Title
NON-AMMONIUM REDUCED NITROGEN SPECIES IN ATMOSPHERIC AEROSOL PARTICLES

Permalink
https://escholarship.org/uc/item/72h0t71q

Author
Dod, R.L.

Publication Date
1983-08-01
To be presented at the Second International Conference on Carbonaceous Particles in the Atmosphere, Linz, Austria, September 11-14, 1983

NON-AMMONIUM REDUCED NITROGEN SPECIES IN ATMOSPHERIC AEROSOL PARTICLES


August 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
NON-AMMONIUM REDUCED NITROGEN SPECIES IN ATMOSPHERIC AEROSOL PARTICLES


Applied Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

ABSTRACT

The traditional belief that ambient aerosol particles contain nitrogen predominantly in the form of inorganic ionic species such as \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) was challenged about 10 years ago by results from x-ray photoelectron spectroscopic analysis (ESCA) of California aerosol particles. A significant fraction (\( \sim 50\% \)) of the reduced nitrogen was observed to have an oxidation state more reduced than ammonium, characteristic of organic nitrogen species. We have used a recently developed thermal evolved gas analysis method (NO\(_x\)) in conjunction with ESCA to confirm the existence of these species in aerosol particles collected in both the United States and Europe. The agreement of EGA and ESCA analyses indicates that these species are found not only on the surface but also throughout the particles.

INTRODUCTION

Particulate nitrogenous air pollutants have traditionally been considered to be largely limited to inorganic compounds containing ammonium and nitrate ions. This view was challenged approximately 10 years ago by results from the then-new technique of x-ray photoelectron spectroscopy (or ESCA), which indicated that as much as half the ambient particulate nitrogen could exist in forms more reduced than ammonium (ref.1). This nitrogen was later postulated to consist of amines, amides, and heterocyclic compounds and was given the collective name N\(_x\) (ref.2). Further indication of the existence of N\(_x\) in ambient particles can be found in total nitrogen combustion analysis, which often reports a greater amount of nitrogen than that found by wet chemical analysis for \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) (ref.3). However, no direct method has been reported that can identify or quantitate the N\(_x\) constituents.

We have developed an NO\(_x\) thermal evolved gas analysis (EGA) system that differentiates among nitrogenous species based on volatility and thermal stability in an oxygen atmosphere (ref.4). EGA, in conjunction with ESCA and ion chromatography, has been applied to the analysis of ambient aerosol particulate samples.

*This work was supported by the Director, Office of Energy Research, Office of Health and Environmental Research, Physical and Technological Research Division of the U.S. Department of Energy under contract DE-AC03-76SF00098 and by the National Science Foundation under contract ATM 82-10343.
collected by filtration to confirm the existence of $N_x$ and to identify characteristics that provide information regarding final speciation.

**ANALYTICAL METHODS**

Analysis of atmospheric particles by ESCA has been described elsewhere (refs. 5,6). This method analyzes for elemental composition as well as the oxidation states of those elements. Quantitation is achieved by comparing analyte photoelectron peak intensities to those for one or more independently determined species within the sample. The sample must be in vacuum, and its surface is analyzed to the escape depth of the photoelectrons ($\approx 20 \text{ Å}$). We have previously determined that ambient aerosol particle nitrogen is usually resistant to vacuum degradation and the particles have similar surface and bulk compositions. Nitrogenous species concentrations were determined from ESCA spectra by reference to sulfur in the samples, which was independently determined by x-ray fluorescence analysis. Deconvolution of the reduced nitrogen peak was based on the peak position and form of the ammonium nitrogen peak in $(\text{NH}_4)_2\text{SO}_4$. All photoelectron spectra were taken with an AEI ES200 spectrometer modified by installation of a Surface Science Laboratories Model 239G position-sensitive detector.

Evolved gas analysis ($\text{CO}_2$ and $\text{SO}_2$) has been used by Malissa, Puxbaum, and Pell to investigate collected aerosol particulate material (ref.7). We have adapted this analytical technique to analysis of particles collected on quartz-fiber filters and have extended it to include visible light attenuation and evolved $\text{NO}_x$ (ref.4). Our system, shown in Fig. 1, uses an NDIR $\text{CO}_2$ detector.

![Figure 1. Schematic diagram of thermal evolved gas analysis apparatus.](image-url)
(MSA LIRA 202S) and a chemiluminescent NO\textsubscript{x} detector (ThermoElectron 14D/E) in series to determine analyte concentrations in a single low-volume gas stream. Detection limits of < 1 ppm for CO\textsubscript{2} and < 0.01 ppm for NO\textsubscript{x} in the gas stream translate to sample sizes required for quantitation with typical ambient particle samples of ~10 \mu g carbon and < 1 \mu g nitrogen.

NO\textsubscript{x} EGA thermograms of sample nitrogen-containing ionic compounds show differentiated features that permit identification of those compounds (Fig. 2). Peaks resulting from low-temperature evaporation and thermal decomposition of these discrete compounds appear quite sharp. Thermograms of some organic compounds containing nitrogen show similar differentiation (Fig. 3). For each compound, the evolved CO\textsubscript{2} and NO\textsubscript{x} are detected simultaneously. Conversion of sample nitrogen to NO and NO\textsubscript{2} is partially dependent on initial oxidation state, especially for inorganic compounds. Nitrogen recovery as NO\textsubscript{x} was 71 ± 18\% for the 13 compounds studied.

DISCUSSION

That N\textsubscript{x} can be distinguished by EGA is illustrated with an ambient particle sample from Ljubljana, Yugoslavia. The N 1s ESCA spectrum (Fig. 4a) shows both NH\textsubscript{4}\textsuperscript{+} and N\textsubscript{x}. The deconvoluted peak areas, which are proportional to atomic populations, show approximately 1.4 times as much NH\textsubscript{4}\textsuperscript{+} as N\textsubscript{x}. The NO\textsubscript{x} thermogram of this sample (Fig. 4b) exhibits a doublet that can be ascribed to (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, a
small shoulder at lower temperature corresponding to NH$_4$NO$_3$, and a substantial amount of NO$_X$ evolved at temperatures greater than 300°C that can be attributed to N$_X$. The ratio of NO$_X$ evolved below 300°C to that evolved above is $\sim$ 1.7. Since it is likely that some of the N$_X$-containing compounds are thermally decomposed or vaporized at temperatures below 300°C, and since EGA, unlike ESCA,
is a bulk analytical technique, this agreement is quite reasonable.

Evidence for a link between the higher temperature evolved NO\textsubscript{X} and the organic component of ambient particles is demonstrated by the behavior of N\textsubscript{X} in a solvent extraction sequence that removes most organic material while leaving the black carbon (refs.8,9). Evolved CO\textsubscript{2} and NO\textsubscript{X} thermograms of a Berkeley, California, sample are shown in Fig. 5a. The dominant nitrogenous species is NH\textsubscript{4}NO\textsubscript{3}, with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and N\textsubscript{X} also present. The coincident CO\textsubscript{2} and NO\textsubscript{X} peaks at ~450°C indicate the linkage of the higher temperature nitrogen species to a carbonaceous component. Sequential extraction with benzene and a 1:2,v:v methanol:chloroform mixture removes nearly all organic carbon as shown by the thermograms in Fig. 5b. The NO\textsubscript{X} thermogram shows that most of N\textsubscript{X} has been removed with the organic material. The high temperature at which the organics associated with N\textsubscript{X} are thermally removed indicates a stability similar to that observed in high molecular weight compounds.

![Graphs showing evolved CO\textsubscript{2} and NO\textsubscript{X} thermograms.](image)

Fig. 5. Evolved CO\textsubscript{2} and NO\textsubscript{X} thermograms of < 1.8 \textmu m ambient particles from Berkeley, California, 22 October 1981. (a) Before solvent extraction. (b) After extraction with benzene and a methanol-chloroform mixture.

Further evidence for a link between N\textsubscript{X} and the organic fraction of carbonaceous particulate material is shown by samples collected in Riverside, California. High-volume samples were collected in parallel with and without removal of large particles (\geq 1.5 \textmu m) by an impactor (Sierra Instruments Model 236). The CO\textsubscript{2} and NO\textsubscript{X} thermograms are shown in Fig. 6a. It is apparent that most of the NO\textsubscript{X} evolved at temperatures greater than 250\degree C is associated with large particles. When the large particle contribution is determined by subtracting the thermograms (Fig. 6b), the correspondence in the form of the evolved NO\textsubscript{X} and evolved CO\textsubscript{2} indicates that the carbon and nitrogen of these particles are present in the same structures or compounds.
CONCLUSIONS

The results presented here confirm the presence of substantial amounts of organic reduced nitrogen species in ambient aerosol particulate material throughout the world. The agreement of NO\textsubscript{x} thermal EGA results with those from ESCA establishes the presence of these species as bulk constituents of the particles. The relatively high temperatures at which NO\textsubscript{x} is evolved from these species indicates that their parent molecules are nonvolatile and therefore unlikely to have entered the particle phase through condensation from gases.

REFERENCES

2 S.G. Chang and T. Novakov, Atmos. Environ. 9 (1975) 495-504.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.