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DETERMINATION OF RELATIVE CONCENTRATIONS OF PRIMARY AND SECONDARY ORGANICS
AND SPECIATION OF SULFUR COMPOUNDS
BY THERMAL ANALYSIS AND PHOTOELECTRON SPECTROSCOPY*

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Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenic aerosol particle burden. The objectives of this presentation are to outline a methodology developed in our laboratory to quantitate the amounts of primary and secondary particulate carbon and to present data on speciation of sulfur compounds by a novel approach using thermal analysis and photoelectron spectroscopy (ESCA).

Primary vs. secondary aerosol carbon. Carbonaceous particles in the atmosphere consist of two major components -- graphitic or black carbon (sometimes referred to as elemental or free carbon) and organic material. The latter can be either directly emitted from sources (primary organics) or produced by atmospheric reactions from gaseous precursors (secondary organics). We define soot as the total primary carbonaceous material, i.e., the sum of graphitic carbon and primary organics.

At the past year's meeting, we reviewed the results of a systematic study of 24-hour average black carbon to total carbon ratios and showed how such measurements could be interpreted to estimate the soot fraction of urban aerosols. This year we present results obtained by thermal analysis that enable an empirical definition and quantitation of primary and secondary carbon fractions in ambient aerosols. The measurements were performed on both 24-hour and 2-hour ambient samples.

Thermal analysis -- effluent gas analysis (EGA) -- involves thermal separation of components in a mixture and is a powerful tool for characterizing the carbon-, sulfur-, and nitrogen-containing components of materials. In EGA the sample is heated at a predetermined rate in an oxidizing or neutral atmosphere. The evolved gases resulting from volatilization, pyrolysis, decomposition, and combustion are monitored (as a function of temperature) by one or more gas-specific detectors. Depending on the purpose of analysis, the purge gas is usually oxygen or nitrogen.

For analysis of carbonaceous materials, the gas detected in the oxygen mode is CO₂. An oxidizing catalyst is used to assure complete conversion of CO, hydrocarbons, and other organic vapors to CO₂. In the nitrogen (or pyrolysis) mode, the evolved hydrocarbons are either detected directly by a FID or oxidized over a post catalyst to CO₂ and detected by a CO₂ detector. Nitrogen- and sulfur-containing materials may be analyzed in an analogous manner by detecting NO_x, SO₂, or total gaseous sulfur. EGA in the oxidizing (O₂) model,² is the most common mode of operation for characterizing carbonaceous materials.

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The actual measurement consists in monitoring the CO₂ concentration as a function of the sample temperature. The result is a "thermogram" — a plot of the CO₂ concentration vs. temperature. The area under the thermogram is proportional to the carbon content of the sample. The carbon content is quantitated by calibrating with a calibration gas (CO₂ in oxygen) and by measuring the flow rate through the system. This calibration is crosschecked by analyzing samples of known carbon content. The thermograms reveal distinct features in the form of peaks or groups of peaks that correspond to volatilization, pyrolysis, oxidation, and decomposition of the carbonaceous groups. Assignment of the thermogram peaks to specific species or groups of species can be made by comparison with standard compounds.

When analyzing atmospheric particulates, it is important to quantitatively determine the content of black or graphitic carbon. To determine which of the thermogram peaks corresponds to black graphitic carbon, the intensity of the light beam (produced by a He-Ne laser) transmitted through the sample is monitored by a photodiode and displayed by the second pen of the chart recorder, simultaneously with the measurement of the CO₂ concentration. An examination of the CO₂ and light intensity traces enables the assignment of the peak or peaks in the thermograms corresponding to the black carbon because they appear concomitantly with the decrease in sample absorptivity.

The greatest strength of this method is its ability to "fingerprint" source-produced carbonaceous particles and to assess their contribution to the ambient aerosols, i.e., to empirically determine the ratio of primary vs. secondary aerosol organics. This differentiation was previously done by a very time-consuming solvent extraction procedure. Thermal analysis provides this information, together with other data mentioned above, in a single run.

The "fingerprinting" capability of the method can be illustrated by the following examples. Figures 1 and 2 show the thermograms of a sample collected in Manhattan (source-enriched street canyon) and one collected in Berkeley (aged ambient aerosol). The common features of both thermograms are the black carbon peak, the peak at $\sim 340^{\circ}\text{C}$, and the peaks occurring below $\sim 250^{\circ}\text{C}$ which correspond to the volatile organics. The Berkeley sample clearly shows the presence of a prominent peak at $\sim 350^{\circ}\text{C}$ which is absent in the thermogram of the New York sample. This peak (or possibly group of peaks) may correspond to secondary organic species.

To check this hypothesis, we have performed solvent extractions on some of the ambient samples and obtained thermograms of the insoluble filter residues, since according to an operational definition of Appel et al.,³ "primary" organic carbon is cyclohexane-extracted carbon; "secondary" carbon is the difference between the total carbon extracted by the benzene, methanol-chloroform sequence and the cyclohexane-extracted carbon. The thermograms of sequentially extracted filters should thus show which peaks can be identified with primary and secondary organics.

The result of one such experiment with a sample collected in Berkeley is shown in Figure 3. Cyclohexane extraction has removed practically the entire volatile organics, which — according to the above definition — should be primary species. The peak at $\sim 350^{\circ}\text{C}$ is removed only with the polar benzene-methanol-chloroform solvent. This is consistent with the preliminary assignment — that this peak is due to secondary species. The black carbon peak, as expected, was not removed by solvent extraction.

The possibility of differentiating secondary and primary organics is further demonstrated in Figures 4 and 5, where the thermograms of an early morning sample and a midday Los Angeles sample (collected during a smog episode) are shown. The morning thermogram is distinctly different from the midday, and it lacks the prominent secondary peak at $\sim 350^{\circ}\text{C}$.

Speciation of atmospheric sulfates. Photoelectron spectroscopy (ESCA) and thermal analysis EGA in the NO_x mode were used to study ambient aerosol particles. ESCA measurements on ambient particles in many instances revealed the presence of reduced nitrogen species other than ammonium. On those instances the ratio of ammonium nitrogen to sulfate sulfur is 1:1, indicating that the sulfate could be in the form of ammonium bisulfate. Wet chemical procedures, when performed on the same samples, indicate however that the principal form of sulfate is ammonium sulfate. In order to resolve this apparent inconsistency, thermal analysis was performed on these samples. Preliminary results of these experiments will be discussed.

References

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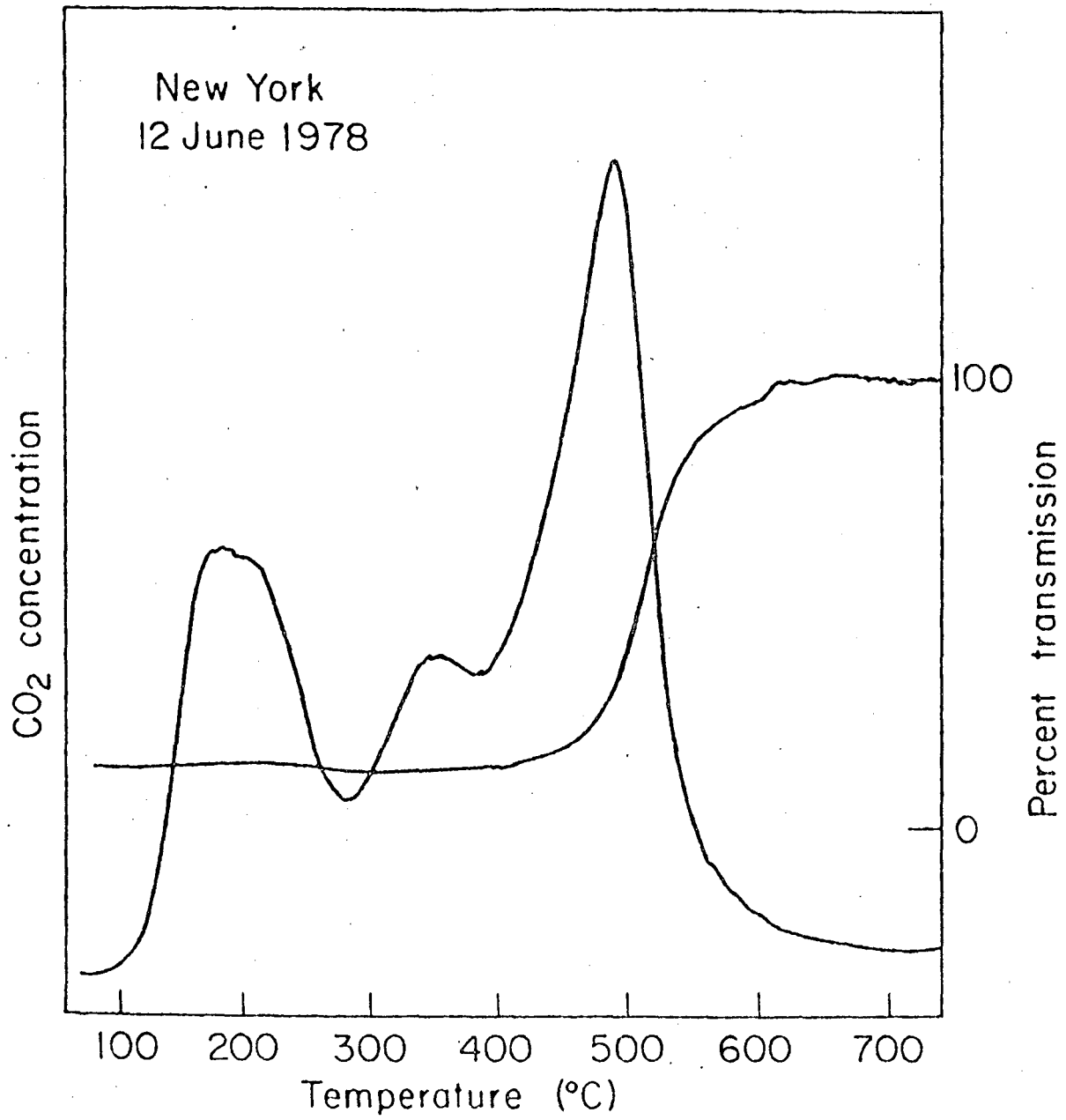


Figure 1. Thermogram of a source enriched ambient sample collected in Manhattan, NY.

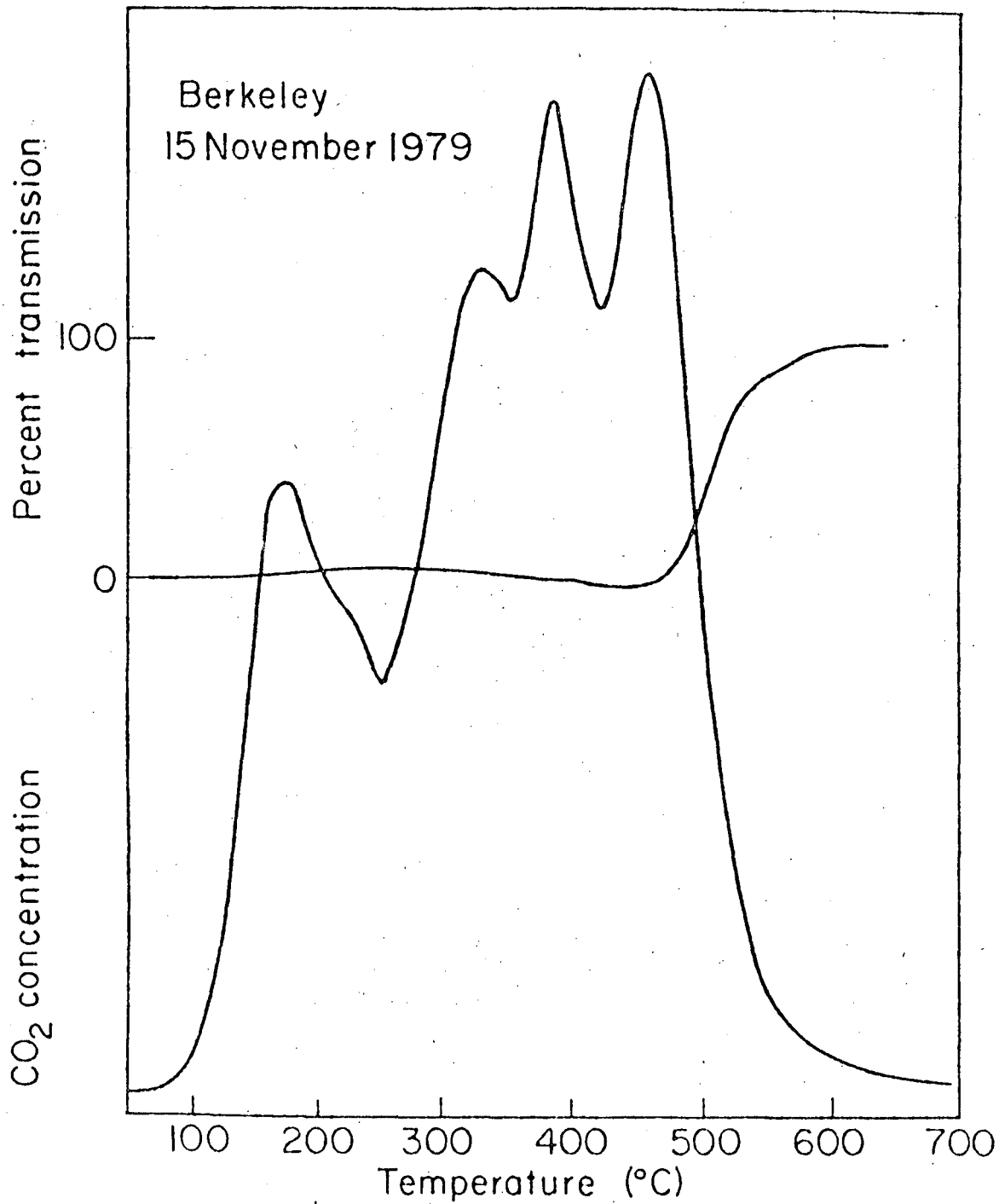


Figure 2. Thermogram of an aged ambient sample collected in Berkeley, CA.

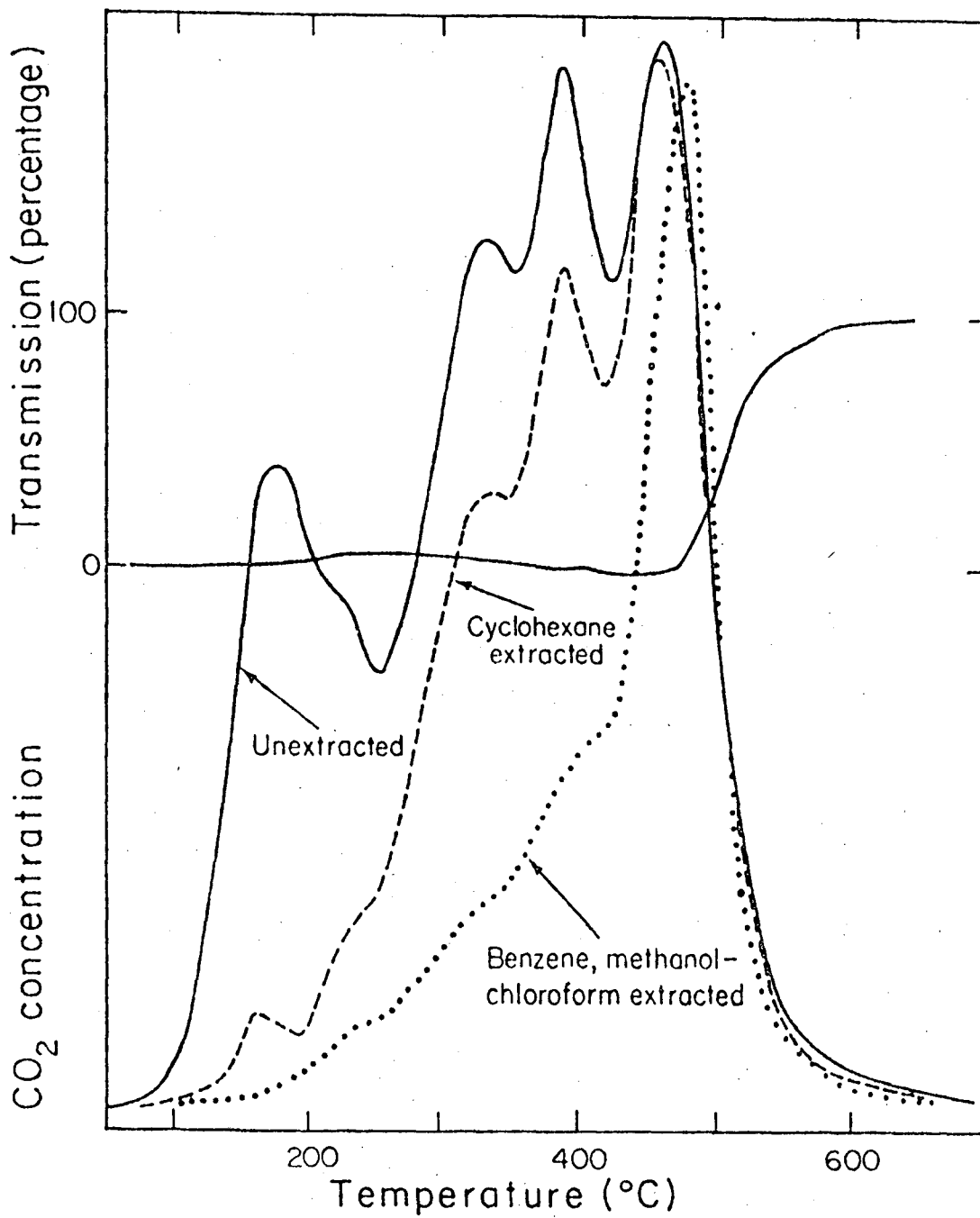


Figure 3. Thermogram of sequentially extracted Berkeley sample.

10-9-80 0700-0900

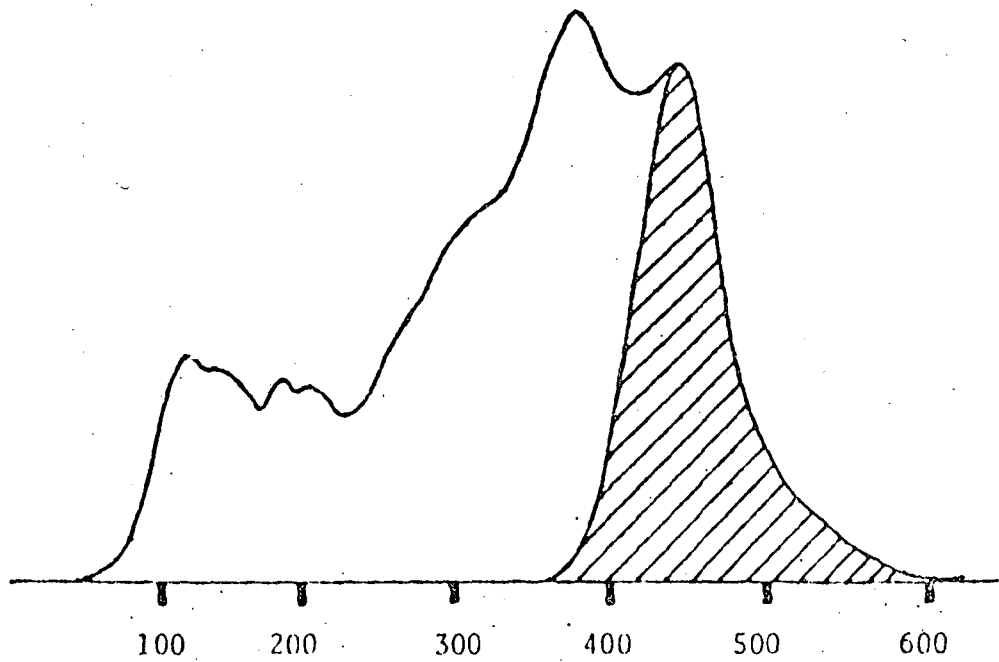


Figure 4. Thermogram of a Los Angeles sample collected during a smog episode between 0700-0900 PDT. Shaded area represents the black carbon.

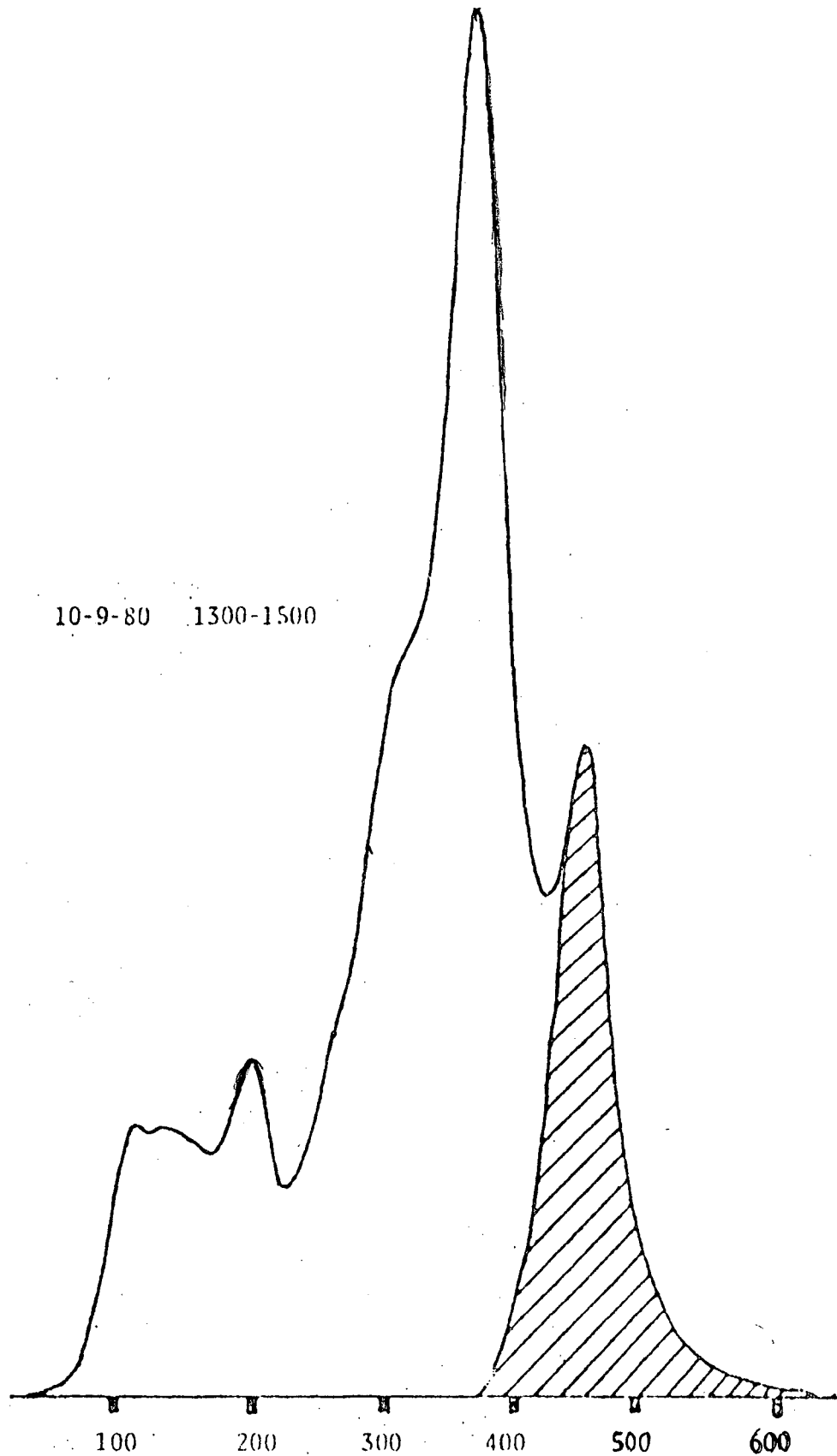


Figure 5. Thermogram of a Los Angeles sample collected between 1300-1500 PDT.

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