The Application of Infra Red (Ir) Spectroscopy For Rapid Characterization Of Clays From Odukpani South Eastern Nigeria.

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Abstract: This paper demonstrates the utility of Infra Red (IR) Spectroscopy for rapid routine analysis of clay samples for the purposes of characterization and to a lesser extent identify them. Specifically, the area of the IR absorption bands (obtained by measurements of absorption bands) have been used to estimate both wave number, absorption bands and type of hydrogen bonding in the clay samples. Results of the investigations on clay samples are presented and discussed.

Keywords: Clays, Characterization and Infra-Red Spectroscopy.

INTRODUCTION:

Frequently used techniques for clay characterization include X-ray diffractometry (XRD), (Emufurietaet al., 1992; Obaje and Ekpenyong, 1997; Oden et al., 2000 and Osaboret al., 2010), atomic absorption spectroscopy (AAS) (Okolo and Chima, 1979, Odigi, 1989) Thermal analysis (Szaboet al., 1974; Osabor et al., 2010). Total Organic Carbon (TOC) (Emufurietaet al., 1992) and other chemical and physical properties (Ekosse, 1990, Attahet al., 2001 and Hassan, 2000).

Some of the analyses are very cost intensive and the instruments are not readily available. To solve these problems to some extent, there are needs for a judicious choice of techniques for detailed analysis. Such selection should be guided by a rapid screening analysis. Three plausible screening techniques as proposed by Szaboet al. (1974) include X-ray diffraction, thermal analysis and recently Infra Red Spectroscopy.

The main phase changes such as exothermic and endothermic occurring in clays by heat treatment are well known. Most of the researches have been directed to study formation of metakaolinite 600-900oC, the spinel 900-1100oC and mullet 1200-1400oC phases and their structures in clays.

The X-ray diffraction analysis gives information on the mineralogy of the clay samples such as Kaolinte, quartz, feldspar, illite, montmorillonite etc. The atomic absorption analysis of clays mainly documents information on the metal and metal oxides compositions. These instruments are not readily available because of their relatively high cost.

The present investigation is based on the infra red (IR) analyses of Odukpani clay samples. It demonstrates the usefulness of IR spectrophotometer for clay characterization. Earlier, infra-red study was directed towards kaolinite structure (Szaboet al., 1974). The method presented here avoids the time consuming procedure for clays identifications and thus makes it particularly valuable as rapid routine and screening tool.

Infra red spectra of carbonaceous samples, like coal and asphaltene are very similar and do not offer the possibility of having the finger prints of these organic substances (Udo and Etuk, 1990).

However, the estimation of the band intensities (via measurement of the absorption bands) in the IR spectra of these carbonaceous substances have prove the IR technique to be very valuable semi quantitative tool based on the functional groups analysis of this complex organic solids. Through such analysis, differences both in wave number and absorption bands can be estimated.

Different vibrational modes such as stretching vibration, bending vibration and molecular vibration (bend) have been used to describe the atomic vibration (Van Dar Marel and Bentelspacher, 1976). The most useful regions of IR spectra for clay minerals are in OH vibrational region, because of access to information are not available from other Analytical methods. IR spectra reveal the bonding energy of the OH bond on the sheet silicate structures. The absorbed water can be investigated using IR methods.

IR spectral analysis is particularly useful in determining the environment of the crystalline water (OH) in clay and the arrangement of octahedrally co-ordinated cations. Szabo et al (1974) investigated the Georgian kaolin using IR spectra. The results obtained showed that the IR spectra between 400 and 1200cm-1 and bands of the following wave numbers (cm-1) were identified σSi-O, 540 Al-O-Si, 700, 755, Vs Si-O-Si, 913 σAl-O-H, 1010, 1040 Si-O, 1100 Vs Si-O-Si. Between 3500 and 3636cm-1 four types of OH absorption bands were observed: 3686cm-1 for free OH group situated at the surface of the dioctahedral layer, 3660cm-1 intra particle hydrogen-bonded OH- groups situated at the dioctahedral surface 3642cm-1hydrogen bonded OH groups situated between layers and 3616cm-1 for inter particle hydrogen bonded OH groups situated at the unoccupied positions of the tetrahedral layer.

The present investigation is based on the use of IR

spectrophotometer as a research tool for clay characterization and identification. The crystallohydrates chosen for this study is the Odukpani clay samples. Earlier works on this clay deposit were mostly related to their chemical compositions and mineralogical properties (Attahet al., 2001 and Oden et al., 2001.)

EXPERIMENTALS:

Ten ditch cutting samples obtained from IkotOmin clay deposit in Odukpani Local Government Area , Cross River state, South-South Nigeria; Fig 1 were analyzed. These samples cover a depth range of 10-40m and were representative of Odukpani clay beds with the cretaceous and tertiary sedimentary sequence in the Niger Delta Basin (EkwUemeet al., 1995).

The ten samples under investigation were air dried for two weeks before being pulverized. The total organic carbon (TOC) was determined by the (Walkey-Blacky, 1934) method. The organic matter (OM) content was estimated by multiplying the TOC values by 1.44.

The Fourier Transform infra red spectra of the samples under investigation were recorded between 400cm-1 – 4000cm-1 on IF 566 V/S beam Spectrometer. Measurements were carried out at room temperature by diffuse reflectance method (mixture of sample with KBr in ratio of approximately 1:20). The KBr window using MIR infra red source operated at 5mbar vacuum at room temperature with a voltage of 220 X 10A single phase and a frequency of 50Hz was used.

RESULT AND DISCUSSIONS:

Table 1 presents total organic carbon (TOC) and organic matter (OM) contents of the clay samples. There is an ordered variation of TOC with depth (from 0.52 to 1.33%) apart from some few fluctuations which are expected in nature. Table 2 presents identified absorption bands in the IR spectra of the samples. Table 3 presents infra red vibrating frequencies (cm-1) for the clay samples. The results for IR spectral studies of the clay samples are presented in Fig. 1 – 3 .

DISCUSSIONS:

The total organic carbon (TOC) and organic matter (OM) of the samples are mainly sediments and exhibited small variations in the total organic carbon contents. The TOC values ranged from 0.52% (samples/K1) to 1.33% (samples/K4) with a mean TOC value of 0.85%. The organic carbon contents of the samples studied is high. Emufurietaet al (1992) reported TOC values of 0.91%, 0.89% and 25% for Ubulu-uku, Awo-omama and Buan clay samples respectively. Table1 also shows the results of the analyses of clay samples from the different locations for organic matter (OM) contents. The results obtained ranged from 0.7488% (sample K5) to 1.9152% (samples/K9) with a mean value of 1.3493%. The organic matter contents of Odukpani clay samples compared favorably well with the 1.54% obtained by Emufurietaet al (1992) for Awo-omama clay samples. The IR spectra between 400 cm-1to 1200 cm-1 the following band separations were identified 430.3, 470.6, Si-O, 538.8 Al-O-Si, 695.8, 754, 796.3, Vs Si-O-Si, 913.4 Al-O-H, 1001.7, Si-O, 1399.9, 1628.6, 1822.2 Vs Si-O-Si. Between 3400 and 3750 cm-1 four types of OH absorption bands were observed and are in agreement with literature data (Szaboet al., 1974). These are 3696 cm-1 for free OH groups situated at the surface of dioctahedral layer, 3652.4 for inter particle hydrogen bonded group situated at dioctahedral surface, 3620.4 cm-1 for intra particle hydrogen bonded OH groups situated between the layers and 3436.6 cm-1 for intra particle hydrogen bonded OH groups situated at the unoccupied positions of the tetrahedral layers.

Figures 1 – 3 show the IR spectra of the clay samples. The main features of all the spectra are somewhat similar on the basis of frequencies of vibrations in the low infra red region between 400 and 1200 cm-1, the bands for the samples under investigation are associated with stretching vibrations of Si-O and Al-O tetrahedral vibrations, Al, Fe and Mg Octahedral and Si-O-Si octahedral vibrations. The vibration modes of OH stretch appears on the infra red region of 3500-3700 cm-1. the results obtained from this investigation compared favorably well with those in the literature (Szaboet al. 1974, Velda, 1992 and Essienet al. 2011). These samples also have very broad bands (between 3600 and 3200 cm-1), this suggests possible effects of hydrogen bonding possibly associated with water adsorbed on these samples.

CONCLUSION:

Clay samples obtained from Odukpani, South-Eastern Nigeria have been characterized using infra red spectroscopy. The use of infra red (IR) spectroscopy as a semi quantitative tool, based on functional group analyses, demonstrates the utility of this technique as a versatile tool for rapid routine analysis of clay samples. The results of infra red (IR) spectroscopy conveniently complete other methods so far utilized in previous studies, viz DTA, TGA/DTG, dilatometry and X-ray analysis. The IR spectra of these samples have helped in characterizing and identifying the wave number and absorption bands of the samples under investigation.

Table 1: Total Organic Carbon (TOC) and Organic Matter (OM) contents

Sample No.	Depth (m)	Sample Code	TOC (%)	OM (%)
1	1	K_1	0.52	0.747

2	3	K_2	0.92	1.325
3	4	K_3	0.60	0.864
4	5	K_4	0.63	0.9072
5	10	K_5	0.52	0.749
6	15	K_6	0.86	1.238
7	20	K_7	1.81	1.166
8	22	K_8	1.10	1.584
9	27	K_9	1.33	1.915
10	30	K_{10}	1.22	1.757

Table 2: Infra-red (IR) Spectral Studies of the Samples.

S/N	Absorbing Group	Vibration Mode	Wavelength of Absorption (cm^{-1})
1	OH	Stretching Vibration	3600 – 3200
2	Si-O-Si	Assymetrical Stretching Vibration	1600 – 2010
3	Si-O	Bending Vibration	1000 – 2000
4	Al-O-H	Stretching	806 – 1000
5	Si-O-Si	Stretching Vibration	600 – 800
6	Al-O-Si	Stretching Vibration	538.8
7	Si-O	Stretching Vibration	400 – 470

Table 3: Infra-red Vibration Frequencies (cm^{-1}) for Odukpani Clay Samples.

K_1	K_2	K_3	K_4	K_5	K_6	K_7
3696.3	3696.7	3696.6	3696.5	3696.8	3496.6	3696.6
3652.4	3652.6	3652.5	3652.4	3652.3	3652.6	3652.6
3620.4	3620.5	3620.3	3620.4	3626.1	3620.5	3620.5
3436.6	3434.4	3433.8	3436.6	3421.2	3434.4	3434.7
1822.2	1633.6	1627.4	1826.7	1635.6	1633.6	1633.6

1628.6	1103.5	1399.9	1628.5	1398.0	1103.5	1103.5
1399.9	1033.3	1399.9	1388.0	1030.0	1007.7	1007.7
1001.7	1007.7	1032.5	1002.9	1001.9	913.3	913.3
913.4	913.3	913.4	913.6	913.8	795.9	795.4
796.3	795.9	796.2	796.3	755.6	695.4	695.4
754.5	753.6	754.5	754.5	696.3	538.3	538.3
695.8	695.4	696.2	752.1	536.0	469.8	469.8
537.8	538.3	539.6	536.9	470.0	430.8	430.8
470.6	469.8	470.4	470.4	431.2		
430.3	430.3	430.0	430.6			

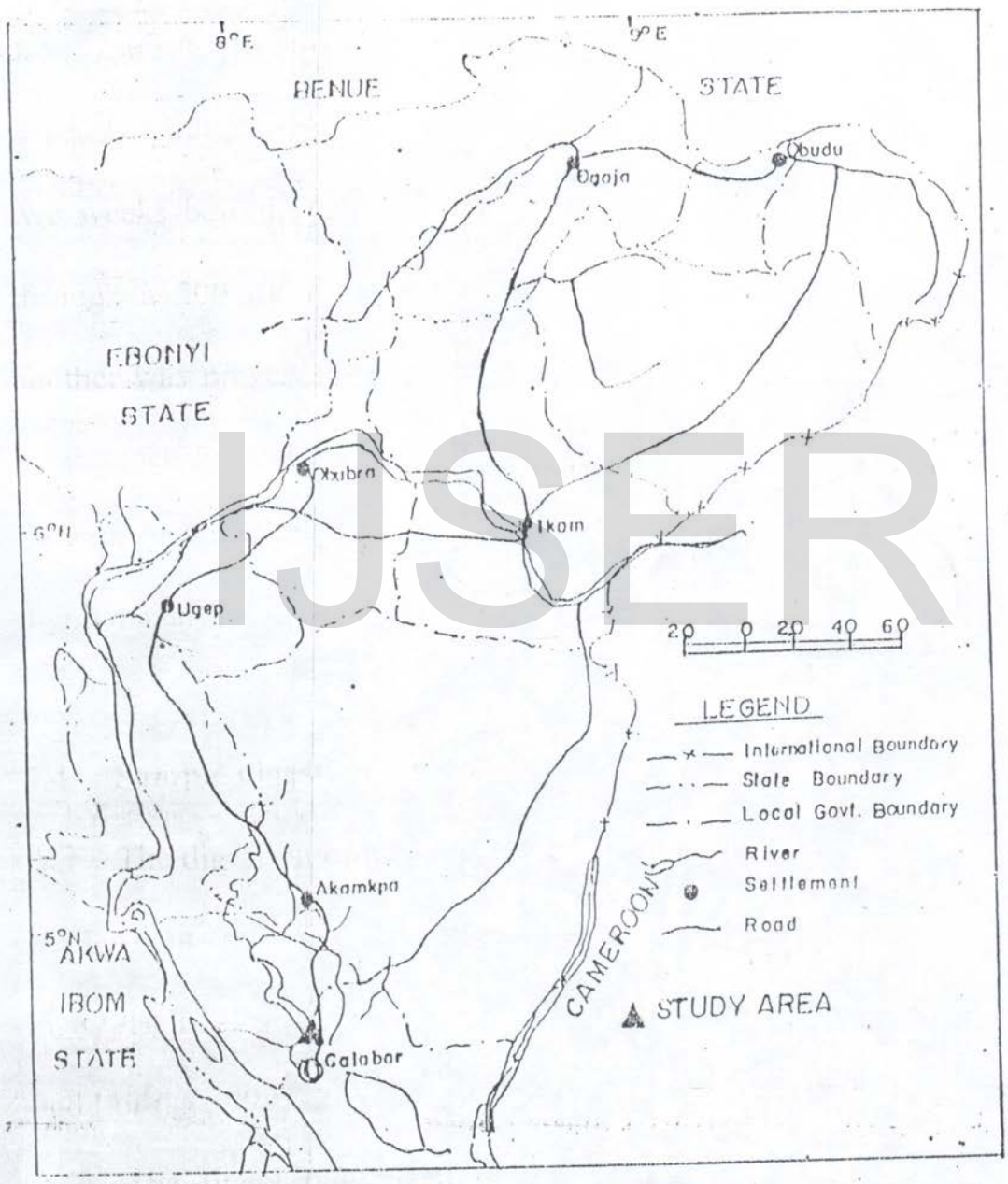
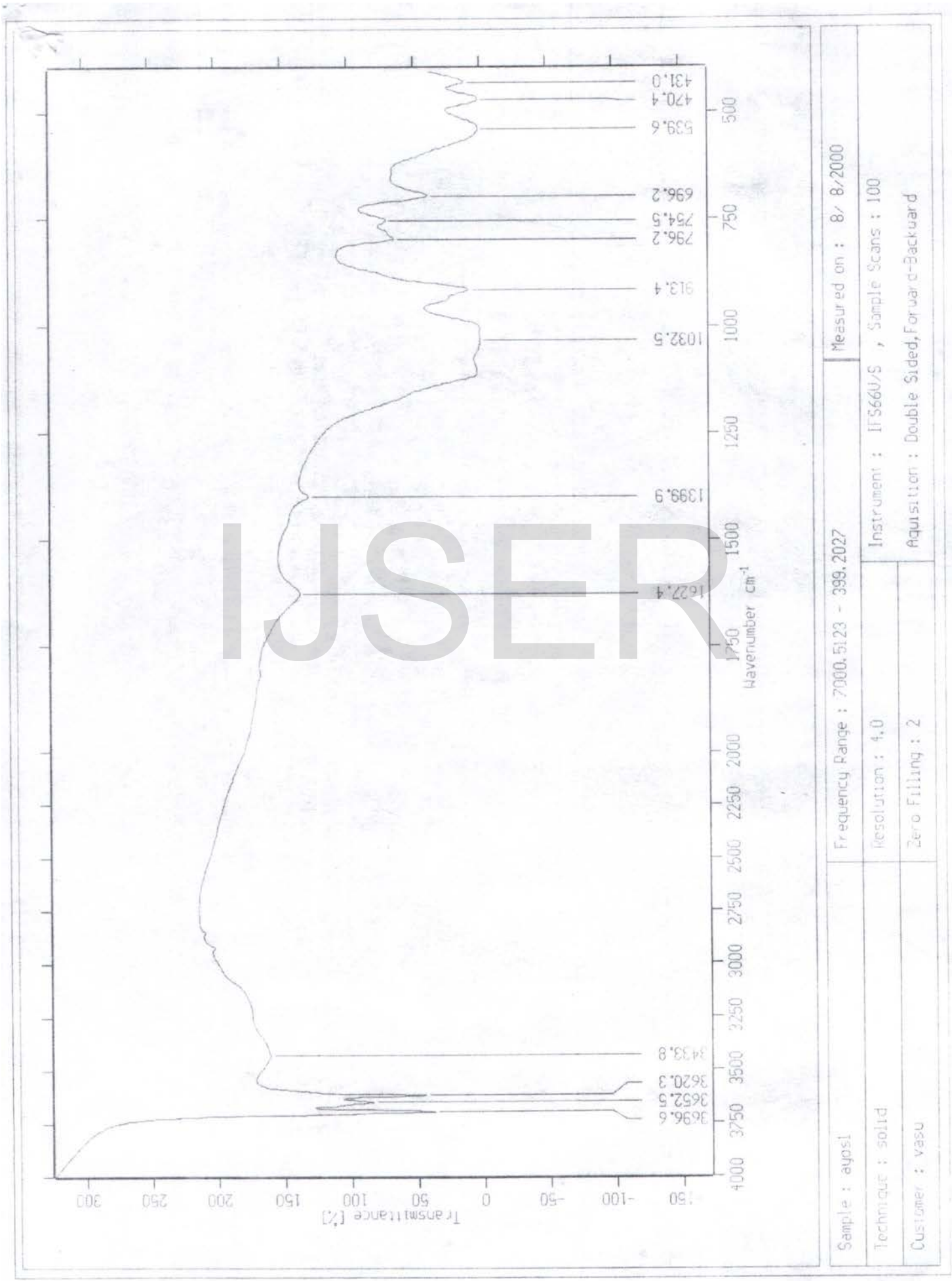


FIG.3.1 Generalised map of Cross River State showing Study Area. (From the State Geological guide Ekwueme et al, 1995).


431.0
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Wavenumber cm-1
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Sample : ayasi
Technique : solid
Customer : vasu
Frequency Range : 7000.5123 - 399.2027
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Measured on : 8/ 8/2000
Instrument : IFS66V/S , Sample Scans : 100
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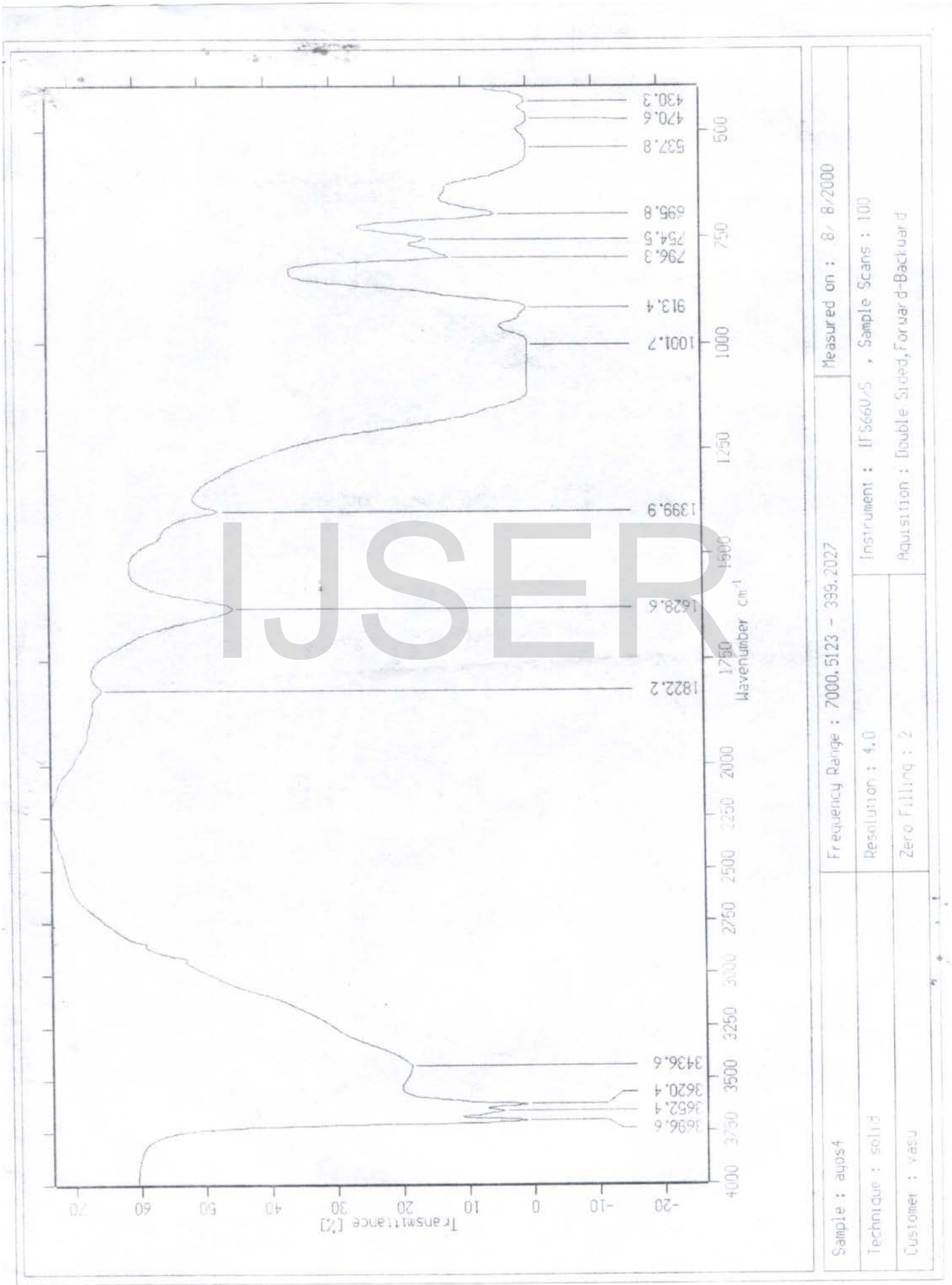
430.3
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3436.6
3620.4
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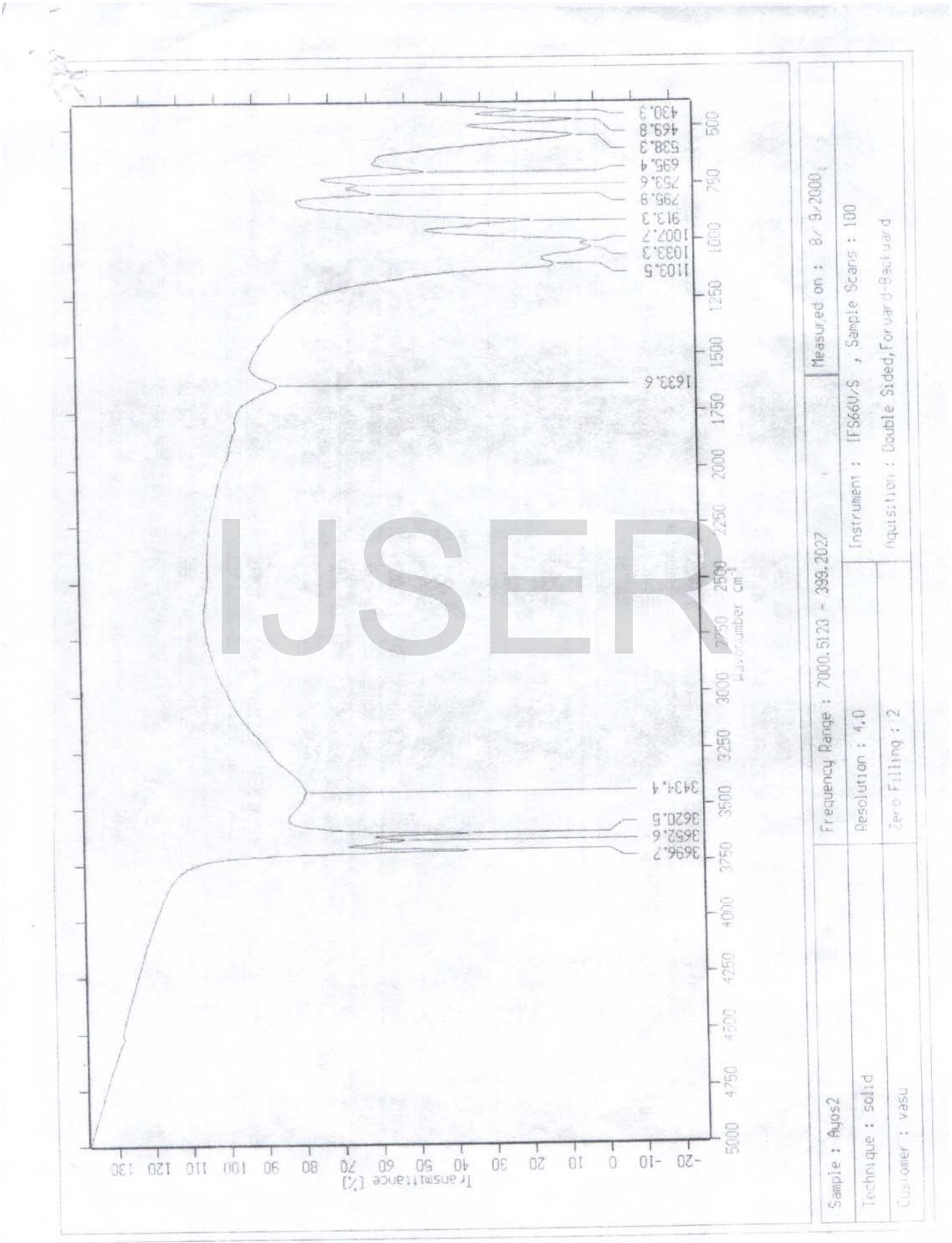
Wavenumber cm-1
Transmittance [%]
Sample : ayos4
Technique : solid
Customer : vasu
Frequency Range : 7000.5123 - 399.2027
Resolution : 4.0
Zero Filling : 2
Measured on : 8/ 8/2000
Instrument : IFS66v/S , Sample Scans : 100
Aquisition : Double Sided,Forward-Backward


Transmittance [%]
Wavenumber cm-1
3696.7
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1633.6
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1033.3
1007.7
913.3
795.9
753.6
695.4
538.3
469.8
430.3
Sample : Ajos2
Technique : solid
Customer : vasu
Frequency Range : 7000.5123 - 399.2027
Resolution : 4.0
Zero Filling : 2
Measured on : 8/ 9/2000
Instrument : IFS66V/S , Sample Scans : 100
Aquisition : Double Sided,Forward-Backward

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