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A THERMOLUMINESCENT METHOD FOR AEROSOL CHARACTERIZATION

by

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16. Abstract A thermoluminescent method has been used to study the interactions of aerosols with ozone. The preliminary results show that ozone reacts with many compounds found in aerosols, and that the thermoluminescence curves obtained from ozonated aerosols are characteristic of the aerosol. The results suggest several important applications of the thermoluminescent method: development of a detector for identification of effluent sources; a sensitive experimental tool for study of heterogeneous chemistry; evaluation of importance of aerosols in atmospheric chemistry; and study of formation of toxic, electronically excited species in airborne particles.					
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(smoke stack, chemical plant, steel mill, etc.) of the aerosols and provide information related to chemical composition.

Recently, Cadle, et al⁽¹⁾ have suggested that heterogeneous reactions may be important in atmospheric chemistry. The technique discussed here is very sensitive for determining the extent of aerosol-ozone reactions and can provide data useful for atmospheric models.

In addition, the possibility that aerosol-ozone interactions produce long-lived, electronically excited species in aerosols may have implications regarding the carcinogenicity of aerosols.⁽²⁾

Experimental Technique

The substances listed in Table I were measured into glass ampules and the ampules were placed in a chamber through which a mixture of 1% ozone in oxygen was passed. Each ampule contained approximately 2 mg of the substance. The samples were exposed to the ozone and oxygen mixture for 5 minutes and then removed from the chamber. A few minutes were allowed for excess ozone to dissipate and a drop of saturated solution of rubrene in benzene was added to each solid sample. The benzene evaporated in a few minutes. The rubrene acted as the fluorescent material which luminesced when excited by the thermal decomposition of the ozonides.⁽³⁾

The apparatus for observing the thermoluminescence is shown in Fig. 1. The solid prepared as above was placed on the heater and heated at a linear rate of 30°C/min to 200°C. The temperature of the heater was controlled by an F&M Scientific Corporation Model 240 M

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temperature programmer and the temperature sensed by a chromel-alumel thermocouple. The thermocouple output was recorded on one channel of a Honeywell Electronik 194 dual pen recorder. The other channel was used to display the signal from an RCA 7265 photomultiplier which was amplified by an Elcor Model A309B electrometer. Fig. 2 is an example of the recorder trace from a sample of 1,2 benzanthracene obtained in this manner.

Results and Discussion

The parameters listed in Table I were measured from the recorded output for each of the substances tested. A comparison of the parameters in Table I indicates that the various substances are distinguishable on the basis of this simple analysis of the glow curves. The temperature maxima and the linewidths at half maximum are all different. The organic compounds in Table I are known constituents of urban aerosols. The cosanes constitute approximately 85% of the organics in urban aerosols. ⁽⁴⁾ $(\text{NH}_4)_2\text{SO}_4$ is a primary sulfate in the atmosphere and a product of SO_2 oxidation. NaCl is an aerosol in the coastal regions. Aluminum oxide did not display a reaction with ozone. A more detailed analysis of line shapes should reveal other characteristics that are unique to the substances.

The aerosols identified as 1293 aerosol and ROGO aerosol were collected at 2 different sites as precipitated particles from the atmosphere and are mixtures of many compounds. The glow curves from these aerosols are reproducible and therefore could be compared with aerosols

from pollution sources to identify the source. Such a comparison would be invaluable for tracing dispersion of pollutants, as well as determining the identity of the source.

The thermoluminescence curves may be useful in qualitative analysis of the aerosol composition. This is accomplished by comparison of the aerosol luminescence curve with curves from a mixture of chemical species that are known constituents of aerosols. For a specific geographical area there would be a limited number of species. A catalog of curves could be produced by measuring aerosols from various sources and analyzing their chemical composition by standard methods. Identification of the aerosol would then be accomplished by simply comparing the glow curves obtained in the field to the cataloged curves.

Four of the samples were examined four hours after ozonation and found to produce glow curves different from those found immediately after ozonation. In the case of one of the aerosols, several peaks were exhibited. Since the ozonides formed initially are unstable, new chemical species are formed at various rates and glow curves such as these could be used as additional data for characterizing the aerosol.

These preliminary experiments were performed to demonstrate the method. The solids were all ozonated in the laboratory at 1% ozone concentration. We have since observed interactions of $(\text{NH}_4)\text{HSO}_4$ with ozone at ozone concentrations of 1 ppm. Trace amounts of ozone are present in the atmosphere at all altitudes; therefore, airborne aerosols are ozonated naturally, though not to the extent produced under our laboratory conditions. With more sensitive photon detection

devices, the ozonides produced naturally could be detected using procedures analogous to those described here. Solid reaction rates as low as 10^{-9} mole/year can be followed with this technique.⁽⁵⁾ The need for artificial ozonation would be eliminated. The advantage of such a system would be that the reactions of aerosols with ozone in the atmosphere could be followed using a thermoluminescence method.

The temperature at which the peak in the glow curve occurs is representative of the stability of the ozonides formed and can be related to the activation energy for the thermal decomposition. For a reaction following first order kinetics, the position of the peak depends only on the type of compounds formed and time after ozonation, and not on the concentration of these compounds in the mixture. Under such conditions the peak in the glow curve will not depend on the amount of ozone that has reacted with the aerosol and is unique to the aerosol.

Concluding Remarks

Heterogeneous interaction between several organic and inorganic atmospheric aerosol compounds with ozone has been observed using a thermoluminescent method. The luminescent spectrum is different for each compound and is thus characteristic of the compound's molecular structure. The spectra also change with time after ozonation, and thus additional chemistry takes place after initial heterogeneous complexing. With meteorological data, these properties make the sensitive thermoluminescent method suitable for detecting and tracking aerosols to their source (smoke stack, chemical plant, steel mill, etc.). The instrumentation requirements make the technique suitable for source identification in the field and for ground truth and flight experiments.

It is recognized that the technique will also be useful for parameter evaluation in atmospheric chemistry models which include aerosols, and in the basic study of heterogeneous chemistry. The observations of luminescence indicate that the aerosol/ozone complex is a high energy species with serious implications with respect to toxic, biological properties such as mutagenicity and carcinogenicity.

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Table I

OZONE/AEROSOL THERMOLUMINESCENCE

<u>SUBSTANCE</u>	<u>INITIAL MAXIMUM</u>	<u>INITIAL HALFWIDTH</u>	<u>MAXIMUM FOUR HR AFTER OZONATION</u>
1293 AEROSOL	97 °C	81 °C	100, 122, 151 °C
ROGO AEROSOL	83	64	102
AMMONIUM SULFATE	110	44	---
SODIUM CHLORIDE	152	52	---
3,4 BENZOPYRENE	103	69	---
1,2 BENZANTHRACENE	99	35	---
CORONENE	85	72	101
N-OCTACOSANE	122	96	130
Al ₂ O ₃	No reaction		

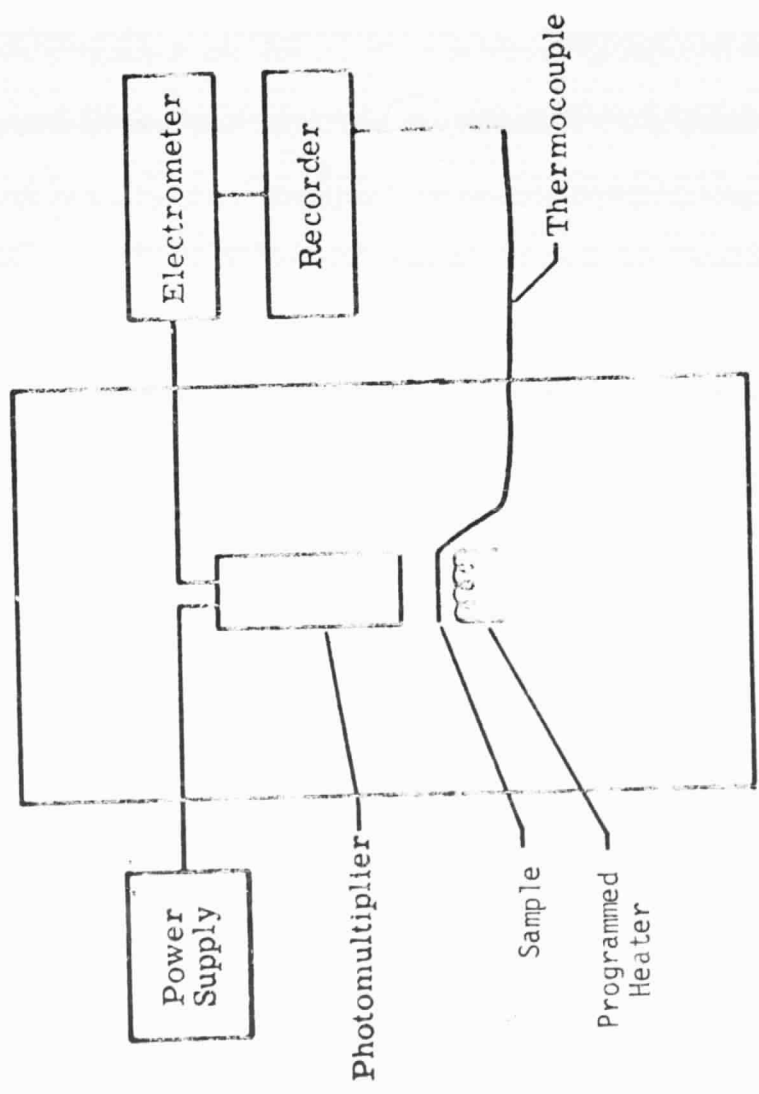


Figure 1. Schematic diagram of apparatus for thermoluminescence analysis.

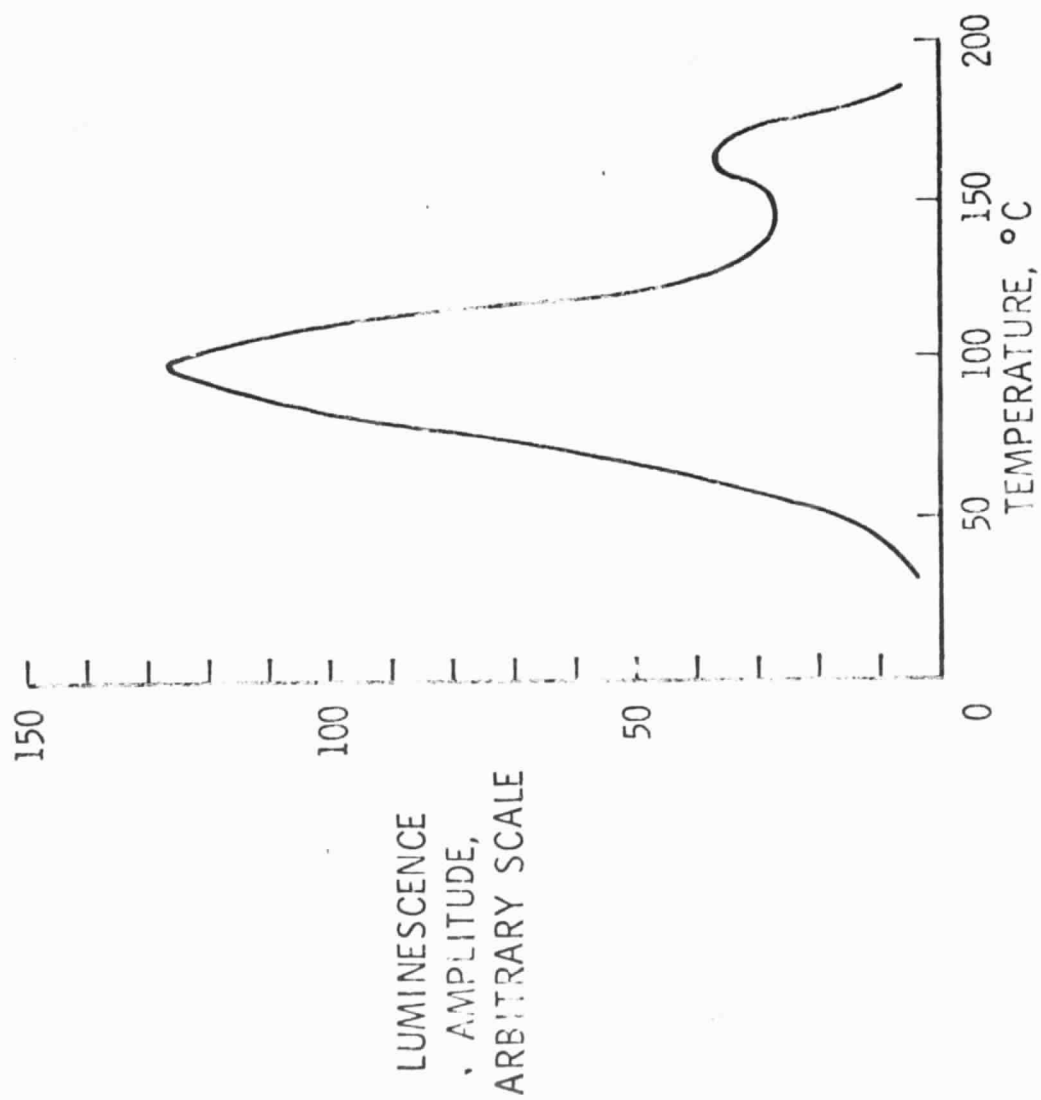


Figure 2. Thermoluminescence curve obtained from a sample of 1,2-benzanthracene.