

Conversion of ATR-IR spectra to Optical Coherence Spectroscopy spectra using the Fresnel equations and single-scatter theory

Yadong Hou

Supervisor: Prof. Stephen J Matcher, Second Marker: Prof. John Rodenburg.

Department of Electronic and Electrical Engineering, The University of Sheffield

Abstract— This project successfully used the Fresnel equations and single-scatter theory to convert the ATR-IR spectrum of the sample from the Sheffield Dermatology Research Group to the OCS spectrum, the ATR spectrum is generated with 10 bounces. The samples studied in this process included water and human skin, and the ATR prism used was diamonds. Both samples used the optical coefficient of water at 6000nm as the real part of the refraction index, which is close to the coefficient of skin, then used to get the absorbance coefficient by the Fresnel equation and Beer-Lambert law. The scattering coefficient is extrapolated from the current scattering data in NIR to generate the power exponential function theoretically. The backscatter coefficient is inferred from the relationship between the total attenuation coefficient at 1300nm. The OCS spectra were obtained by integration calculations. The obtained OCS spectra have stronger OD values than the ATR spectra. For example, the highest peak of the water's OCS spectrum is up to 2.7 at 3250 cm⁻¹, whereas in the previous ATR spectrum it was only around 0.76. Besides, the skin's OCS spectrum absorbance value increases to 6 times the ATR spectrum absorbance value. The waveform displayed by the OCS spectrum amplifies the smaller absorption peaks in the ATR spectrum, and the entire waveform is more obvious while narrowing the gap between the maximum and minimum absorption peaks.

I. INTRODUCTION

The human skin is the first barrier to protect the body's immune system and consists mainly of the epidermis, dermis, and subcutaneous tissue and is between 50 and 150 microns thick. The EEE Biophotonics Group is actively collaborating with the Sheffield Dermatology Research Group to investigate the use of infrared absorption spectra of the stratum corneum (SC) to predict whether a newborn has a skin condition such as eczema. [1] Also, the EEE Biophotonics Group is developing a related technique, Optical Coherence Spectroscopy (OCS), which differs in the way it works from the ATR-IR technique. The project aims to write a MATLAB script to convert an ATR-IR spectrum into an OCS spectrum for both samples of water and human skin in the near-infrared (NIR) and middle infrared (MIR), and vice versa. This paper focuses on exploring the differences between the two techniques and the relationship between the measurement techniques, meanwhile, analyzing the results from the converted spectrums.

A. Background

1) Skin of stratum corneum

The stratum corneum tested is the outermost layer of the epidermis, consisting mainly of keratinocytes and lipids. The thickness of the stratum corneum is usually between 10-20 microns thick. Its main function is to protect the body from external physical and chemical irritants, as well as to protect the body from water loss. [1] The composition of the epidermis is relatively stable, and when lesions occur, the protein structure,

for example, can deteriorate. The use of ATR-IR is a non-invasive tool to assess changes at the molecular level. [1]

2) ATR-IR

Attenuated total reflection (ATR) is a technique for the direct detection of solids or liquids in combination with infrared spectroscopy. When operating, a beam of infrared light is directed at an angle into the crystal and this light is reflected internally to produce an evanescent wave that extends from the surface of the crystal to the sample being detected by continuous reflection. The evanescent wave continuously attenuates or changes the energy absorbed according to the infrared spectrum of the sample. Each time the energy is attenuated, it is transferred back into the detector by the infrared beam through the other end of the crystal to produce the infrared spectrum. Usually can detect samples between 0.5 and 2 microns. To have the desired data, the sample must be in good contact with the ATR crystal and the refractive index of the sample should be less than the refractive index of the crystal to ensure that internal reflection can occur. [2]

The multiple reflected IR beams produce mutually independent swift waves that interact with the sample after each bounce, and the absorption between these waves is additive. Due to the higher signal-to-noise ratio after multiple bounces, the bounce allows for more sensitive recording of spectral data.[3]

The most commonly used ATR crystal materials are zinc selenide (ZnSe) and germanium. Of these, zinc selenide is the most commonly used material ideal for studying liquids, pastes and gels. Germanium has the highest refractive index and therefore the best effective penetration depth. The most ideal

dielectric material is diamond, especially for hard samples, but its price is the most expensive. [2]

3) OCS

The technique of scanning and imaging with low coherent light from an optically scattering medium is known as optical coherence spectroscopy (OCS) and offers the advantages of no sample preparation and direct imaging without contact compared to conventional detection methods. [3] In addition, the depth of penetration into the sample is much higher than that employed using the ATR technique, with OCS probing samples up to a depth of 500 μm or more. [3] Also, OCS has a higher resolution compared to ATR spectroscopy, allowing sample features to be more clearly observed. However, because the OCS technique is more complex, the implementation will be more difficult and the cost required will also increase. This project aims to convert ATR spectra to OCS spectra using MATLAB code and to theoretically explore the characteristics of the two spectra.

II. IMPACT OF COVID-19

Had to participate in online individual meetings to communicate with supervisors Due to the Covid-19, and face-to-face communication was not possible. All the information comes from the Internet, and it is impossible to learn how ATR obtains the spectrum on the spot.

III. METHODOLOGY

A. Absorbance spectrum of OCS

The attenuation caused by absorption and scattering is defined as $I(z) = I_0 \exp(-(\mu_a + \mu_s)z)$, where I_0 is the incident light intensity and z is the propagation distance. Combine with the backscatter coefficient can have the light intensity for OCS. Which is:

$$I_{OCS} = \mu_b \int_0^\infty I(z) dz \quad (1)$$

Since the absorbance is equal to $\log_{10}(I_0/I_{OCS})$ thus the incident light intensity can be canceled. The final absorbance spectrum of OCS is:

$$\text{absorbance} = \log_{10} \frac{1}{\mu_b \int_0^\infty \exp(-(\mu_a + \mu_s)z) dz} \quad (2)$$

The above relationship shows that if the OCS spectrum is to be obtained then the coefficients must first be solved.

A. Backscatter coefficient

The scattering characteristics of a medium can be quantified by the backscattering coefficient. The backscattering coefficient is the differential scattering cross-section per unit volume at a reflection angle of 180degree, expressed as μ_b . It is used to detect the echo signal generated by the scattering of light as it passes through the medium.[9]

The backscatter coefficient is equal to the $0.05\mu_t$ for Stratum Corneum in 1300nm. [8] Meanwhile, the μ_s have more effect for μ_t . [8] thus the μ_b can simplify equal to $0.05\mu_s$ in 1300nm. Conjecture the ratio still work in the NIR and MIR region, meanwhile, it is assumed that the backscatter coefficient for water still holds because water has optical properties similar to skin.

B. Total attenuation coefficient

The attenuation coefficient is the attenuation of energy that occurs as the light beam passes through the medium. Transparent media have a small attenuation coefficient, usually expressed as μ_t . The attenuation coefficient is the sum of the absorption and scattering coefficients, i.e. $\mu_t = \mu_a + \mu_s$. [7][8] However, within the NIR, μ_s is much larger than μ_a , thus $\mu_t \approx \mu_s$.

C. Scattering coefficient

The change in the polarization and phase of the light direction is described by scattering write as μ_s is the scattering coefficient. [11] The μ_s is a power law curve a/λ^n in near-IR wavelengths. According to the current paper can have the scattering coefficient of human's skin is changed as Fig.1 within 1600nm. Choose the two points of females under 40 because the project is service for newborn babies.

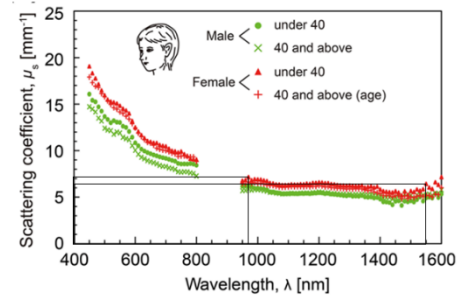


Fig.1. Average values of scattering coefficient in different ages [10]

The first point is $\mu_s = 7.1 \text{ mm}^{-1}$ with wavelength 970nm, the second point is $\mu_s = 6.3 \text{ mm}^{-1}$ with wavelength 1600nm. Use the data fit the above equation can solve the a and n . thus the scattering coefficient can be calculated as:

$$\mu_s (\text{mm}^{-1}) = 36.70 / \lambda (\text{nm})^{0.2389} \quad (3)$$

Same as above, the (3) is also used to calculate the scattering coefficient of water.

D. Absorption coefficient

The absorption coefficient of a medium is expressed as μ_a . The reduction of light energy is called absorption. The beam intensity falls with propagation distance z as $I(z) = I_0 \exp(-2 * \text{Im}(n_2) * k_0 * z)$. k_0 is the vacuum propagation number of the wave equal to $2\pi/\lambda_0$. Meanwhile, the fall due to the absorption can be calculated by the Beer-Lambert law, $I(z) = I_0 \exp(-\mu_a z)$. Thus the absorption coefficient is :

$$\mu_a (\text{nm}^{-1}) = n_1 * 4\pi / \lambda_0 (\text{nm}) \quad (4)$$

E. R_{TE} calculation

The n_1 in the (4) is the refractive index which should be calculated from the ATR spectrum.

The first step is converting the absorbance of the ATR-IR

spectrum to the reflection coefficient. The absorbance is a dimensionless ratio by the incident beam intensity I_0 divide the detected intensity I . I_0/I also can be represented as R is the amplitude reflection coefficient. Meanwhile, the project spectrum was collected using 10 bounces which means the absorbance should divide 10. Thus, the relationship is:

$$\text{Absorbance}/10 = \log_{10}(I_0/I) = \log_{10}(1/R) = 2\log_{10}(1/|r|) \quad (5)$$

Thus the R can be calculated as

$$R_{TE} = 10^{(-\text{absorbance}/10)} \quad (6)$$

F. n_I calculation

The project is going to generate the ATR-IR spectra by using a diamond as the ATR prism, which is the upper-medium. And the samples for the lower medium are water and skin respectively. The ratio of the speed of light in a vacuum to the speed of light in a sample is known as the refractive index, and the refraction that occurs when light passes through two substances with different refractive indices is also known as the relative refractive index. [4]

The available research material describes the variation of their reflectance at infrared wavelengths. For optically transparent materials such as diamond, only the refractive index is real. According to Phillip and Taft's curve, the reflection index of the diamond from 0.0354 μm to 10 μm , the value remains at 2.38 in the NIR and IR wavelengths thus $n_1=2.38$. The sample is generally absorbing, so the reflection index is a complex number, the collected coefficient of water is measured by Hale and Querry from 0.2 to 200 μm , [5] which shows the real part of the coefficient does not vary significantly in the infrared region and can therefore be assumed to be a fixed value, corresponding to a real part of the index of reflection $\text{Real}(n_2)=1.32$ at 6100 nm. [6] Because the coefficient of skin is close to the water, thus use 1.32 as the real part of the refractive index also.

The imaginary part can be found by combining the ATR spectrum and the Fresnel equation under suitable boundary conditions.

The refractive index of two median is equal to the ratio of the refractive index of ATR prism (upper medium) n_1 divided by sample (lower medium) n_2 . Which means $n=n_2/n_1$.

Adding suitable boundary conditions at the interface allows r the complex amplitude reflection coefficient to be calculated utilizing Fresnel equations.

$$r_{TE} = \frac{\cos\theta - \sqrt{(n_R^2 - n_I^2 - (\sin\theta)^2) + 2jn_R n_I}}{\cos\theta + \sqrt{(n_R^2 - n_I^2 - (\sin\theta)^2) + 2jn_R n_I}} \quad (7)$$

Where θ is the angle of incidence of the light wave at the interface. n_R is the real part of the relative refractive index of two media, n_I is the image part of the relative refractive index of two media. To facilitate the calculation, directly take the square of the modulus of Eq3 which means convert r_{TE} to R_{TE} for calculation.

1). Newton-Raphson method

There are two methods used in solve the equation to have the n_I , first is using the Newton-Raphson method, Newton's method was originally proposed by Isaac Newton. The method

sets a variable with a function close to zero, calculates the corresponding value and the value of the derivative, and then calculates the point of intersection of the tangent line with the x-axis. Simplify the equation can write as:

$$x_{n+1} = x_n + \frac{f(x_n)}{f'(x_n)} \quad (8)$$

A more accurate result can be obtained if this position converges after setting a suitable tolerance and a maximum number of iterations. To obtain accurate data for this project, the tolerance was set to 10^{-20} and the maximum number of iterations to 150. $f(x)$ is the $\text{abs}(\text{Equation 3})^2 - R_{TE}$, with the x is n_I . the other data is known.

2). Symbolic math method

Another method is solving the function directly. The first is to expand the root sign, the root of complex number $a+jb$ is equal to $\frac{\sqrt{2}}{2}(\sqrt{a^2+b^2}+a + j\sqrt{a^2+b^2}-a)$, according to the Euler formula. Therefore, Eq3 reduces the equation to a complex form with real and imaginary parts by using MATLAB to calculate the sum of the squares of the real and imaginary parts to calculate the square of the mode. The final solve() function is used to calculate n_I when R_{TE} has different values.

IV. DISCUSSION

A. Sample of water

The ATR-IR spectrum is the result of a detected sample of water from 2500nm to 15000nm with 10 bounces, which was provided by the Sheffield Dermatology Research Group. The spectrum is shown in Fig.2.

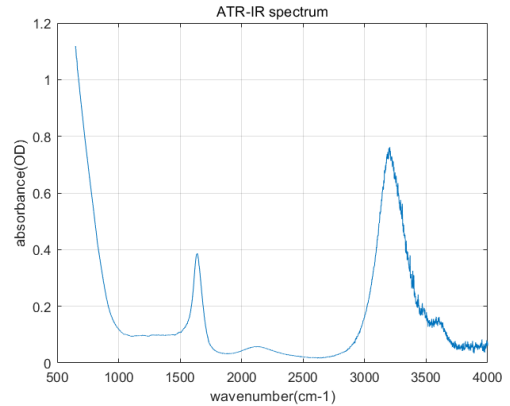


Fig. 2. ATR-IR spectrum of water

Fig.2 is of the ATR absorption spectra for the sample of water. Two absorption peaks can be identified by observation, at approximately 3100nm and 6100nm respectively. After 10,000 nm, the absorption values show a continuous increase. There is a small peak between 4000 and 6000 nm, and between 7000 and 10000 nm, it remains more or less constant.

The R_{TE} is calculated as Fig.3 which has a value lower than 1, which is opposite to the variation in the ATR-IR spectral waveform, and all values are below 1.

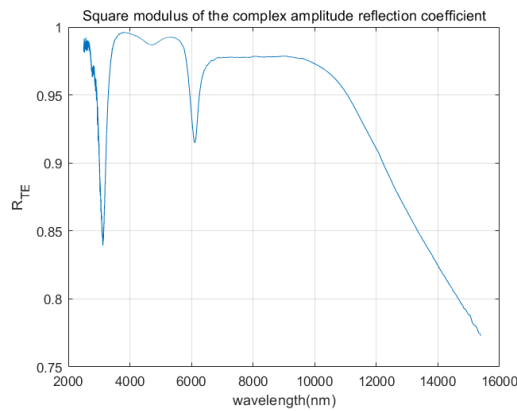


Fig. 3. R_{TE} spectrum of water

Fig. 3 shows the variation of R_{TE} calculated from the absorption spectra. At the same time, the values of R_{TE} are less than 1. Fig.4 includes three waves for water's refractive index. The two overlapping sets below are the n_i waveforms obtained by bringing in the previous R_{TE} using the Newton-Raphson method and the Symbolic math method respectively, and the other one is a reference waveform from the Hale & Query data. By recording the processing times for the two methods, it can be seen that d runs for 17860.969498 seconds and the Symbolic math method runs for 61146.416592 seconds.

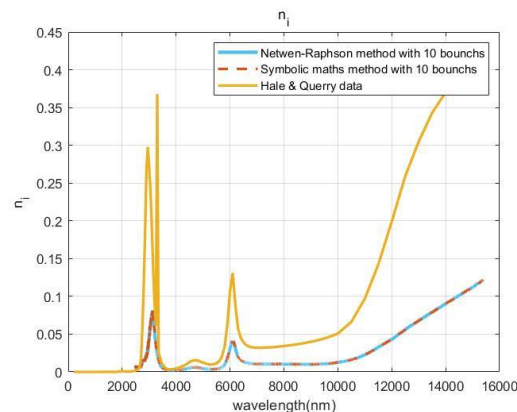


Fig. 4. Compare for n_i calculated from two methods with the Hale & Query data for the sample of water

The results obtained for both calculations of n_i are the same, but when comparing the run times, the Newton-Raphson method requires a much smaller run time than the other method. Therefore, the Newton-Raphson method is preferred for the same accuracy.

Hale & Query's data includes the full range of n_i . A comparison shows that the calculated values are smaller than the measurements recorded in the literature. In particular, after two peaks and 10,000nm.

This may be because the real part of the sample's real refractive index is calculated directly using a constant to simplify the calculation, but the actual n_r is constantly changing. These problems may result in the calculated results differing significantly from the measured values in the literature. Besides, The probe used in the ATR system manufactured by Nicolet

does not define the number of bounces well.

Fig.5 is the absorption coefficient of water which has large fluctuations with peaks above 100mm^{-1} with similar waveforms with n_i which is based on the ATR spectrum of water and refraction index of water.

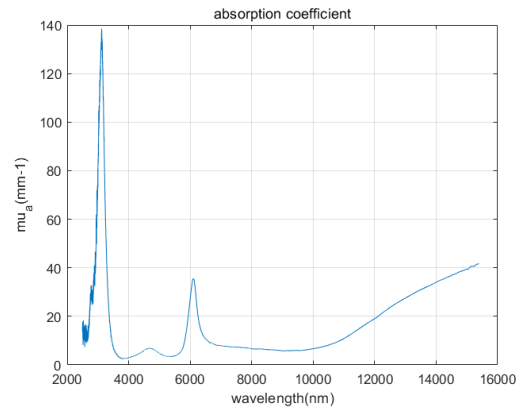


Fig. 5. The absorption coefficient of water

The overall trend is consistent with the trend in the ATR absorption spectra, but the values are in the tens and even 138, which are much higher than the μ_s values. When comparing the data in the literature, it was found that the n_i corresponding to wavelengths above 2000nm becomes rapidly larger, [6] and the corresponding μ_a is also influenced to become larger, so this change is reasonable.

Fig.6 shows the scattering coefficient decreases exponentially in the NIR region (2500nm to 15000nm) from 5.6mm^{-1} to 0 for the sample of water.

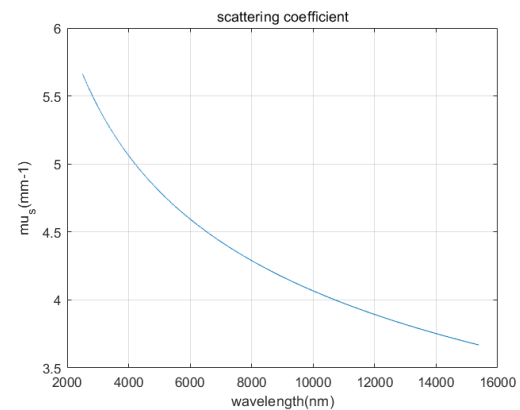


Fig. 6. Scattering coefficient of water

The results for μ_s are consistent with the prediction of a power exponential decrease from 5.6mm^{-1} to 3.7mm^{-1} .

The total attenuation coefficient here is more in line with the waveform of the absorption coefficient.

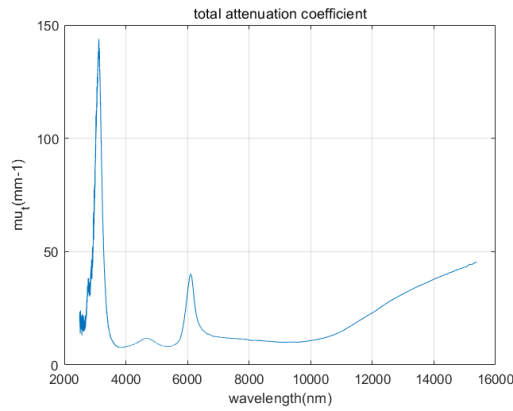


Fig. 7. Total attenuation coefficient of water

The μ_t is more affected by μ_s in the visible region [11] than in the NIR, where μ_t is more affected by μ_a . The backscatter coefficient is minimums with decreases exponentially.

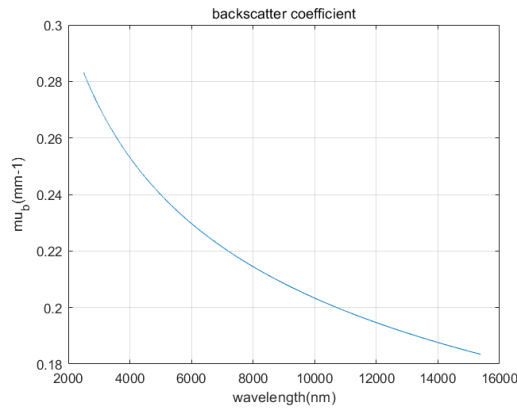


Fig. 8. Backscatter coefficient of water

The μ_b in this project is still based on the assumption that μ_t is mainly determined by the variation in μ_s and therefore the data obtained is questionable. The final OCS absorbance spectrum of water is shown below.

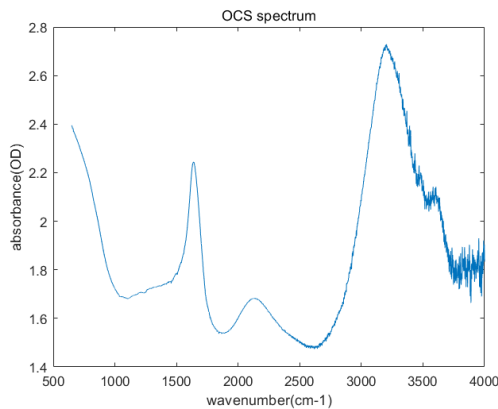


Fig. 9. OCS spectrum of water

For the final obtained absorption spectra of OCS a comparison with the previous ATR--IR spectra can be made that the absorption values are much larger. Moreover, the intensity of the individual wave peaks is enhanced and the obtained curve variations are easier to observe.

B. Sample of skin

Fig.10 is the ATR spectrum of skin with a tiny absorbance value from 2500nm to 25000nm, the absorbance in the MIR (15000nm to 25000nm) is 0OD.

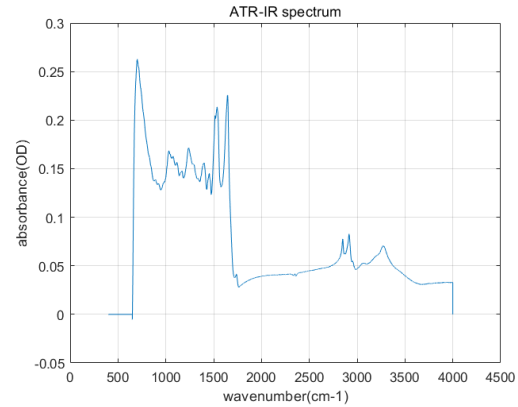


Fig. 10. ATR spectrum of skin

From the ATR spectrum can be seen that the spectrum is more complex for the skin compared with the spectrum of water. The absorbance value of the skin is small, between 0- 0.26OD. Fig.11 is the R_{TE} for human skin, which is from 0.94 to 1 in the NIR and MIR.



Fig. 11. RTE spectrum

Fig.12 with the same waveform as R_{TE} is the n_i , the range from 0 to 0.0255. the method is only used the Newton-Raphson method because the fastest running time, which is 1011.209659 s.

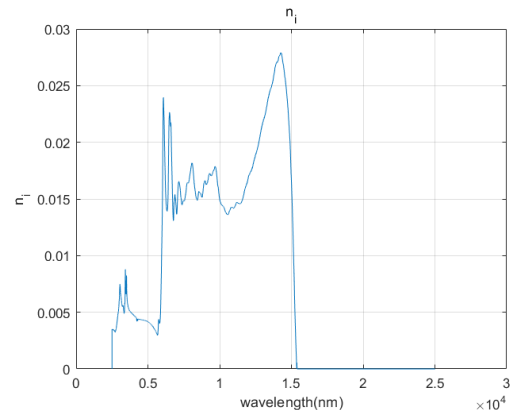


Fig. 12. n_i for skin

The absorption coefficient is much larger, the waveform is different from n_i , which highest peak in Fig12 is decrease.

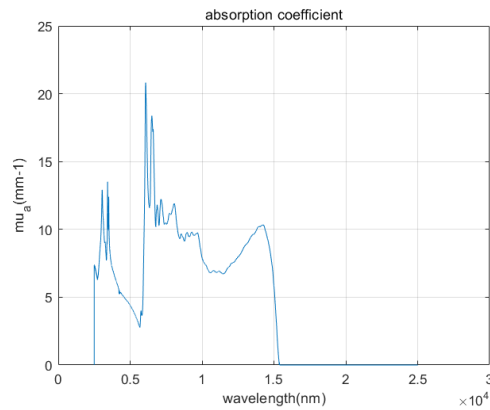


Fig. 13. Absorbance coefficient of skin

The scattering coefficient is an exponential function decrease from 5.7mm^{-1} to 3.3mm^{-1} .

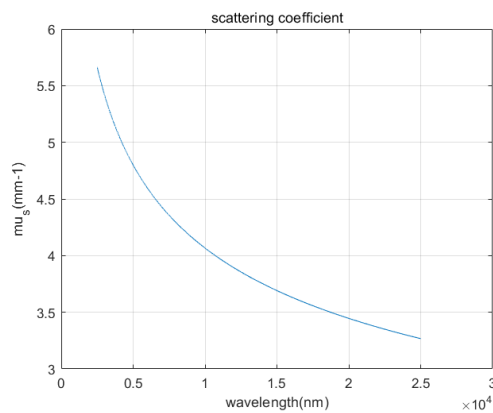


Fig. 14. Scattering coefficient of skin

The total attenuation coefficient is with the same wave as the absorbance coefficient but the value increased by the effect of the scattering coefficient.

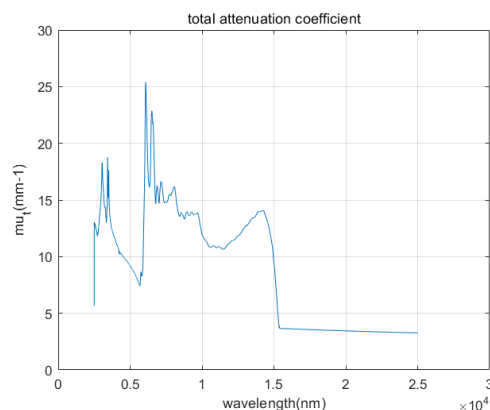


Fig. 15. Total attenuation coefficient of skin

The Absorbance coefficient is still larger than the scattering coefficient, but the difference in values is smaller, so the total attenuation coefficient is affected by both.

The backscatter coefficient decreases from 0.28mm^{-1} to 0.16mm^{-1} .

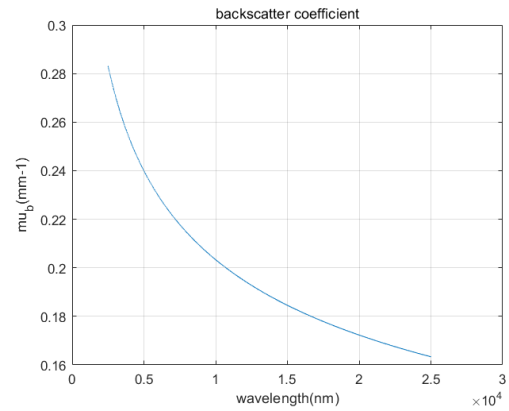


Fig. 16. Backscatter coefficient of skin

The backscatter coefficient is still deduced from μ_s and used directly to solve the final OCS spectrum. Errors in the choice of coefficients are also the main cause of the final error.

The final result is the OCS spectrum of skin which absorbance value belongs to 1OD to 2OD range.

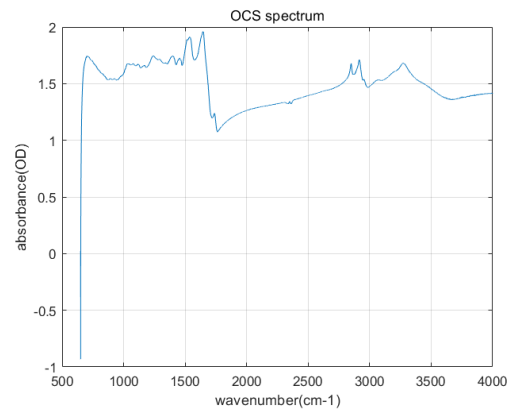


Fig. 17. OCS spectrum of skin

The final OCS spectrum values of the skin are mainly concentrated between 1OD and 2OD, much larger than the ATR spectrum of the skin.

V.CONCLUSIONS

The project successfully used MATLAB to convert the ATR-IR spectrum into an OCS spectrum based on human skin and water as samples. The OD value of the converted OCS spectrum was much higher than that of the ATR-IR spectrum. At the same time, the OCS spectrum can more clearly amplify the change law of the sample's absorption spectrum, and the results are easier to observe. However, there are several problems with the conversion process. First, the relative refractive index of the sample is a changing, complex number. The real part of the calculation is chosen to simplify the calculation by assuming a constant, which will lead to subsequent error calculations. Secondly, the relationship between the absorption and scattering coefficients in the near-infrared region is different from the conversion relationship in the visible region, which affects the total attenuation coefficient. In addition, since the relationship between the total attenuation coefficient and the backscatter coefficient in the literature only refers to the

effectiveness of the keratinous surface of human skin at a wavelength of 1300nm, it is uncertain whether it is still applicable to the NIR and MIR regions, so the accuracy of the backscatter coefficient can not be guaranteed. Finally, because the two samples have the same optical coefficient, the sample of water uses the scattering coefficient of skin and the sample of skin uses the refraction index of water directly, which will cause the final result to be inaccurate.

VI. FUTURE WORK

In summary, the calculations for this project are currently only rough calculations, and the accuracy of the results is still uncertain. The Kramers-Kronig relationship should be further studied in future work. For the real and imaginary parts of the refractive index, because they are not independent of each other, a suitable solution needs to be found later. A more precise relationship will be sought to ensure the accuracy of the backscatter coefficients and to ensure that the total attenuation coefficient should tend to be mainly attributed to absorption or scattering in the near-infrared region and all the coefficients used should be the same as the sample.

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