Colloid Thruster Propellant Stability after Radiation Exposure[◊]

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We present a characterization of the stability of critical characteristics of the ionic fluid EMI-Im ($C_8H_{11}F_6N_3O_4S_2$) to the operation of colloid microthrusters in gamma radiation environments. This propellant was selected by Busek Co. for their colloid microthruster that will be flown on Space Technology 7 Disturbance Reduction System (ST7-DRS) demonstration mission because of its high conductivity, low vapor pressure and performance as an electrospray. The complicated nature of this propellant and the radiation environment of the ST-7 spacecraft warranted this investigation to ensure that the performance of the thruster will remain stable and predictable throughout the mission. In this investigation the fluid was exposed to 2x and 20x the expected mission dose of gamma radiation. The fluid viscosity, conductivity, chemistry, contact angle, and I-V characteristics in the colloid micro thruster were characterized before and after the exposures to determine the impact of the exposures on them. The results showed that the radiation induced slight changes in the contact angle of the fluid on gold and stainless steel, the refractive index of the fluid and some breakdown of the parent compound to liberate trace amounts of CF_3 and SO_2.

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1 Introduction

Colloid microthrusters will be used continually for three months during the ST7-DRS mission at 1 AU to control the spacecraft position within 10 nm/√Hz. During the entire year-long mission, a maximum total dose of less than 5 kRad has the potential to change critical characteristics of the propellant and interfere with proper thruster operation.

Because of the complicated nature of the propellant, there were concerns that the radiation environment can breakdown propellant molecules, change important physical characteristics of the liquid propellant, and produce volatiles that may interfere with proper thruster operation. The liberation of any vapors from the fluid or from the internal walls of the propellant system, including the stainless steel and gold needles, could result in the formation of bubbles that will get entrained with the fluid flowing through the needles and result in unpredictable and unstable thrust. The formation of particulates in the propellant or at the interface between the propellant and the feed system walls could result in unstable thrust if the particles get entrained in the fluid in the needles and/or restrict flow through valves and filters. Changes in the propellant viscosity, conductivity or wetting characteristics will affect the flow rate of the propellant and current-voltage characteristics of the thruster.

To address these concerns about the stability of critical characteristics of the ST-7 colloid thruster propellant, EMI-Im, these characteristics of the fluid were quantified before and after exposure to gamma radiation. Propellant samples in stainless cylinders were exposed to radiation levels at 0, 10 and 100 krad. The propellant viscosity, conductivity, color, chemical composition, contact angle, and I-V characteristics in the thruster were measured for the radiated and non-radiated samples to determine the effect of Gamma radiation on these properties of the fluid. The containers used for the experiments allow for the detection of any gasses that are produced during the exposure or during the storage of the propellants. The procedure followed in the investigation and the results of this investigation are discussed in the following sections of this paper.

2 The propellant test volumes

The propellant test cylinders were fashioned from 316L stainless steel with VCR fittings on each end and internal volumes of approximately 75 mL. The cylinders were electropolished to 20 Ra. One end of the cylinders had a 315L stainless steel Veriflo 944 Diaphram valve and the other end was capped after it was filled with the propellant.

Each cylinder was thoroughly cleaned before being filled with propellant. They were rinsed with 30 ml of acetone that was filtered through 2 um stainless steel frits three times and then 30 ml of isopropyl alcohol that was filtered through 0.5um stainless steel frits three times. They were dried with a nitrogen purge through 0.5 um filters. The cylinders were filled with approximately 65-70 ml of EMI-Im through 0.5 um filters. The fluid was pressure fed through the filters with nitrogen or helium.

All nine of the cylinders were then connected at the valves by a manifold to a pumping station to evacuate the open volume in the cylinder. The estimated final pressures in the cylinders are identified in Table 1.

3 Radiation exposure

During the ST-7 mission with the spacecraft in an Earth trailing orbit at 1 AU, the expected radiation dose is 3-5 krad of gamma and proton radiation. This dose includes the dose for the mission and the orbit insertion time.

A Co-60 Shepard irradiator at JPL was used as the gamma radiation source for the fluid exposures. In this facility, the decay of cobalt-60 produces a 1.17 MeV and a 1.33 MeV

gamma photon. These photons produce secondary electrons via Compton scattering which produce ionization within the test object. A Radcal 2025 ionization chamber was used for dosimetry with 10 % accuracy. The radiation intensity was 25 Rad/s at the cylinder location. The attenuation coefficient for stainless steel for this gamma radiation is about 0.45/cm. Therefore, the incident radiation on the fluid, I = Io x exp[-0.45 x thickness (cm)].

The radiation doses to the fluid in the cylinders are identified in Table 2. The radiation doses to the cylinders were 10 and 100 krad.

4 Stability of critical propellant characteristics in gamma radiation environment

The results of the fluid characterizations before and after their exposure to gamma radiation are discussed in this section. Dielectric constant measurements were attempted, but the conductivity of the fluid was too high for these measurements. Particulate density distribution measurements were attempted using a dynamic scattering approach. However, the concentration of particulates did not exceed the minimum detectable by the instrument, $3x10^7/cm^3$.

4.1 Chemical Composition of the Fluid

The molecular formula for 1-ethyl-3-methylimidazolium bis(triflouromethylsulfonyl)imide, EMI Im, is $C_8H_{11}F_6N_3O_4S_2$. Chemical analysis of the fluids from cylinders 1,3,7 was conducted using vibrational spectroscopy, Diffuse Reflectance/Fourier Transform Infrared (DRIFT/FTIR) and Raman, and examining the transmission spectrum in the UV (200-2500 nm). FTIR and Raman provide chemical functional group information for quantitative identification of materials. UV-Vis (200-800) transmission spectroscopy was conducted using a 1-centimeter quartz cell in a Cary 500 spectrometer. Near Infrared (800-2500) transmission spectroscopy using a 1-centimeter quartz cell in a Cary 500 Spectrometer and Karl Fisher water titration were employed to identify the water content in some of the fluid samples.

The results of the chemical analysis are presented in Figures 1 and 2. Figures 1 and 2 show that there were no significant changes in the bulk composition of the fluids from the radiation exposures. The results shown in Figure 3 support the observation that the fluids slightly yellowed with radiation dose. The yellowing of the solution could be a result of the formation of SO_2 as revealed by the mass spectrometer results on the vapor analysis. The changes in the baseline in the non-absorbing regions indicate there is small differences in the refractive index of the exposed solutions that increase with radiation exposure. Figures 4 and 5 show that water concentration was less than 100 ppm in samples 1,3 and 7 and that they varied by ~10% with no correlation to radiation dose.

4.2 Vapor Constituents

The chemical composition of the vapor in the open volume of the cylinders was detected by opening the valve on the cylinders to a mass spectrometer. The results of these measurements were also verified with a gas chromatograph. These measurements were conducted at JPL.

The effect of radiation on the composition of the vapor in the cylinders is shown in Table 3 as a comparison of the percent of the total pressure that corresponds to the most abundant constituents. It is important to note that the volume of fluid in the cylinders varied, and therefore, the volume of gas also varied. The results of the measurements suggest that the radiation increased levels of hydrogen, fluorocarbons (CF_3), isopropyl alcohol, CO_2 and SO_2. The results also suggest that the radiation exposure decreased levels of oxygen and argon in the vapor.

4.3 Physical Appearance of the fluid

The appearance of the fluid before the radiation exposures was clear. The 10 kRad exposure very slightly yellowed the fluid. The 100 krad exposure yellowed the fluid slightly more.

4.4 Viscosity of the fluid

The viscosity of the fluids in cylinders 5, 6 and 8 was measured at 10, 20 and 30°C at Saybolt Laboratories using the ASTM-445 procedure. The measured viscosities are shown in Table 4. The results show that radiation had no effect on the viscosity of the fluid.

4.5 Conductivity of the fluid

The conductivity of the fluid was measured at Brookhaven Instruments using one of their commercial instruments. The results of the measurements are shown in Table 5. These data also show that the radiation had no effect on the conductivity of the fluid. The conductivity was also measured on a fluid sample that was not radiated, however it was exposed to an extremely humid environment

4.6 Contact Angle of the fluid

The Busek colloid thruster that will be flying on ST-7 employs stainless steel needles with gold coated tips. The contact angle measurements were taken at 25 °with First Ten Angstroms instrument and software. The contact angle of the EMI-Im was measured on both stainless steel and gold.

The results of these measurements indicate that the contact angle is affected by the radiation exposure. They are presented in Table 6. The contact angle decreased with radiation exposure on the stainless steel substrate and increased with radiation exposure on the gold substrate.

5 Conclusions

In response to concerns by the ST-7 flight program about the stability of the colloid microthruster propellant EMI-Im in radiation environments, critical characteristics of the fluid were quantified before and after exposure to gamma radiation levels that were 2x and 20x the expected mission dose. The results of the measurements showed that

-there were no significant changes in the bulk chemistry from the radiation exposure

-CF_3(10,100kRad), and SO_2 (100 kRad) degradation products were formed at low concentration from radiation exposure, indicating breakdown of the parent compound.

-the fluid yellowed slightly from the radiation exposure (expected from SO_2 formation).

-refractive index was affected by radiation exposure.

-the viscosity of the fluid was not affected by the radiation exposure

-the conductivity of the fluid was not affected by the radiation exposure

-the contact angle of the fluid increased on gold and decreased on stainless steel with radiation exposure.

Acknowledgements

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References

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TABLES

Table 1. The cylinder open volume pressure before the radiation exposure.

Cylinder	Pressure
1	4.0×10^{-5}
2	3.3×10^{-5}
3	2.9×10^{-5}
4	2.7×10^{-5}
5	2.1×10^{-5}
6	3.3×10^{-5}
7	9.0×10^{-6}
8	3.0×10^{-5}
9	1.5×10^{-5}

Table 2. The radiation dose to the fluid in each of the cylinders.

Cylinders	Radiation Dose (kRad)
1, 5, 9	0
2, 7, 8	9.28
3, 4, 6	92.8

Table 3. The percent of total pressure of the most abundant constituents in the vapor trapped in the open volume of many of the cylinders.

Sample #	**#5**	**#9**	**#2**	**#8**	**#4**	**#4**
Dose (kRad)	**0**	**0**	**10**	**10**	**100**	**100**
Po	2×10^{-5}	1.5×10^{-5}	3.3×10^{-5}	3.0×10^{-5}	2.7×10^{-5}	2.7×10^{-5}
P (Torr)	3.4	11.1	11.5	9.4	1.0	1.0
Nitrogen	75.9 %	73.9 %	89.2 %	91.2 %	19.1 %	8.23 %
Oxygen	13.7 %	14.6 %	4.38 %	1.55 %		
Argon	2.73 %	4.19 %	1.63 %	1.14 %	5,124 ppm	5,154 ppm
CO_2	1,613 ppm	615 ppm	1,200 ppm	1,397 ppm	1.36 %	1.23 %
Moisture	1.28 %	2,893 %	3,758 ppm	5,341 ppm	21.6 %	29.6 %
Hydrogen		257 ppm	8,175 ppm	1.15 %	3.7 %	2.61 %
Helium	1.69 %	5.94 %				
Flourocarbon			1,746 ppm	2,663 ppm		
SO_2					3,942 ppm	5,931 ppm
ISP-ALC	3.59 %	9,652 ppm	3.28 %	4.03 %	52.4 %	56.1 %
Methanol	9,540 ppm				9.253 ppm	1.18 %
Notes					Flourocarbon (69, but no 119)	Flourocarbon present also- mass 69, but no 119

Table 4. Viscosity measurements on the EMI-Im after 0, 10, and 100 kRad radiation doses at 10, 20 and 30°C.

Sample	**Viscosity cSt (cP) at 10C**	**Viscosity cSt (cP)at 20C**	**Viscosity cSt (cP) at 30C**
Sample #5, 0 rad	39.0 (59.67)	26.60 (40.7)	17.50 (26.79)
Sample #8 10 kRad	37.91 (58.0)	24.53 (37.53)	17.12 (26.19)
Sample #6, 100 KRad	38.73 (59.26)	25.01 (38.27)	17.08 (26.13)

Table 5. Conductivity measurements on the EMI-Im after 0, 10, and 100 kRad radiation doses and after extreme hydration.

Sample	**Conductivity** u-Seimens/ cm	**Conductivity after hydration** u-Seimens/ cm
#9 (0 kRad)	7950	9230
#2 (10 kRad)	6380	
#4 (100 kRad)	7660	

Table 6. Contact angle measurements of the EMI-Im on Stainless Steel and Gold after 0, 10, and 100 kRad radiation doses.

Sample	**Contact Angle Stainless Steel**	**Contact Angle Gold**
Sample #1, 0 kRad	27.2	35.1
Sample #7 10 kRad	25.9	37.1
Sample #3, 100 kRad	25.2	40.7

FIGURES

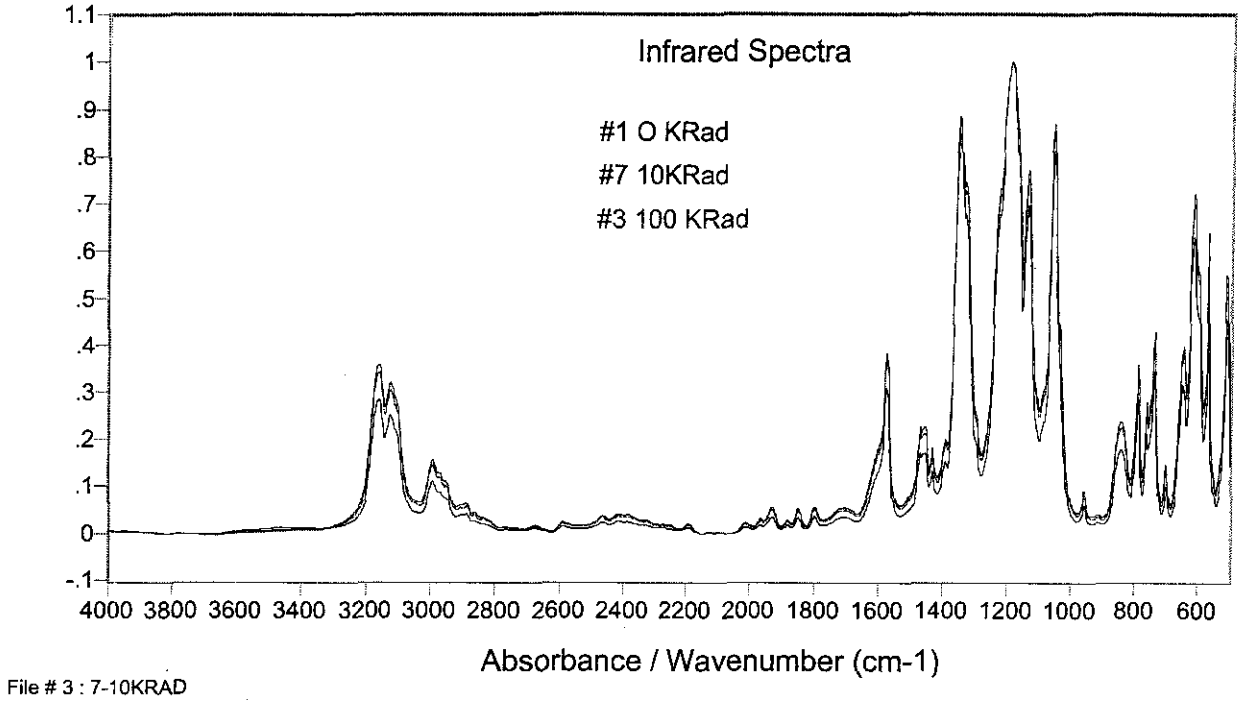

Figure 1. Comparison of the infrared spectra for fluids with varying levels of radiation exposure.

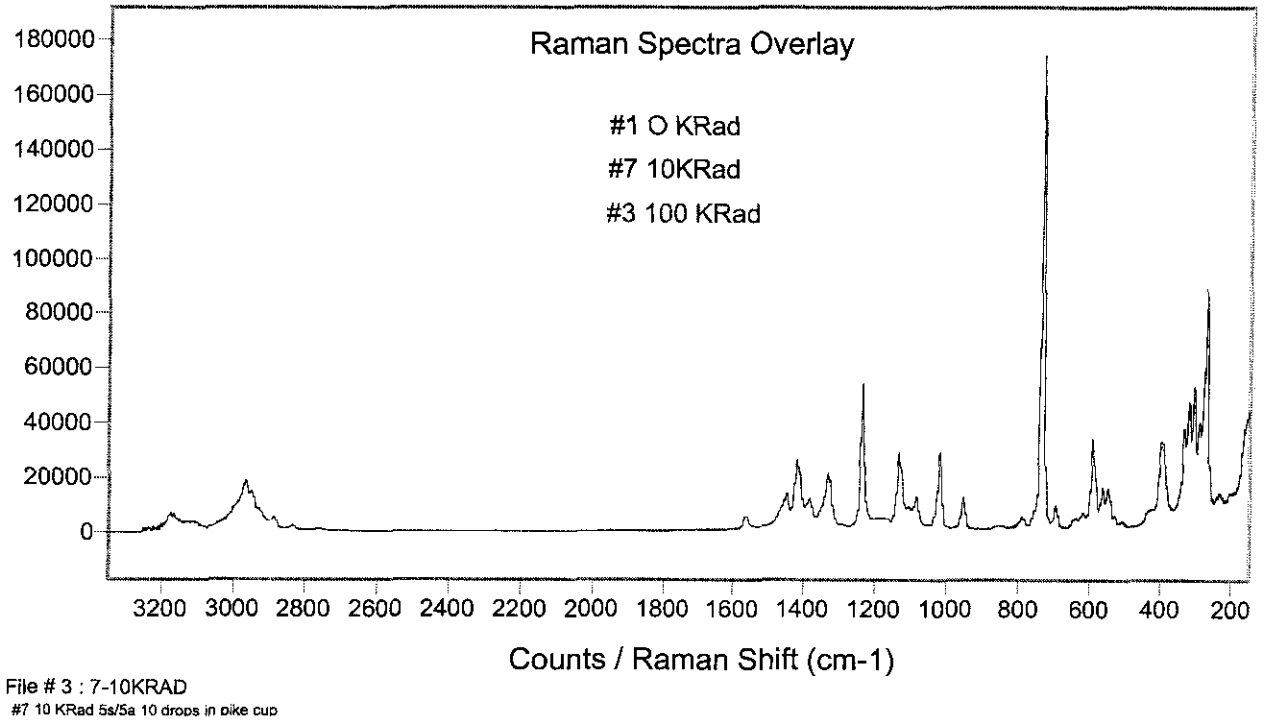

Figure 2. Comparison of the Raman Spectra for fluids with varying levels of radiation exposure.

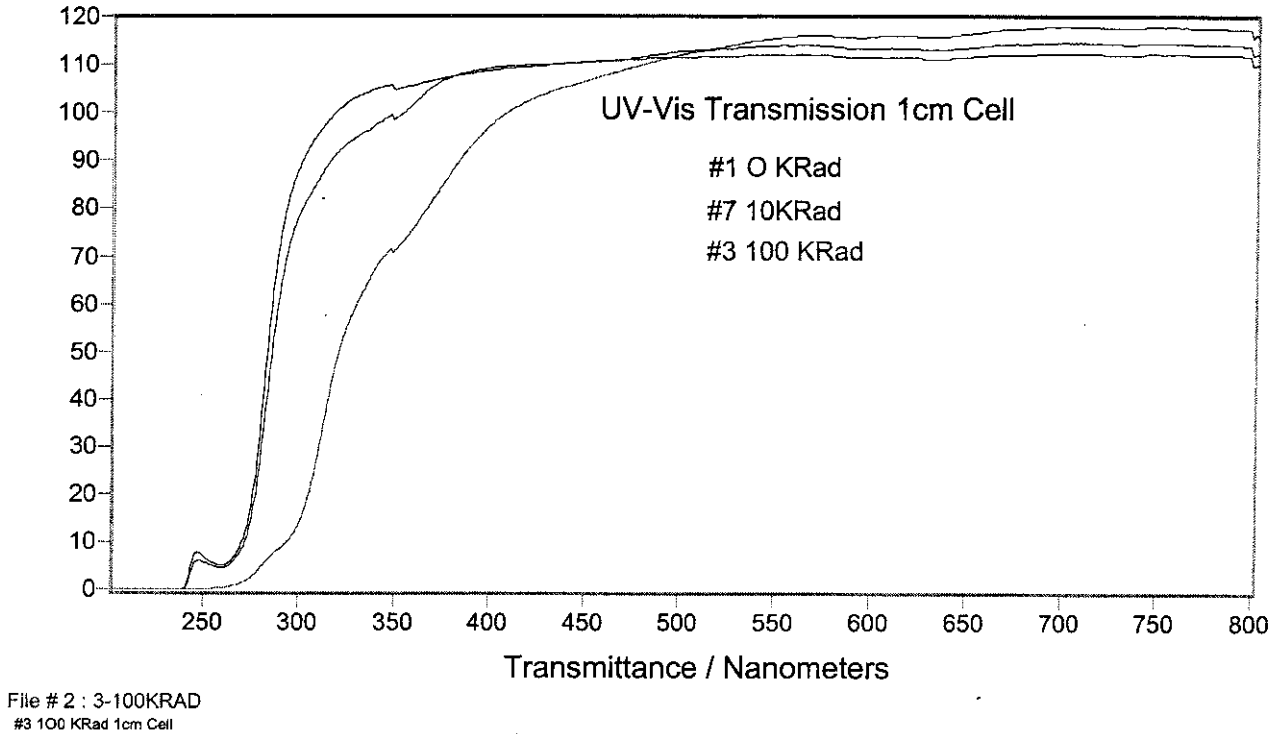

Figure 3. UV-Vis transmission spectroscopy data.

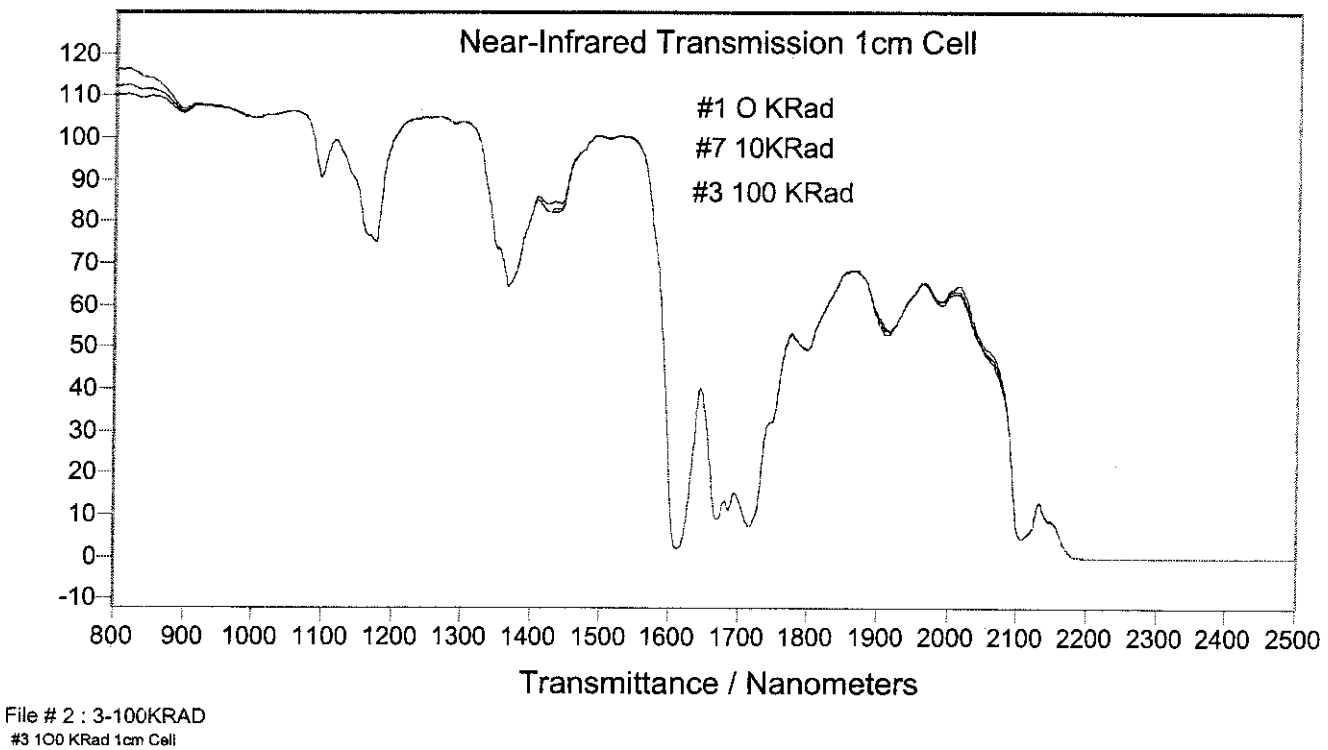

Figure 4. Near-Infrared transmission spectroscopy data.

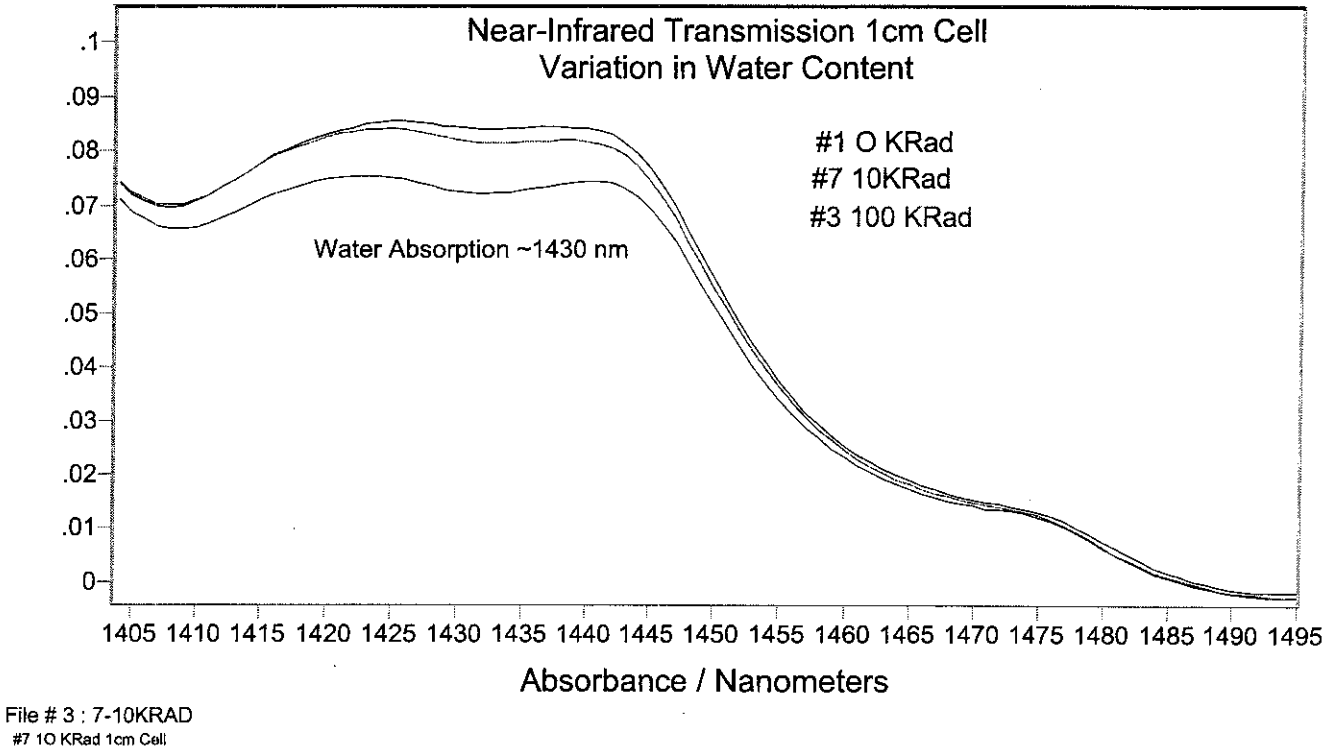

Figure 5. Near –Infrared transmission spectroscopy data showing variations in water content.