

Raman Spectroscopic Investigation Of Multicomponent Aerosols From The Environment Of Sugar Factory

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It is well understood fact that, the presence of aerosol can cause respiratory or cardiovascular diseases, enhance the formation of cloud precipitation and affect the earth scattering and absorption of radiation. Because of the public health dangers, it is important to have accurate and sensitive analytical method for detection and chemical speciation of these particles. In this paper we will assess the laser Raman scattering and its application for the chemical identification of atmospheric aerosols collected from the environment of sugar factory in the month of March 2008 at the Rahuri in the state of Maharashtra (INDIA). In the application of Raman spectroscopic technique, a beam of monochromatic visible laser light is focused on the aerosol sample to obtain the Raman Spectra. This spectrum includes 25 independent Raman peaks representing 25 Raman frequencies which represent various chemical species present in the aerosol sample. As documented, all Raman peaks are found within Raman frequency range 521 cm^{-1} to 3396 cm^{-1} . As illustrated in Spectra, (Not shown) three Raman peaks observed at 521 cm^{-1} , 572 cm^{-1} and 760 cm^{-1} show the presence of Aryl nitro compounds, however Raman peaks at 1015 cm^{-1} , 1066 cm^{-1} and 1275 cm^{-1} exhibit the occurrence of mono and di-sub compounds. Similarly, two peaks which are visible at 2367 cm^{-1} , 2344 cm^{-1} are recognized as P-H str compounds. There are total nine Raman peaks ranging between 2514 cm^{-1} to 3396 cm^{-1} which are characterized as primary and secondary amides which seem to be the major composition of the aerosol samples. In addition to these, alkyl isocyanate, Diesters are also found as trace elements which are the compounds of Ammonia and Nitrogen. Thus, the aerosol samples constitute different types of elements which are far from being single component system. The technique developed in the present work has made it possible to identify the mixed salts which may be present in ambient aerosols, as a result of changing atmosphere conditions.

Keywords: Raman scattering, Aerosols, Raman Spectra, Sugar Factory, Human health. Chemical species monochromator organic and inorganic compounds

1. Introduction

There is great deal of evidence indicating that the increase in the aerosol emissions in the atmosphere of the urban area is great concern to human health and reduction of visibility. The presence of aerosol can cause respiratory and cardiovascular diseases, enhance the formation of cloud precipitation and affect the earth energy balance by scattering and absorption of radiation (Ramnathan V. et al. 2001; Finlayson Pitts J.N. 2000; Scienfield J.H. and Pandis S.N.; 1998). In urban atmosphere, the chemical make up of aerosol particle is quite complex (K leeman and Class, 1998) comprising carbon compound (both elemental and organic) as a major fraction. This is especially true for particles produced by motor vehicles (Kirch Stetter et al: 1999) as well as for many other important classes of aerosol particles, including secondary organic aerosols (Bathelnie and Pryor, 1997) and those produced in cooking and many common industrial processes. Because of the public health dangers, it is important to have accurate and sensitive analytical method for the detection and chemical speciation of those particles, which has always been formidable challenge due to their complexity. In pursuing these requirements; other techniques have fallen short of the mark, because these techniques do not provide a basis for molecular or crystal identification. Only Raman spectroscopy appears to offer a distinct possibility for effective application in this direction. In order to better assess the origin and the environmental effects of aerosol particles, Raman scattering technique hold considerable promise as a non destructive, sensitive and selective method for characterization of aerosol particles. In this paper, we will assess the laser Raman scattering technique and its application obtain to the Raman spectra of ambient aerosol particles. This technique is employed to obtain information related to the molecular composition of micro samples of atmospheric aerosol. We report, in this paper, the analytical potential of laser Raman spectroscopy for the chemical characterization of atmospheric aerosols collected from the environment of sugar factory at Rahuri in the state of Maharashtra (INDIA) in the year of 2008.

2. Experimental

The spectroscopic measurements carried out in the investigation is performed with laser Raman spectrometer. It permits the acquisition of analytical quality of Raman Spectra of atmospheric aerosol sample collected from the environment of sugar factory. In the application of Raman Spectroscopic technique, a beam of monochromatic visible laser light is focused on the aerosol sample. The radiation scattered by the sample contain weak lines, at frequencies both lower and higher than exciting radiations. The frequency difference, called Raman shift is the characteristics of the sample and the independent of exciting frequency. The spectra obtained with the spectrometer are called Raman Spectra. These arise from molecules, which scatters photons of the lower and higher frequency than that of exciting line. The molecules which scatter photons with lower frequency is called as Stokes lines and that of with higher frequency is called Antistokes lines. Thus, the Raman pattern which they represent, provide a molecular fingerprint for the identification and characterization of aerosol particles. The measurements were carried out using Raman spectrometer which is shown in fig-1. It uses double monochromator with diffraction grating having groove density 1800 grooves per mm and diode laser (532nm wavelength) with 25mW power. The light scattered by aerosol sample is collected and transferred into a double monochromator which is detected by cooled photo multiplier (S-20 response) and processed by photon counting electronics. In Raman spectroscopy measurements, the sample is usually excited in a region where the

sample does not absorb. Appreciable absorption of exciting radiations generally leads to sample heating which will further manipulate and destroy the sample. In such measurements, the problem can be severe because of the high irradiances (power/ unit area) that must be employed to the sample. A major potential limitation in all Raman work is sample fluorescence which may totally swamp the Raman Effect. With choice of laser frequencies, problems of radiation, absorption and sample fluorescence can be minimized, if not virtually eliminated.

3. Selection of susbrate(filters) and aerosol, Sampling

The most conventional method of sampling ambient aerosols involves their collection on the filters. Several types of plastic films are commonly used as filter media (e.g. Millipore, Nucleopore, etc.) for the collection of ambient aerosols. The filter materials made with inorganic binders, teflon, polycarbonate or other polymeric materials, however, give unacceptable levels of background fluorescence and therefore are unaccepted (Barthelmie R.J. and Pryor S.C. 1997). We have collected the aerosol samples from environment of sugar factory at Rahuri in Ahnednagar District of Maharastra state (INDIA). The samples of ambient aerosol were obtained in five days which are collected through the use of standard high volume air sampler employing quartz filters. Before the use of collection, these filters are baked at 300°C for at least 2 hours at constant relative humidity between 20% to 40% as followed by (Qin Y. and Oduyemi K. 2003) and at constant temperature 150°C to 300°C. This is achieved by placing a filter paper in desiccators at least 24 hours before investigation for chemical composition using Raman Spectrometer. With this procedure, lowest manipulation of the aerosol samples is expected

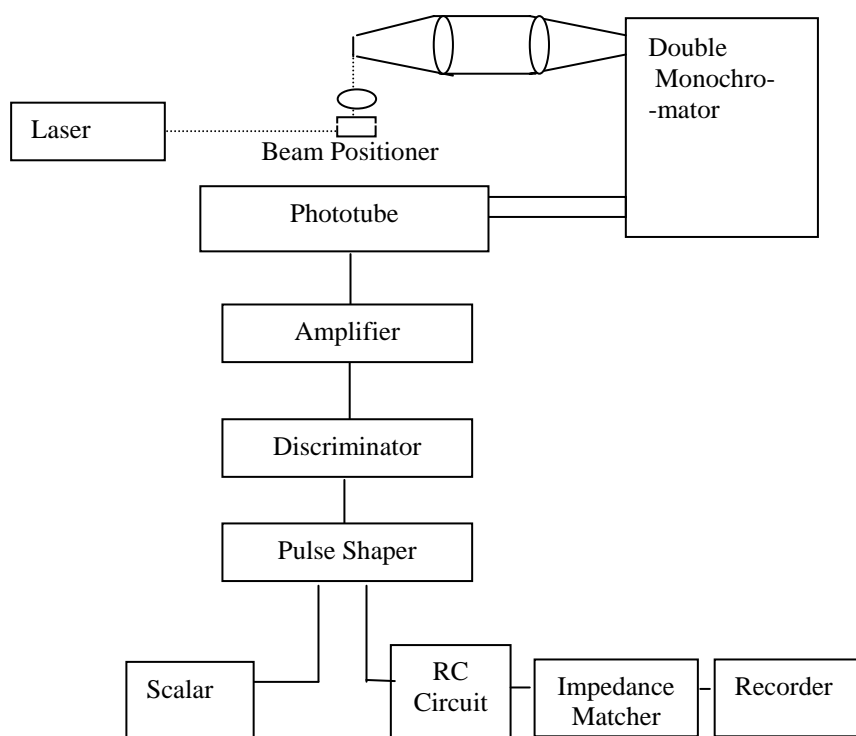


Figure (1) Block diagram of Raman spectrometer

atmospheric aerosols is highly complex and vary considerably with time and location. It is quite obvious that aerosols encountered in the environment occur as a mixture of substances or nuclei coated with dissimilar materials these impurities or coating may introduce spectral interferences or cause serious health problems due to strong absorption of the laser beam. As pointed out (Brosset, 1975, Lunminsham and Johnson, 1970) the Raman lines of particular species may be different from those of the pure component salt or they may represent a slight displacement from standard Raman frequency. For example, Raman Spectrum of NH_4NO_3 show Raman Line at 1043 cm^{-1} is only slightly displaced from that of pure component. NH_4NO_3 at 1050 cm^{-1} . In case of homogeneous particle, the condition of the heating caused by the absorption of the laser beam suggest that the thermal resistivity of the particle substrate interference will determine the temperature rise in the particle. It is quite obvious that, aerosol encountered in the environment occurs as a mixture of substances of nuclei coated with dissimilar materials. These impurities or coating may introduce spectral interference or may cause serious heating problems due to small absorption of the laser beam.

Table(1): Raman frequencies(cm^{-1}) and observed chemical species for atmospheric aerosol

No.	Raman Shift (cm^{-1})	Groups	Raman Frequencies (cm^{-1})	Chemical Species
1	521	-	580-515	Aryl nitro compound
2	572	-	580-515	Aryl nitro compound
3	760	-	735-775	Aryl nitro compound
4	980	-	980-950	Format and acetatet
5	1015	-	1045-1015	Mono-subst. compound
6	1066	-	1080-1060	di-subst. compound
7	1275	-	1395-1250	di-subst. compound
8	1316	-	1325-1210	p=o str
9	1611	Doubled bond, aromatics Heterocycles	1625-1600	Alkyl ($\text{CH}=\text{N}=\text{N}=\text{CH}$) Aryl azines
10	1642	Doubled bond, aromatics Heterocycles	1650-1620	$\text{O}=\text{C}=\text{N}$ isocynates
11	1737	Carbonyl groups	1740-1735	Diesters
12	1803	Carbonyl groups	1900-1650	$\text{C}=(7,8,9,10,11,12)$
13	1856	Carbonyl groups	1900-1650	$\text{C}=(7,8,9,10,11,12)$
14	2327	-	2440-2300	P-H str
15	2344	-	2440-2300	P-H str
16	2436	-	2440-2300	P-H str
17	2514	NH CH SH	3500	NH CH SH
18	2559	NH CH SH	3180-3140	NH CH SH
19	3010	NH CH SH	3100-3000	CH_2 Cyclopropane
20	3058	NH CH SH	3070-3000	NH_4^+
21	3065	NH CH SH	3065-3000	Primary thiomides
22	3141	NH CH SH	3180-3140	Secondary amides bonded NH
23	3144	NH CH SH	3500-3100	NH(12,14) CH(3)
24	3315	NH CH SH	3335-3250	Primary amides
25	3396	NH CH SH	3450-3250	Secondary amides

5. Conclusions

The Raman spectroscopic techniques described above has demonstrated the feasibility of obtaining useful Raman spectra from aerosol samples collected from the environment of sugar factory. These results suggest a positive potential for the Laser Raman technique as a analytical tool. The technique developed in the present work has made it possible to identify the mixed salts which may be present in ambient aerosols. as a result of changing atmosphere conditions. The Raman frequencies documented in the presence study serve as useful guide to chemical and physical characterization of aerosol particles.

6. References

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