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THERMAL ANALYSES OF AEROSOLS

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Thermal analysis as an analytical tool has been applied to the study of suspended liquid and solid matter in air. The aerosol is heated in a glass pipe, and the light scattering coefficient is used for the *in situ* detection of aerosol. Results of thermal analysis of the Los Angeles smog, and of St. Louis aerosol on dry and humid days, are presented, all indicating distinctly different thermo-nephelograms. On polluted days in St. Louis, over 50% of the light scattering coefficient is lost at about 100°, which indicates the presence of H_2SO_4.

Suspended liquid or solid matter in air, commonly referred to as aerosols, are receiving increasing attention because of their important role as health hazards, their effects on the global climate and weather, damage to buildings and vegetation, and other environmental effects. Because of these effects, aerosols, in particular atmospheric aerosols, constitute one of the most damaging components of the current air pollution problem.

In recent years much has been learned about the physical and chemical characteristics of atmospheric aerosols. Unfortunately, chemical analyses of aerosol samples deposited on filter or other substrates could only yield partial information regarding the aerosol which is suspended in air. A major uncertainty about the suspended aerosol concentrations exists due to inadequate data on the content of water and other volatile matter such as light organics in the ambient aerosols [1]. The present study was initiated with the purpose to elucidate the volatile aerosol fraction and, if possible, derive quantitative data on the volatility, i.e. under what conditions (mainly temperature) and how much of the ambient aerosol is driven from the aerosol to gas phase. For this purpose, we adapted thermal analysis as the analytical tool.

Results of controlled thermal exposure and analyses of urban aerosols were first reported by Goetz, Preining and Kallai [2]. They showed that deposited marine aerosol changes insignificantly after exposure to 80° air, i.e. it is not volatile at that temperature. On the other hand, about 80% of the Los Angeles smog aerosol in the size range below 0.5 μm volatilized at 80°. They found that at this temperature the subrange between 0.5 and 1.3 μm did not change substantially.

Thermal analysis, i.e. aerosol analysis as a continuous function of temperature has been used by other investigators to study the behavior of natural aerosols

[3, 4]. In the present work, the light scattering component (0.2 – 0.6 μm) of urban aerosols was thermally analyzed using an *in situ* detection technique, nephelometry.

Experimental setup

Description of the equipment

The experimental setup used for thermal analyses of aerosols is shown schematically in Fig. 1. It consists of three major components, the heater, the aerosol sensor and the data recorder. Aerosol is heated by a pyrex glass heating pipe before it enters the nephelometer. Fin-like obstructions extending from the inner wall to the center of the pyrex pipe insure the mixing and uniform heating of the aerosol sample. The first section of the pipe is wrapped with a heating strip, and the aerosol passing through this section can be heated up to 300°. The rate of heating is controlled by the power input, and the air flow rate. A timer turns the power on or off, and hence it controls the heating time. The aerosol flow rate through the heater is set at 500 cm^3/s. After heating, the aerosol passes through the other half of the pyrex pipe and cools down to about 30°, and then enters the nephelometer.

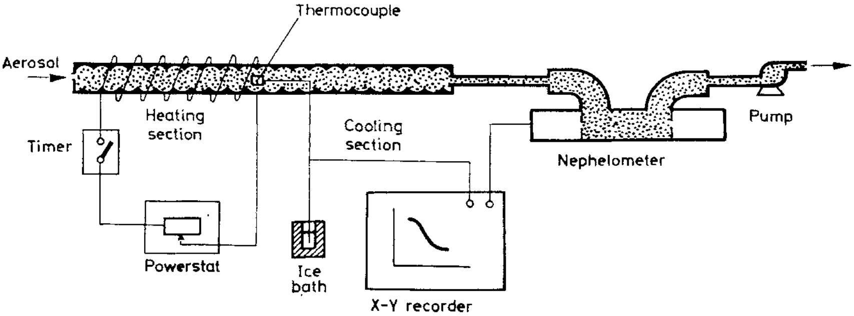

Fig. 1. Schematics of the experimental setup for the aerosol thermal analyses

The temperature of the heated aerosol is measured by a thermocouple which is placed in a teflon radiation shield and rests at the end of the heating section of the pipe. Hence it measures the maximum temperature that the aerosol has been heated to.

There are several convenient devices available for the monitoring of aerosol properties. Optical devices, using the light scattering by aerosols as the signal, can provide a simple means for the continuous and *in situ* measurement of particles in the 0.20 – 5 μm particle diameter range.

In the present work, the aerosol is monitored by a nephelometer [5] which measures the total light scattering coefficient, b_{scat}, in the visible wave length range. The particle diameter range that the nephelometer is most sensitive to is between 0.2 and 0.6 μm [6]. The output signal is sent to two recording units: a continuous strip chart recorder which records the time history of the total light scattering during heating and cooling periods, and an X-Y recorder which plots the total light scattering coefficient against temperature.

Calibration of the instruments

The calibration procedures for the nephelometer are described in the manufacturer's manual (Meteorology Research, Inc.). The possible loss of the aerosol particles in passing through the heating tube is checked by bypassing the heating system and comparing the readings of the nephelometer with and without the heating tube. For atmospheric aerosol, no observable loss of b_{scat} in the heating system was found.

Based on a number of temperature vs. time curves, the settings of the powerstat and the timer were chosen such that the maximum temperature of the aerosol after heating was about 300° and the heating-and-cooling cycle lasted less than 30 minutes. It was observed that at 300°, the light scattering coefficient, b_{scat}, approached an almost constant value for most of the substances.

Thermo-nephelograms of known aerosols

Aerosol particles of volatile substances will diminish in size due to evaporation or decomposition upon heating, and hence the amount of light they scatter will be reduced. A plot of the total light scattering, b_{scat}, versus the temperature, T, of an aerosol sample reveals the thermal behavior of the aerosol; and such a plot will be called a thermo-nephelogram or TNG hereafter. Because of their different thermodynamic properties, aerosols of various substances will exhibit their own particular TNG's. Hence by comparing the TNG's of aerosol of unknown composition with those of known aerosols, one may seek information regarding the composition of the unknown aerosols.

Tests were performed using NaCl, H_2SO_4, ammonium sulfate, polystyrene latex, cigarette smoke and dioctyl-phthalate (DOP) aerosols. These aerosols, except cigarette smoke, were prepared by a nebulizer filled with either water or alcohol solutions of the particular substances. The median diameter of the nebulizer droplets was about 6 μm and, using solutions of 0.1 weight per cent, the resulting dry particles were of submicron size (≈ 0.6 μm).

The results of TNG experiments on known substances are shown in Figs. 2 and 3. First, it was observed that the heating of the non-volatile polystyrene latex aerosol has minimal effect on the light scattering. The 10% decrease of b_{scat} observed at the end of heating process may partly be attributed to the loss of the particles in the system. Sodium chloride has a boiling point of 1413° and it is considered non-volatile. Accordingly, it shows almost no decrease in b_{scat}

upon heating. The sudden decrease in the beginning of the heating process is attributed to the loss of hydrated water in the NaCl crystal.

Thermo-nephelometric analyses of sulfuric acid and ammonium sulfate reveal that these substances have well defined evaporation or decomposition temperatures. H_2SO_4 evaporates in the temperature range of 80–120° while $(NH_4)_2SO_4$ decomposes and evaporates at 180–220°.

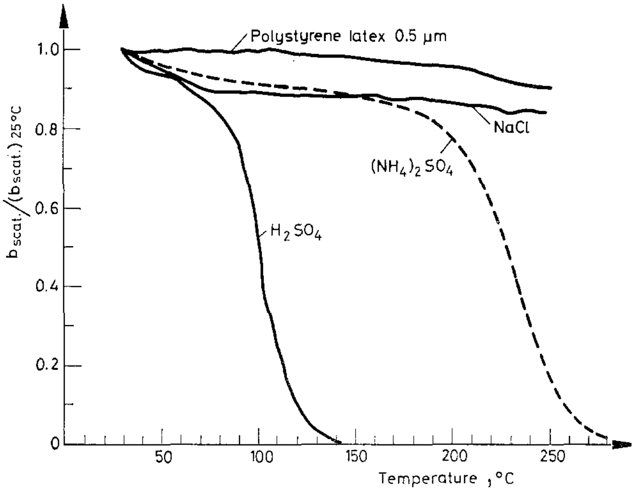

Fig. 2. Thermo-nephelograms of known substances

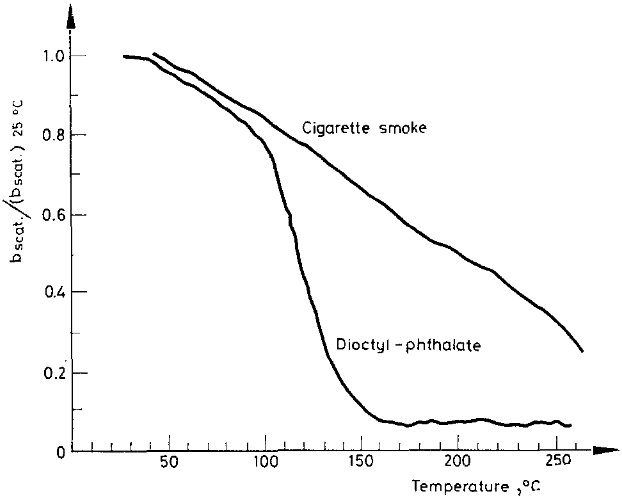

Fig. 3. Thermo-nephelograms of known volatile substances

The TNG's of volatile substances are considerably different from those observed above. Cigarette smoke, for instance, responds to the heating immediately and its b_{scat} decays almost linearly with increasing temperature. Dioctyl-phthalate (DOP), aerosol, first decays slowly and at about 100° it starts to drop sharply and reaches almost zero b_{scat} at about 150°. At this point, it is appropriate to comment that we have observed no condensation during the cooling process. Hence it is concluded that there is no recondensation after heating for aerosols of low vapor pressure substances.

These sets of data shown above are of interest for serving as reference data for analyzing the TNG's of atmospheric aerosols.

Thermal analyses of atmospheric aerosols

Thermal analyses of atmospheric aerosols were performed in Pasadena, California, and in St. Louis, Missouri. It is beyond the scope of this presentation to discuss these results in much detail. It is instructive, however, to observe several TNG's that were found typical for the Los Angeles and St. Louis respectively.

Inspection of TNG data for Pasadena revealed that the aerosol in the Los Angeles basin exhibits two distinctly different type of thermal behavior as shown in Fig. 4. One occurred on cloudy, hazy days with relatively low photochemical activity ("hazy" in Fig. 4) and the other type occurred on "smoggy" days with high ozone, eye irritation and the typical smell of photochemical smog. On smoggy days, the TNG exhibited a reverse S shaped curve while on hazy days, the b_{scat} decreased linearly with temperature up to 150°.

The above data demonstrate that simple thermal analyses of the Los Angeles aerosol can reveal some important information about its origin and its volatile fraction. More detailed discussion of these results is given elsewhere [7].

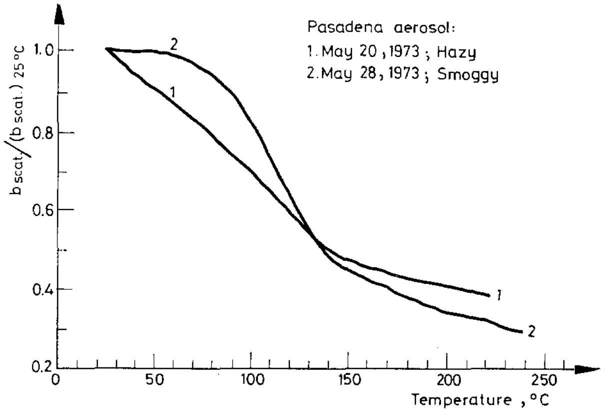

Fig. 4. Comparison of TNGs obtained on "hazy" and "smoggy" days in the Los Angeles basin

Results of thermal analyses of St. Louis aerosol are shown in Fig. 5. The curves 1 and 2 represent typical data for clear, dry days and for humid, polluted air respectively. On dry days, the b_{scat} exhibits little change up to 300°. On the other hand, on humid and polluted days, over 50 % of the light scattering coefficient is due to volatile components. It is interesting to note that the vaporization temperature for pollution aerosol is between 80° and 120° which corresponds to the vaporization of H_2SO_4. These data, therefore, provide strong support to other observations [8] that in the midwestern United States a large fraction of the sulfate aerosol is in form of sulfuric acid.

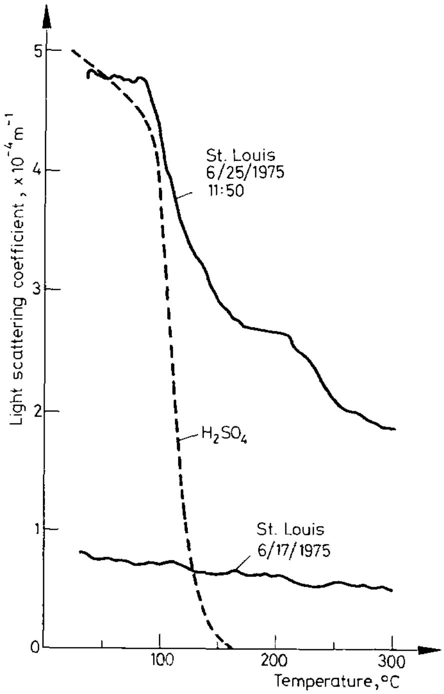

Fig. 5. Thermo-nephelograms recorded on clear and on hazy-polluted days in St. Louis

Discussion

In this work, thermal analysis, as an analytical tool, was applied to the study of liquid and solid matter suspended in air. Based on the presented data and experience, we consider that thermal analysis may yield substantial amounts of new information regarding the physical and chemical characteristics of complex aerosol systems, such as urban aerosols. In particular, the *in situ* characterization of aerosol volatile fraction is of importance because in the classical aerosol sampling techniques, which involve aerosol deposition, many of the volatile components escape before analyses. We also recognize, however, that at present the technique yields only qualitative information and that strong need exists for fundamental studies to quantify the results.

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Résumé — Application de l'analyse thermique comme moyen d'analyse des matériaux liquides et solides en suspension dans l'air. L'aérosol est chauffé dans un tube de verre et le coefficient de diffusion de la lumière est utilisé pour analyser *in situ* l'aérosol. Les résultats de l'analyse du brouillard de Los Angeles et de l'aérosol de St. Louis par temps sec et humide sont présentés, indiquant tous des néphélogrammes thermiques différents. Les cas de pollution à St. Louis se traduisent par une déperdition du coefficient de diffusion de la lumière de plus de 50% à 100° environ, ce qui indique la présence de H_2SO_4.

Zusammenfassung — Die Thermoanalyse wurde als analytische Methode zur Untersuchung von in Luft suspendierten flüssigen und festen Substanzen eingesetzt. Das Aerosol wird in einem Glasrohr beheizt und Lichtstreuungskoeffizient zum *in situ* Nachweis des Aerosols verwendet. Die Ergebnisse der Thermoanalyse von Smog aus Los Angeles und von Aerosol aus St. Louis an trockenen und feuchten Tagen werden bekanntgegeben; diese zeigen deutlich verschiedene Thermonephelogramme. An Tagen bei besonders starker Verschmutzung in St. Louis, gehen mehr als 50% des Lichtstreuungskoeffizienten bei etwa 100° verloren, was auf Gegenwart von H_2SO_4 zurückzuführen ist.

Резюме — Термический анализ, как аналитический метод, был использован для изучения суспендированного жидкого и твердого вещества в воздухе. Аэрозоль нагревали в стеклянной трубке, а коэффициент рассеивания света использовали для определения аэрозоля. Представленные результаты термического анализа лос-анжелесского смога и сент-луизианского аэрозоля в сухие и влажные дни, показывали отчетливо различные термонефелограммы. В загрязненные дни в Сент-Луизе наблюдали уменьшение коэффициента рассеивания света больше, чем на 50% при 100°C, что указывает на присутствие серной кислоты.