\) region before applying the Kramers-Kronig transformation.

Absorption index in the ultra violet/visible region. The spectra in the UV/VIS region were measured using an Agilent 8454E photodiode array spectrophotometer. The spectra were recorded in the wavelength
range from 220 nm to 1100 with a resolution of 1 nm. The integration time was set to 0.5 s. To obtain the imaginary refractive index – the absorption index, $k(\lambda)$ – a different method was applied in this wavelength region. The expression of $k(\lambda)$, derived from the Beer-Lambert law, is given by:

$$k(\lambda) = \ln(10) \frac{A(\lambda) \cdot \lambda}{4\pi d}$$  

(1)

where $\lambda$ is the wavelength, $d$ is the path length through the sample, and $A(\lambda)$ is the dimensionless absorbance, expressed as $-\log(I/I_0)$, that is the ratio of the monochromatic radiant power transmitted through the sample to that incident on the sample. The true absorbance cannot be measured directly because the solution to be studied is enclosed by two cell windows. Reflection and scattering losses can, and will, occur at the cell walls at the various interfaces of the cell. To compensate for these losses it is common in UV/Visible spectroscopy to use a cell containing only the solute and use this spectrum as $I_0(\lambda)$. In the present case this is not an appropriate method as the solvent (water) is an integrated part of the sample. Instead we employed another method using four cells with different path lengths. We may then use the following relation, assuming that the scattering losses in the solution can be neglected

$$S_i(\lambda) = R_f(\lambda) + A(\lambda) \cdot d_i$$  

(2)

where $R_f(\lambda)$ is the reflection loss, $S_i(\lambda)$ is the experimental spectrum and $d_i$ is the corresponding path length of the cell; in the present case 1.0, 5.0, and 10.0 mm. The absorbance spectrum corrected for the reflectance losses, $A(\lambda)$, was then obtained by a least square calculation, and this spectrum was used in equation (1) to derive the absorption index, $k(\lambda)$. We note that the reflection loss was very small for all the samples studied.

3 Results and discussion

Optical properties in the infrared region. Table 1 shows that the most concentrated sample with respect to inorganic ions and total organic carbon (TOC) is the one collected on 31 December 1998. The infrared region refractive and absorption index of the fog sample collected at this day are presented in Figure 1.
The figure also shows that the differences between our data and those of Bertie and Lan$^{12}$ for pure water are very small – that is the refractive and absorption index is entirely dominated by the properties of water. The presence of the organic and the inorganic compounds at the concentrations present in the fog samples, Table 1, do not influence the refractive and absorption index significantly in this wavelength region. There is, though, minute differences in the OH stretching and in the sulphate absorption regions,$^{10}$ but these differences are negligible for all practical purposes. The results for the other samples are similar.

Absorption Index in the UV-visible region. Figure 2 shows the absorption index in the UV-Visible region. Results for all three samples are shown, with water included for comparison. The figure illustrates the absorption index in the UV/VIS region to be small, but distinctly different from that of water at shorter wavelengths; already at 400 nm the absorption index is approximately 100 times that of water. The observed spectral characteristics compare with reference data in Percampus$^{13}$ and seem to be consistent with the presence of the classes of organic compounds: neutral species, mono- and dicarboxylic acids and polycarboxylic acids, suggested by Fuzzi et al.$^9$ The contribution from sulphate and nitrate species is not important at these low concentrations.

![Absorption Index of fog samples](image)

*Figure 2. Absorption Index of fog samples collected in the Po Valley 31 December 1998, 5 January and 27 February, 1999. Data for pure water is included for comparison.*

The multiphase cloud chemistry is essential in the partitioning of atmospheric trace compounds between the gas, aerosol and cloud droplet phases. Chemical constituents in the liquid phase of clouds derive from the incorporation of the soluble species contained in the aerosol particles on which cloud droplets nucleate or from aerosols scavenged by the droplets themselves. In addition, there is also dissolution of trace gases in the droplets. Facchini et al.$^{14}$ have presented results showing that aerosol-derived water-soluble organic compounds (WSOC) are also present in substantial amounts in cloud and fog samples. Blando and Turpin$^{15}$ suggest that there is a potential for secondary aerosols production in clouds. The proposed mechanism is that soluble or partly oxidised gases can be absorbed into water droplets and undergo chemical reactions and result in addition of organic material to the particle phase when the droplet evaporates. Recently Fuzzi et al.$^9$ have carried out detailed analyses of samples collected in the Po Valley in the period 1998-1999 (the same time period and the same field stations from which the present samples originated). They present results showing that the inorganic ions account for an average of 76 % of total fog water solute, the concentration of WSOC, ~25 %, in the samples is by no means negligible. They also found that acidic compounds are the dominant WSOC in fog water, accounting for an average of 60 % of soluble organic carbon mass. Their conclusion is that the organic chemical composition of fog...
water exhibits substantial similarities with that observed for the water-soluble fraction of the fine aerosol collected at the same field station. Their results are consistent with the mechanism proposed by Blando and Turpin.\textsuperscript{15}

According to Blando and Turpin\textsuperscript{15} there are many possible precursors to secondary formation of aerosols through cloud droplets. Among these are monocarboxylic acids and methanol and they suggested that the dicarboxylic acids are a particle-phase product. Oxalic acid and acetic acid are commonly detected in aerosol and fog water samples - also in the Po Valley.\textsuperscript{9,16-18} Figure 3 compares the absorbance spectra of these carboxylic acids and methanol to that of the sample collected at 31 December 1998 in the Po Valley. The Figure also includes the spectrum of benzoic acid representing the water-soluble aromatic compounds. It should be noted that most phenolic compounds have very similar UV spectra to that shown. Oxalic acid is only observed in small amounts in the samples collected in the Po Valley but acetic acid is observed at higher concentrations.\textsuperscript{9} The results presented in Figure 3 are in accordance with the presence of oxalic acid at lower concentrations than acetic acid. However, the spectral characteristics of acetic acid can not explain the main spectral variations observed. Methanol is a very weak absorber in the UV/Visible region compared with the other components investigated and does not contribute significantly to the spectrum. In conclusion, the UV/VIS spectra of the fog and cloud droplets can not be explained by the explicitly identified classes of compounds.\textsuperscript{9}

![Figure 3: Absorbance of two common organic species present in cloud droplets: oxalic acid, acetic acid and the sample collected on 31 December 1998. Methanol is also included as a possible fog droplet component.](image)

There is a large uncertainty in the cloud-radiative interaction and some of this may be linked to the absorption index.\textsuperscript{13} We have carried out simplified calculations of the single scattering albedo using the experimentally obtained absorption indexes. The results indicate that the observed difference between the absorption index of water and the fog samples from the Po Valley has negligible effect in the reduction of the single scattering albedo of clouds and fog droplets. This indicates that the single scattering albedo of fog and clouds, even in polluted regions like here, can be treated as pure water in radiation calculations.
4 Summary

In this work we have investigated the optical properties of fog samples collected in the Po Valley. We present data for the real and imaginary refractive index in the infrared region, 6500-400 cm\(^{-1}\), 1.49-25 \(\mu\)m. In the region from 230-1100 nm we only present data for the absorption index.\(^5\) The optical parameters in the IR are nearly identical with those of water, whereas in the UV-Visible the absorption index is about hundred times higher than for pure water, and daily variations in the samples investigated can be as much as 80 % at short wavelengths. Nevertheless, calculations of the single scattering albedo indicate that the anthropogenic influenced clouds and fog can be treated as pure water in radiative calculations.

To the best of the authors' knowledge this is the first time the absorption index has been measured of authentic field samples. The results of the work conform to the observations and analysis of Fuzzi et al.\(^9\) Further, the results are consistent with the Blando and Turpin mechanism,\(^15\) in which soluble or partly oxidised gases may be absorbed into water droplets, undergo chemical reaction, and result in additional organic material in the particle phase when the droplets evaporate.

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References

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*All spectroscopic data sets are available from the authors upon request.