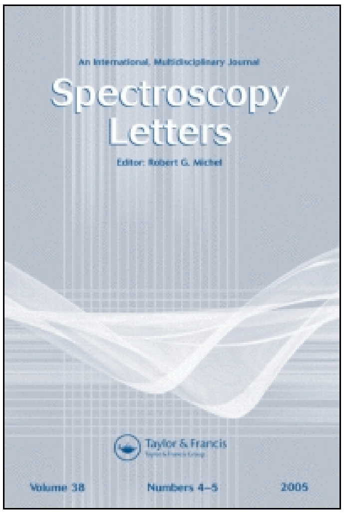

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Characterization of Humic Substances by Laser Raman Spectroscopy

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CHARACTERIZATION OF HUMIC SUBSTANCES BY LASER RAMAN SPECTROSCOPY

Key Words: Humic substances, Raman spectroscopy, Graphite-like structure

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ABSTRACT

The laser Raman scattering signals of a fulvic acid from weathered coal and four humic acids from soils have been observed. The results are similar to those of disordered graphite and the conclusion is supported with X-ray and electron diffraction data. It is found that the Raman signals aren't obviously influenced by the existing forms and states of humic substances and the presence of inorganic minerals. Therefore Raman spectroscopy will become a powerful tool for characterising humic substances in real environment.

INTRODUCTION

Humic substances (humic,fulvic acids and related substances) play a vital role in terrestrial and aquatic ecosystems, consequently their composition, structure and

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physical and chemical properties have attracted much attention[1-2]. Although many methods (e. g. X- ray diffraction, NMR, IR, electron microscopy) have been used to characterize and elucidate the structure of humic substances[1], much remains to be learned about the " building blocks " of this materials and little is known on how the " building blocks " align and what structural arrangement they produce. Besides, most of the presented methods are very difficult for characterising humic substances in real environment due to their inherent shortcomings[1].

Laser Raman spectroscopy should be particularly suitful for the study of humic substances in wet state as in the natural environment and can provide information relating to the structural arrangement of humic substances because water is a very poor scatter. However, the reports of Raman spectral mearsurement of humic substances are very scarce up to now. The main aim of this preliminary investigation is to explore the feasibility , advantages and difficulties of Raman spectroscopy for characterising humic substances. X-ray diffraction and electron diffraction analyses are also made to compare and support the result obtained from Raman spectral measurements.

EXPERIMENTAL

Reagents and Procedures

A fulvic acid from weathered coal of Gongxian (Henan province, P.R. China) was extracted and purified by ion exchange method[3]. By IR and EPR spectroscopies,X- ray diffraction, atomic absorption analysis and ash content determination ,it was found that the raw FA mainly exists as sodium,calcium and magnesium salts, ferric and copper complexes and contains 24.3 % ash which includes sulfates and silicates. However. the ash content of the purified sample was reduced to 0.75%. Higher carbon content (54.75%) and lower hydrogen content (1.98%) showed that the fulvic acid (FA) had higher humification degree. Both the raw and purified FA were used for Raman spectral measurements.

A humic acid (HA) from boggy soil was a generous gift from Prof. P. Zheng. It contained 56.87% carbon , 4.02% hydrogen and 5. 21% ash content. The humic acid was used without further purification. Four soil humic acids (Shitara Black, Komagahara, Anjo Black and Yamamono)[4] and a fulvic acid from sea water[5] were use without further purification.

The neutralized samples with different pH values were obtained by adding 0.1 mol/dm^3 hydroxide sodium solution to the FAs or HAs solutions or suspensions. Ca, Mg, Fe(III) and Cu(II) fulvates or humates were obtained by adding 0.1 mol/dm^3 chloride of metals to the FAs or HAs solutions with pH8. Distilled water was used in all experiments. The solid samples were obtained by freeze-dried.

Raman Spectral Measurement

Normal Raman spectra were recorded on a Spex Model 1403 double-grating spectrometer equipped with a Spectra-Physics Model 2025-5 Ar ion laser operating on the 514.5nm line or a Spectra- Physics model 165 Krypton ion laser on the 647.1nm line. The spectra did not change when 488.0 or 457.9nm radiations were used. The measurement of the Raman spectra of the solid samples were carried out by rotating KBr discs at 3000 rpm. The spectra of the solutions or suspensions were recorded with capillary tubes. In order to minimize laser- induced reactions, sample solutions were circulated through glass capillary tubes using a peristaltic pump. Data acquisition conditions were as follows : Laser power 150 mw, integration time 1 s, scan step length 1 cm^{-1}/s, slit width 400 um. In such a typical experiment, a satisfactory spectrum could be obtained with three scans.

The Fourier Transform Raman spectra were recorded on a Perkin -Elmer 2000 FT-IR-Raman spectrometer.The 1.064 um line of an Nd: YAG laser was used as exciting radiation, and an InGaAS detector was employed. The spectra were scaned in the range 3500--400 cm^{-1} at resolution of 3 cm^{-1}. 100 scans were co-added with 50 mw laser power.

The X-ray diffraction for powered samples were measured by using a Rigaku Denki X- ray diffractometer. Thecondition and the procedure were very similar to ref. 6. The electron- diffraction experiments were carried out by a Philips EM-400T electromicroscoper.

RESULTS

As a typical example, the normal Raman spectrum of the purified FA solution (60 g/dm^3) from weathered coal is shown in Fig.1A. The other spectra of its salts and complexes in solid state and in wet state (solutions or suspensions) aren't shown since all these spectra are very similar to Fig.1A. Only two broad bands at 1386 cm^{-1} and 1608 cm^{-1} are observed. Half width at 1386 cm^{-1} is 119 cm^{-1} and half width at 1608 cm^{-1} is 60 cm^{-1}.In addition, the relative intensity ratio (I_{1386}/I_{1608}) is equal to 0.86.

Fig.1B is the normal Raman spectrum of the raw FA material containing large amounts of impurities.It is found that the spectrum does not seem to be influenced by the impurities and only two similar bands are observed.

The normal Raman spectra of the HA from boggy soil in concentrated solution are shown in Fig.2. Fig.2A is recorded by using Ar^+ laser (514.5 nm) and Fig.2B is recorded with Kr^+ laser (647.1nm) . Clearly, using Kr^+ laser is better than using Ar^+ laser at least for avoiding or weakening fluorescence background.Similar Raman spectra of the HA can be obtained in its wet state and solid state when Kr^+ laser is used and the detection limit is 60 g/dm^3. However, these results cann't be obtained due to too strong fluorescence when Ar^+ is used.

Three kinds of humic acids with high degree of humification (Anjo Black, Shitara Black and Komagahara) [4] and their salts or complexes in wet state (suspension or concentrated solutions) and in solid state can be also successfully

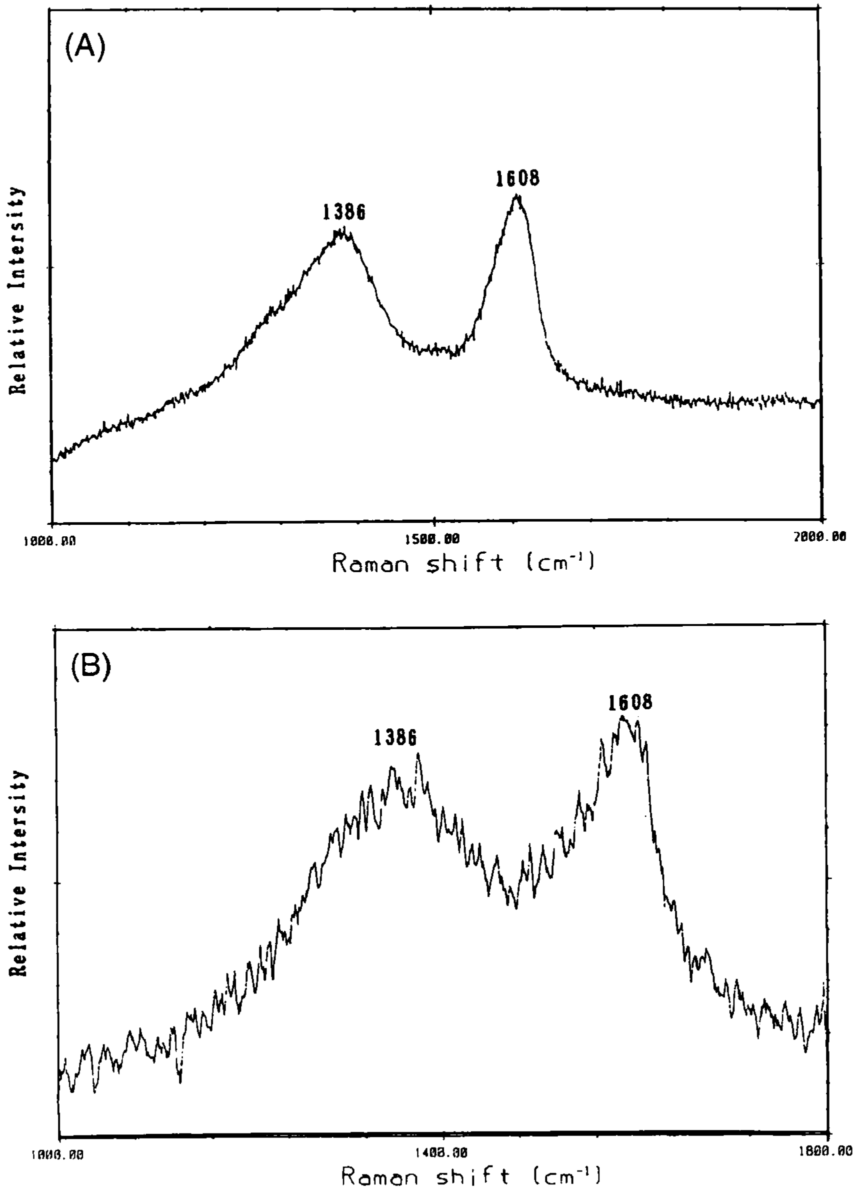
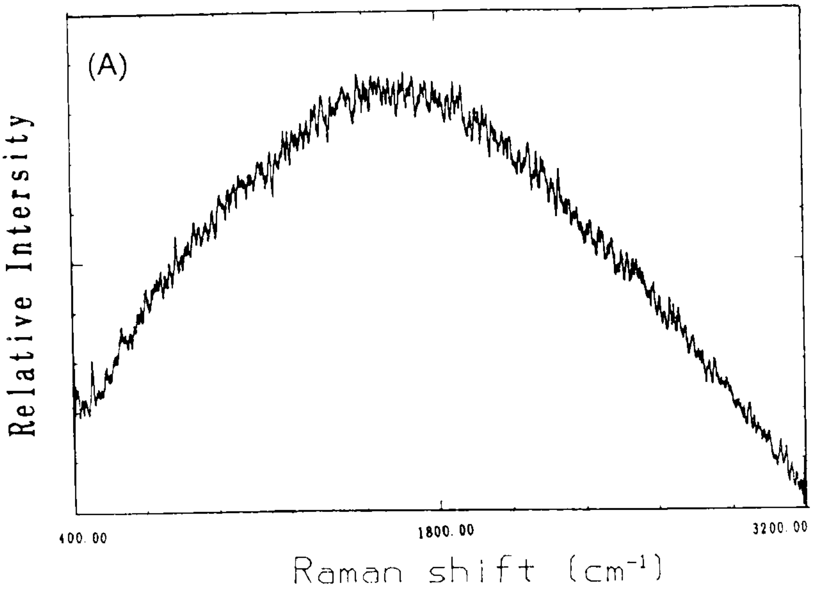


Fig.I Raman spectra of the fulvic acid from weathered coal, Ar^+ laser is used.

A. For the purified FA solution

B. For raw FA in solid state



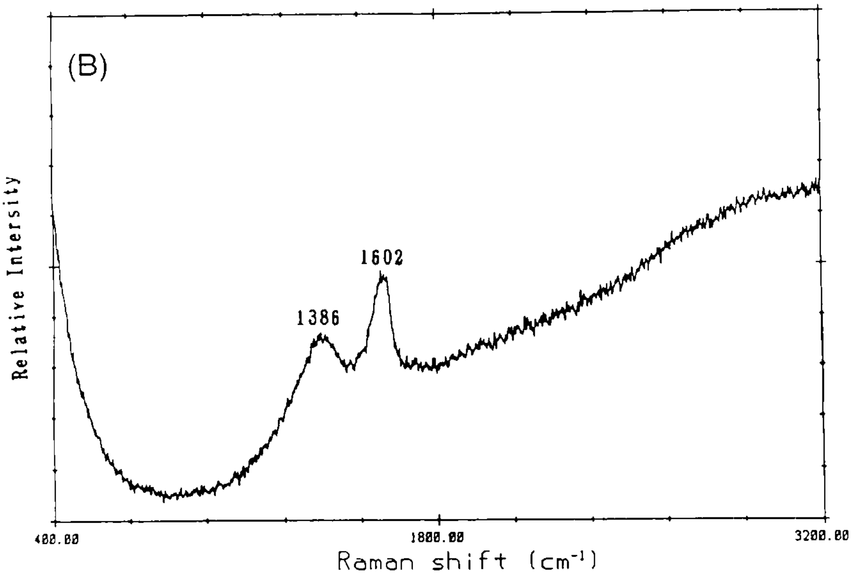


Fig.II Raman spectra of the HA from boggy soil in concentrated solution (80 g/l, pH9.0)

A. Ar^+ laser is used.

B. Kr^+ laser is used.

characterized by Raman spectroscopy. The spectra are also very similar to Fig.1 and Fig. 2. The detection limits for their solutions are also ca.60 g/dm^3 when Kr^+ laser is used.

The Raman spectra shown in Fig.1 and 2 are very similar to the ones of typically disordered graphite-like materials[7,8]. The 1386 cm^{-1} band has been assigned to in-plane c-c phonons at the M point of the Brillouin zone and is called the D band[7,8] The band at 1608 or 1602 cm^{-1} originates from the zone-center E_{2g} mode of graphite and is called the G band[7,8]. Both are mostly used to diagnose graphitic materials[7,8].

To substantialize the conclusion, the FA and HAs are analyzed by using X- ray and electron diffraction methods. The X- ray diffraction pattern of the purified FA in fine powder state is shown as Fig.3. It is very similar to that of A type HAs reported by Matsui et .al[6] and exhibits two peaks at d= 3. 5 Å and near 2. 1 Å due respectively to (002)- and (10)- bands of graphite. The HA from boggy soil has no enough quantity for X- ray diffraction analysis. The salts and/or complexes of the FAs and HAs cann't be analyzed by this method due to the same reason. The X-ray diffraction pattern of the other HAs have been given and characterized their graphite- like structure.[6]

The electron diffraction pattern (× 80000 folds) from the purified sodium salt (pH 9.0) of the FA from weathered coal is shown as photo 1. The analytical data obtained according to ref.9 is shown in Table 1.

The results of other samples are not presented here, since this result here is a typical example. Most of the spacings in Table 1 are almost identical with those of Graphite 2H[10]. Undoubtedly, the structure arrangement of the "building blocks" of these samples are graphite-like with crystal defection, and they also support the conclusion from Raman spectral analysis.

However, the normal Raman spectra of a soil HA (Yamamono) [4] and a FA from ocean[5] cann't be observed since Kr^+ laser is used. To slove this problem, we try to use FT-Raman spectroscopy[11].Unfortunately, although fluorescences background disappears, another source of strong background has buried Raman scattering from most

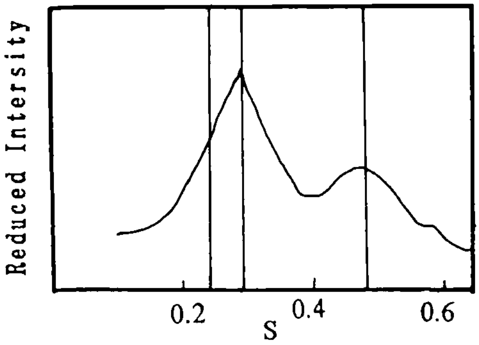


Fig.III X-ray diffraction pattern of the purified FA from weathered coal in fine power state

Photo.1 Electron diffraction pattern from the purified Na fulvate from weathered coal

Table 1 Analyses of Electron Diffraction Pattern

	r (mm)	d(Å)	hkl indices	Lattice Parameter a=b(Å)	Lattice Parameter c(Å)
1	8.85	3.34	002		6.69
2	10.75	2.75			
3	14.50	2.04	101	2.47	6.69
4	16.90	1.75	102	2.37	6.69
5	17.80	1.66	004		6.65
6	20.53	1.44	103	2.17	6.69
7	22.80	1.30	110	2.57	6.69
8	25.00	1.18	112	2.53	6.69

of the samples. The strong background results from continuous blackbody radiation emitted by particles of carbon[11].It is difficult to avoid that due to the "native" deep colours of humic substances. Fig. 4 is the FT-Raman spectrum of the fulvic acid from ocean water[5]. Since the FA is reddish, there are still three Raman bands at 2940 cm^{-1} (asymmetric CH stretch of -CH$_2$, -CH$_3$)[12], 1601 cm^{-1} (aromatic C=C stretch) [12] and 1317 cm^{-1} (-CH$_2$ torsional vibration)[12] on strong background from thermal emission. Clearly, the "building block" of the FA has a large derivative from disordered graphite and should be ascertain by further study.

DISCUSSION

On the basis of these results from Raman spectral measurements, it can be concluded that the feasibility of Raman spectroscopy to characterization of humic substances has been demonstrated.

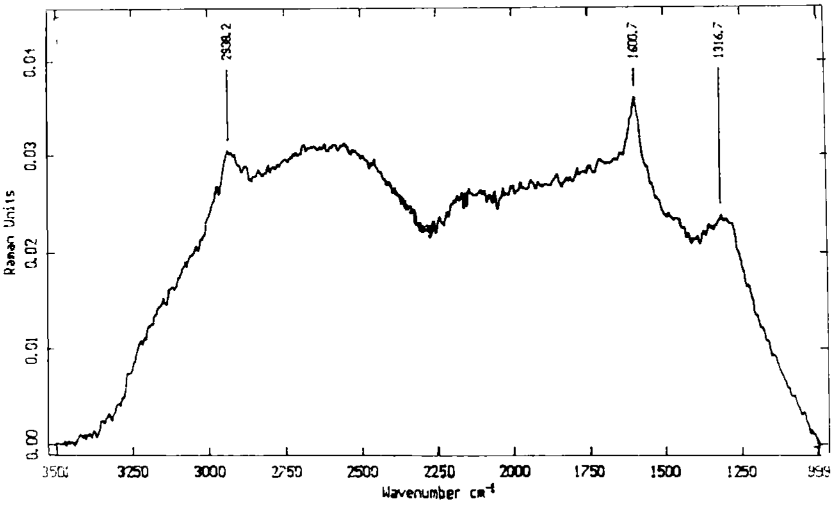


Fig.IV FT-Raman spectrum of the FA from sea water in solid state

Since more and more evidences have shown that humic substances exist as large aggregates in solid state and in wet state (suspension and/or concentrated solution)[2], disordered graphite structures of humic substances should be thought as the structural arrangement of the building blocks from aggregation of small molecules. The very important advantages are that Raman spectroscopy can be easily used to detect humic substances in their "native" wet state as well as in solid state, and the structural information of humic substances provided by this technique aren't influenced by the existing forms of humic substances and the presence of inorganic minerals. Besides, another advantage is that only a small amount of samples is used for Raman spectral measurement

Thus, it is very possible that Raman spectroscopy provides a new, promising approach for "in situ" charactering humic substances in real environment and is also very useful for building "bridge" among their different states.

By the way, since disordered graphite structure of some humic substances have been detected in concentrated solutions, anisotropy must have a important contribution for broadening ^{13}C NMR peaks of some humic substances because the ^{13}C NMR spectra were often recorded in their concentrated solution (e. g. 100 g/dm^3) [2]. This problem should be noticed in further ^{13}C NMR measurements.

One shorting is that strong fluorescent background is often the obstacle in normal Raman spectral measurement. Besides, humic substances are colour and will absorb energy from the exciting beam and therefore Raman scattering is weak. Due to the same reason, thermal emission gives very strong background in FT-Raman measurement.However, we believed that these problems are only tentative. If coherent anti-Stokes Raman or Surface-enhanced Raman scattering are used, fluorescence should be quenched or weaked, and dilute solution is tested at the same time[13] . Thus thermal emission and adsorbance should be avoided in normal and FT-Raman spectral measurement. Further study is testing these assumptions.

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