



Project Summary

Fourier Transform Infrared Spectrometry of Ambient Aerosols

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Fourier transform infrared (FTIR) spectrometry has been evaluated as a method for determining the concentration of selected species present in ambient aerosols collected on Teflon[®] filters. The filters are analyzed by transmission measurements after collection of the fine fraction (< 2.5 μm diameter) of the ambient particles on 2 μm pore size Teflon filters. The spectra of the blank filters are subtracted from the spectra of the loaded filters and the area of the specific absorbance bands for ammonium, nitrate, and sulfate are measured and compared to calibration curves. The filter orientation must be maintained for all measured infrared spectra.

Calibration curves were developed for sulfate and ammonium nitrate from measurements of laboratory-generated particles. The lower limit of detection (LLD) for laboratory-generated sulfate, calculated from measurements of the 620 cm^{-1} absorption band, is 1.7 $\mu\text{g}/\text{cm}^2$ (3σ). The LLD for the sulfate band at 1117 cm^{-1} is 0.2 $\mu\text{g}/\text{cm}^2$; however, this band cannot be used in the analysis of ambient aerosol samples because of spectral interferences. The LLD for laboratory-generated ammonium nitrate is 1.32 $\mu\text{g}/\text{cm}^2$. Multicomponent analysis methods were developed to analyze ammonium nitrate in the presence of ammonium sulfate.

Ambient aerosols were collected during the Carbonaceous Methods Species Methods Intercomparison (CARB) study. The filters were analyzed for sulfate by both FTIR and Ion Chromatography (IC). There is good agreement between sulfate analysis by IC and analysis of the FTIR transmission spectra of the air filters. The LLD for ambient sulfate was measured to be 5.8 $\mu\text{g}/\text{cm}^2$. If filter orientation is maintained the LLD is estimated to be 1 - 2 $\mu\text{g}/\text{cm}^2$.

The CARB study samples were also analyzed for elemental carbon using FTIR. Intercomparisons were made with results obtained from the analysis of co-collected quartz filter samples using a thermal combustion method of analysis. Good correlation was found between the infrared absorbance in the 650 - 666 cm^{-1} region of particles collected on Teflon filters and the elemental carbon determined from analysis of the quartz filters. Attempts to develop a direct elemental carbon calibration standard on Teflon filters were unsuccessful. It was concluded that calibrations must be made with co-collected air samples on quartz filters analyzed by thermal methods.

The chemical interactions on the filter between ammonium nitrate and ammonium sulfate were studied. It was determined that both compounds can interact to form the nonvolatile mixed salts $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ and $3\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$. NH_4NO_3 was found to react on the filter with NaCl to form NaNO_3 and volatile NH_4Cl . A procedure based on

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this reaction is proposed as a method to retain nitrate ion on Teflon filters.

In order to analyze large numbers of filter samples, the FTIR spectrometer was modified by the addition of an automatic sample changer. The sample changer compartment accepts the filter carousel from a Sierra/Anderson model 245* automated dichotomous sampler. The motion of the sample changer is completely controlled by the FTIR computer.

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

The collection and analysis of ambient aerosols is an important means of studying the chemistry of the troposphere. The major constituents of the fine fraction ($< 2.5 \mu\text{m}$ diameter) of the particulate matter in the atmosphere are ammonium sulfate, ammonium nitrate, and elemental and organic carbonaceous particles. Knowledge of the origins, interaction, and deposition of these compounds is important in the study of visibility degradation, atmospheric chemistry, acid deposition, and the effects of these particles on human health and terrestrial ecology.

Ambient aerosols are typically collected with dichotomous air samplers which collect particles in two size fractions. The fine fraction particles are $< 2.5 \mu\text{m}$ in diameter and the coarse fraction particles are in the $2.5 - 15 \mu\text{m}$ diameter size range. The size fractions correspond to the bimodal distribution of particles sizes found in the atmosphere. The particles are collected on various filter media including Teflon, Nylon, quartz, and paper filters. The choice of filter media depends, among other things, upon the compounds to be measured, on the analysis technique to be used, and the cost of the filters.

There are a number of chemical analysis techniques available to measure the concentrations of elements and compounds collected on air filters. Sulfate and nitrate ions collected on the filters are typically measured using ion chromatography. Ion chromatography is a very sensitive but destructive analytical technique for the determination of sul-

fate, nitrate, and a number of other ions. The method requires liquid extraction, followed by separate analysis of cations and anions, and provides no direct information concerning compound speciation of the ions. In addition, the extraction procedure can alter the species found on the filter.

Another method for determining sulfate collected on filters is x-ray fluorescence (XRF) analysis. This nondestructive method of analysis has been used in an automated system to determine elemental sulfur, as well as other elements, deposited on Teflon filters. Sulfate concentrations can be inferred by assuming that all of the sulfur is in the form of sulfate. Ion chromatography analysis for sulfate has been compared to XRF analysis for sulfur on Teflon air filters and the two methods have been shown to provide equivalent results for sulfate. X-ray fluorescence provides no information concerning nitrate deposition due to the low energy of the characteristic nitrogen x-ray emission.

X-ray diffraction is a nondestructive technique that can provide for compound identification. It is difficult to obtain quantitative results using x-ray diffraction for two reasons: (1) The sensitivity of this technique is relatively low. Consequently, high particle loadings are required to obtain adequate measurements for accurate compound identification. High particle loadings introduce the possibility of chemical reactions between particles concentrated on the filter. (2) Water in the sampled air can promote recrystallization of particles on the filter. This introduces a preferred orientation in the sample which will change the peak ratios in the diffraction signals causing difficulties in calibration.

Recently, another method for particle analysis on Teflon filters has been reported by other researchers who have shown that ammonium and sulfate can be measured directly on Teflon filters using FTIR transmission spectrometry. Their results showed the equivalence of XRF and FTIR spectroscopy for the quantitative determination of sulfate. They also reported quantitative measurements of the ammonium cation. In addition to the discrete absorption bands associated with the vibrational modes of specific molecular species, the mid-infrared spectrum of these ambient aerosols shows continuous absorption across the entire spectrum which is characteristic of carbonaceous particles. To the extent that a relationship between this absorption and the elemental carbon

content can be established, a method for nondestructive automated analysis of carbon particle concentration simultaneously with that for sulfate, ammonium, and nitrate particles could result. Finally, this technique is appealing because it makes use of a common filter media. Teflon, is nondestructive, requires no sample preparation, is amenable to automation, and can provide simultaneous analysis of compounds that typically require different types of analysis on different filter media.

This report describes an experimental program intended to build on previous work reported in the literature, where a number of suggestions are proposed to improve lower limits of detection for sulfate. This study has implemented and tested those suggestions. Experiments to test analytical methods to quantitatively determine sulfate, nitrate, ammonium, and elemental carbon on laboratory-generated samples and ambient samples are also described.

An FTIR spectrometer was modified with the addition of an automatic sample changing compartment. The FTIR instrument and sample changing compartment will be described; however, a detailed description of the FTIR system can be found in the operating manual accompanying the instrument.

Conclusions

Automated FTIR analysis of aerosol samples using a Nicolet model 5DXB Fourier transform infrared spectrometer has been realized with the design and construction of a specialized sample handling system. The sample compartment directly accepts the sample carousel from a commercial air sample produced by Sierra/Anderson Inc thereby minimizing sample handling. Software was developed and added to the existing data collection and analysis programs in the Nicolet FTIR to allow complete control of the position of any filter. Software was also written to analyze ambient air samples by automatically providing an optimal background subtraction and integration of absorption bands of interest of the collected particles. This instrument provides automated nondestructive sulfate analysis of up to 40 Teflon air filters with minimal sample handling and operator intervention.

Quantitative spectral analysis methods were developed to analyze sulfate in aerosols collected on Teflon filters. Laboratory experiments showed that detection limits are eight times lower for

analysis using the sulfate absorption band at 1117 cm^{-1} than for the band at 620 cm^{-1} . However, spectral interferences found in ambient samples prevented use of this former band for routine sulfate analysis. Analysis of air samples collected in Los Angeles during the California Air Resources Board CARB study showed good correlation of the FTIR method of analysis for sulfate with ion chromatography (IC) analysis of the same sample filters.

Small improvements in the detection limit for sulfate using the 620 cm^{-1} band were realized by using $2\text{ }\mu\text{m}$ pore size Teflon filters, saving reference spectra of each blank filter prior to air sampling for use during background subtraction, and maintaining the physical orientation of the filters during infrared spectral measurements. All of these practices contribute to more accurate background subtraction which leads to a more accurate measurement for sulfate. The lower limit of detection for sulfate in ambient aerosols using the 620 cm^{-1} absorption band was measured to be $5.8\text{ }\mu\text{g}/\text{cm}^2$ during the CARB study in which the filter orientation was not maintained throughout the analysis. If filter orientation is maintained, then the lower limit of detection is estimated to be $1 - 2\text{ }\mu\text{g}/\text{cm}^2$ for ambient sulfate.

Spectral analysis methods were developed to quantitatively measure ammonium nitrate in the presence of interferences due to ammonium sulfate. Ammonium nitrate measurements were accurate to within 3 - 5% after ammonium sulfate spectral interferences were removed on laboratory-prepared aerosol samples. The lower limit of detection for the measurement of ammonium nitrate was found to be $1.32\text{ }\mu\text{g}/\text{cm}^2$ for laboratory-generated samples.

A high degree of correlation was found between elemental carbon measurements on infrared spectra of ambient samples collected on Teflon filters and elemental carbon measured by thermal methods on samples collected on quartz filters. However, attempts to develop a direct elemental carbon calibration standard on Teflon filters using laboratory generated soot particles was unsuccessful. It was concluded that calibrations must be made with co-collected air samples on quartz filters analyzed by thermal methods.

The sensitivity of infrared analysis to specific compounds represents a unique advantage for performing quantitative chemical measurements of ambient aerosols. The 2:1 and 3:1 mixed salts of

ammonium nitrate and ammonium sulfate were identified on ambient filters collected during the CARB study. The Fourier transform infrared spectrometer also provides an ideal means for studying the dynamics of chemical reactions occurring on the filter. Laboratory experiments showed that nitrate ion could be trapped on the filter by reactions of ammonium nitrate with NaCl, but experiments with ambient samples were inconclusive.

Recommendations

It is recommended that this technique and instrument be incorporated into an air sampling and analysis network in order to develop an intercomparison database to further evaluate this instrument relative to other methods of analysis. This instrument can easily be incorporated into an existing air sampling network because it uses a common filter medium, Teflon, performs nondestructive analysis, and is designed to handle large numbers of samples in an automated system. Additional ambient samples are required to:

1. Determine collection parameters, such as sampling time and flow rates, to provide adequate samples for analysis within the constraints of the sensitivity of the analytical method.
2. Determine the type of spectral interferences that will occur in various sampling environments.
3. Confirm the correlation for sulfate measured by Fourier transform infrared analysis and ion chromatography.
4. Collect carbon samples on quartz filters in parallel with Teflon filter samples to develop a calibration for elemental carbon.
5. Collect a sufficient number of samples containing ammonium nitrate and carbon to develop an empirical method to determine the baseline underneath the ammonium nitrate absorption band.

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The complete report, entitled "Fourier Transform Infrared Spectrometry of
Ambient Aerosols," (Order No. PB 88-213 236/AS; Cost: \$14.95, subject
to change) will be available only from:

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