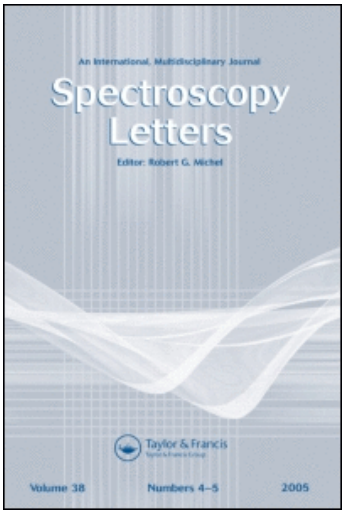

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Infrared Analysis of the Chemical Composition of Particulates in Subway Air

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INFRARED ANALYSIS OF THE CHEMICAL COMPOSITION OF PARTICULATES IN SUBWAY AIR

KEY WORDS: AIR QUALITY, PARTICULATES, INFRARED SPECTRAL ANALYSIS

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ABSTRACT

The chemical composition of particulates in subway air collected during nonheating and heating seasons were determined by infrared analysis. The inorganic constituents were found to include sulfate, nitrate, bromate and silica. The principle sulfate compounds were ferrous sulfate and zinc sulfate. The infrared spectra also indicate the presence of an α, β unsaturated aldehyde such as acrolein. Some variation of composition with particle size was found. The possible presence of $(NH_4)_2SeO_4$ was also observed, but only during the heating season. The principle sources of the pollutants appear to be emissions from automobiles, power plants, incineration, and braking operations and track-wheel abrasion of the subway cars.

INTRODUCTION

Infrared spectrophotometry has been found useful as a complementary analytical tool to other techniques (e.g., atomic absorption spectroscopy, X-ray fluorescence spectroscopy) for the analysis of atmospheric particu-

lates. The characterization and analysis of the chemical composition of airborne particulate material has been reported as a function of both particle size and time using infrared spectroscopy[1,2]. Microspectrophotometric techniques have been used to obtain full scale, high resolution infrared absorption spectra from microgram quantities of atmospheric dust[3,4]. In principle in such studies, most polyatomic (except diatomic homonuclear species) reactant, product, or even relatively stable intermediate species can be identified by their own distinct infrared spectra but only with difficulty by classical methods.

A complete understanding of the variation in particle composition is essential for proper evaluation of the potential health hazards posed by airborne particulates and for the selection of appropriate control methods necessary for the reduction of the levels of airborne particulate material to acceptable values[5,6]. Such information could also provide insight into the relative importance of various mechanisms that have been proposed for the formation of particulates from gaseous constituents of the atmosphere. Presently, these reaction mechanisms are not well understood. For example, it is not certain whether the reactions take place homogeneously or heterogeneously. Further, it is not yet possible to predict how various species are distributed between the gas and the particle phases from theory and/or from experiments. As an example, it is thought that the product of the reaction between NH_3 and HNO_3 is formed either in the gas phase or on aerosol particles[7]. Further, nitrate ion has been identified by infrared spectroscopy as being present in the bulk of the particle (absorption bands at 1768, 1360 and 840 cm^{-1}) formed through the chemisorption of gaseous NO_2 on the particulate surface[2]. It is apparent that chemical reactions involved in phase changes are very complex and are currently an area of active research. It is hoped that this study would make some contribution to a better understanding of this area.

As part of a comprehensive study of the air quality in underground transit systems, a 24-hour air sampler has been installed in an underground station of the Newark subway system. Size distributions of suspended particulates have been gravimetrically determined for the nonheating season[8]. The purpose of this study was the infrared spectral analysis of the polyatomic species present in the particulates collected in the subway system during the heating and nonheating season.

Air quality in an underground mass transit system is very important to public health since a large number of people may be exposed for prolonged periods of time. Limited studies have appeared on air quality in a subway environment[9-13]. A comprehensive study of air quality in an underground transit system is needed in order to develop a suitable model which can systematically obtain and evaluate the parameters necessary for the identification and correlation of atmospheric pollutants with location and source. The Newark City Subway, a small underground transportation system consisting of single electrically powered cars, was selected for development of the model. The chemical composition of the particulates obtained in this study from infrared spectral analysis should aid in the determination and evaluation of the parameters of the model.

METHODS

A six stage suspended particle fractionating sampler of the cascade impactor type was used (Research Appliance Company, Model 2354). The effective cutoff particle diameters for each of the five stages of the cascade impactor and the back-up filter (i.e., stage 6) are as follows: 3.156μ, 2.344μ, 0.969μ, 0.531μ and 0.313μ for stages 1 through 6, respectively.

Samples were collected over a continuous 24 hour weekday period at flow rates ranging from 4 to 5 cfm. The sampler was set up at an under-

ground station located beneath a heavily travelled urban thoroughfare. The sampler was located approximately 12 feet above station level, on a wall adjoining the train tracks, and at a point some 20 feet off the outgoing end of the station. The nearest air vent was situated at least 100 feet from the sampler.

Samples were collected by placing aluminum foil impaction discs (i.e., filters) of 3.25 inch diameter on the collection/backup plate in each stage. Sample collection was undertaken during the nonheating season (August-September, 1974) and the heating season (January-February, 1975). After collection the samples (usually 1-5 mg) from stages 1 through 5 were scraped from the aluminum foil discs, mixed with about 180-200 mg of infrared grade potassium chloride, ground to a fine particle size with mortar and pestle and pressed into 13 mm diameter discs with a Carver Laboratory Press for subsequent infrared spectrophotometric analysis. For stage 6, since the samples could not be removed from the filter freely, 400 mg of potassium chloride were ground and poured over the samples on the filter. After being carefully mixed, about 200 mg of the mixture were taken off the filter to make pellets for infrared analysis. Infrared spectra of the samples were obtained over the range 2.5μ to 15μ (650 cm^{-1} to 4000 cm^{-1}) using a Perkin Elmer 137B NaCl Spectrophotometer. The wavelengths were measured to ±0.02μ. A beam attenuator from Barnes Engineering Co. was used to obtain full scale absorption spectra for several of the samples. All runs were done in triplicate and were found to be reproducible. Each run involved a sample from a different collection.

Infrared spectra of the potassium chloride pellets containing known amounts of ferrous sulfate, ferric sulfate, zinc sulfate, lead sulfate, lead nitrate, zinc nitrate, ferric chloride, sodium silicate and silica gel, and the mixtures of ferrous sulfate and zinc sulfate, ferrous sulfate

and silica gel, sodium silicate and ferrous sulfate, potassium bromate and zinc chloride, lead chloride and potassium bromate, ferrous chloride and potassium bromate, and ferric chloride and potassium bromate were also obtained for purposes of comparison. These substances were chosen because X-ray fluorescence study of the particulates collected in the six stages in the subway station indicated the presence of iron, zinc, lead and manganese[8].

RESULTS

Representative infrared spectra obtained for the samples from stages 1 through 6 collected during the nonheating season are shown in Figures 1 and 2, and they are summarized in Table 1. The representative infrared spectra obtained for the samples from stages 1 through 6 collected during the heating season are shown in Figures 3 and 4, and they are summarized in Table 2. Inferences that could be drawn from the presence of specific infrared absorption bands are also summarized in Tables 1 and 2. These assignments were made, in general, by comparing the spectra of the samples collected on the stages with the infrared spectra of known substances (Figures 5-7), available from commercial sources, and with the spectra reported in the compilations of Hunt, et al.[14], Miller and Wilkens[15], Miller, et al.[16], Nyquist and Kagel[17], and Gadsden[18]. The following analysis of the experimental data reported in Tables 1 and 2 are based upon these comparisons.

The band near 3.0μ from the spectra of the subway dust for all stages in different seasons can be due to the presence of water or ammonium ion. The pressed disc method has the disadvantage that the O-H and N-H stretching regions are obscured by the O-H absorption of water normally present as residual water in hygroscopic halide.

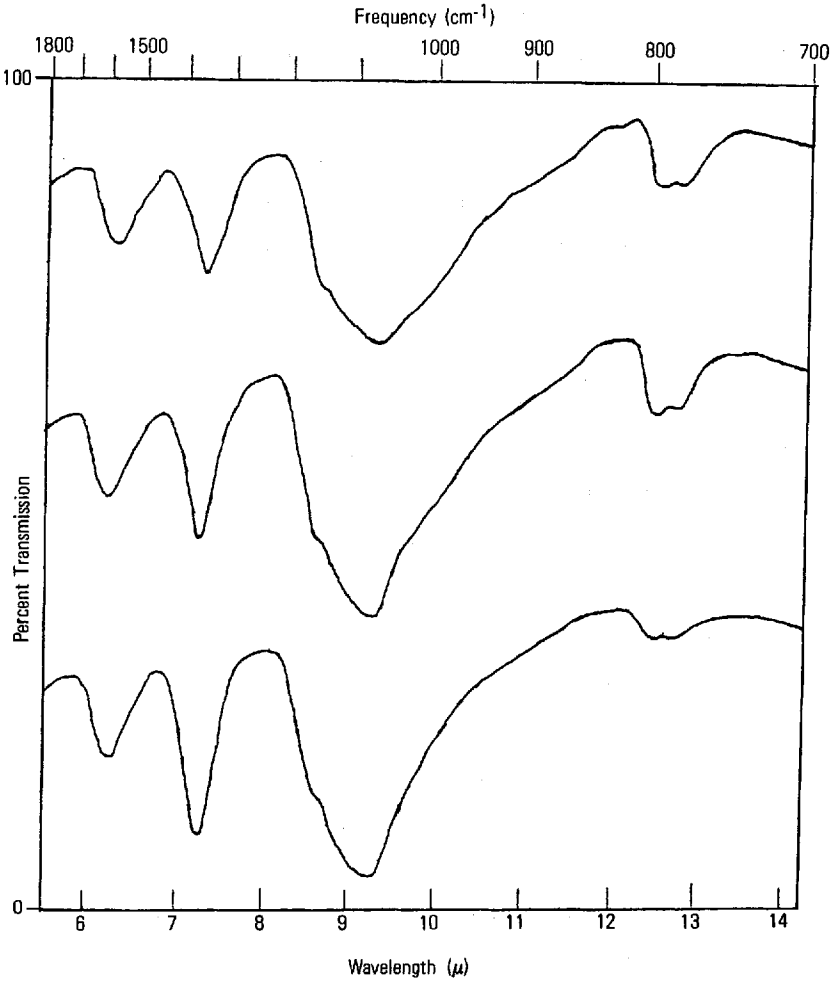

FIG. 1. Infrared spectra (1800-700 cm^{-1}) of respirable dust of subway air in Newark during nonheating season (A: Stage #1, B: Stage #2, C: Stage #3).

The band at 3.5μ arising from C-H stretching vibrations is due to the presence of organic substances in all stages.

A weak absorption band at 5.90μ appears only in stages 5 and 6 for both nonheating and heating seasons. The wavelength of the band is too low

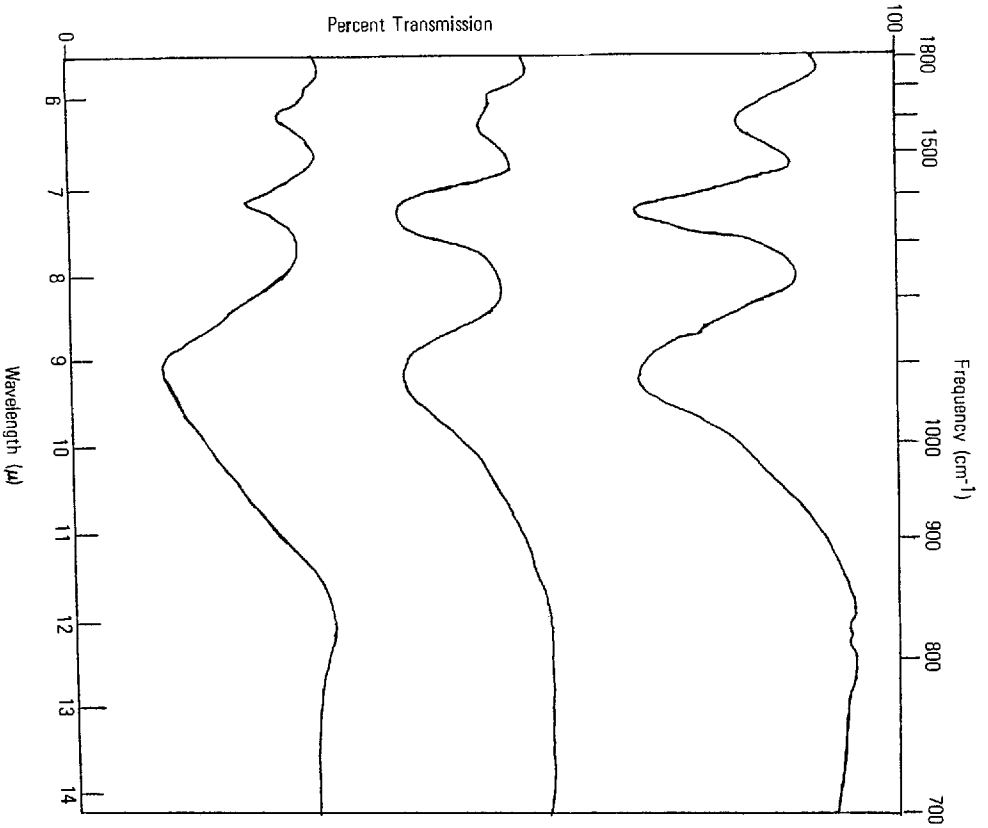

FIG. 2. Infrared spectra (1800-700 cm^{-1}) of respirable dust of subway air in Newark during nonheating season (A: Stage #4, B: Stage #5, C: Stage #6).

to assign to possible inorganic species. The absorption could be due to the presence of an α, β-unsaturated aodehyde[19], such as acrolein.

The absorption band ranging from 6.15 to 6.18μ in all stages is probably due to the presence of ferrous sulfate[15] in the samples.

An unusual feature of the infrared study was the appearance of a weak absorption band at 7.0μ in the spectra of samples from stages 1 through 4 collected during the heating season only, i.e., this band was not observed

TABLE 1. FREQUENCIES OF INFRARED BANDS OF SUBSTANCES PRESENT IN RESPIRABLE DUST OF SUBWAY AIR IN NEWARK, NEW JERSEY

NONHEATING SEASON

Stage #1	Stage #2	Stage #3	Stage #4	Stage #5	Stage #6	Remarks & Inferences
3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	2.98μ(m) 3356 cm^{-1}	Water of hydration and/or NH_4^+ ion.
3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	Organic substances (C-H stretching vibrations).
				5.90(w) 1695	5.90(w) 1695	α-β-unsaturated aldehyde (e.g., acrolein).
6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.15(m) 1625	Ferrous sulfate.
7.25(m) 1379	7.25(m) 1379	7.25(m) 1379	7.25(m) 1379	7.20(s) 1389	7.20(m) 1389	Surface nitrate species.
8.70(sh) 1149	8.70(sh) 1149	8.70(sh) 1149	8.70(sh) 1149			Ferrous sulfate and possibly zinc sulfate.
				9.10(s) 1099	9.10(s) 1099	Zinc sulfate.
9.20(s) 1087	9.20(s) 1087	9.20(s) 1087	9.20(s) 1087			Ferrous sulfate.
12.50(w) 800	12.50(w) 800	12.50(w) 800	12.50(w) 800			Bromate species and some silica.
12.85(w) 778	12.85(w) 778	12.85(w) 778	12.85(w) 778			

NOTE: vw = very weak w = weak m = medium s = strong sh = shoulder

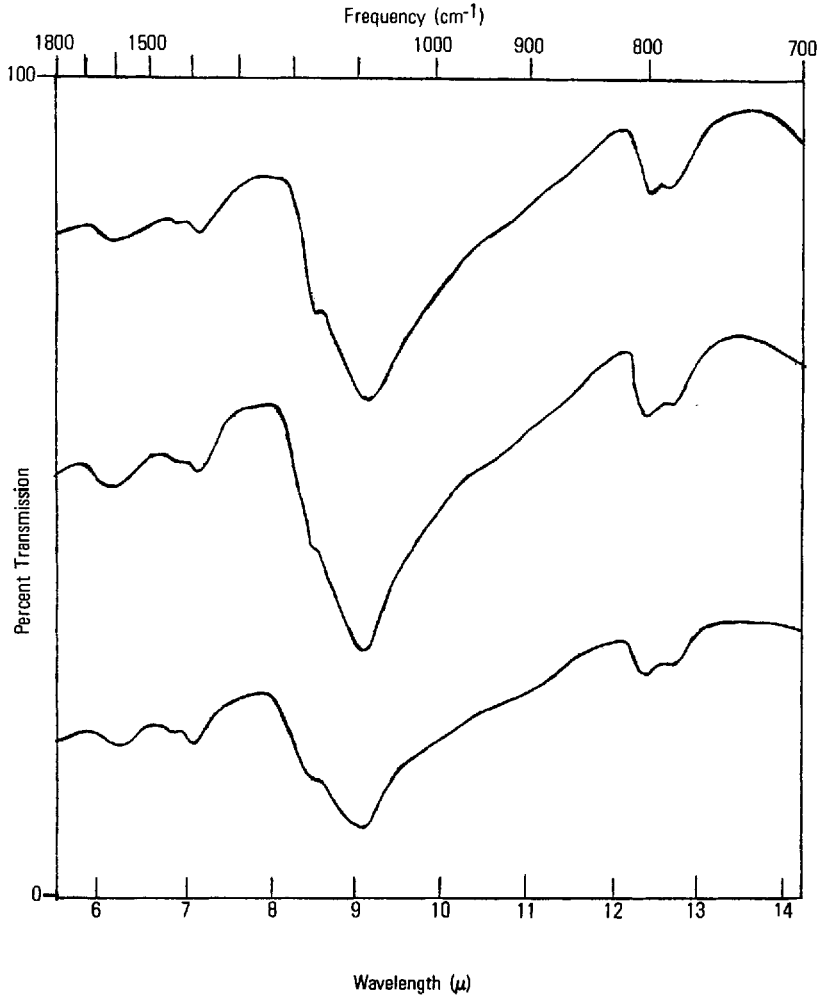

FIG. 3. Infrared spectra (1800-700 cm^{-1}) of respirable dust of subway air in Newark during heating season (A: Stage #1, B: Stage #2, C: Stage #3).

in the spectra of any sample collected during the nonheating season. The ammonium ion should show an absorption band in the 6.9-7.2μ region[18]; of the several possible ammonium compounds, ammonium selenate shows a band (7.05μ) near the observed absorption band.

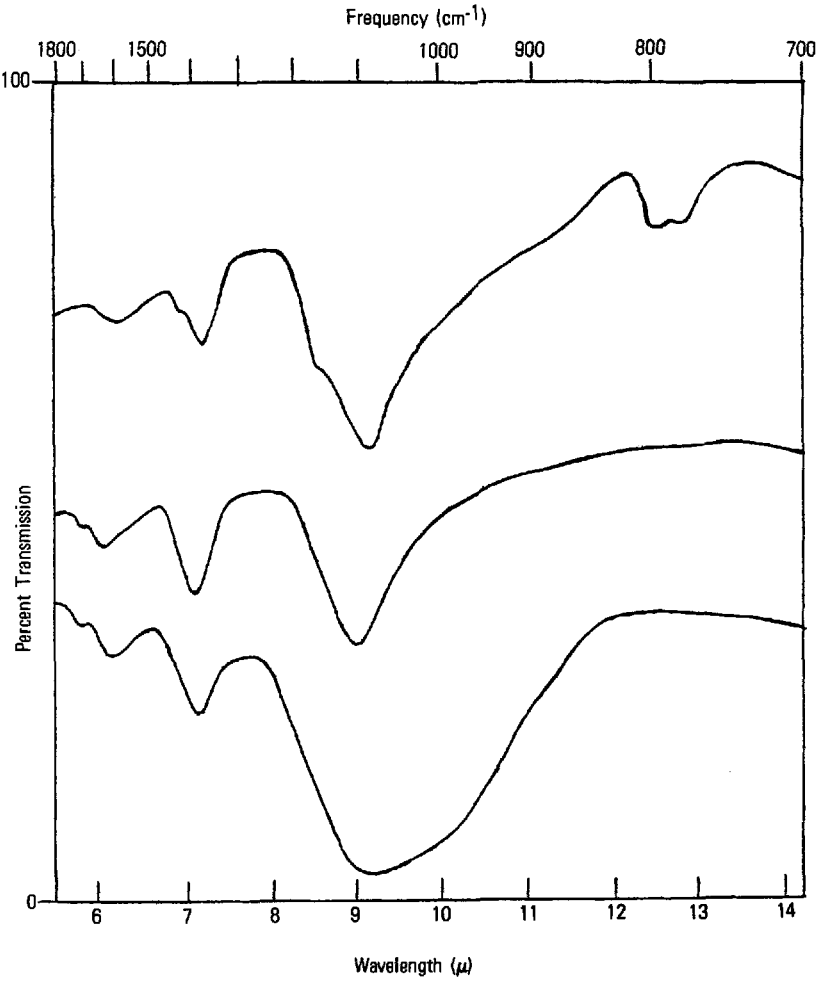

FIG. 4. Infrared spectra (1800-700 cm^{-1}) of respirable dust of subway air in Newark during heating season (A: Stage #4, B: Stage #5, C: Stage #6).

The medium to strong absorption band appearing at approximately 7.20 to 7.25μ in all samples could be due to the presence of surface nitrate[2]. The surface nitrate is formed through the chemisorption of atmospheric NO_2 on the particulate surface.

TABLE 2. FREQUENCIES OF INFRARED BANDS OF SUBSTANCES PRESENT IN RESPIRABLE DUST OF SUBWAY AIR IN NEWARK, NEW JERSEY

HEATING SEASON

Stage #1	Stage #2	Stage #3	Stage #4	Stage #5	Stage #6	Remark & Inferences
3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3333 cm^{-1}	3.00μ(w) 3356 cm^{-1}	Water of hydration and/or NH_4^+ ion.
3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	3.50(vw) 2857	Organic substances (C-H stretching vibrations).
				5.90(w) 1695	5.90(w) 1695	α-β-unsaturated aldehyde (e.g., acrolein).
6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.18(m) 1618	6.15(m) 1625	Ferrous sulfate.
7.00(w) 1429	7.00(w) 1429	7.00(w) 1429	7.00(w) 1429			Trace of ammonium selenate ($[NH_4]_2SeO_4$).
7.25(m) 1379	7.25(m) 1379	7.25(m) 1379	7.25(m) 1379	7.20(s) 1389	7.20(m) 1389	Surface nitrate species.
8.70(sh) 1149	8.70(sh) 1149	8.70(sh) 1149	8.70(sh) 1149			Ferrous sulfate and possibly zinc sulfate.
				9.10(s) 1099	9.10(s) 1099	Zinc sulfate.
9.20(s) 1087	9.20(s) 1087	9.20(s) 1087	9.20(s) 1087			Ferrous sulfate.
12.50(w) 800	12.50(w) 800	12.50(w) 800	12.50(w) 800			Bromate species and some silica.
12.85(w) 778	12.85(w) 778	12.85(w) 778	12.85(w) 778			

NOTE: vw = very weak w = weak m = medium s = strong sh = shoulder

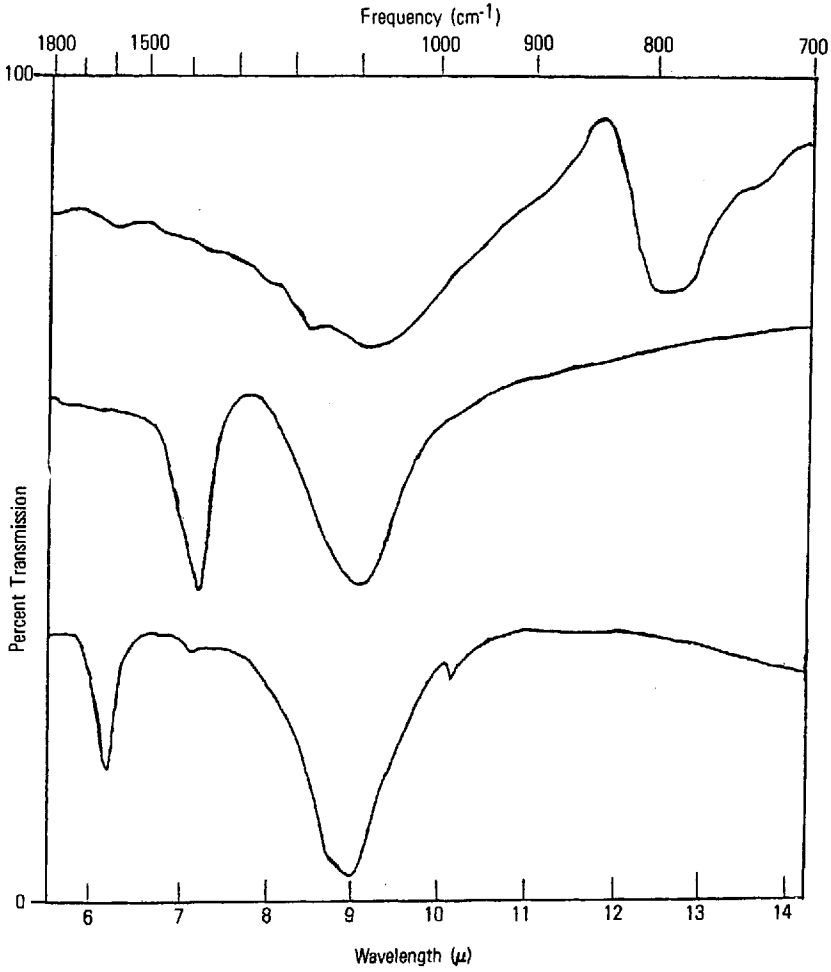

FIG. 5. Infrared spectra (1800-700 cm^{-1}) of (A) silica powder, (B) ammonium sulfate, (C) zinc sulfate.

The sulfate ion shows a strong, usually broad absorption in the 8.3-9.6μ region, which may be a single band or multiple bands depending on the cation to which the sulfate is coordinated[17]. Ferrous sulfate has absorption bands 8.7 and 9.2μ[15] and zinc sulfate has bands at about 8.7 and

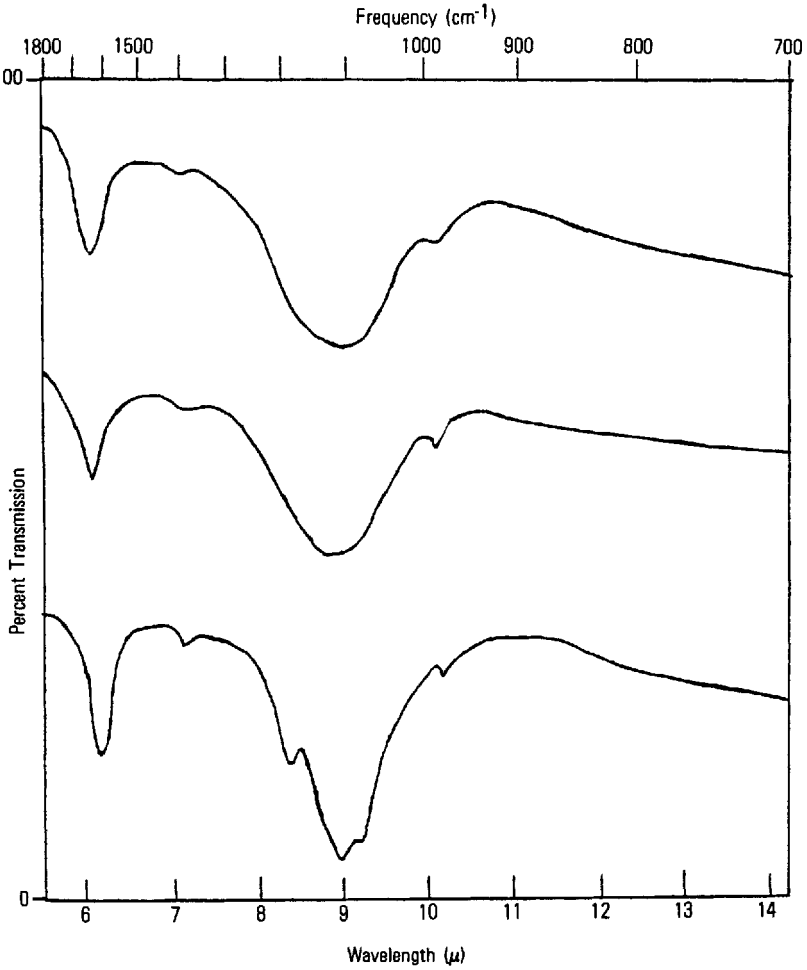

FIG. 6. Infrared spectra (1800-700 cm^{-1}) of (A) ferrous sulfate, (B) 2:1 by weight of $FeSO_4$ and $ZnSO_4$, (C) 1:1 by weight of $FeSO_4$ and $ZnSO_4$.

9.1μ[17,18]. Thus, ferrous sulfate was apparently collected on stages 1 through 4 and zinc sulfate on stages 5 and 6. Some zinc sulfate may also have been collected on stages 1-4 but the small amount that would be present is difficult to confirm in the presence of the ferrous sulfate. The

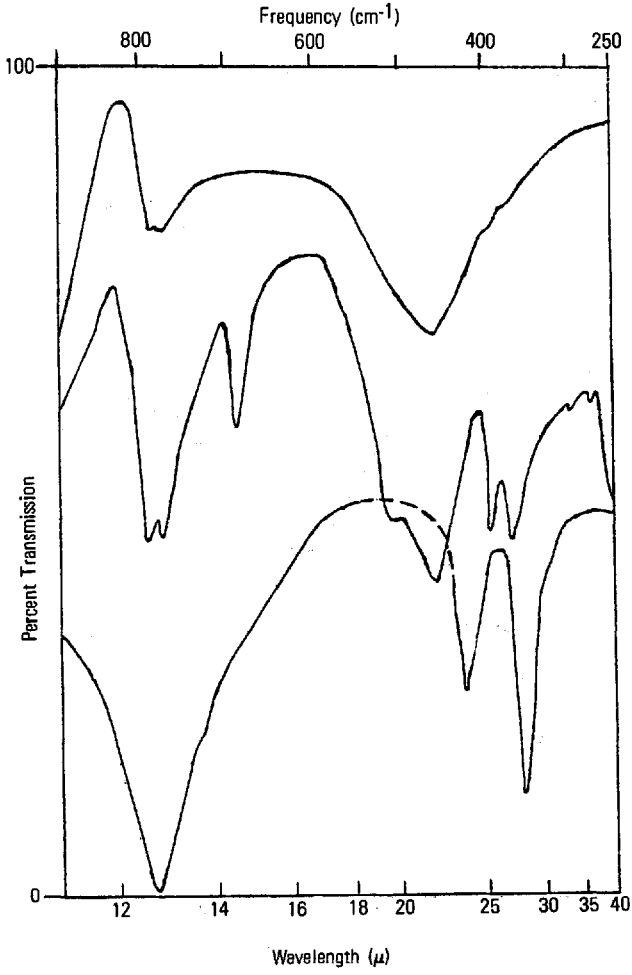

FIG. 7. Infrared spectra (900-250 cm^{-1}) of (A) respirable dust of subway air during nonheating season: Stage #1, (B) silica powder, (C) potassium bromate.

presence of trace amounts of manganese sulfate can not be ruled out since its major absorption at 8.8μ[15] would be buried by the absorptions due to ferrous sulfate and zinc sulfate. Similarly, the major absorption bands

TABLE 3. FERROUS SULFATE DISTRIBUTIONS BY WEIGHT PERCENT

Impactor Stage	Non-Heating Season		Heating Season	
	Weight Fraction of Sample in Disk	$FeSO_4$ wt.%	Weight Fraction of Sample in Disk	$FeSO_4$ wt.%
1	0.00636	44.8	0.00492	50.8
2	0.00565	54.8	0.00485	59.8
3	0.00565	51.3	0.00533	65.7
4	0.00856	47.9	0.00533	56.3
5	0.00659	47.0	0.00425	43.5

of lead sulfate at 9.0 and 9.5μ[17] would not be apparent if trace amounts were present.

The doublet at 12.50μ and 12.85μ is somewhat more difficult to analyze. Bromates as well as silica exhibit such doublets in their infrared spectra[17,20]. Further, the spectra of these compounds are also similar in the region above 15μ. Infrared spectra (12-40μ region) of silica and a bromate were obtained in this laboratory on a Perkin-Elmer 457 Infrared Spectrophotometer and are shown in Figure 7. The only available bromates were $KBrO_3$ and $NaBrO_3$ and they showed identical infrared spectra. For comparison, the infrared spectrum of a dust sample collected on stage 1 of the sampler is also shown in Figure 7. Figure 7 indicates the possibility that bromate and silica could be present. However, silica shows an infrared absorption band about 14.4μ which is not present in the bromate spectrum and does not appear in the spectrum of the sample of respirable dust of subway air. Thus, the coublet at 12.50 and 12.85μ is associated primarily with the presence of bromate in the samples which were collected during both the nonheating and heating seasons in stages 1 through 4. Neither band is observed in stages 5 or 6. Silica is probably also present in the samples but the absence of the band near 14.4μ indicates that only trace amounts of the silica are present.

Experimental difficulties prevented the analysis of the chemical constitutents in the particulates quantitatively. However, it was possible to obtain the relative quantities of sulfate from its major compounds present, i.e., ferrous sulfate and zinc sulfate. For the analysis, the band at 9.2μ was used when ferrous sulfate was the predominant species and the band at 9.1μ was used when zinc sulfate was predominant. The results are shown in Table 3.

The undertainties of the results of Table 3 are probably in the range of 3-5 weight percent of sulfate in the dust. Thus the differences in

sulfate between the nonheating season and the heating season for stages 1, 3 and 4 (Table 3) should be significant.

It should be pointed out that the data in Table 3 may not represent absolute values of sulfate in the particulates. There could be extensive overlap between the zinc sulfate bands and the ferrous sulfate bands with it being difficult to estimate the effect of such overlap on the quantitative analysis of sulfate. At best, one might say that the data represents the minimum quantity of sulfates present in the particulates. In any case, comparisons between stages and comparisons between heating season and nonheating season data appear valid.

DISCUSSION

The results of this study combined with x-ray fluorescence data[8] indicate that the chemical composition (inorganic substances) of the particulates collected in the subway environment in Newark during both the nonheating season and heating season include sulfate, nitrate, bromate and silica. The prevelant sulfates are ferrous sulfate and zinc sulfate. Further, there is some evidence for the presence in the particulates of a α,β-unsaturated aldehyde such as acrolein. Since not all species appeared in every stage it is apparent that there is some variation of composition with particle size. Only one difference between the nonheating season and the heating season is apparent from the infrared spectra of the collected samples. Ammonium selenate appears to be present on stages 1 through 4 for samples collected during the heating season only.

This study indicates that the principle sources of the particulates are from automobile emissions, fossil fuel fired power plant emissions, and incineration emissions, entering the system through ground level ventilation ducts, as well as from braking operations and track-wheel abrasion.

The subway station where these studies were made is located in a highly urbanized center (downtown Newark) at an intersection that has heavy vehicular traffic which is approximately constant regardless of season. This is consistent with the data in Tables 1 and 2 which show sulfate, nitrate, bromate and silica present in samples from several stages in both the nonheating season and the heating season.

It should be possible to correlate the analysis of the metals by atomic absorption spectroscopy with the results reported here to obtain further information on the chemical composition of the particulates. The separation and further identification of the organic constituents of the particles is now in progress.

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