Title

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AMMONIUM SULFATE ANALYSIS ON TEFLON AIR FILTERS

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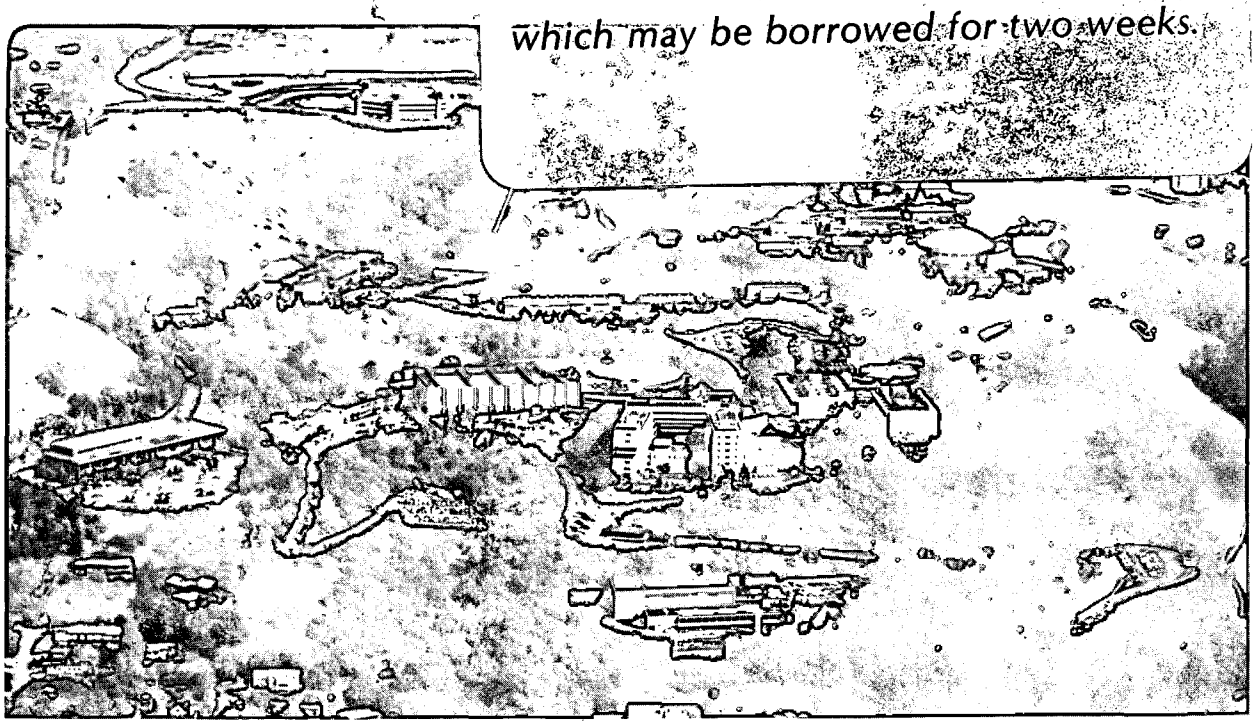

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FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AMMONIUM SULFATE ANALYSIS ON TEFLON AIR FILTERS

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Abstract

This paper reports on the improvement and automation of a method of analyzing ammonium sulfate particles collected on Teflon* membrane filters. The filters were analyzed by transmission measurements using Fourier transform infrared spectroscopy after collection with dichotomous air samplers. The spectra of the blank filters are subtracted from the spectra of the loaded filters and an integration of the 1000-1135 cm^{-1} absorbance band for sulfate leads to a lower limit of detection of 0.2 $\mu g/cm^2$ on 37 mm 2 micron Teflon filters. This corresponds to an ambient concentration of 0.1 $\mu g/m^3$ for a 24 hr, 21.6 m^3 air sample. Ammonium sulfate particulate standards were prepared by sampling the output of a laboratory particle generator. Concentrations were then determined by x-ray fluorescence analysis. An automatic sample changer was constructed which accepts the filter carousel from a Sierra/ Anderson model 245* automated dichotomous sampler. The sample changer is controlled by the FTIR computer. The analysis is nondestructive, automated, and requires no sample preparation.

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Introduction

Sulfur in atmospheric aerosols is generally present in the form of ammonium sulfate. Ammonium sulfate is important in visibility studies, SO_2-to-sulfate conversion processes, and health effects. It also comprises the major portion of the fine particle fraction (< 2.5 μm) of atmospheric aerosols.

Sulfur aerosols are collected with dichotomous air samplers[1] which collect particles in two size fractions, < 2.5 μm and 2.5-15 μm particles to reflect the bimodal distribution of inhalable particulates in the atmosphere. There have been two approaches to automating dichotomous samplers for unattended sampling over time periods of days, weeks, or months. One approach is the linear slide tray sampler developed at Lawrence Berkeley Laboratory (LBL). Another approach is a rotating sample carousel. This second approach is incorporated in the Sierra/ Anderson Series 245 automatic dichotomous sampler.

One means of analyzing the filters is elemental analysis with x-ray fluorescence (XRF)[2]. This is a nondestructive technique that measures the mass of the elemental sulfur on the filter. The chemical form of the sulfur is not determined in this measurement although it is widely assumed that it is predominantly ammonium sulfate.

Another means of analysis for ammonium sulfate is ion chromatography[3]. This is a destructive technique that requires a wet chemical extraction of the filters. It can detect as little as 0.5 μg of ammonium and sulfate ions per sample with 10-12% error for ammonium and 5% error for sulfate. The extraction procedure could alter the species found on the filter.

With the shortcomings of the previous two methods in mind, an alternate analysis technique was sought that would be 1) non-destructive, 2) sensitive, 3) could identify species collected on the filter, 4) was amenable to automation, and 5) required no sample preparation. W. A. McClenny, et al have shown that Fourier transform infrared spectroscopy (FTIR) is a feasible approach[4]. The goal of this present research was to determine if the sensitivity and accuracy of the technique could be improved for ammonium sulfate analysis. In addition, the FTIR instrument was to be configured for automated sample analysis.

Experimental Methods

The FTIR was a Nicolet model 5DXB* which is capable of 2 wavenumber resolution. It is equipped with a 36 megabyte hard disk, a 1 megabyte floppy disk, and 640 kilobytes of extra memory to provide adequate programming and file storage space. It is also equipped with a flipper mirror option to direct the infrared beam out of the main optical bench and into an automatic sample changer compartment containing the loaded Sierra sampler filter carousel. The sample compartment was not enclosed at the time of this study so no purging of laboratory air was possible for these experiments. An airtight enclosure is under construction. Additional sample focusing mirrors were mounted in the carousel compartment to direct the infrared beam through the Teflon filters and into the deuterated triglycerine sulfate (DTGS) detector. The Teflon filters are placed in circular filter holders which are in turn placed in the circular carousel. The carousel holds 20 pairs of filters. The infrared beam covers an approximately 15 mm diameter area on the Teflon filter to average any non-uniformity in particle deposition. The filters are located as close to

the detector as possible to increase the collection of light that is scattered by the filter. The carousel is mounted horizontally over the DTGS detector. There is also sufficient space to install a mercury cadmium telluride (MCT) detector if desired. A stepper motor rotates the carousel to position the filters for analysis. Another stepper motor moves the carousel horizontally to select either the inner or outer concentric circle of filters.

The Nicolet 1280* computer controls data collection, data storage, and the positioning of the correct filter in the infrared beam. It communicates to a microcomputer (BASICON model 2N, Portland, OR*) through an RS232 interface. This microcomputer controls and monitors the carousel stepper motors and microswitches and can be programmed in TINY BASIC or machine language for control applications.

Laboratory ammonium sulfate was generated for calibration purposes and to provide samples to study in the absence of soot and other compounds. Air is passed through 1.4 kg of indicating Drierite* and a series of particulate filters. This clean air is then used to aspirate a solution of ammonium sulfate in water. The liquid particles are passed up through a heater tube, a drying column, a Kr 85 particle deionizer, a final heating tube, and then into the dichotomous air sampler inlet. The laboratory-generated particles produce an absorption spectrum that is identical to that seen in actual ambient samples. Scanning electron micrographs show that the laboratory-generated ammonium sulfate particles are on the order of 2 microns in size while ambient ammonium sulfate particles are in the 0.1-1 micron range. There is also a humidifying option which was not used in these experiments. The apparatus was designed by Roland Otto and built with the help of William Searles at LBL.

Two micron pore size Teflon filters (Gelman TEFLO PTFE* with polymethylpentene support ring) were placed in the Sierra Sampler filter holders and into the carousel. Reference spectra of each blank filter were automatically taken with the number of scans varying from 10 to 1000. Each set of spectra for each filter were then stored on disk for future use in background subtraction. The blank filters were then removed from the Sierra filter holders and put into the 2 by 2 in. filter slide holders suitable for use in the linear slide tray of the LBL automated dichotomous air sampler. A Sierra automated dichotomous air sampler was not available for use. The Teflon filters were then loaded with laboratory-generated ammonium sulfate with depositions ranging from 2-50 $\mu g/cm^2$. The filters were analyzed for total sulfur using x-ray fluorescence. They were then removed from the filter slides and returned to the Sierra filter holders for analysis.

During actual air sampling, the Sierra automated dichotomous sampler samples air with a total flow rate of 1 cmh with a flow rate of 0.9 cmh for the fine particle fraction and 0.1 cmh for the coarse particles. Typical sampling periods are 6, 12, or 24 hr which represents 5.4, 10.8, and 21.6 m^3 of sampled air on the fine particle filters.

Results

Figure 1 shows an FTIR spectrum obtained from a 2 micron Teflon filter loaded with approximately 58.7 $\mu g/cm^2$ of laboratory-generated ammonium sulfate. Figure 2 shows the spectra of a 1-micron (solid line) and a 2-micron (dashed line) blank Teflon filter. The vibrational bands of importance for sulfate are from 596-640 cm^{-1} with a peak at 620 cm^{-1} and from 1000-1200 cm^{-1} with a peak at 1116 cm^{-1}. The ammonium band of interest is from 1300-1550 cm^{-1} with peak at 1420 cm^{-1}. Another ammonium band

from 2400-3520 cm^{-1} was not used because it lies in an area of significantly higher baseline noise levels. The ammonium band at 1420 cm^{-1} does not overlap any other band but it does lie in a region of maximum water absorption which would indicate that the instrument should be purged of water vapor to achieve maximum noise reduction for this band. Both sulfate bands overlap Teflon bands in the regions 1150-1250 cm^{-1} and 600-675 cm^{-1}. The Teflon band at 1116 cm^{-1}, below the two strongly absorbing Teflon bands, can clearly be seen because of the relatively high loading of this sample. The smaller sulfate band at 620 cm^{-1} can also be seen by careful comparison to Figure 2.

Figure 3 is a graph of the mass loading in $\mu g/cm^2$ as determined by x-ray fluorescence versus the integrated areas of the ammonium and sulfate bands after background subtraction using the blank filter spectra taken earlier. A linear least squares line was fit to each set of data and a clear linear relationship can be seen. The error in the slope and intercept for each line was calculated and a lower limit of detection (LLD=3σ) was determined using a propagation of errors approach[5]. Table I shows the calculated lower limits of detection for ammonium and sulfate on 37 mm, 2 micron Teflon filters for each absorption band. The last column shows the equivalent ammonium sulfate particulate concentration in air for a 24 hr sampling period (21.6 m^3 sampled air). The data in Figure 3 represents 100 spectral scans with the FTIR spectrometer.

Discussion

Figure 4 shows the spectra of an actual air sample taken in Portage, Wisconsin (note the expanded scale). The ammonium sulfate peaks are exactly the same as those found in the laboratory generated samples. This

filter spectra represents one of the higher particulate concentrations measured in this city with the majority of the measurements being much lower than the concentration on this filter. Similar filter samples from Steubenville, Ohio have much higher particulate concentrations the highest having absorbances greater than 2.0. On all air filter samples soot will be found in the fine particle fraction and will be evident as a continuous increase in the baseline of the spectra. No nitrate was found on any of the filters from Portage or Steubenville. Ammonium nitrate particles generated on our particle generator show a prominent nitrate peak at 1340 cm^{-1} overlapping the ammonium peak at 1420 cm^{-1} and a weaker nitrate peak at 828 cm^{-1}.

This technique will not work for glass fiber filters, paper filters, or Nylasorb* filters because these materials cause too much scattering and absorption. Two micron Teflon filters (Gelman TEFLO PTFE with polymethylpentene support ring) are preferred to 1 micron filters because of their lower absorption. The highest absorption peak for the 2 micron filters represents approximately 10-15% transmission while those for the 1 micron filters are totally absorbing. Teflon filters also have a remarkably simple absorption spectrum (see Figure 2). The 2 micron filters have the same collection efficiency as the 1 micron filters.

Integration of the 1116 cm^{-1} sulfate band the provides the best measure of ammonium sulfate. Analysis of the sulfate bands requires subtraction of the blank Teflon filter spectra from the spectra of the same filter after particulate collection in the air sampler. Background subtraction is not an entirely straightforward technique. Subtraction of absorbance bands is extremely sensitive to slight distortions in the spectral data. The subtraction of two spectral files with small differences in absorbance band

shapes can result in derivative-like noise far in excess of what would be expected simply by propagation of errors in the subtraction process. This effect can negate any signal-to-noise improvement obtained by increasing the number of scans on the data. Figure 5 illustrates this effect clearly by showing the result of an uneven subtraction of the two Teflon peaks at 1135-1250 cm^{-1}. This subtraction was performed on two spectra of the same blank filter after 1000 scans for each spectra. Spectral distortion may be related to light scattering effects on the detector that result from moving the filter into and out of the infrared beam between spectral scans. The subtraction artifacts can be worse if the spectra from two different filters are subtracted from each other because there can be significant absorption variability between filters. As a result of these "subtraction problems", the sulfate peak at 1116 cm^{-1} was integrated in the region from 1000-1135 cm^{-1} which is in a region removed from the subtraction artifacts due to the large Teflon absorption peaks.

The baseline noise will improve with the square root of the number of scans that are averaged. The number of scans used has to be weighed against the 1.5 sec needed per scan. The analysis for 100 scans requires about 3.5 min per filter while that for 1000 scans requires almost 27 min. The scan speed can be increased by decreasing the resolution of the scan but this would lead to greater subtraction problems. An MCT detector is both quieter per scan and has a greater scan speed at the same resolution but it has less dynamic range than a DTGS detector. This could lead to subtraction problems as well. An MCT detector has not yet been thoroughly tested for this application.

Conclusions

Fourier transform infrared transmission spectroscopy can provide an accurate and sensitive means of quantifying ammonium sulfate deposition on 2 micron Teflon filters. A necessary requirement, however, is that reference spectra be obtained and stored before sampling to be used in background subtraction. Further increases in sensitivity may be possible with the use of a mercury cadmium telluride detector. If analysis time is not a consideration, then increasing the number of scans should decrease the lower limit of detection. The instrumentation is automated and no sample preparation is required. Specific species can be observed by the presence and identification of absorbance peaks in the spectrum. The analysis is nondestructive.

Further work will consist of analyzing actual air samples and comparing these results with analysis by x-ray fluorescence and ion chromatography. Work will proceed toward quantifying the mass loading of soot as well.

Acknowledgments

We would like to thank Robert Giauque for performing the x-ray fluorescence measurements, William Searles for the mechanical construction of the sample changer, and Roland Otto for use of the particle generator.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Department of Energy to the exclusion of others that may be suitable.

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under Contract No. DE-AC03-76SF00098, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. B. W. Loo, R. S. Adachi, C. P. Cork, F. S. Goulding, J. M. Jaklevic, D. A. Landis, and W. L. Searles, "A second generation dichotomous sampler for large-scale monitoring of airborne particulate matter," Lawrence Berkeley Laboratory Report LBL-8725, (1979).

2. J. M. Jaklevic, D. A. Landis, and F. S. Goulding, "Energy dispersive x-ray fluorescence spectrometry using pulse x-ray excitation", Advances in X-ray Analysis, R. W. Gould, C. S. Barrett, J. B. Newkirk, and C. O. Rudd, eds., Kendahl/Hunt, Dubuque, IA, 1976, 19: pp 253-265.

3. E. Sawicki, J. D. Mulik, E. Wittgenstein, eds., Ion Chromatographic Analysis of Environmental Pollutants, Ann Arbor Science, Ann Arbor, MI, 1979, Volume 1.

4. W. A. McClenny, J. W. Childers, R. Röhl, and R. A. Palmer, "FTIR transmission spectrometry for the nondestructive determination of ammonium and sulfate in ambient aerosols collected on teflon filters," Atmos. Environ. 19: pp 1891-1898 (1985).

5. G. L. Long, J. D. Winefordner, "Limit of detection, a closer look at the IUPAC definition," Anal. Chem., 55(7): pp 712-724A, (1983).

Table I

Lower Limits of Detection

	Filter concentration $\mu g/cm^2$	Ammonium Sulfate 24 hours, 21.6 m^3 sample $\mu g/m^3$
Sulfate 596 - 640 cm^{-1}	1.70	0.86
Sulfate 1000 - 1135 cm^{-1}	0.20	0.10
Ammonium 1300 - 1550 cm^{-1}	0.15	0.20

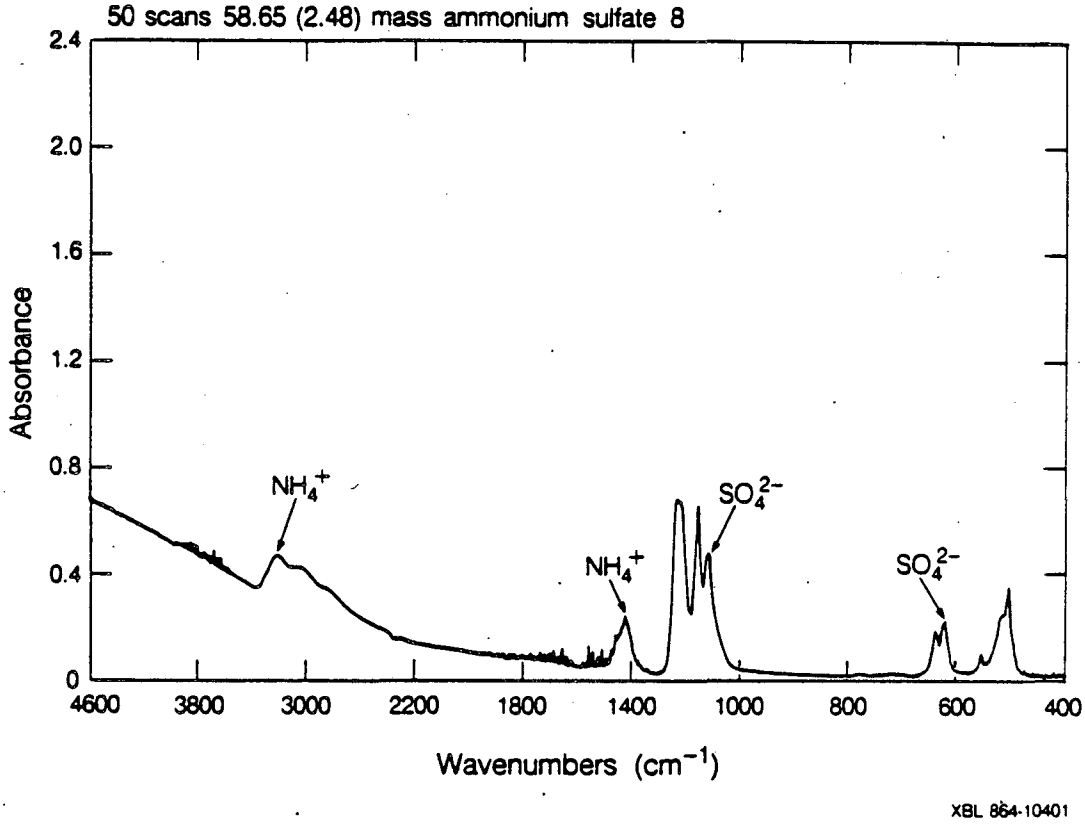

Figure 1. 70 μg/cm^2 ammonium sulfate on a 2-micron Teflon filter.

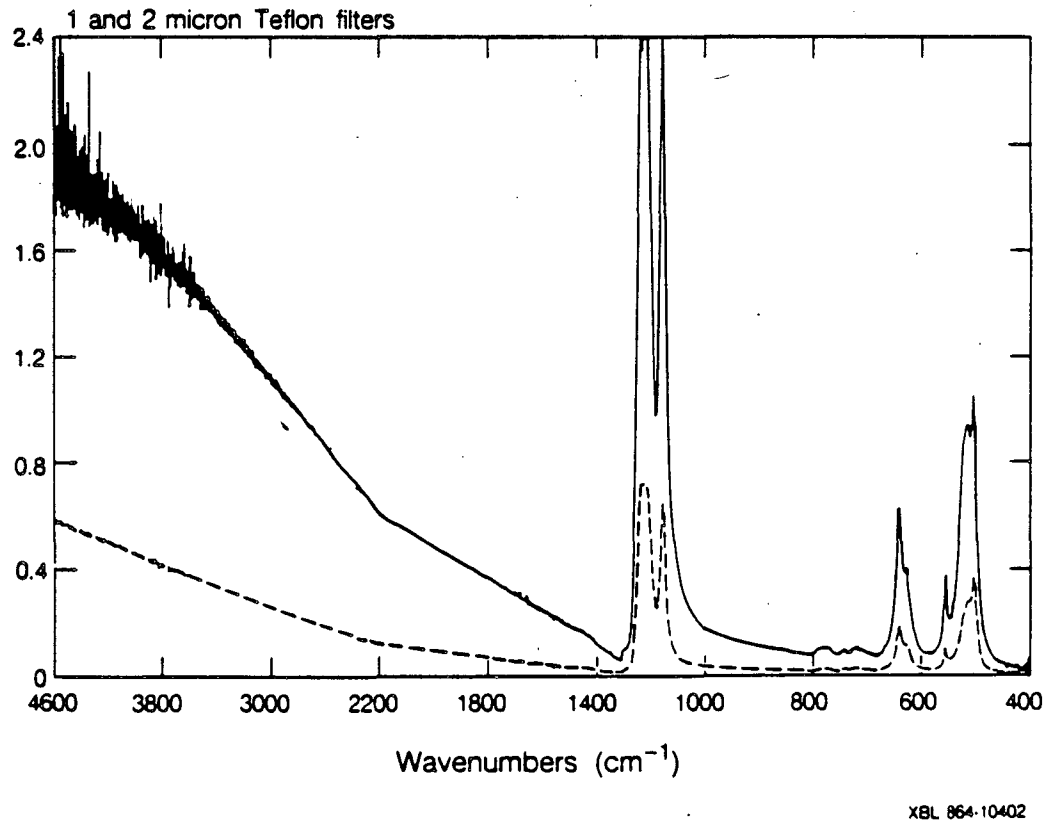

Figure 2. One-micron (solid line) and 2-micron (dashed line) blank Teflon filters.

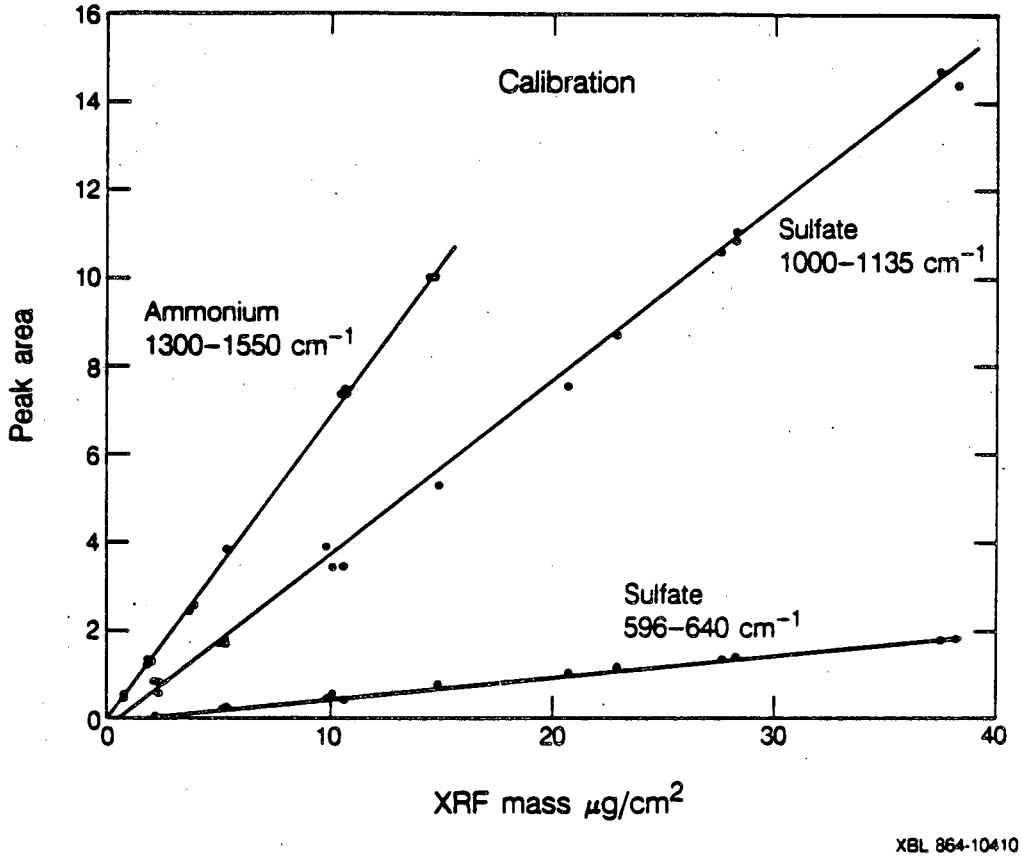

Figure 3. Calibration of ammonium and sulfate.

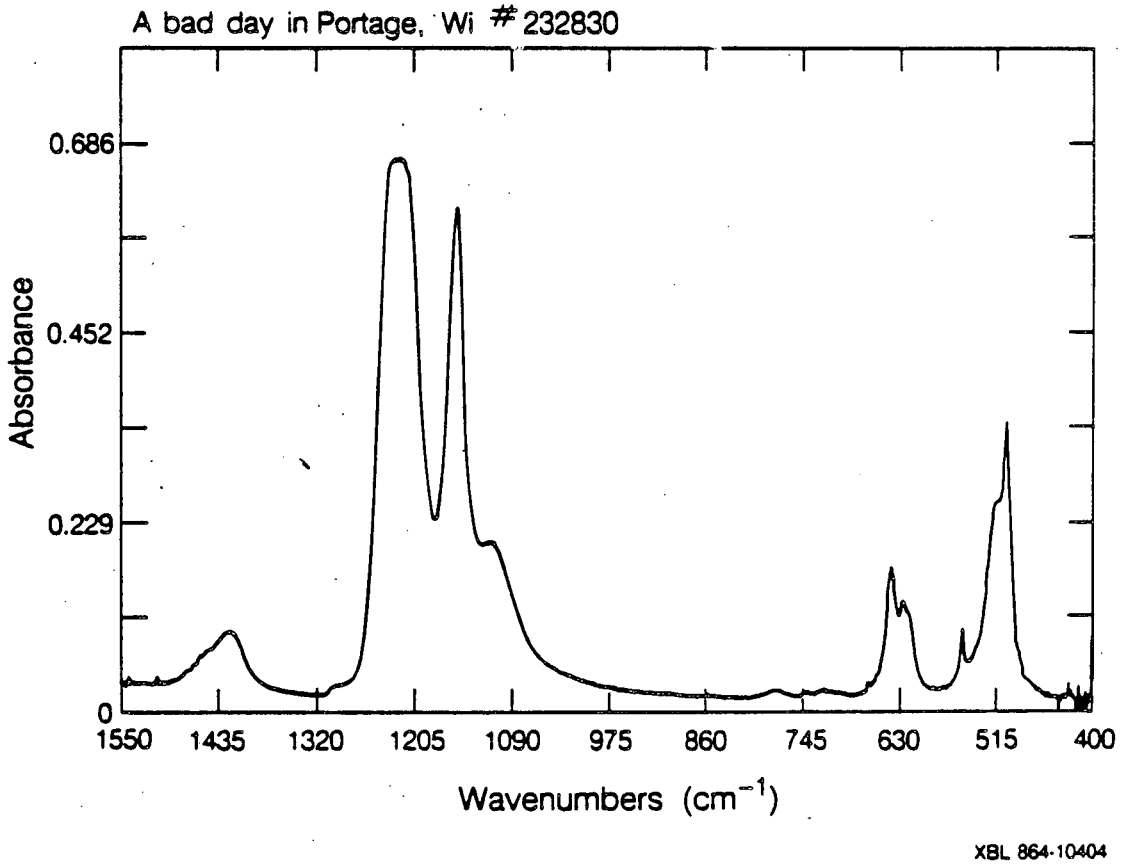

Figure 4. High ammonium sulfate loading for Portage, Wisconsin.

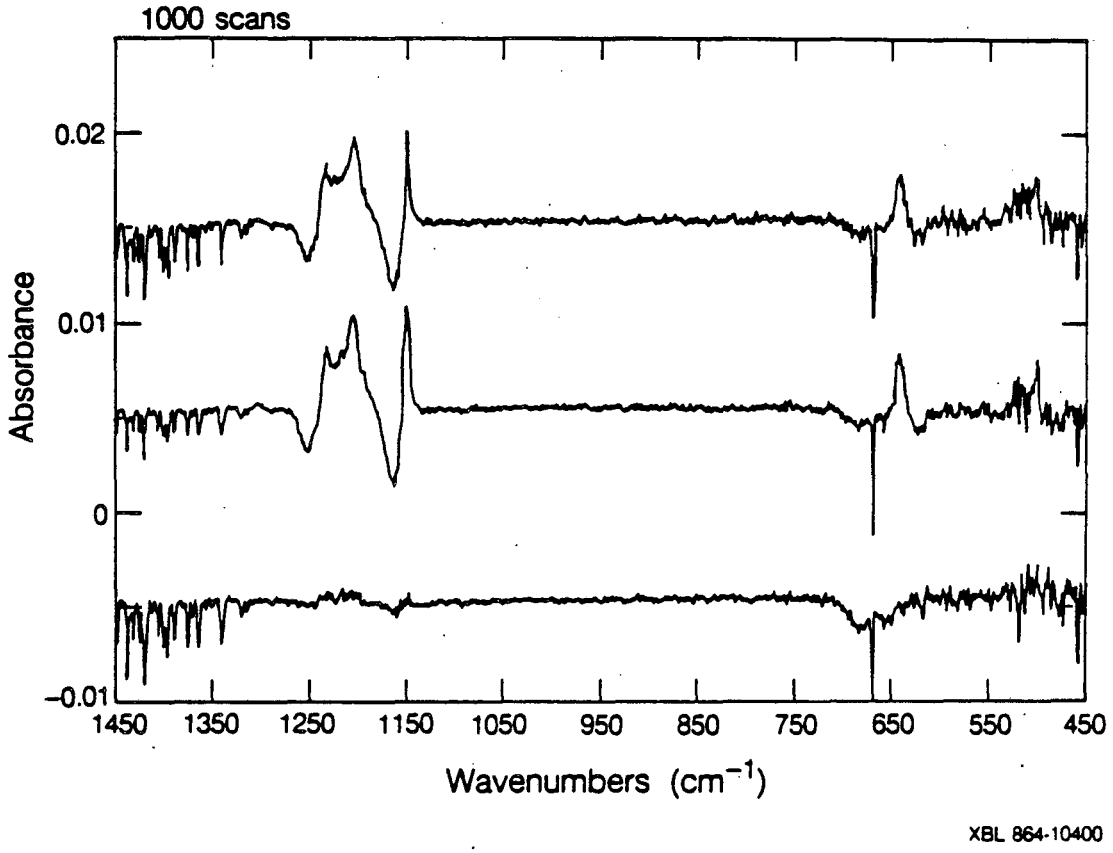

Figure 5. Subtraction artifacts due to blank Teflon filters.

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