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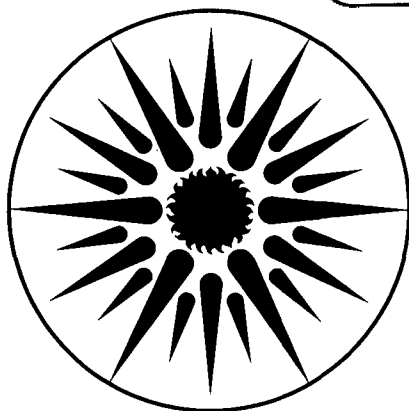
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R.L. Dod, L.A. Gundel, W.H. Benner, and T. Novakov

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NON-AMMONIUM REDUCED NITROGEN SPECIES IN ATMOSPHERIC AEROSOL PARTICLES*

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ABSTRACT

The traditional belief that ambient aerosol particles contain nitrogen predominantly in the form of inorganic ionic species such as NH_4^+ and 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 NH_4^+ and 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

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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 ($\sim 20 \text{ \AA}$). 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 (CO_2 and 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 NO_x (ref.4). Our system, shown in Fig. 1, uses an NDIR CO_2 detector

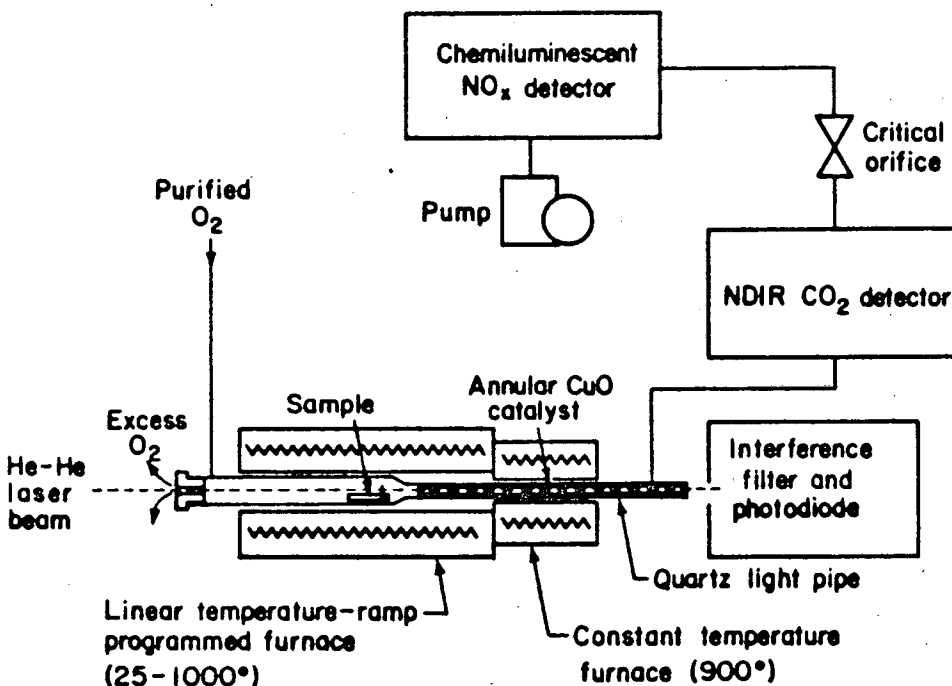


Figure 1. Schematic diagram of thermal evolved gas analysis apparatus.

(MSA LIRA 202S) and a chemiluminescent NO_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_2 and < 0.01 ppm for NO_x in the gas stream translate to sample sizes required for quantitation with typical ambient particle samples of ~ 10 μg carbon and < 1 μg nitrogen.

NO_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_2 and NO_x are detected simultaneously. Conversion of sample nitrogen to NO and NO_2 is partially dependent on initial oxidation state, especially for inorganic compounds. Nitrogen recovery as NO_x was $71 \pm 18\%$ for the 13 compounds studied.

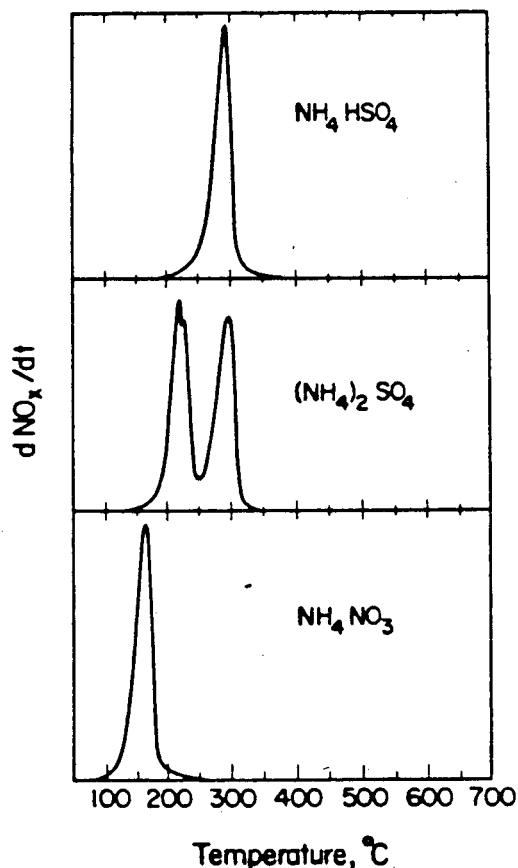


Fig. 2. Evolved NO_x thermograms of inorganic compounds reported to be present in atmospheric particles.

DISCUSSION

That N_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_4^+ and N_x . The deconvoluted peak areas, which are proportional to atomic populations, show approximately 1.4 times as much NH_4^+ as N_x . The NO_x thermogram of this sample (Fig. 4b) exhibits a doublet that can be ascribed to $(\text{NH}_4)_2\text{SO}_4$, a

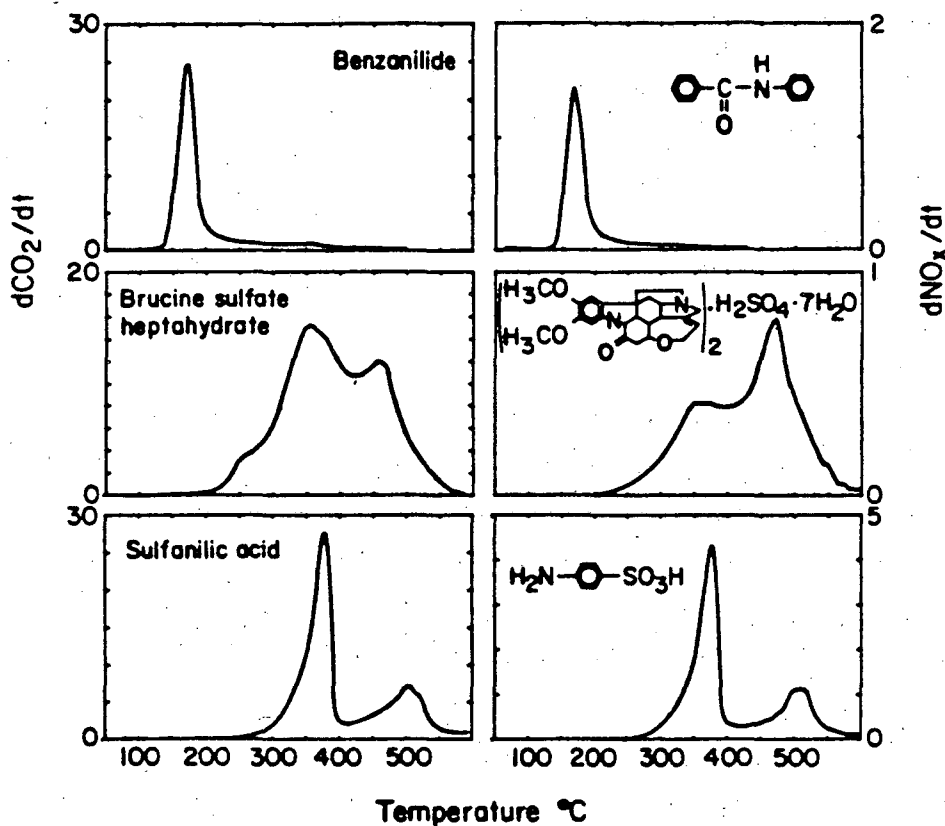


Fig. 3. Evolved CO_2 and NO_x thermograms of some pure organic compounds that contain nitrogen.

small shoulder at lower temperature corresponding to NH_4NO_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 ~ 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,

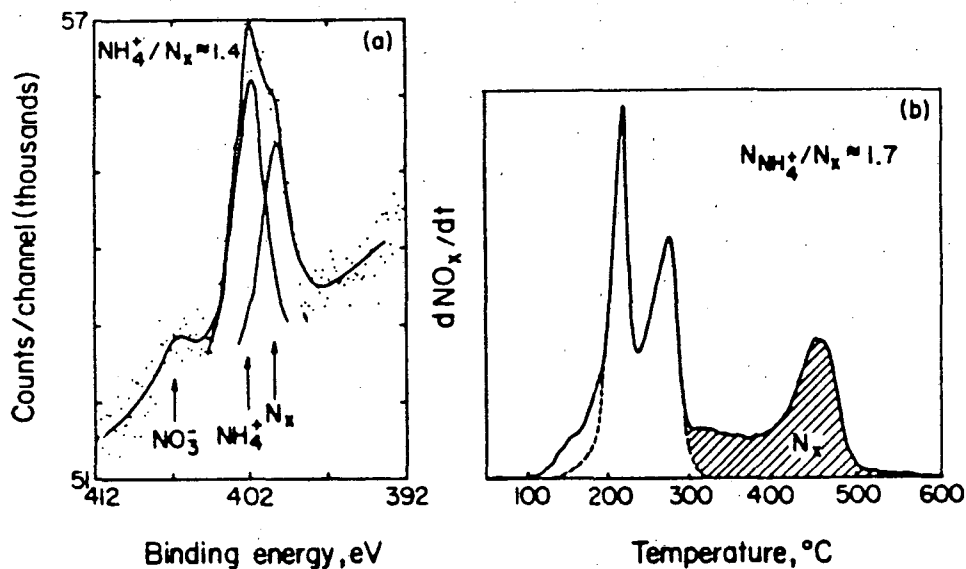


Fig. 4. Nitrogen speciation for Ljubljana, Yugoslavia, ambient particles, 15-17 January 1983. (a) N 1s ESCA spectrum showing the presence of NO_3^- , NH_4^+ , and N_x . (b) Evolved NO_x thermogram showing inorganic and organic (N_x) nitrogen.

is a bulk analytical technique, this agreement is quite reasonable.

Evidence for a link between the higher temperature evolved NO_x and the organic component of ambient particles is demonstrated by the behavior of N_x in a solvent extraction sequence that removes most organic material while leaving the black carbon (refs.8,9). Evolved CO_2 and NO_x thermograms of a Berkeley, California, sample are shown in Fig. 5a. The dominant nitrogenous species is NH_4NO_3 , with $(\text{NH}_4)_2\text{SO}_4$ and N_x also present. The coincident CO_2 and NO_x peaks at $\sim 450^\circ\text{C}$ 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_x thermogram shows that most of N_x has been removed with the organic material. The high temperature at which the organics associated with N_x are thermally removed indicates a stability similar to that observed in high molecular weight compounds.

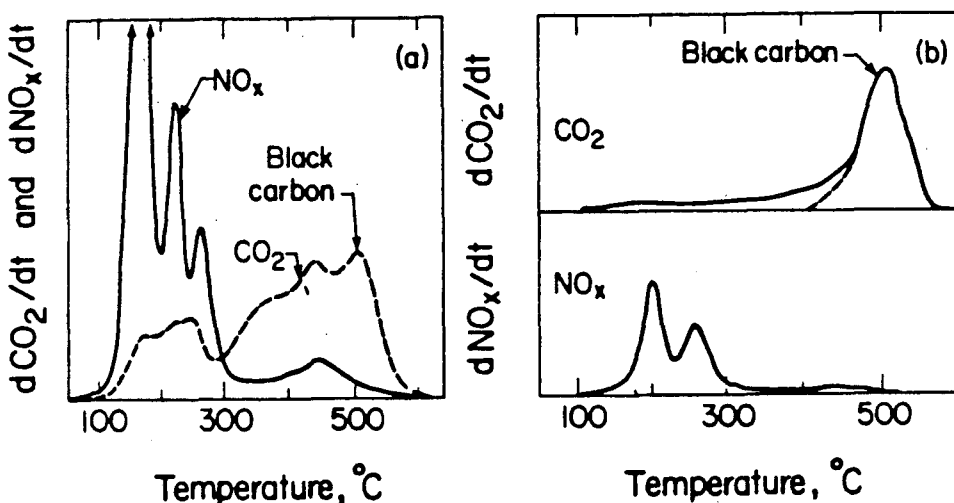


Fig. 5. Evolved CO_2 and NO_x thermograms of $< 1.8 \mu\text{m}$ ambient particles from Berkeley, California, 22 October 1981. (a) Before solvent extraction. (b) After extraction with benzene and a methanol-chloroform mixture.

Further evidence for a link between N_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 ($\geq 1.5 \mu\text{m}$) by an impactor (Sierra Instruments Model 236). The CO_2 and NO_x thermograms are shown in Fig. 6a. It is apparent that most of the NO_x evolved at temperatures greater than 250°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_x and evolved CO_2 indicates that the carbon and nitrogen of these particles are present in the same structures or compounds.

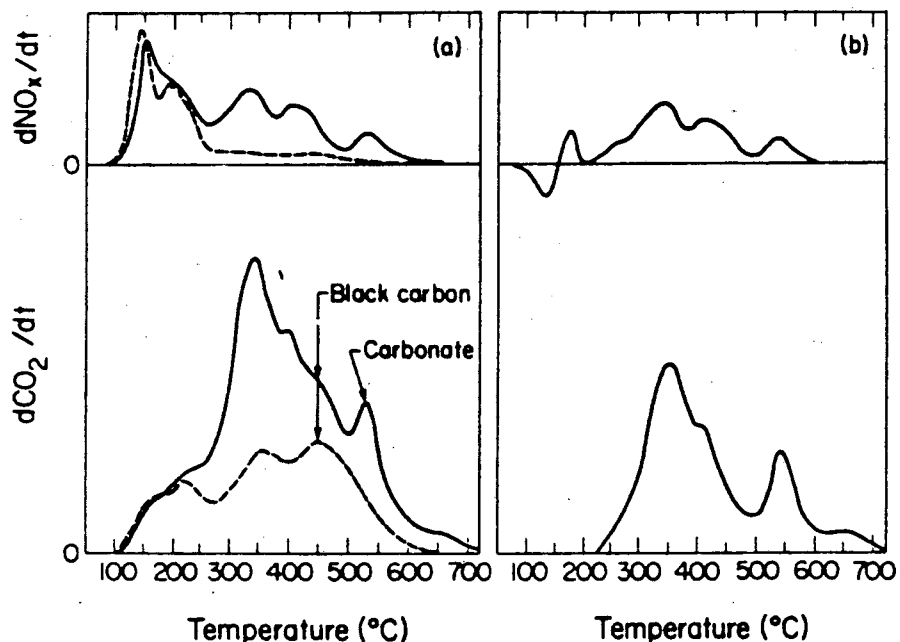


Fig. 6. Evolved CO_2 and NO_x thermograms for ambient particles from Riverside, California, 17 June 1981. (a) Thermograms for total particle sample (solid lines) and $< 1.5 \mu\text{m}$ particle sample (dashed lines) collected in parallel. (b) Thermograms of large particles determined by difference between total and small particle thermograms.

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_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_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

- 1 T. Novakov, P.K. Mueller, A.E. Alcocer and J.W. Otvos, *J. Colloid Interface Sci.*, 39 (1972) 225-234.
- 2 S.G. Chang and T. Novakov, *Atmos. Environ.* 9 (1975) 495-504.
- 3 C.W. Spicer, *Atmos. Environ.*, 11 (1977) 1089-1095.
- 4 R.L. Dod and T. Novakov, in L.A. Casper and C.J. Powell (Eds.), *Industrial Applications of Surface Analysis*, American Chemical Society, Washington, D.C., 1982, pp. 397-409.
- 5 T. Novakov, S.G. Chang and R.L. Dod, in D.M. Hercules, G.M. Hieftje, L.R. Snyder and M.A. Evenson (Eds.), *Contemporary Topics in Environmental and Clinical Chemistry*, Vol. 1, Plenum, New York, 1977, pp. 249-286.
- 6 B.R. Appel, J.J. Wesolowski, E. Hoffer, S. Twiss, S. Wall, S.G. Chang and T. Novakov, *Intern. J. Environ. Anal. Chem.*, 4 (1976) 169-181.
- 7 H. Malissa, H. Puxbaum and E. Pell, *Z. Anal. Chem.*, 282 (1976) 109-113.
- 8 B.R. Appel, E.M. Hoffer, E.L. Kothny, S.M. Wall, M. Haik and R.L. Knights, *Environ. Sci. Technol.*, 13 (1979) 98-104.
- 9 L.A. Gundel, R.L. Dod and T. Novakov, Lawrence Berkeley Laboratory report LBL-11986 (1981), pp. 5-26 - 5-30.

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