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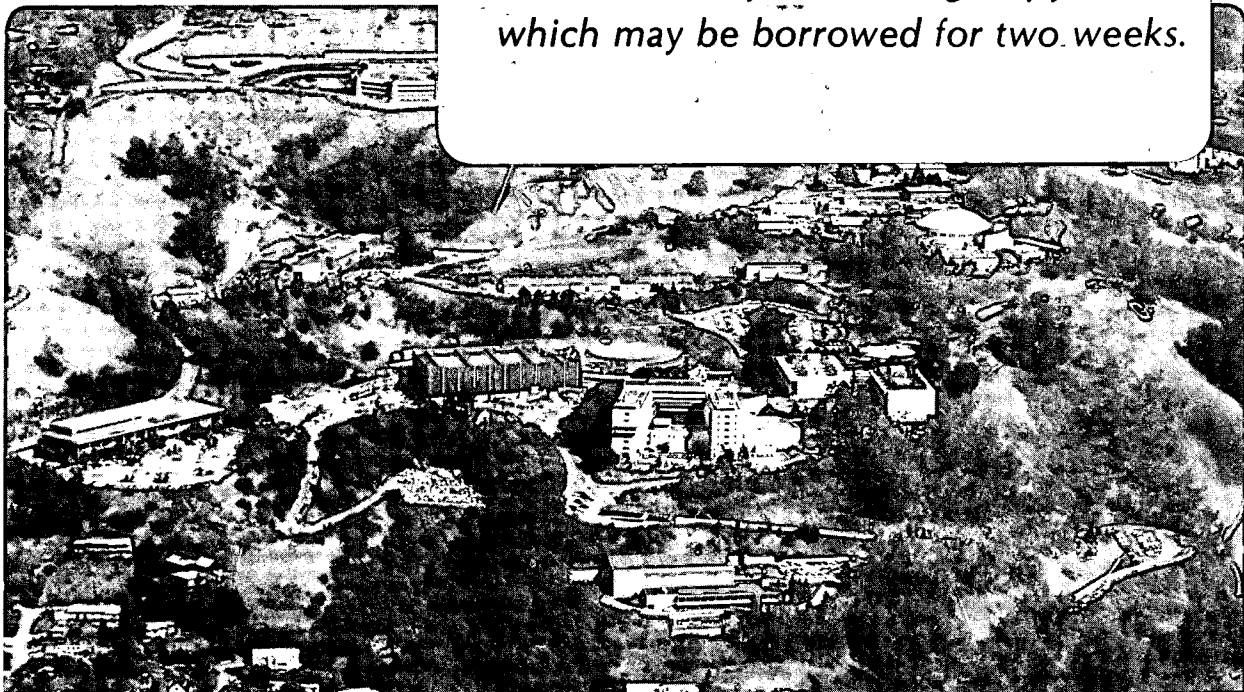
### FTIR and Ion Chromatographic Sulfate Analysis of Ambient Air Samples

M. Pollard, J. Jaklevic, and J. Howes

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FTIR AND ION CHROMATOGRAPHIC SULFATE ANALYSIS  
OF AMBIENT AIR SAMPLES

Martin Pollard and Joseph Jaklevic  
Lawrence Berkeley Laboratory, Berkeley, CA 94720 U.S.A.

James Howes  
Environmental Monitoring and Services, Inc.  
Camarillo, CA 93010 U.S.A.

ABSTRACT

Fourier transform infrared (FTIR) spectrometry has been evaluated as a method for determining the sulfate concentration of ambient aerosol particulate samples. Samples were collected on Teflon\* filters. 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 difficulties incurred during background subtraction of the infrared spectra are described.

Key word index: Aerosols, ambient; Sulfate, aerosol; Fourier Transform Infrared Spectroscopy; Ion Chromatography

## INTRODUCTION

The predominant chemical species of the fine (less than 2.5  $\mu\text{m}$  aerodynamic diameter) ambient aerosol mass is ammonium sulfate (Milford, 1987). Knowledge of the origins, interactions, and deposition of sulfate compounds is important in the study of visibility degradation, atmospheric chemistry, and their effects on human health. We will present the results of an air sampling study in which ambient air filters were analyzed for particulate sulfate first nondestructively by FTIR transmission spectrometry followed by ion chromatography (IC) analysis.

The composition of ambient air particles is determined by first sampling a known volume of air on a filter. Chemical analysis is then used to determine the identity of the particle compounds and their concentration on the filters. The ambient air concentration of the particles is then calculated from the filter mass concentration and the volume of air sampled. 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 sulfate, nitrate, and a number of other ions (Mulik et al., 1976). The method requires liquid extraction, separate analysis of cation and anions, and provides no direct information concerning compound speciation of the ions. Another method used to determine sulfate collected on filters is x-ray fluorescence. This nondestructive automated method of analysis has been developed and used successfully to determine elemental sulfur, as well as other elements, deposited on Teflon\* filters (Jaklevic, 1976). 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 (Stevens, 1978). X-ray fluorescence provides no information concerning nitrate deposition.

Recently, another nondestructive analysis method for particle analysis on Teflon\* filters has been reported. McClenny et al., (1985) have shown that ammonium and sulfate can be measured directly on Teflon\* filters using fourier transform infrared (FTIR) transmission spectroscopy. Their results showed the equivalence of XRF and FTIR spectroscopy for the quantitative determination of sulfate. The technique requires no sample preparation, is amenable to automation, and the infrared spectrum of the filter particles simultaneously provides information for ammonium, nitrate, and sulfate species as well as carbon particle loading.

Pollard (1986) investigated the sensitivity of the FTIR transmission technique using laboratory prepared ammonium sulfate particulate samples. McClenny et al. reported limits of detection that were larger than ion chromatography but lower than the average sulfate collected on samples from remote regions assuming a  $21.6 \text{ m}^3$  sample volume. Their measurements were based on the absorption of a weakly absorbing sulfate band at  $615 \text{ cm}^{-1}$ . Pollard showed that the use of a more strongly absorbing sulfate band at  $1115 \text{ cm}^{-1}$  improved the sensitivity of the technique by a factor of 8 for laboratory prepared ammonium sulfate samples. This improvement was achieved by incorporating suggestions by McClenny to (1) analyze each filter prior to sampling and (2) use 2 micron pore size filters rather than the 1 micron filters examined by McClenny et al. Both of these actions improved background spectral subtraction by more closely matching reference spectra to sample spectra and reducing the magnitude of the absorbance of the interfering Teflon\* absorption bands.

The purpose of this study was to (1) apply analytical methods developed in the laboratory to improve the sensitivity of the FTIR technique to sulfate on freshly collected field filter samples, (2) investigate the effects of co-collected volatile compounds, such as ammonium nitrate and carbonaceous compounds, not present on laboratory standards or archival samples examined by McClenny et al., (3) develop automated methods of sample manipulation and analysis for use in large sampling studies, and (4) establish the equivalence of the measurement of sulfate between FTIR and IC analysis. In pursuit of these goals we participated in the Carbonaceous Species Methods Intercomparison (CARB) Study conducted by the California Air Resources Board during August of 1986 in Glendora, CA. The primary purpose of the CARB study was to collect and analyze aerosol carbon species. In addition to collecting air samples for carbon species analysis, air samples were collected on Teflon\* filters and analyzed for sulfate, nitrate, and ammonium ions using ion chromatography. The FTIR transmission method was used to analyze the same filters for sulfate.

#### EXPERIMENTAL SECTION

Ambient air samples were collected by Environmental Monitoring and Services, Inc. (EMSI) at Citrus College, in Glendora, CA during the time period August 12 - 21, 1986. The samples were collected for the 12-hour intervals, 0800-2000 and 2000-0800 each day. Three air samplers, operated in parallel, collected 108 samples of which 30 were analyzed by both ion chromatography (Howes, 1987) and fourier transform infrared spectroscopy. In addition to these filters there were five field blanks analyzed by FTIR as well. All filters were analyzed at the conclusion of the air sampling study.

The air samplers were modified Sierra/Andersen Model 245\* automated dichotomous samplers. The modification consisted of removing the virtual impactors and replacing them with identical inlets. Each inlet was equipped with a cyclone to admit particles  $\leq 2.5 \mu\text{m}$  aerodynamic diameter. The regulated flow rates were approximately 24 lpm. The air filters were 37 mm diameter, 2 micron pore size Teflon\* membrane filters supported on a polyolefin support ring. The filters were supported in circular polypropylene filter holders. The collection area of the filters is  $6.38 \text{ cm}^2$ . The filters, in their filter holders, are placed in a circular sample carousel which is then mounted in the air sampler. The air sampler rotates the sample carousel automatically to place a pair of filters at the air inlets at the beginning of each sampling period. During the CARB study the samplers were operated in the manual mode. All of the filters were analyzed at the conclusion of the CARB Study. The filters were analyzed nondestructively by FTIR prior to ion chromatography analysis.

The infrared analyses were performed on a Nicolet 5DXB\* Fourier Transform Infrared Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Spectra were taken in dry purge air using a  $2 \text{ cm}^{-1}$  resolution over the spectral range  $4600 - 400 \text{ cm}^{-1}$  and signal-averaged for 100 scans. Spectra of the blank Teflon\* filters were measured before air sampling to be used as background reference spectra. The filter spectra were measured again after air sampling and before IC analysis. The sample filters were measured with the particle loaded side facing the infrared beam. The ratio of the spectra to the open-beam spectra at the time of measurement was calculated and stored as absorbance data files.

The FTIR spectrometer was modified for automatic sample analysis by directing the infrared beam out the side of the spectrometer into a chamber containing the filter samples and the DTGS detector. The sample wheel from the Sierra/Andersen\* dichotomous sampler can be mounted directly in the sample changer with no handling of the filters. A pair of stepper motors, under direct program control from the FTIR computer, can rotate and horizontally position the sample wheel to move any filter into the infrared beam for analysis. The infrared beam was directed down through the filters in the sample carousel to the detector underneath the carousel. The entire chamber can be sealed and flushed with purge air if desired.

Analysis of the filter spectra for sulfate concentration requires spectral background subtraction because both sulfate bands, at  $615\text{ cm}^{-1}$  and  $1115\text{ cm}^{-1}$ , overlap absorption bands of the Teflon\* substrate. Correction for substrate background is achieved by subtracting the spectrum of the blank filter from the spectrum of the same filter after air sampling. The resulting spectrum is due only to absorption of the collected particles and not due to absorption of the Teflon\* filter. Figure 1 is the mid-infrared spectrum of an aerosol sample obtained during the CARB Study. The dashed line is the spectrum of the blank Teflon\* filter before sampling. The absorbance scale for this spectrum is on the right side of the figure. The solid line is the spectrum of the collected aerosol particles after subtraction of the Teflon\* filter background spectrum. The absorption scale for this spectrum is on the left side of the figure. The ammonium, nitrate, and sulfate absorption bands are indicated in the figure. The overlap of the sulfate and Teflon\* absorption bands can be seen by comparing the two spectra in Fig. 1.

The subtraction, on the Nicolet 5DXB FTIR\*, is performed according to the following formula:



$$\text{RESULT SPECTRUM} = \text{SAMPLE SPECTRUM} - \text{FCR} * \text{REFERENCE SPECTRUM}$$

where the variable FCR is a scale factor approximately equal to one. The variable FCR is determined by an iterative procedure. The subtraction is complete when all of the absorption due to the reference background has been nulled. This requires that there be a region where the absorbance due only to Teflon\* can be measured. In spectra of actual ambient filter samples there are no regions free of absorption due to collected compounds. Carbon compounds, organic and inorganic, absorb over the entire mid-infrared region of  $4600 - 400 \text{ cm}^{-1}$ . This means that the criteria for the determination of the completion of the background subtraction must account for the overlapping carbon absorption.

The subtraction criteria are described as follows: in the region  $700 - 400 \text{ cm}^{-1}$ , the carbon absorbance is assumed to be linear with increasing wavenumber. Since the Teflon\* band at  $514 \text{ cm}^{-1}$  does not interfere with any sulfate, nitrate, or ammonium bands, this band can be subtracted to yield a linear background due only to the carbon absorption spectrum. The carbon absorption in the region of the Teflon\* band is assumed to be a linear interpolation of the carbon absorption on both sides of the  $514 \text{ cm}^{-1}$  Teflon\* band. This interpolation is calculated to be the least squares fit line to the data in the region  $572 - 567 \text{ cm}^{-1}$  and  $480 - 447 \text{ cm}^{-1}$  (regions A and B in Fig. 2). The FCR value is varied until the area of the  $514 \text{ cm}^{-1}$  band is zero above the carbon spectrum. Figure 2 illustrates the background subtraction procedure. After each iteration of the FCR value, a linear least squares fit line is calculated for the data in regions A and B. The area of the spectrum above this line and between regions A and B is calculated. In curve 1 a value of  $\text{FCR} = 1.1000$  subtracts too large a multiple of the Teflon\* absorption band resulting in a negative area. FCR

is decreased in curves 2 and 3 until the area above the curve is zero as is true for curve 3 in Fig. 2.

Following subtraction of the background due to the substrate the area of the sulfate bands above the carbon absorption baseline was calculated for the bands at  $615 \text{ cm}^{-1}$  and  $1115 \text{ cm}^{-1}$ . The baseline under the  $615 \text{ cm}^{-1}$  absorption band was calculated to be the least squares fit line to the absorption data between  $670 - 660 \text{ cm}^{-1}$  and  $590 - 565 \text{ cm}^{-1}$ . The baseline under the  $1115 \text{ cm}^{-1}$  sulfate absorption band was calculated to be the least squares fit line to the absorption data in the region  $815 - 680 \text{ cm}^{-1}$ . The sulfate band areas were used to calculate a sulfate filter concentration from a sulfate calibration curve.

Calibration standards were prepared by depositing particles of ammonium sulfate on blank Teflon\* filters. The particles were generated using a constant output collision nebulizer (TSI model 3075\*) (May, 1973). The ammonium sulfate solution was prepared by mixing  $2 \text{ mg ml}^{-1}$  of the reagent grade compound with water. The particles from the nebulizer are dried with a silica diffusion dryer and are charge neutralized in a Kr-85 diffusion discharger. The aerosol from the particle generator was deposited on the filter through the fine particle ( $2.5 \mu\text{m}$  cut point) inlet of a dichotomous air sampler. The sulfate concentration on the filters was inferred from sulfur measurements using x-ray fluorescence analysis. The sulfate concentration of the calibration standards varied between  $2 - 38 \mu\text{g cm}^{-2}$ . Independent calibration curves were calculated based on the band area associated with the sulfate absorbance bands at  $1115 \text{ cm}^{-1}$  and  $615 \text{ cm}^{-1}$  respectively. There is no overlapping soot background to consider in the analysis of the laboratory standards but the same algorithm was used to perform background subtraction and area calculations as was used for the field samples.

Following the FTIR analysis, the filters were sent to EMSI for ion chromatography analysis. The sulfate analysis (Howes, 1987) was performed on a Dionex\* model 10 ion chromatograph with an anion separator column and an anion fiber suppressor. One hundred microliters of ethyl alcohol was pipetted onto each filter to promote wetting during the extraction procedure. The Teflon\* filters were extracted in 15 ml. of deionized water for 30 minutes in an ultrasonic bath. Extraction reagent blanks were prepared for every 30 samples. Filter spikes for  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NH}_4^+$  were prepared for every 30 samples. For the sulfate levels found on the ambient filter samples, the accuracy of the IC analysis was 2% with a precision of  $\pm 2\%$ . Assuming a 5% sampling error, the overall IC measurement error is approximately 5.4%.

## RESULTS AND DISCUSSION

A number of problems are encountered when we apply the FTIR analysis protocol to ambient aerosol samples. The ambient spectrum in Fig. 1 illustrates the difficulties in the analysis of sulfate due to interferences from co-collected compounds on the filters. The major components of the fine fraction of ambient air particles collected on Teflon\* air filters are ammonium sulfate, ammonium nitrate, and both elemental and organic carbonaceous particles. Distinct ammonium, sulfate, nitrate, and Teflon\* bands are visible in the spectra of Fig. 1. Each sulfate absorption band is seen to overlap Teflon\* bands. The nitrate absorption band overlaps both a Teflon\* band and the ammonium band. Carbonaceous particles absorb continuously across the entire spectrum and can be seen as the nonzero baseline gradually rising in absorption with increasing wavenumber.

To achieve an accurate band integration two steps must be accomplished. First it is necessary to achieve a correct background subtraction of the

spectrum of the blank Teflon\* filter from that of the sample filter. Second, the carbon baseline must be estimated underneath the sulfate peak.

Two difficulties were encountered in the attempt to achieve an accurate area integration of the  $1115\text{ cm}^{-1}$  sulfate band which were not encountered during the development of analytical techniques in the laboratory. The first is attributable to absorption in this region due to carbon compounds. Unlike the linear behavior of the carbon spectrum across the  $514\text{ cm}^{-1}$  Teflon\* band, the carbon spectrum cannot be linearly interpolated across the  $1300 - 1000\text{ cm}^{-1}$  region. This can be seen in Fig. 1 by noting that the carbon baseline increases linearly between  $1000 - 400\text{ cm}^{-1}$  but it has decreased in absorbance at  $1525\text{ cm}^{-1}$  just above the ammonium band. Infrared measurements of propane soot deposited on KBr pellets also show variation in the spectra of soot in this region consistent with the spectra of the collected components in the CARB samples. There is also evidence in the literature of this structure in the infrared spectra of elemental carbon (Friedel, 1970; Akhter, 1985). It should also be noted that the carbon absorbance in Fig. 1 is due to both elemental and organic carbon. Functional group absorption due to organic compounds could also influence the variation of total absorbance in this region.

The second difficulty is due to the inability to determine the point at which the Teflon\* bands in the  $1300 - 1000\text{ cm}^{-1}$  region have been completely nulled in the subtraction process. Laboratory experiments on blank filters indicate that the scale value (FCR) that nulls the  $514\text{ cm}^{-1}$  Teflon\* band does not necessarily null the Teflon\* bands in the  $1300 - 1000\text{ cm}^{-1}$  region. Figure 1 shows that the nitrate band also overlaps the Teflon\* bands. Since the nitrate and carbon spectra are variable and unknown, it is impossible achieve a successful background subtraction because there are no

interference-free Teflon\* bands in this region to serve as a background reference in the subtraction process.

In a previous study (McClenny et al., 1985), the difficulty of completely subtracting the strong Teflon\* absorbance bands in the  $1300 - 1000 \text{ cm}^{-1}$  region for 1 micron pore size filters was described. It was suggested that this problem might be mitigated by use of less absorbing 2 micron filters. The subtraction difficulties encountered using 1 micron pore size filters can be attributed to the fact that absorbance subtraction is extremely sensitive to small deviations in the absorbance values of the spectra (Hirschfeld, 1975a, 1975b, 1976) particularly for strongly absorbing bands. The 2 micron pore size filters do not absorb as strongly as the 1 micron pore size filters because of the greater mass of the 1 micron filters. While it is true that the subtractions are better for the 2 micron filters, the ultimate limitation in the analysis of ambient filters using the  $1115 \text{ cm}^{-1}$  sulfate band is not the fundamental difficulties of background subtraction but the uncontrolled variability of spectra due to co-collected nitrate and carbon found in ambient air samples.

The background subtraction techniques previously described for the  $615 \text{ cm}^{-1}$  region were applied to the samples collected during the CARB study. Figure 3 is a histogram of data for the daily sulfate concentrations determined by both ion chromatography and fourier transform infrared spectroscopy. The FTIR sulfate concentrations in Fig. 3 are based on the area measurement of the weak sulfate absorption band at  $615 \text{ cm}^{-1}$ . The sampling periods are labeled for days 2 - 10. The daytime sampling periods are labeled with the number 6 and the nighttime sampling periods are labeled with the number 7. The first sampling period began during the day of August 12, 1986. All measurements are corrected to standard conditions of  $25^\circ\text{C}$  and 760 mm Hg.

It is clear from Fig. 3 that both the FTIR and the IC measurements follow the same trends throughout the entire study period. From the beginning of the study through day 6 the agreement between the FTIR and IC measurements is very good. The differences between the two measurements is less than 10%. From day 7 through the end of the study almost all of the FTIR measurements are  $2 \mu\text{g m}^{-3}$  lower than the IC measurements and since the absolute sulfate concentrations were low during this period of the study, the relative differences between the FTIR and IC measurements is quite high, exceeding 100% in some cases. All of the filters, both the calibration filters and the CARB study samples, were analyzed by the same objective criterion in the automated background subtraction program written for the FTIR computer. The consistently low FTIR measurements might indicate a bias in the calibration but this is ruled out because there is no such bias in the measurements during the first part of the study. The absolute error becomes greater as the concentration of the sulfate in the atmosphere decreased indicating a high lower limit of detection for the FTIR method of analysis. In fact measurements of the field blanks showed a large variation in the area measured in the  $615 \text{ cm}^{-1}$  band region. A calculation, based on the calibration spectra and the five field blanks from the CARB study, showed that the lower limit of detection for the determination of sulfate in the atmosphere was  $5.8 \mu\text{g m}^{-3}$ . The last ten samples measured by ion chromatography were below the calculated lower limit of detection for the FTIR analysis using the  $615 \text{ cm}^{-1}$  absorption band.

Sulfate concentrations were also calculated using the  $1115 \text{ cm}^{-1}$  band after background subtraction based on the  $514 \text{ cm}^{-1}$  Teflon\* band. The  $514 \text{ cm}^{-1}$  Teflon\* band was used because of the difficulties of subtracting the Teflon\* bands in the  $1300 - 1000 \text{ cm}^{-1}$  region described earlier. A

carbon baseline underneath the sulfate peak was calculated based on an interpolation of the carbon data in the region  $815 - 680 \text{ cm}^{-1}$ . There was poor agreement between ambient sulfate concentrations calculated using this band and with the ion chromatography analysis indicating that the  $514 \text{ cm}^{-1}$  Teflon\* absorbance band is too far from the  $1115 \text{ cm}^{-1}$  sulfate band to provide an adequate background subtraction as was discussed earlier. The results for the  $1115 \text{ cm}^{-1}$  sulfate band are not presented here.

The large variation in the field blank measurement values indicated problems that can lead to a high lower limit of detection. One possible source of the variation in the field blanks is the scattering effects due to filter orientation. Electron micrographs of Teflon\* filters show that the filters do not have a uniform fibrous structure but rather a banded structure consisting of thick Teflon\* fibers with smaller interconnecting Teflon\* fibers. The thick fibers defined a specific orientation for each filter. There is significant scattering due to the blank Teflon\* filter above  $1500 \text{ cm}^{-1}$ . The effects of filter orientation on measurements at the  $615 \text{ cm}^{-1}$  sulfate band region were investigated by measuring the spectra of a single blank filter at various relative orientations from  $0 - 90$  degrees. It was determined that the variation in the measured area for subtracted spectra of randomly oriented filters was five times that for subtracted spectra where filter orientation was maintained. The areas were determined with the same automatic background subtraction program used to analyze the calibration spectra and the CARB field samples. Maintaining filter orientation throughout the analysis procedure could lower the lower limit of detection to  $1 - 2 \mu\text{g m}^{-3}$ . There are distinctive features to the subtraction spectra of filter measured at  $90$  degrees relative orientation to each other. These features were observed in a number of the subtraction spectra of the CARB

study samples confirming that this problem does exist in the analysis of the CARB study samples.

There is good correlation between the sulfate measurement obtained by integrating the  $615\text{ cm}^{-1}$  sulfate band and sulfate measured by ion chromatography. Figure 4 is a scatter plot of the FTIR sulfate measurements and the ion chromatography sulfate measurements on the thirty ambient air filters as shown in Fig. 3. The regression line in Fig. 4 is calculated from the twenty data points above the FTIR detection limit. The regression equation has a slope of  $B = 0.92$ ,  $\sigma_b = 0.1$ , an intercept of  $A = 1.26$ ,  $\sigma_a = 0.94$ , and a linear correlation coefficient of 0.912. The cause of the significant non-zero intercept is unknown.

#### CONCLUSIONS

There is good agreement for measurements of particulate sulfate on Teflon\* air filters using fourier transform infrared transmission spectroscopy and ion chromatography analysis. The sensitivity of the FTIR absorbance measurements were not adequate to accurately measure all of the samples collected during the CARB study. The lower limit of detection, based on the  $615\text{ cm}^{-1}$  band, could be improved by a factor of 4 - 5 by maintaining filter orientation during measurement of the reference and sample spectra. This should also improve the accuracy of measurements above the lower limit of detection as well. An improvement of this magnitude in the detection limit would have brought the FTIR measurement sensitivity low enough to accurately measure ambient concentrations throughout the CARB study. The stronger sulfate absorbance band at  $1115\text{ cm}^{-1}$  could not be used because of spectral interferences of components co-collected on the filters and the practical limitations of spectral absorbance subtraction. The suitability of this



technique, as well as all techniques, depends on the sampling scheme used. Longer sampling times and higher sampler flow rates would provide adequate samples for accurate measurements for typical ambient concentrations.

There is an abundance of information available in the infrared spectra shown in Fig. 1. In addition, it should be possible to quantitatively and simultaneously measure ammonium, nitrate, and possibly elemental carbon concentrations on the filter as well as sulfate. The overlapping nature of the spectra make simple absorbance subtraction analysis techniques unsuitable as an analysis method. A number of multicomponent analysis techniques are being investigated to aid in the analysis of ammonium and nitrate.

An appealing feature of this instrument is the automated analysis capabilities. The instrument is capable of direct, simultaneous measurements of spectra of components collected on the filters, automated analysis, and minimal sample handling for large number of samples. Both sample manipulation and background subtraction procedures have been successfully incorporated into the instrument for a fully automated analysis. This feature could prove to be extremely useful for filter analysis in large sampling networks.

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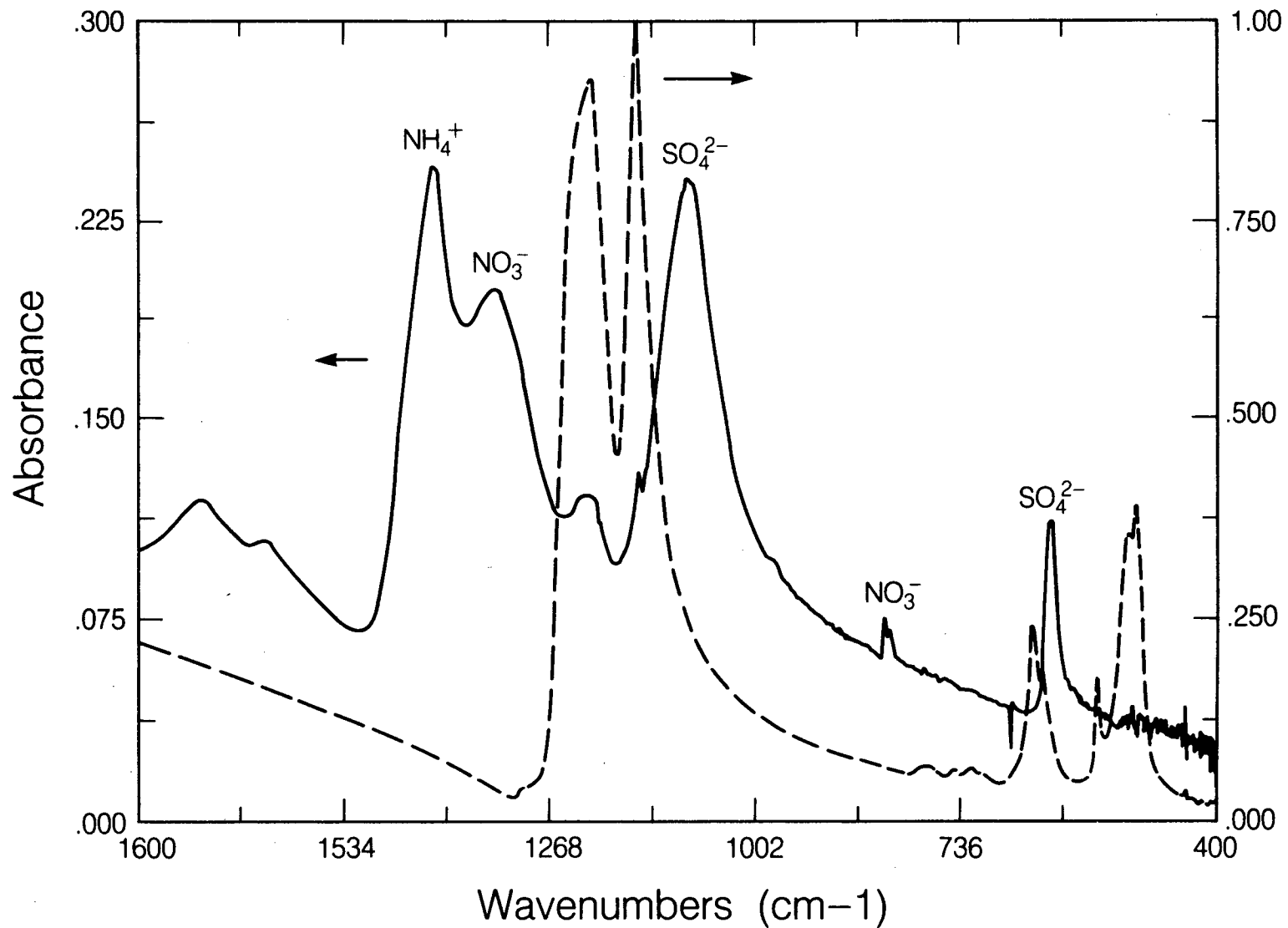
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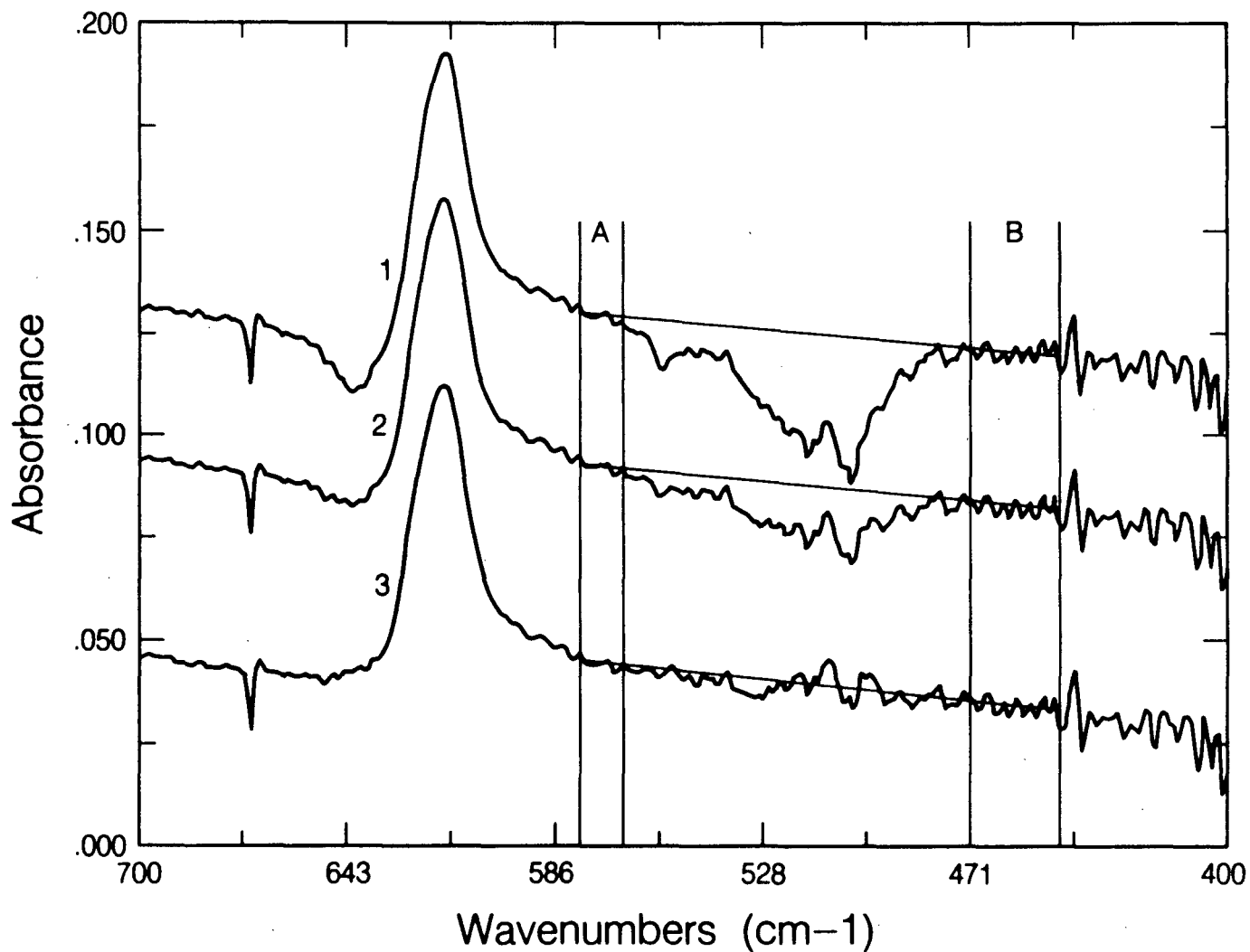
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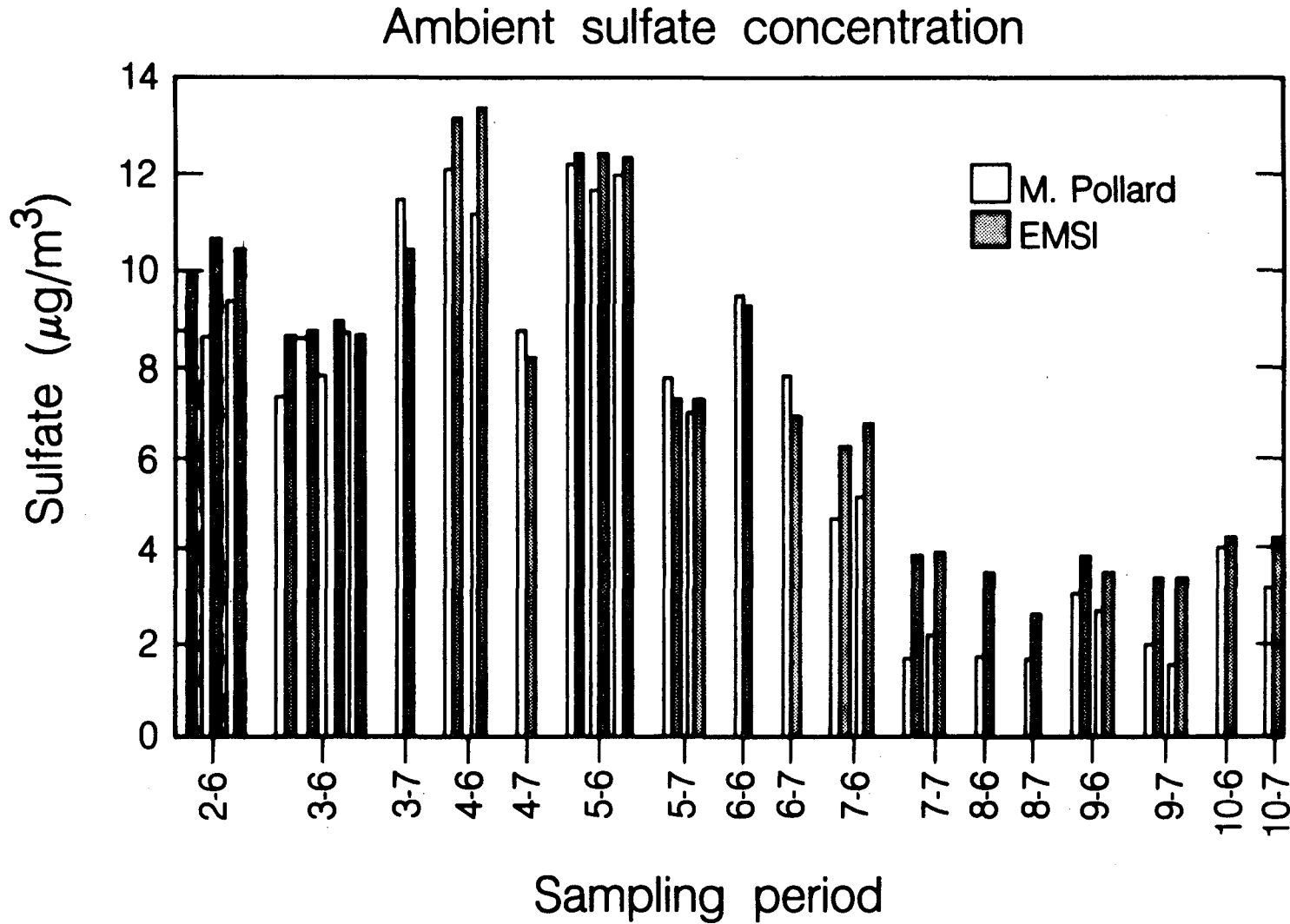
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Figure 1. The background corrected infrared spectrum of an ambient aerosol sample (solid line) and the blank Teflon\* filter (dashed line) before sampling. The arrows indicate the respective absorbance scales for the two spectra.



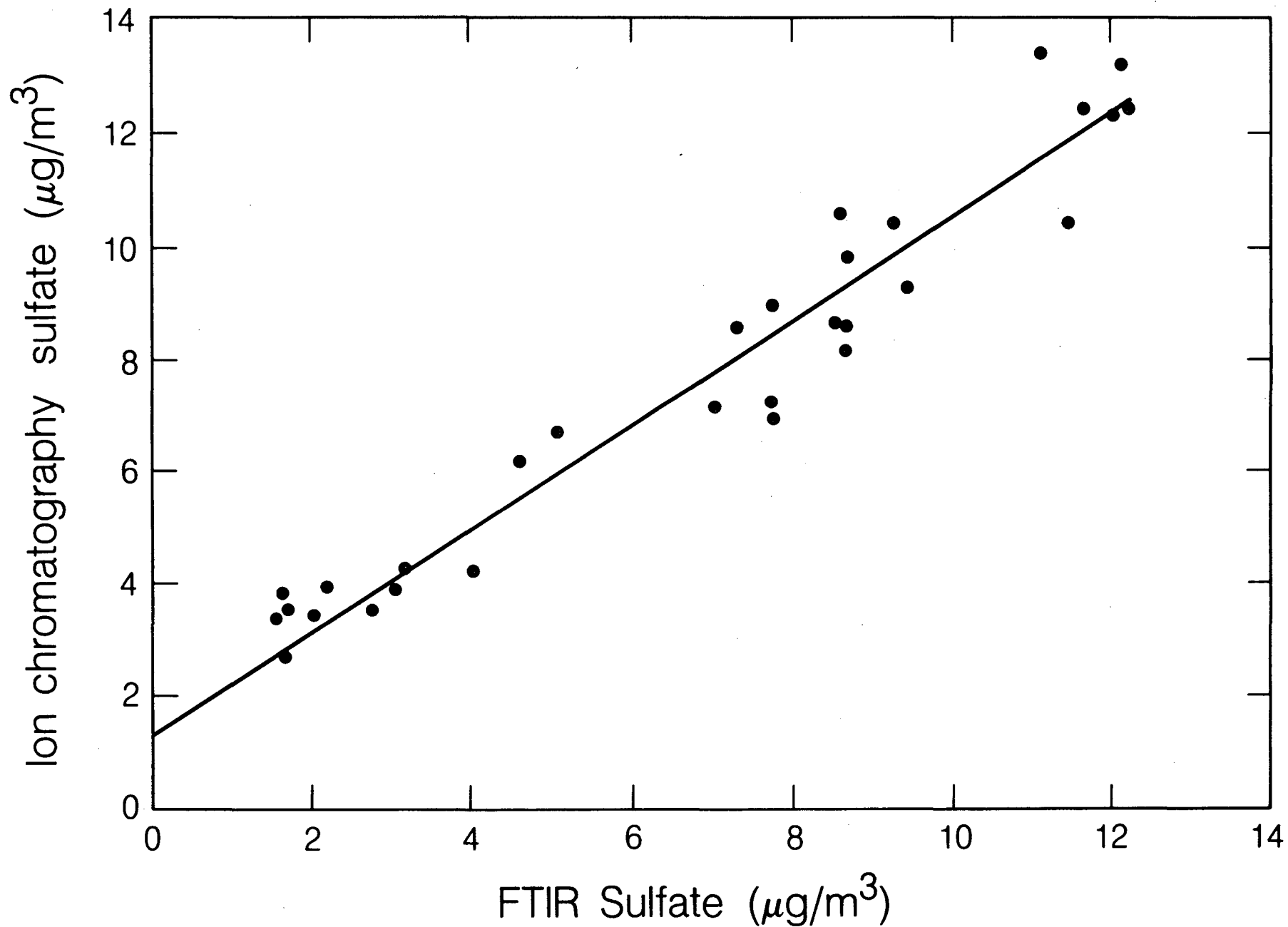
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Figure 2. Determination of the proper subtraction of the Teflon\* absorption band in the vicinity of the  $615\text{ cm}^{-1}$  sulfate band. Curves 1 and 2 show the negative peak due to oversubtraction of the Teflon\* band. Curve 3 shows complete subtraction of the Teflon\* band based on the estimated position of the carbon baseline determined from the carbon baseline data in regions A and B.



XBL 879-10342

Figure 3. A comparison of ambient sulfate concentrations measured during the CARB study. The sulfate measurements by M. Pollard are from FTIR analysis of the sample filters. The sulfate measurements by EMSI are by ion chromatography analysis of the same sample filters.



XBL 879-10339

Figure 4. The linear regression line showing good agreement between the FTIR and ion chromatography measurements of sulfate concentrations in the atmosphere.



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