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CHARACTERIZATION OF PARTICULATE AMINES*

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ABSTRACT

As determined by proton activation analysis, water washing removes between 75 and 98% of the total nitrogen associated with ambient particulate matter (Berkeley, winter, 1977-78). ESCA measurements show that the nitrogen remaining on the filter after water washing is entirely reduced nitrogen, which is thought to consist of amine, amide, and nitrile species.\( \text{NH}_4^+ \) and \( \text{NO}_3^- \) are completely removed by water washing, as is most of the \( N_x \). ESCA measurements for the evaporated extracts show evidence for the conversion of some \( N_x \) to \( \text{NH}_4^+ \) during water washing, and we suggest that this may be due to the hydrolysis of amides. We conclude that extraction of particulate material with water may chemically change the nitrogen species so that the chemical composition of the extract is not representative of the original sample.

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INTRODUCTION

In addition to nitrate and ammonium species, a large fraction of the nitrogen associated with ambient particulate matter occurs in two or more chemically reduced forms. These reduced species, \( N_x \), have been tentatively identified as amine, amide, and possibly nitrile species by means of x-ray photoelectron spectroscopy (ESCA or XPS). For simplicity and in the absence of a more rigorous term, we shall refer to these reduced species as particulate amines or \( N_x \). \( N_x \) species occur in combustion-generated and ambient particulates, and species with similar ESCA spectra and thermal behavior in vacuum can be produced by reaction of soot or graphite with \( \text{NH}_3 \).

Studies of reduced particulate nitrogen species by other workers have emphasized determination of \( \text{NH}_4^+ \) and identification of basic organic compounds. Basic organic compounds are typically aza-arenes, many of which are carcinogenic. Recently, high resolution mass spectroscopic studies have found evidence for amides associated with ambient particulate samples.

The purpose of this paper is further chemical characterization of particulate amines, which we approach here by combining ESCA measurements with determination of total nitrogen by proton activation. The solubility of ambient particulate nitrogen in water and organic solvents has been explored in this way, and our most important result is that only a small part (\( \sim 15\% \)) of \( N_x \) is not removed by water. \( N_x \) species with this behavior could be water-soluble stoichiometric compounds such as amines, and surface species such as amides and nitriles which can undergo hydrolysis. Since hydrolysis would convert amide nitrogen to soluble ammonium ion, such behavior could explain the observed discrepancies between ammonium concentrations as determined by ESCA and wet methods. We will present other evidence of a significant perturbation of the species present on the filter by solvent washing. This adds a note of
caution to interpretation of results of wet chemical determinations of species associated with ambient particulates.

CHEMICAL CHARACTERIZATION OF PARTICULATE NITROGEN BY ESCA AND PROTON ACTIVATION ANALYSIS

ESCA has proved to be a very useful tool in identifying the variety of nitrogen species associated with ambient particulates, and its use has been extensively reviewed.\textsuperscript{10-12} The following observations about ambient particulate nitrogen are based on ESCA measurements on silver filter samples from several locations (Los Angeles, St. Louis, and Berkeley); the experimental evidence has been presented earlier\textsuperscript{4,10-12} and will not be repeated here.

1. Besides the expected salts — ammonium sulfate (\((\text{NH}_4\text{)}_2\text{SO}_4\)) and ammonium nitrate (\(\text{NH}_4\text{NO}_3\)) — which are relatively stable in vacuum, a more volatile ammonium species, probably ammonium chloride (\(\text{NH}_4\text{Cl}\)) or adsorbed \(\text{NH}_3\), is often associated with ambient particulate matter.

2. Particulate amines (\(\text{N}_x\)) typically account for up to half of the total nitrogen as determined by ESCA.

3. ESCA determinations of total reduced nitrogen (\(\text{NH}_4^+ + \text{N}_x\)) agree with determination of \(\text{NH}_4^+\) by wet methods.\textsuperscript{4} Since \(\text{N}_x\) is often more abundant than \(\text{NH}_4^+\) in ambient samples, there is a serious discrepancy which is consistent with the conversion of \(\text{N}_x\) to \(\text{NH}_4^+\) during the analytical procedure\textsuperscript{13} to determine \(\text{NH}_4^+\).

4. Nitrate nitrogen is typically much less abundant than ammonium nitrogen. Nitrate species are more volatile in vacuum than \(\text{NH}_4\text{NO}_3\), indicating that adsorbed nitric acid may be present. Wet methods tend to find much more (3-5x) nitrate than ESCA.\textsuperscript{4} Besides the volatility of \(\text{HNO}_3\), artifact nitrate on glass fiber filters\textsuperscript{14} can account for some of this difference.

5. Based on studies of winter aerosol samples from Berkeley, California,\textsuperscript{15} ESCA inventories nitrogen as 25% nitrate, 25% ammonium, and 50% \(\text{N}_x\), as indicated
in Table 1. Indirect evidence obtained in another laboratory\textsuperscript{16} supports the existence of $N_x$ by showing that nitrate and ammonium cannot account for all nitrogen associated with ambient particulates. The average nitrogen deficiency is 25%.\textsuperscript{16}

Both ESCA and traditional analytical methods have helped characterize particulate nitrogen, but their results for $\text{NH}_4^+$, $N_x$, and $\text{NO}_3^-$ do not agree. Whereas ESCA samples are subject to volatility losses in high vacuum, especially for $\text{NO}_3^-$, wet methods may modify the chemical composition of the samples by reactions such as hydrolysis, so that the technique affects the results obtained by using it. In order to reconcile the existing information and to further characterize particulate amines, we have used a new nondestructive nitrogen determination\textsuperscript{9} (discussed below) in conjunction with ESCA for ambient particulate samples, before and after solvent washing. ESCA has also been used for the evaporated solvent extracts. Thus further information has become available which may answer the following questions:

1. How much nitrogen is removed by solvent washing? (PAA)

2. Which nitrogen species are removed? (ESCA)

3. What are the relative concentrations of nitrogen species in the evaporated solvent extracts? (ESCA)

4. How does nitrogen speciation on the particulate sample before solvent treatment compare with that of the evaporated extract? (ESCA)

The answer to the last question may help resolve the technique-dependent difference in results which we mentioned earlier. Before presenting these results, we shall introduce the nitrogen determination technique.

Proton activation analysis (PAA) relies on inducing the nuclear reaction $^{14}\text{N}(p,\alpha)^{11}\text{C}$ with energetic protons generated in the LBL 88-inch cyclotron. The radioactive decay of $^{11}\text{C}$ with 20.4-minute half life is followed by its 0.511-MeV
positron annihilation radiation. We can relate the count rate at the end of bombardment for the $^{11}$C component of the aerosol sample and the nitrogen standards to their total nitrogen loading. Further details about proton activation analysis (PAA) appear elsewhere. We have used proton activation to determine total nitrogen in samples collected during a severe haze episode in Berkeley in November, 1976. Table 1 presents data obtained by PAA and by combustion for parallel samples on Ag and quartz fiber filters respectively. In general the agreement is very good: the average deviation of PAA compared with the combustion results is approximately 10%. Because PAA is nondestructive, further measurements can be performed on the same filter, as we have done here with ESCA. PAA provides a quantitative foundation for the speciation determined from ESCA, so that the techniques are complementary.

SOLUBILITY BEHAVIOR OF PARTICULATE NITROGEN

A series of ambient particulate samples collected on silver filters during autumn and winter in Berkeley, California, have been washed with water and organic solvents, with PAA and ESCA analyses performed after each step. Static extraction with distilled deionized water at room temperature for two hours removed a large fraction of the original nitrogen, as shown in Table 2. Further sequential Soxhlet extraction with benzene followed by methanol and chloroform (1:2 v:v) removed only a small fraction of the remainder. Nitrogen remaining on the filter accounts for between 2 and 25% of the initial nitrogen. Water-washing of all the winter 1977-78 samples (Table 2) changes the nitrogen-to-carbon ratio from 0.32 ± 0.26 to 0.040 ± 0.020. For comparison we find that untreated vehicle exhaust collected in a highway tunnel has nitrogen-to-carbon ratio lower than untreated ambient particulates (0.046 ± 0.010). The ESCA results in Figure 1 show the effect of water washing on one of the samples (Dec. 1977). The other samples exhibit similar behavior except that they
Figure 1. ESCA spectra in the nitrogen region for ambient particulate material collected in December, 1977, in Berkeley, California. Binding energy for nitrogen species: NO$_3^-$, 407 eV; NH$_4^+$, 402 eV; Nx, 400 eV. Top: Untreated particulate material. Middle: H$_2$O-washed ambient particulate on Ag. Bottom: Dried H$_2$O extract.
contain less nitrate. The nitrate peak occurs at binding energy close to 407 eV, \( \text{NH}_4^+ \) close to 402 eV, and \( N_x \) close to 400 eV. The reduced nitrogen peaks have been resolved into contributions from \( \text{NH}_4^+ \) and \( N_x \) by comparison with standards. The untreated particulate material contains roughly equivalent amounts of ammonium, particulate amine, and nitrate species, with total nitrogen equal to 5.0 \( \mu g \) m\(^{-3}\). After water washing, the remaining nitrogen is \( N_x \). It can be seen from Table 2 that 4.8 \( \mu g \) m\(^{-3}\) of the initial nitrogen has been removed by water extraction.

The chemical speciation of the evaporated extract may be expected to reflect the initial speciation; however, as seen from Figure 1, the extract contains much less \( N_x \) than \( \text{NH}_4^+ \) and shows a higher \( \text{NO}_3^- \)-to-\( \text{NH}_4^+ \) ratio. These findings suggest two interpretations. First, assuming that all nitrogen removed in water washing appears in the dried extract, \( N_x \) present in the untreated extract has been converted to \( \text{NH}_4^+ \) during the extraction procedure or during evaporation. Hydrolysis of amides would convert \( N_x \) to \( \text{NH}_4^+ \), and we shall discuss this further. The second observation, that more nitrate appears in the extract than in the untreated sample, implies that nitrate present in the untreated sample is quite volatile, and that a substantial fraction of the original nitrate is lost in the ESCA spectrometer. From the dependence of the nitrate peak intensity on X-ray and vacuum exposure time (Figure 2), we can estimate the original \( \text{NO}_3^- \) intensity. It is important to note that the nitrate associated with the ambient sample is more volatile in vacuum than expected for a salt such as \( \text{NH}_4\text{NO}_3 \). The water extraction has changed the chemical composition of the sample, so that conclusions based on methods employing extraction may not accurately characterize the original particulate material.

\( N_x \) species can be hydrolyzed during \( H_2O \) extraction and thus converted to \( \text{NH}_4^+ \). The expected reaction, illustrated for particulate amides, is
Figure 2. Dependence of the nitrate peak intensity on high vacuum and X-ray exposure time during ESCA. Top curve: Dried extract. Lower curve: Untreated ambient particulate sample (December, 1977; Berkeley, California).
\[
\text{R-C-NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{R-C-OH} + \text{NH}_4^+.
\]

ESCA distinguishes amide (N\textsubscript{x}) from NH\textsubscript{4}\textsuperscript{+}; and, indeed, the ratio of N\textsubscript{x} to NH\textsubscript{4}\textsuperscript{+} is smaller in the extract than in the ambient sample, as mentioned previously. Amine salts would appear in the extract as N\textsubscript{x}. In Table 3 we present nitrogen speciation for the Berkeley sample from December, 1977, whose ESCA spectra were shown in Figure 1. Total nitrogen loadings derive from PAA and speciation from ESCA, with volatility corrections for NO\textsubscript{3}\textsuperscript{-} in the untreated sample based on vacuum behavior of nitrate in ESCA. We have assumed that all nitrogen removed from the sample during water extraction is retained in the evaporated extract so that the concentrations of dissolved species can be expressed in \(\mu\text{g m}^{-3}\). The fact that NO\textsubscript{3}\textsuperscript{-} concentrations for the untreated sample and the extract agree within 0.1 \(\mu\text{g m}^{-3}\) provides a self-consistency check. We note that more NH\textsubscript{4}\textsuperscript{+} appears in the extract than was present on the untreated sample; less N\textsubscript{x} appears in the extract than was present on the untreated sample. The N\textsubscript{x} deficiency in the extract (1.0 \(\mu\text{g m}^{-3}\)) matches the surplus in NH\textsubscript{4}\textsuperscript{+} (0.9 \(\mu\text{g m}^{-3}\)). These results provide evidence which is consistent with amide hydrolysis.

Removal of N\textsubscript{x} by dissolution in water without hydrolysis can occur when N\textsubscript{x} species are soluble stoichiometric compounds such as amines. Our results indicate that about half the original N\textsubscript{x} is removed by hydrolysis and the other half by dissolution, as expected for a mixture of amine, amide, and nitrile functional groups. Some of the species may be present as stoichiometric compounds and others possibly occur as surface species.

CONCLUSIONS

Our principal results can be summarized as follows:

1. A large fraction of N\textsubscript{x} (85%) originally present in ambient particulate matter can be removed by water extraction (whereas NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} are completely removed).
2. Compared with the untreated sample, $\text{NH}_4^+$ concentration in the extract increases by approximately the same amount as the $N_x$ concentration decreases. We attribute this behavior to the hydrolysis of amide groups.

Extraction of particulate material with water may chemically change the nitrogen species so that the chemical composition of the extract is not representative of the original sample. Therefore, analytical methods based on extraction may give erroneous results. The conversion of particulate amides to $\text{NH}_4^+$ during extraction may yield $\text{NH}_4^+$ concentrations which are too high.
REFERENCES


Table 1. Nitrogen inventory (μg/m³) for Berkeley particulates, November 5-6, 1976.

<table>
<thead>
<tr>
<th>Collection date</th>
<th>4-5 Nov 76</th>
<th>5 Nov 76A</th>
<th>5 Nov 76B</th>
<th>5-6 Nov 76</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection time</td>
<td>18:39(11-4)-</td>
<td>9:54-</td>
<td>11:48-</td>
<td>18:05(11-5)-</td>
</tr>
<tr>
<td></td>
<td>9:45(11-5)</td>
<td>11:40</td>
<td>18:00</td>
<td>22:00(11-6)</td>
</tr>
<tr>
<td>Nitrogen b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total N, PAA (LBL)</td>
<td>7.53</td>
<td>15.60</td>
<td>10.29</td>
<td>3.06</td>
</tr>
<tr>
<td>Total N, combustion (Battelle)</td>
<td>7.40</td>
<td>19.15</td>
<td>11.14</td>
<td>3.69</td>
</tr>
<tr>
<td>NH₄⁺ (as N)</td>
<td>1.9-2.3</td>
<td>～4</td>
<td>～3</td>
<td>～1.0</td>
</tr>
<tr>
<td>Nₓ (as N)</td>
<td>3.8</td>
<td>～8</td>
<td>～4</td>
<td>～1.2</td>
</tr>
<tr>
<td>NO₃⁻ (as N)</td>
<td>1.5-1.9</td>
<td>～4</td>
<td>～3</td>
<td>～1.0</td>
</tr>
<tr>
<td>NO₃⁻ (as N), wet chemistry (Battelle)</td>
<td>5.07</td>
<td>14.16</td>
<td>5.87</td>
<td>2.58</td>
</tr>
<tr>
<td>Carbon b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total C, combustion (LBL)</td>
<td>21.56</td>
<td>60.54</td>
<td>40.94</td>
<td>15.96</td>
</tr>
<tr>
<td>Total C, combustion (Battelle)</td>
<td>23.75</td>
<td>62.64</td>
<td>38.01</td>
<td>15.82</td>
</tr>
<tr>
<td>Mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSP = 3.1 × 10⁵ b scat</td>
<td>143c</td>
<td>313</td>
<td>229</td>
<td>81</td>
</tr>
</tbody>
</table>


bParallel quartz fiber and Ag membrane filters. LBL ESCA and proton activation analysis (PAA) used Ag filters. Analyses performed at Battelle by C.W. Spicer employed quartz filters.

cTSP units μg/m³ as in the remainder of the table.
Table 2. Solubility behavior of ambient particulate nitrogen. PAA results (μg/m^3).

<table>
<thead>
<tr>
<th>Air quality episode</th>
<th>Haze</th>
<th>Overcast</th>
<th>Moderate haze</th>
<th>Sunny</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>5 Nov 76</td>
<td>9-12 Dec</td>
<td>30 Jan-1 Feb</td>
<td>19-23 Jan</td>
</tr>
<tr>
<td>Duration, hr</td>
<td>6</td>
<td>72</td>
<td>48</td>
<td>96</td>
</tr>
<tr>
<td>Total weight loading(^a)</td>
<td>229(^b)</td>
<td>71</td>
<td>49</td>
<td>22</td>
</tr>
<tr>
<td>Total N</td>
<td>8.9(^c)</td>
<td>5.0</td>
<td>2.2</td>
<td>0.67</td>
</tr>
<tr>
<td>N after H(_2)O wash(^d,e)</td>
<td>4.6 (0.52)</td>
<td>0.23 (0.05)</td>
<td>0.08(^f) (0.04)</td>
<td>0.17 (0.25)</td>
</tr>
<tr>
<td>N after H(_2)O, Bz, MC wash(^g)</td>
<td>0.89 (0.10)</td>
<td>0.22 (0.04)</td>
<td>0.05 (0.02)</td>
<td>0.17 (0.25)</td>
</tr>
<tr>
<td>Total Ch</td>
<td>40.9</td>
<td>8.28</td>
<td>9.31</td>
<td>5.93</td>
</tr>
<tr>
<td>C after H(_2)O wash(^e,i)</td>
<td>na</td>
<td>4.26 (0.51)</td>
<td>3.97(^f) (0.43)</td>
<td>3.69 (0.62)</td>
</tr>
<tr>
<td>C after H(_2)O, Bz, MC wash</td>
<td>na</td>
<td>0.83 (0.10)</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

\(^a\)Net mass loading, except as noted.
\(^b\)TSP
\(^c\)Drop of 14% compared with earlier measurement (see Table 1) made about 6 months earlier.
\(^d\)Static extraction — 2 hours with deionized H\(_2\)O at 20°C except as indicated.
\(^e\)Numbers in parentheses give the fraction of initial total nitrogen.
\(^f\)Static extraction — 2 hours with deionized H\(_2\)O at 80°C.
\(^g\)Bz = benzene, MC = methanol + chloroform (1:2 v:v)
\(^h\)Total C by combustion (LBL). Prefired quartz hi-vol filters were used for collection.
\(^i\)Numbers in parentheses give the fraction of initial total carbon.
Table 3. Effect of water washing on December 1977 ambient particulate.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th>Ambient</th>
<th>H\textsubscript{2}O extract\textsuperscript{c}</th>
<th>Extract-ambient</th>
<th>H\textsubscript{2}O-washed ambient</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textsuperscript{NH\textsubscript{4}}\textsuperscript{+} as N</td>
<td>1.4</td>
<td>2.3</td>
<td>+0.9</td>
<td>0.0\textsuperscript{d}</td>
</tr>
<tr>
<td>fraction</td>
<td>0.28</td>
<td>0.47</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>\textsuperscript{N\textsubscript{x}} as N</td>
<td>1.7</td>
<td>0.7</td>
<td>-1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>fraction</td>
<td>0.34</td>
<td>0.14</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>\textsuperscript{NO\textsubscript{3}}\textsuperscript{-} as N</td>
<td>1.9\textsuperscript{e}</td>
<td>1.8</td>
<td>-0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>fraction</td>
<td>0.38</td>
<td>0.39</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Total nitrogen (\textmu g m\textsuperscript{-3})</td>
<td>5.0</td>
<td>4.8</td>
<td>-0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}9-12 December 1977 Berkeley particulate on Ag filters (Table 2). Total nitrogen in \textmu g m\textsuperscript{-3}.

\textsuperscript{b}Speciation is based on integrated areas under curves shown in Figure 1. Total nitrogen is from PAA except for H\textsubscript{2}O extract. H\textsubscript{2}O extract total nitrogen is the difference between ambient total N before and after H\textsubscript{2}O washing.

\textsuperscript{c}Values for N are based on the assumption that all N removed by H\textsubscript{2}O appears in the evaporated extract.

\textsuperscript{d}ESCA results in Figure 1 may show a small amount of \textsuperscript{NH\textsubscript{4}}\textsuperscript{+}.

\textsuperscript{e}The volatility correction is calculated from results presented in Figure 2.
FIGURE CAPTIONS

Figure 1. ESCA spectra in the nitrogen region for ambient particulate material collected in December, 1977, in Berkeley, California. Binding energy for nitrogen species: NO$_3^-$, 407 eV; NH$_4^+$, 402 eV; N$_x$, 400 eV. Top: Untreated particulate material. Middle: H$_2$O-washed ambient particulate on Ag. Bottom: Dried H$_2$O extract.

Figure 2. Dependence of the nitrate peak intensity on high vacuum and X-ray exposure time during ESCA. Top curve: Dried extract. Lower curve: Untreated ambient particulate sample (December, 1977; Berkeley, California).
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