



## Project Summary

# Survey of Direct Analysis Methods for Organic Compounds in Particulate Matter

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Spark source, secondary ion and direct probe mass spectroscopy and infrared, Raman and photoacoustic optical spectroscopy were evaluated for their present and potential usefulness in direct (i.e., without prior concentration) qualitative and semiquantitative analysis of aromatic hydrocarbons in particulate matter. It was found that spark source and secondary ion mass spectroscopy, and Fourier-Transform infrared, Raman and photoacoustic spectroscopy did not provide sufficient sensitivity for the determination of environmental levels (low ppm by weight) of polycyclic aromatic hydrocarbons in particulate matter. Direct probe thermal desorption mass spectroscopy was found to be capable of detection and quantification of organic compounds, particularly high molecular weight species not detected with the usual extraction and gas chromatography or gas chromatography/mass spectroscopic analysis. The National Bureau of Standards (NBS) Standard Reference Material 1648 was used to evaluate the various techniques. It is further concluded that the organic material absorbed on ambient particulate matter may be much more complex than previously suspected.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Current methodology for analysis of organic material in particulate matter involves extraction procedures which are tedious, time consuming, and may contaminate the sample. Analytical techniques normally employed for determining the identity and concentration of extracted species include gas chromatography (GC), liquid chromatography (LC), or GC combined with mass spectrometric detection (GC/MS). The utility of GC and GC/MS techniques is limited by the low volatility of many of the organic species of interest, and the efficiency of extraction is thermodynamically limited by the relative free energies of adsorption and solution. Because the current state-of-the-art of quantitative analysis is time consuming, costly, and can yield uncertain or incomplete results, a study was undertaken of experimental methods currently available which might prove capable of yielding such information without prior sample extraction. There are several emerging techniques which may be used to determine organic compounds in particulate matter without extraction, i.e., direct methods. The present study addresses the question of whether these direct methods have sufficiently low detection limits (i.e., low ppm by weight) and quantitative capabilities to be useful in monitoring applications.

The objective of this particular program was to evaluate five candidate direct methods and to make recommendations for further development of the most promising ones. A direct method is

defined as one for which the sample preparation involves no liquid extraction or other concentration steps. The techniques which were evaluated were (a) temperature-programmed direct probe mass spectrometry; (b) spark source mass spectrometry; (c) photoacoustic spectroscopy; (d) Fourier transform infrared absorbance and Raman spectroscopy; and (e) Fourier transform reflectance spectroscopy. The NBS Standard Reference Material 1648, ambient particulate matter, was used in the evaluations. These techniques were evaluated for qualitative and semiquantitative analyses of polynuclear aromatic hydrocarbons. Additionally, a limited investigation was made of the applicability of secondary ion mass spectrometry (SIMS) to organic compounds adsorbed on the surface of particulate samples.

Fluorescence spectroscopy, which is expected to have greater sensitivity than the optical techniques covered here, was not evaluated since it was being studied in another project.

## Conclusions and Recommendations

The results of this experimental assessment of presently available direct analysis techniques show that only the thermal desorption mass spectrometry technique has much chance of being of general applicability. The spark source MS technique does not work in enough cases to be of practical value. Fast atom bombardment and molecular secondary ion mass spectrometry are both sensitive but are not always effective for particulate samples because the polycyclic aromatic material in the

particulate sample is not readily accessible at the surface exposed to the ion beam. The optical techniques studied suffer from the same problem since the organic compounds have selected energetically favorable sites in the particulate phase, and these sites can be optically shielded from the probing radiation. Therefore the thermal desorption mass spectrometry technique is the most likely candidate for successful direct analysis of organic compounds in particulate matter. This technique can yield quantitative data. Results obtained on the National Bureau of Standards SRM 1648 generally duplicated those obtained by extraction procedures, but thermal desorption is more efficient. It was shown that significant quantities of polycyclic aromatics with heteroatoms, which are generally missed by the usual extraction-GC-MS technique, are present in particulate matter. Whether these occur in nature or were formed on the particles after sample collection cannot be ascertained at this time. However, their presence in such abundance needs to be addressed in any overall protocol involving extraction and subsequent GC-MS analysis.

Some preliminary experiments with a state-of-the-art quadrupole mass spectrometer have indicated that the number and quantity of organic species in particulate matter may be even higher than indicated by the mass-limited scans made with the quantitative direct probe mass spectrometric technique.

It is recommended that direct probe thermal desorption mass spectrometer studies should be continued in order to better define the limitations of the technique and to develop temperature programming which will enhance thermal fractionation of organic species. It does not seem possible at this time to fully identify and quantify all the thermally desorbed species in particulate matter. Consequently, future efforts should be directed toward simplification of the mass spectra by careful temperature control. Possible simplification in compound identification should be explored through the utilization of chemical ionization with several different reagent gases. Additional studies directly comparing the thermal desorption/MS approach with conventional extraction/GC or GC/MS approaches should be conducted.

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*The complete report, entitled "Survey of Direct Analysis Methods for Organic Compounds in Particulate Matter," (Order No. PB 84-154 723; Cost: \$10.00, subject to change) will be available only from:*

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