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# Chemical Identification of Urban Air Particulates in the Environment of Pune City (India) By Raman Spectroscopy

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## Abstract

The Raman spectra of urban aerosols were obtained for the characterization of aerosols and a qualitative interpretation of the spectra is presented. An experiment was carried out using a double monochromator with a diffraction grating frequency of 1,800 grooves/mm, a diode laser with a 532-nm wavelength, and with a power source of 25 mW for excitation. The spectra exhibited the presence of various inorganic compounds, including carbonates, sulphates, persulphate of ammonium and potassium, nitrates of ammonium ($NH_4$), potassium and strontium, etc. as well as organic species dominated by the carbon group. In the environmental research, this kind of analytical capability is very useful for the chemical identification of atmospheric aerosol.

***Keywords*:** Monochromator; Air pollutants; Air sampler; Raman spectrometer.

## INTRODUCTION

The role of atmospheric aerosols in modifying the regional and global radiative balance and thereby perturbing the climate is widely recognized among researchers internationally. Increases in aerosol emissions in the atmosphere of large cities have resulted in the reduction of visibility and in growing concerns for human health (Vincent, 1989). The presence of aerosol can cause respiratory and cardiovascular diseases, can enhance the formation of cloud precipitation, and affect the earth's energy balance by the scattering and absorption of radiation (Ramanathan *et al.*, 2001; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998). Therefore, in order to increase understanding of aerosols in various environmental processes and public health, it is necessary to

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accurately characterize them physically and chemically. Chemical characterization includes the characterization of the gas phase, as well as the particle phase of particulate matter.

In atmospheric sciences, the characterization of individual aerosol particles, their size distribution and chemical composition is of great relevance for the modeling of atmospheric and environmental processes (Pruppacher and Klett, 1978; Andreae, 1995). Detail knowledge of chemical compositions is vital for understanding the kinetics of heterogeneous chemical characterization of a particle and the gas molecules surrounding it. The need for chemical characterization of particles becomes even more obvious when considering the fact that such heterogeneous processes are occurring in everyday life and are also involved in many energy conversion systems, manufacturing processes, and health-related areas, as well.

Various spectroscopic techniques have been applied for the chemical characterization of particulate matter (PM) and most of these techniques can be adopted as routine analytical procedure for bulk samples. Each of these techniques has its advantages and disadvantages. For in situ characterization of aerosol particles, however, Raman scattering is the most promising technique currently available in the field of characterization. This technique is used for the chemical characterization of aerosols at Pune, India, an agricultural region producing sugarcane as a major crop and dominated by low rainfall and a dry climate with a relative humidity around 40%. Pune City, densely populated with about three million residents and a large number of two wheelers and automobiles, is considered one of the most polluted urban environments in India. In this study, three 24-h aerosol samples were taken during or near the diwali festival on 12th, 19th and 21st November, 2004. The diwali festival, which is from 10th to 15th, is the most popular festival in India when people use firecrackers for celebration and burn oil lamps for decoration and open fire for cooking.

## EXPERIMENTAL

Raman Spectroscopy (RS) is an ideal tool for investigating chemical composition of aerosols (Escribano *et al.*, 2001), since spectra of aerosols have been found to respond to changes in microscopic structure. This technique is especially selective, giving information not only about the identity of molecules, but about their immediate environment, also. Schweiger (1999) gives a very informative discussion of the theory of RS of aerosol.

The study reported on in this paper explored the use of RS for the characterization of aerosol particles in urban, rural and industrial areas. The aerosol samples were collected on pure quartz filters with a high-volume aerosol sampler. Spectra were obtained using a Raman spectrometer, a complete block diagram of which is shown in Fig. 1. It uses a double-monochromator with diffraction gratings having a groove density of 1,800 grooves/mm, and a diode laser (532-nm wavelength) with 25-mW power. The spectra of aerosol samples were collected perpendicular to the incident laser beam from the surface of the quartz filter containing aerosols. Various aerosol samples collected on different days were investigated using this spectroscopic technique.

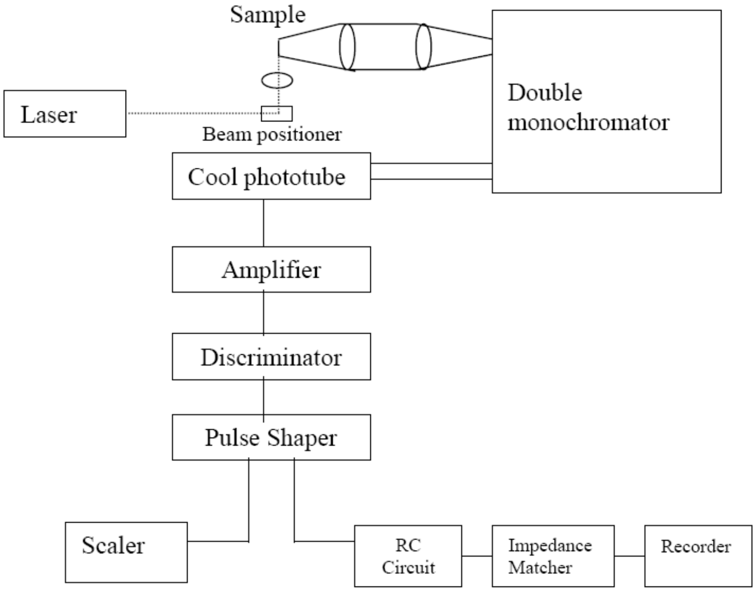

**Fig. 1.** Block diagram of Raman spectrometer.

### *Advantages of Raman spectroscopy*

Various spectroscopic techniques, such as infrared spectroscopy and chromatography, are used for chemical characterization. While infrared measurements can provide a wealth of information, their sensitivity is not high and substantial efforts may be needed to extract unambiguous information about the particles. In comparison, Raman Spectroscopy has the following advantages:

(a) RS is a popular, nondestructive, reasonably rapid tool for structural characterization of crystalline, non-crystalline and amorphous material.
(b) In many cases, sample preparation is often simpler for RS than for infrared.
(c) RS can provide higher sensitivity with comparable selectivity and chemical speciation.
(d) A Raman spectrometer is usually capable of covering lower wave numbers than an infrared spectrometer, extending down to 100 cm$^{-1}$, where most infrareds stop at 200 cm$^{-1}$.
(e) RS is equally useful for any state of matter, such as gas, solid, or liquid, and can identify any type of inorganic, organic and biochemical species in liquid, gas or solid form.
(f) Since aerosol properties can be altered by sampling, and many related processes are transient in nature, an in-situ technique is required.
(g) Most organic and inorganic molecules are Raman active.

### *Selection of filters*

The most conventional method of sampling ambient particles involves their collection on filters. While sampling and examining them for chemical characterization, it is desirable to avoid excessive manipulation of samples. For this purpose, we designed the Raman spectrometer so that the spectra of the samples were directly collected from the filters. Acceptable results were obtained using pre-treated quartz filters. Teflon, polycarbonate or other polymeric materials give unacceptable levels of background fluorescence; and therefore were not used (Barthelmie and Pryor, 1997).

### *Sampling of aerosols*

Ambient aerosol samples were collected from an urban site in central Pune City, in Shukrawar Peth region. The samples were collected on the second-floor terrace of a two-story building by short-term (24 hours) collections with a standard high volume (2 $m^3$/min.) air sampler employing quartz filters baked at 300°C for at least two hours to reduce organic carbon levels. The filters were then equilibrated for 24 hours at a constant relative humidity between 20 and 40%, and at a constant temperature between 15-30°C (Qin and Oduyemi, 2003). This was achieved by placing the filter paper in desiccators for at least 24 hours before investigation for chemical composition using the Raman spectrometer. With this procedure, the lowest manipulation of the aerosol samples is expected.

## RESULTS AND DISCUSSION

The Raman spectra, shown in the Figs. 2, 3a, 3b and 4**,** were obtained from the 24-hr aerosol samples collected in the Pune City urban environment, during 12th November to 19th November and 21st November 2004. The spectra illustrate the kind of spectroscopic information obtain using Raman spectroscopic technique. The wavelength shifts in arbitrary units for Raman stokes lines are displaced on the horizontal axis using a calibration procedure. The spectrometer can be calibrated easily for a high degree of precision by using the emission spectrum of neon. A neon lamp covers the whole electromagnetic spectrum normally used in Raman Spectroscopy (3100 Å to 8900 Å) with an average spacing of about 20 Å. The spectra of neon lines obtained in this study are found on the stokes side of the laser line. These lines match standard lines obtained by Burns *et al.* (1950). Raman shifts in wave number were obtained by considering the exciting wavelength ($\lambda$= 5320 Å) of the laser source. The wavelength calibrations are obtained by using neon emission lines.

Fig. 2 (12th November) represents four major Raman bands in the range of 198-2,180 $cm^{-1}$. Details are given in Table 1. According to reference spectra (Degen and Newman, 1993; Degen, 1997), the Raman bands obtained in our experiments demonstrate the presence of various chemical species in the urban aerosol sample. The bands at 1,988 $cm^{-1}$ and 2,002 $cm^{-1}$ exhibit

C=C=C in the alkane group and benzene rings, respectively. However, the Raman band at 2,052 $cm^{-1}$ and 2,180 $cm^{-1}$ treated as KSCN (Potassium thiocynate) and presence of C≡C in thiocynate. Thus, it is dominated by the presence of carbon and thiocynate compound. For the characterization, we selected only four major bands and no attempts were made to analyze weak Raman bands. The existence of thiocynate (KSCN) is evident from the following explanation.

The chemical compound KSCN is used in the printing industry and for photo development processes. While no printing press was located at the sampling site, some photo studios were located nearby. Therefore, there was a possibility that this compound came from such sources.

The Raman bands exhibited in Figs. 3a and 3b are the resolved spectra of the same sample taken on 19th Nov.2004. The figures are presented separately for better resolution and identification of the chemical species. The Raman group frequencies corresponding to Fig. 3a are expressed in Table 2. They demonstrate various bands in the frequency range of 2,876 to 3,103 $cm^{-1}$. They are identified as organic compounds alkane ($CH_3$), methylene ($CH_2$) and (CH) stretch vibration of alkane (Degen and Newmann, 1993; Degen, 1997). In addition, other spectra exhibit the presence of inorganic compounds of $NH_4$ (ammonium), such as $(NH_4)_2S_2O_6$ (ammonium persulphate) and $NH_4HB_4O_7.3H_2O$ (ammonium tetra borate).

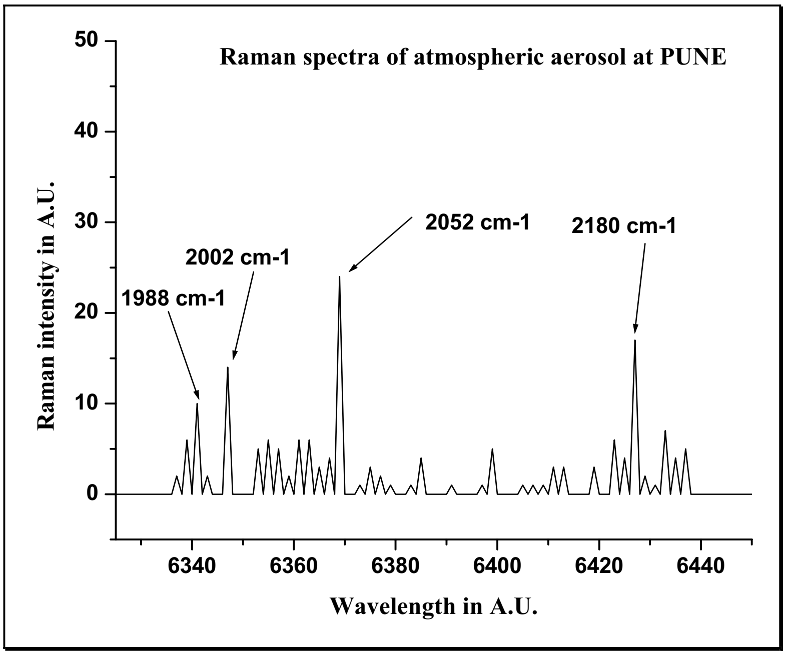

**Fig. 2.** Raman spectra of atmospheric aerosol, date 12th November.

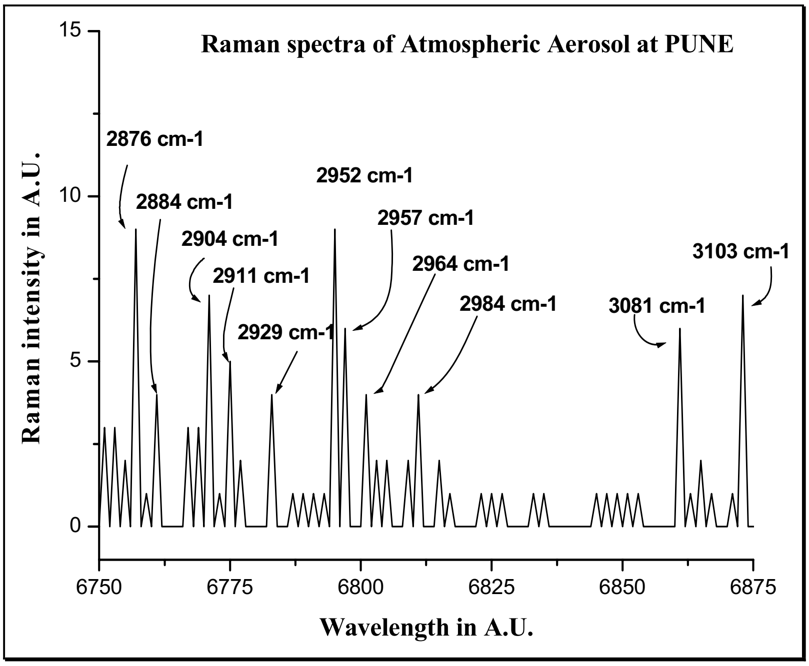

**Fig. 3a.** Raman spectra of Atmospheric Aerosol, date 19th November

Fig. 3b represents the Raman bands in the frequency range of 3,152 to 3,331 $cm^{-1}$. Within this range, eight Raman peaks are observed. Each peak exhibits individual chemical species as identified in Table 3. These species are dominated by ammonia compounds, such as nitrates, sulphates, etc.

The Raman spectrum shown in Fig. 4 was taken from a 24 hours filter sample on 21st November 2004, which exhibits six Raman modes with frequency shifts ranging between 1,229 $cm^{-1}$ to 1,514 $cm^{-1}$. The qualitative comparison of these shifts with the reference spectra (Degen. and Newman, 1993) show various chemical species present in the ambient aerosols samples are given in Table 4. The frequency shifts 1,229 $cm^{-1}$ and 1,287 $cm^{-1}$ are interpreted as ammonium persulphate [$(NH_4)_2S_2O_8$] and potassium persulphate [$K_2S_2O_8$] respectively. While 1,345 $cm^{-1}$ and 1,403 $cm^{-1}$ show the presence of potassium nitrate [$KNO_3$] and strontium nitrate [$Sr(NO_3)$]. The other two bands centered around 1,460 $cm^{-1}$ and 1,514 $cm^{-1}$ indicate the presence of lithium carbonate [$Li_2CO_3$] and cycloalkanes. These are the chemical species identified in our urban aerosol samples at Pune.

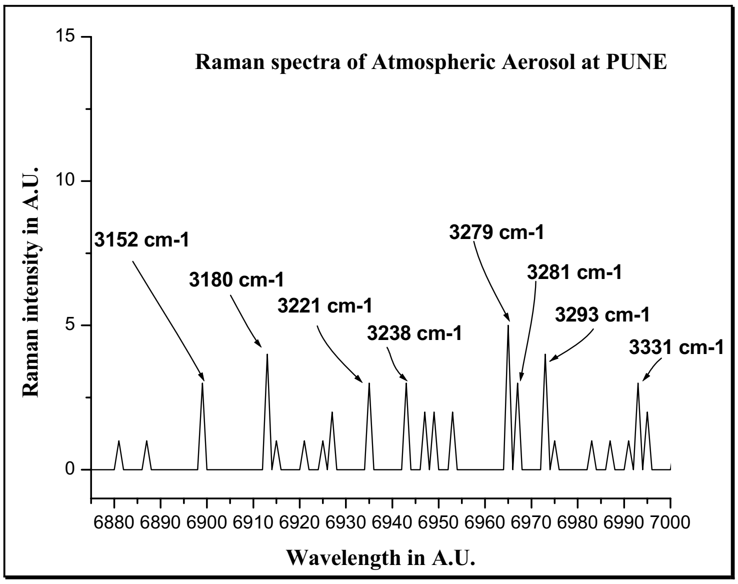

Fig. 3b. Raman spectra of atmospheric aerosol, date 19th November

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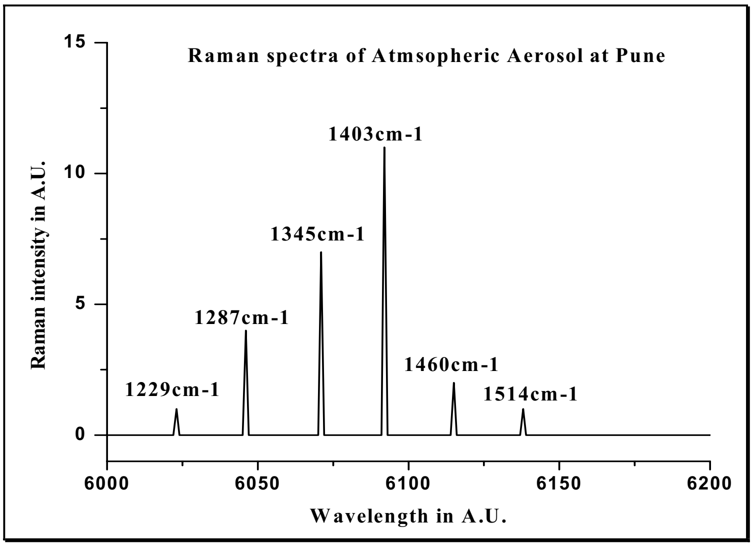

**Fig. 4.** Raman spectra of atmospheric aerosol, date 21st November

**Table 1.** Raman frequencies ($cm^{-1}$) and observed chemical species for atmospheric aerosol, date 12th November

| Sr. No. | Raman frequencies ($cm^{-1}$) | Chemical species |
|---|---|---|
| 1 | 1988 | C= C= C in allenes |
| 2 | 2002 | Benzene ring |
| 3 | 2052 | KSCN, Potassium thiocynate |
| 4 | 2180 | C ≡ C in thiocynate |

**Table 2.** Raman frequencies (cm$^{-1}$) and observed chemical species for atmospheric aerosol, date 19th November

| Sr. No. | Raman Frequencies (cm$^{-1}$) | Chemical Species |
|---|---|---|
| 1 | 2876-2884 | $CH_3$ in alkanes |
| 2 | 2904-2929 | -$CH_2$ – methylene, or CH- stretch vibration in alkanes |
| 3 | 2952-2964 | $CH_3$ in alkanes |
| 4 | 2984 | $CH_3 = C$– in alkenes |
| 5 | 3081 | $(NH_4)_2S_2O_6$, Ammonium persulphate |
| 6 | 3103 | $NH_4 H B_4 O_7 .3H_2O$, Ammonium tetra borate monobasic |

**Table 3.** Raman frequencies (cm$^{-1}$) and observed chemical species for atmospheric aerosol, date 19th November

| Sr. No. | Raman frequencies (cm$^{-1}$) | Chemical species |
|---|---|---|
| 1 | 3152 | $NH_4HSO_4$, Ammonium bisulphate |
| 2 | 3180 | -NH-Stretch; in secondary amide |
| 3 | 3221 | $NH_4NO_3$, Ammonium nitrate |
| 4 | 3238 | $H_3BO_3$, Boric Acid |
| 5 | 3279-3281 | $Fe(NH_4)_2(SO_4)_2.6H_2O$, Ferrous ammonium sulphate |
| 6 | 3293 | $NaBO_2.4H_2O$, Sodium meta borate |
| 7 | 3331 | -NH- Valence; in R-R-NH |

**Table 4.** Raman frequencies (cm$^{-1}$) and observed chemical species for atmospheric aerosol, date 21st November

| Sr. No. | Raman frequencies (cm$^{-1}$) | Chemical species |
|---|---|---|
| 1 | 1229 | $(NH_4)_2S_2O_8$, Ammonium persulphate |
| 2 | 1287 | $K_2S_2O_8$, Potassium persulphate |
| 3 | 1345 | $KNO_3$ , potassium nitrate |
| 4 | 1403 | $Sr (NO_3)_2$ , Strontium nitrate |
| 5 | 1460 | $Li_2CO_3$ , Lithium carbonate |
| 6 | 1514 | Cycloalkanes |

## CONCLUSIONS

We have shown that Raman Spectroscopic analysis provides a means for obtaining qualitative information on the molecular composition of aerosol particles. Thus, the molecular nature of the species appears to be important variables in the aerosol particles. The question related to concentration of species or its abundance in the particle, the compositional complexity and various effects related to morphology of the aerosol particles have not been addressed in this work. What is evident from the present results, however, is that a broad variety of environmentally significant materials in particulate form can be characterized by this approach. The technique and its applications, described here, offer the possibility of identifying with greater certainty the sources of air borne particles and detailed mechanisms of atmospheric reactions and transport processes.

Thus, Raman Spectroscopy permits the chemical characterization of broad variety of environmentally significant materials existing within the aerosol in the form of organic and inorganic species. In any program of environmental research this kind of analytical capability can be expected to yield new answers to problems that could only be partially addressed before.

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