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# Evaluation of Curing Reaction Kinetics of Epoxy Siloxane Hybrid Polymers

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Tämä insinöörityö tehtiin Teknos Deutschland GmbH:lle syksyllä 2014. Tarkoituksena oli selvittää ja arvioida pii-epoksi hartsin kovettumisreaktion kemiallisia reaktioita sekä kinetiikkaa. Tällä hybridi hartsilla on kaksi reagoivaa osaa: epoksi rengas ja pii hartsi. Tämän vuoksi reaktioita oli useampia, kun epoksi rengas reagoi epoksi-amiini kovetus reaktiona samalla kun pii hartsi reagoi kondensaatio reaktiolla.

Työn kokeellinen osuus tehtiin Fuldassa, Saksassa. Kokeellinen pinnoite-erä valmistettiin ilman pigmenttiä tai lisäaineita, jotta tulokset olisivat selkeämmät, ja jaettiin tilavuuksiltaan samankokoisiin pisaroihin. Pisarat laitettiin teflon levylle, jota säilytettiin ilmastokaapissa. Näitä näytepisaroita tutkittiin FTIR spektrometrilla, käyttäen ATR- metodia. Tuloksena saatuja spektrejä verrattiin ja tutkittiin.

Tulokset tukevat reaktioiden osalta hypoteesia, mutta kinetiikasta saatiin uutta tietoa. Kovettumisreaktioon tarvittava aika vaihtelee reaktiosta ja pinnoite kerroksesta. Esimerkiksi epoksi reaktio käynnistyi heti pisaran päällä, mutta kesti useita päiviä ennen kuin reaktio alkoi pisaran pohjalla.

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This study was performed for Teknos Deutschland GmbH in autumn 2014. The main aim was to explore and evaluate chemical reactions and kinetics in the curing process of epoxy-siloxane hybrid resin. This hybrid resin have two main reagents: an epoxy ring and silicone resin. Therefore, there is competing reactions when the epoxy ring reacts with epoxy-amine curing reaction and the silicone resin reacts with condensation reaction.

The experimental part was carried out in Fulda, Germany. The experimental coating batch was made without pigments or additives so that the results would be clearer. The batch was divided in to drops that have equal volume. Drops were put on the Teflon layer and kept in the climate chamber. These drops were measured with an FTIR spectrometer using ATR method. The results were spectra, which were compared and analyzed.

The results were not only supported the hypothesis about the reactions but also gave some new information about the kinetics. The curing process took a different length at time, depending on the layer and the reactions. For example the epoxy reaction took place in the top of the drop immediately while at the bottom of the drop it took several days. This information could be utilized in product development to improve quality or create even better resin.

Keywords FTIR, Polymer, Curing

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# 1 Introduction

## 1.1 Context

During the past decades, chemical regulation in the European Union (EU) has been changing as new knowledge has been provided. These changes have forced the paint and coating industry to react. Nowadays we have more information about hazardous paints, and for example lead-based paints are controlled all around the world. That is why manufacturers have been developing lead-free paints and coatings with great success when white lead has been replaced with titanium dioxide.

European legislation controls also solvents, which paints rather often contain. Previously common solvents, glycol ethers were put under the Registration, Authorization and Restriction of Chemicals (known as the REACH) regulations in 2006. These solvents were much more toxic than previously thought. Therefore, the coating and paint industry has to keep improving safety and developing cheaper solvent- free solutions and with better toxicological profiles for customers and consumers. One example for these kind of coatings is NISO (non-isocyanate) coatings. [1]

## 1.2 Teknos

Teknos Oy was founded in 1948 and is now days one of the biggest suppliers of coatings and paints to the finishing and painting trade in Europe. It has production in seven countries, including Finland, Sweden, Denmark, Russia, Poland, Germany and China. The headquarters is located in Helsinki where there is also another research center. [2]

Teknos expanded to Germany in 1999. Teknos Deutshland GmbH is located in Fulda providing work to 50 people. It has a rather small production capacity for a local market and a product research and development department. One segment develop and produce paints for general industry, while the other segment develop wood paints.

## 1.3 Silikopon EF

Silane coupling agents are organosilicon compounds that have two different functional groups, including one that reacts with organic materials and one that reacts with inorganic materials. Therefore, they have unique characteristic enables to bond organic materials to inorganic materials. [3]

Silikopon EF resin is a new resin complex which has epoxy reactions as well as condensation reactions with silicone resin part. It is used in protective coatings which must be, for example, isocyanate-free and long lasting regarding weather resistance. With this two-layer-system, the needed coating layer is also thinner than that with standard three-layer-system and therefore, it is cheaper to use. [3]

## 1.4 Purpose

This study was made to learn more about the new resin, since there was no previous study about Silikopon EF reactions and kinetics in order to improve products and to develop quality. The purpose was not to study the reactions themselves but to confirm the hypotheses of reactions mechanisms. Therefore, the used ATR-method with the FTIR spectrometer is sufficient. The experimental part was carried out in Fulda, Germany.

IR-spectra are rather clear to read and compare. That is why rough evaluation of kinetics is easy but it does not give any specific details. No certain conclusions, but except for the confirmation of the hypotheses of reaction mechanism can be made.

To evaluate the kinetics of the curing reaction, samples were in form, drop form and measurements were taken from the top and from the bottom of the sample drops. Again, this experimental method gives only rough information about the reactions in different layers in the samples and nothing more. Still it provide enough information to just evaluate reactions and kinetics.

## 2 Coatings Chemistry

Coating materials are used to provide decoration or protection to a surface. [4]. Architectural or decorative coatings are used to coat, for instance a house or an office building. Industrial coatings are used for example, on ships, cars, furniture and appliances. [5; p.1, 4]

The raw materials of coatings must be carefully considered in order to achieve the desired characteristics, which depends on surface, application technique and curing method. [4] The four most common components are resin, pigments, additives and the carrier fluid or solvent (Figure 1). [5; p.1]

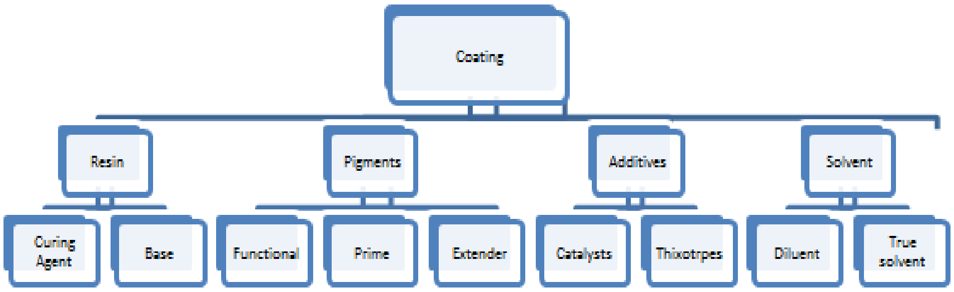


Figure 1. Coating components

Resin is the essence of the coating and establishes most of the physical and chemical properties of the coating. [5; p.1] The type of resin (or binder) usually gives the coating formulation its name. Common binders are polyesters, acrylics, epoxies and urethanes. [4]

The main purpose of solvents is to make the coating application possible. It can also be used to control the reactivity of the system by blocking the access of reactive components before and during the application process. During the drying they also helps to forming the film. Solvents are usually a mix of several different organic solvents ( and/or water) depending on the coating and applications. [5; p.2]

Pigments could be inorganic compounds such as silicates or organic, based on carbon chains and rings like Naphthol. Pigments add color and opacity to the paint but when carefully selected also other properties like UV-light and corrosion resistance, fire retardence and antifouling capabilities. [5]

There are numerous additives, and, depending on the vehicle type and intended application of the coating, those can vary widely. Modifiers are counted as an additive and are used to control consistency and viscosity. They also improve sag resistance and pigment settling. A catalyst is also one type of additive in the coating formulation that, when added in small quantities to chemical reaction, will remain unchanged or will not consumed by the reaction, but will increase the reaction rate. Two- component coatings also include hardener which is needed to get the coating hard and solid.
[5; p.3]

## 2.1 Resin

The main focus was on resin-hardener reactions and kinetics together with a catalyst. The used resin was Silicone-Epoxy which combines an epoxy resin with a silicone resin and provides properties of both resins (Figure 2). While the aliphatic epoxy resin gives corrosion and chemical resistance, the alkoxy silicone resin provides UV resistance and low yellowing.

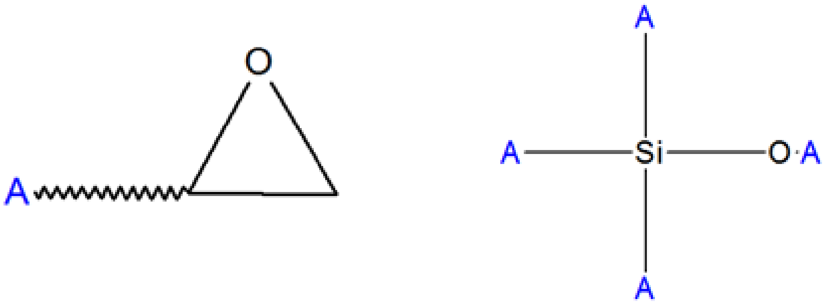


**Figure 2. Epoxy resin (left side) and silicone resin (right side), where A is alkyl group**

### 2.1.1 Epoxy System

Basically, an epoxy system could be any polymer system which enables either binder synthesis or curing with an oxirane or epoxide ring. The reactive group and the structure of the particular product gives these resins a high- performance profile. Oxirane is very reactive and can react with, for example, the amine group. [5; p.187, 2]

The curing of epoxy resins could cause thermal degradation (if not controlled) since it is a highly exothermic reaction. Epoxy may achieve curing by reacting with itself or by reacting with the hardener and forming a copolymer in a copolymerization process. Copolymerization is utilized with two- component coatings, where the resin monomer and the hardener monomer unite together to polymerize. Other method is polyaddition reaction, where readymade polymers react with hardener. The curing reaction could be accelerated by addition of a small amount of catalyst, like carboxyl acid, alcohols or amines. [5; p. 187, 6, 7]

In Figure 3 epoxide ring opens and form carbon-nitrogen bond with amine group, creating also functional alcohol group (OH).

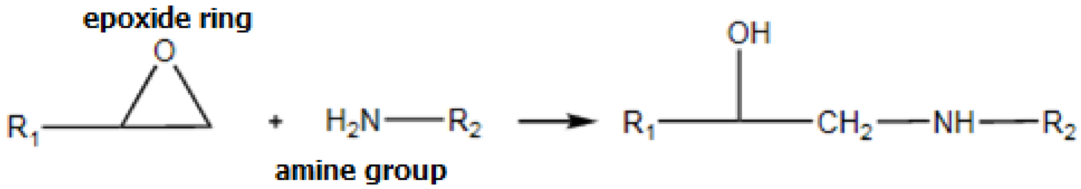


**Figure 3. Epoxide ring react with amine group**

### 2.1.2 Silicone Resin

The silicone resin is based on a silicon atom which in many ways is analogous to carbon. Low surface energy and strong resistance of oxidation are characteristic of silicone resin. This means that silicone resin has excellent hydrophobic properties caused by the low surface energy, but because of resistance of oxidation, it also has high temperature application. Si-O-Si bond has higher bond strength than C-O-C bond, which also improves temperature resistance profile. [5]

Silicone resin forms a linear siloxane-linked polymer (silanol structure) in a hydrolysis reaction, and the condensation product is water. [5; p.267, 6]

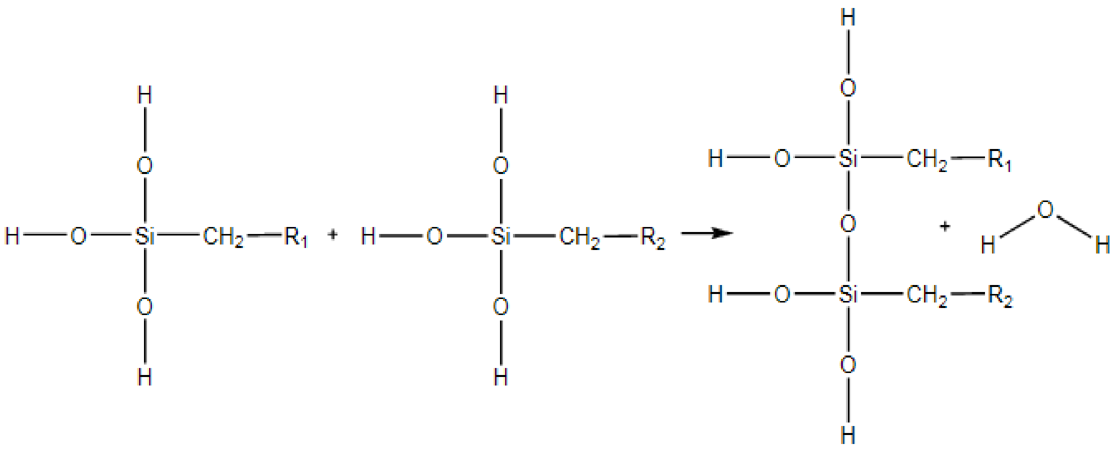
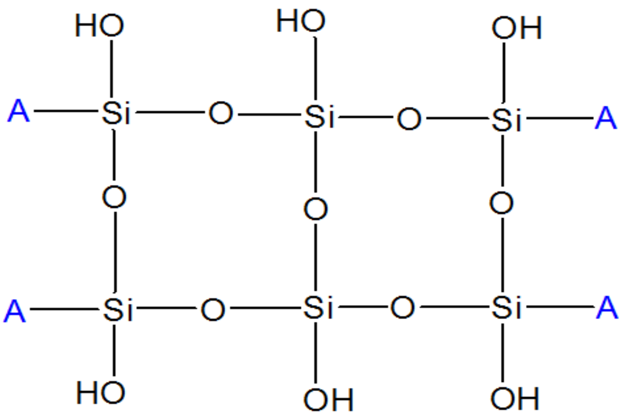


Figure 4. Silicone resins condensation reaction

Normal environment resin is non-cross-linked but when heat is increasing, the resin start to crosslinking. This structure behaving explain silicon resin `s great heat resistance. [2; p.269]



Where A is an alkyl group

Figure 5. Corosslinked silicone resin

### 2.1.3 Hardener

The hardener is Amino alkoxy silane, Dynasylan AMEO, which provides like epoxy resin corrosion protection and chemical resistance in the polymermatrix with the epoxyresin. [6, 7]

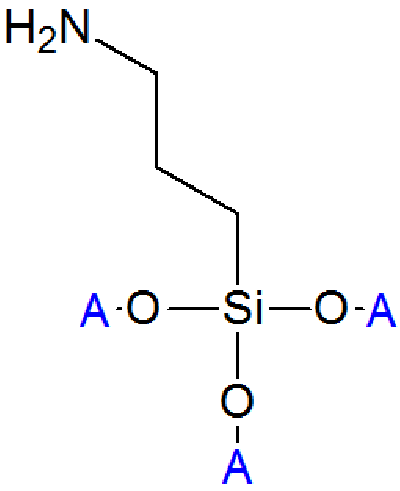


Figure 6. Amino alkoxy silane hardener

It has an amino group that reacts with epoxy in the curing process.

## 2.2 Proposed Mechanisms

Silikopon EF has the chemical crosslinking via the dual-cure mechanism at room temperature: the nucleophilic opening of the epoxide ring by the amine and the hydrolysis / condensation reaction of the alkoxy groups. [6, 7]

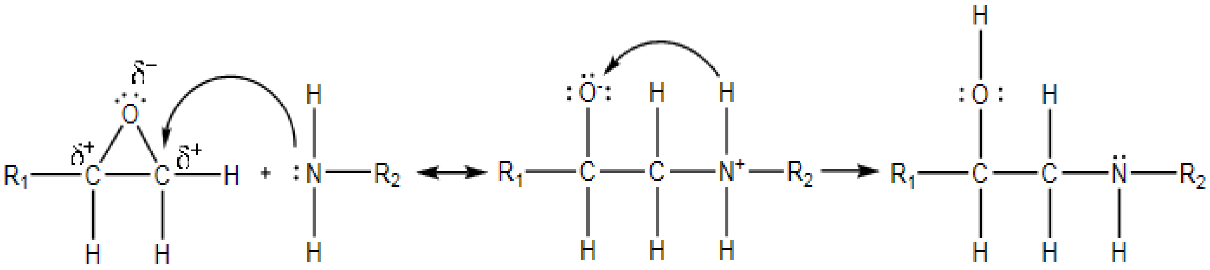


Figure 7. Nucleophilic opening of the epoxide ring

Aminosilanes are the curing agents whose amine groups react with the resin`s epoxy group, while the alkoxy group of the agent reacts with the silicone resin`s free alkoxy group in the presence of water. [6, 7]

With Silikopon EF resin and Dynasylan AMEO hardener, TIB KAT 318 is used in small amounts (the mixing ration of catalyst is 1% to 3%) as a catalyst to accelerated the silicone resin reaction. The catalysis react with silicon resin and there could be carboxyl acid as a side product.

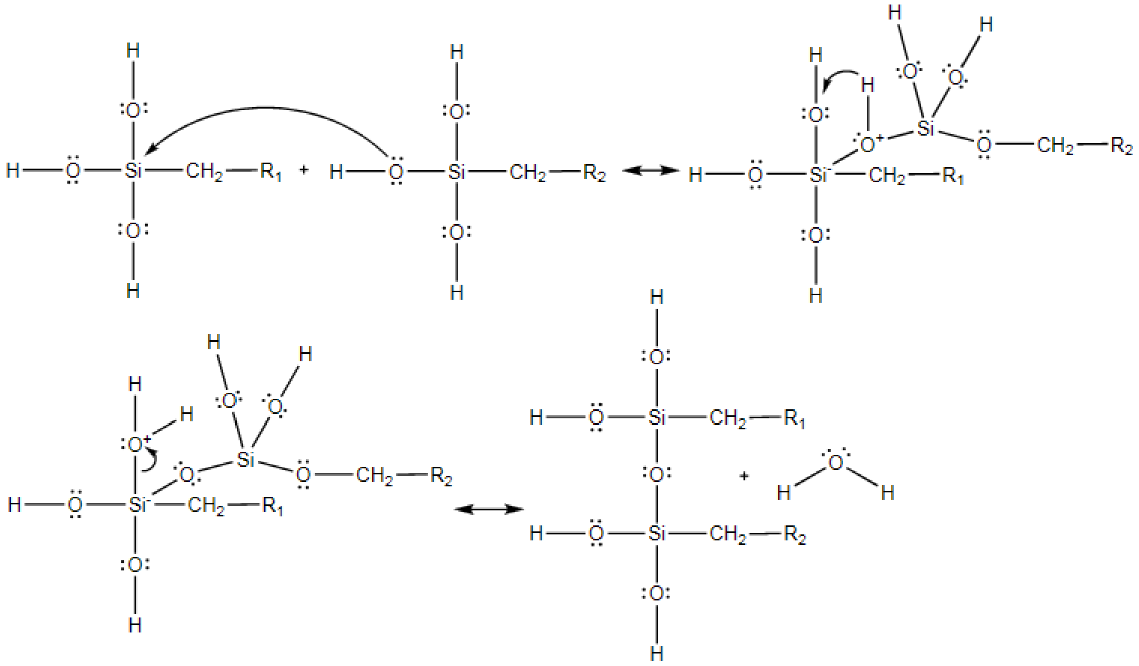


Figure 8. Condensation reaction of the alkoxy groups

[6, 7, 8]

Understanding the reactions mechanisms is essential when the results are analyzed.  The FTIR spectrometer can rather easily detected functional groups, like alcohols and esters. Therefore, it is easy to identify the right peaks from the spectra, when the reaction mechanisms are known.

# 3 FTIR

The FTIR spectrometer is one of the most important instruments for analyzing organic substances in laboratory. It can be used to study different organic compound structures, functional groups and the purity of samples. Organic molecules absorb infrared radiation and the results obtained (absorb spectrum) can be analyzed. Every organic compound has its typical infrared spectrum; therefore, all compounds can be identify. IR analytics is used, for example, in the medical industry and in materials research for quality control and product development. [9, 10]

## 3.1 Theory

FTIR combines Raman modes with Lambert-Beer`s law that relates the substance concentration and properties through which the light is traveling to the absorption of light.

$I = I_0 10^{\varepsilon[J]L}$ Lambert-Beer`s law [9] (1)

, where
I= intensity of the transmitted radiation
$I_0$= intensity of the incident radiation
$\varepsilon$ = molar absorption coefficient
L = the path length (thickness of the sample)
[J] = substance concentration

Definition of Transmittance (T) is determined as follows:

$$T = \frac{I}{I_0}$$

Definition stays that transmittance is intensity of the transmitted radiation divided by incident radiation, while absorbance is common logarithm of incident radiation divided by transmitted radiation.

Definition of Absorbance (A) is determined as follows:

$$A = log\frac{I_0}{I} \qquad (2)$$

According to the law and definitions of transmittance and absorbance, there is a logarithmic correlation between the transmission and absorbance [9] :

$$A = -logT \qquad (3)$$

,where
A= absorbanse
T= transmission of light
[9; p. 414-416, 10]

However, there are some deviations under certain circumstances: the deviations due to the limitations of the law itself and real limitations, deviations due to how measurements are made and deviations due to specific chemical species of the sample have to be considered  when the results are analyzed. [9, 11]

With higher concentrations solvent and other solute molecules and even hydrogen bounds might cause interaction. Therefore, the law could be applied only to low concentrated substance. However, the concentration should not be too low or it may cause other errors. The relative error may occur when the sample absorbs a very small amount of light or nearly all the light. Therefore, too low concentration could lead to relative errors when there are not enough molecules in the sample and adsorption is unsubstantial. In other words transmittance should be always more than 0. [9, 11]

Standards should be run when results are study more than one spectrometer, because the absorptivity may vary from instrument to instrument. The media can also absorb radiation and that is why background measurements without substance are critical. [9, 11]

Another instrumental factor that can cause deviation is when stray light falls on the detector. Lambert-Beer`s law is based on the assumption that at infinite concentration all the light is absorbed and the light falling on, the detector is zero. Therefore, stray light falling on the detector causes a negative deviation from the law and errors with results.

[11; p. 439-441]

There could be also errors if the substance is active and equilibrium is nonsymmetrical. One example is a weak acid that has an anion that does not absorb at all, but the acid itself has a particular wavelength in which it absorbs:

$$HA \leftrightarrow H^+ + A^-$$

(absorb) (transparent)

The best way to avoid these kind of larger chemical deviations is by proper buffering of pH. [9, 10, 11; p. 441-442]

## 3.2 Measuring Principles

### 3.2.1 Vibration of Bonds

In the infrared area, absorption is caused by vibrations of chemical bounds. The radiation absorption is unique for every functional group and shows in different wavelengths. With the FTIR spectrometer, these absorption areas can be detected as a downtrend curve, called transmission minimums. From the minimums, can be determined which functional group(s) the analyzed sample contains. Normal measurement range is 4000 – 400 cm-1 and samples can be in solid, liquid or vapor phase. [9, 12]

A molecule could have more than one absorption area, where its bonds vibrate. In this case, the molecule shows more than one transmission minimum. It depends on the molecule`s degree of freedoms. Degree of freedoms occur because of the movement of atoms in the molecule. There can be translational, rotational and vibrational degrees of freedom. [9, 12]

Table 1. Degrees of freedom

| | **Monoatomic** | **Linear molecules** | **Non-linear molecules** |
|---|---|---|---|
| **Translation** | ***3*** | ***3*** | ***3*** |
| **Rotation** | ***0*** | ***2*** | ***3*** |
| **Vibration** | ***0*** | ***3N-5*** | ***3N-6*** |
| **Σ** | ***3*** | ***3N*** | ***3N*** |

Depending on the degree of freedom, the molecule can vibrate in different ways. The vibration can be symmetric or asymmetric stretching and bending. [9, 12]

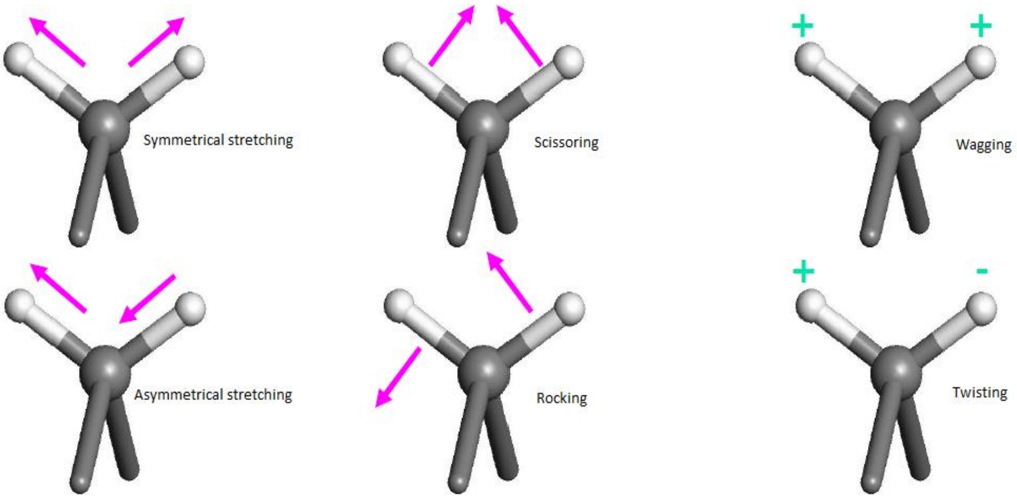


Figure 9. Bendings of molecyles

The FTIR technique can give an idea of what the sample might contain, but not necessarily the whole truth. IR radiation absorbs only if there is a rhythmic change in the molecule’s dipole moment. For example, symmetric and asymmetric stretching of the water molecule are not causing rhythmic change and therefore these can be detected. [9, 12]

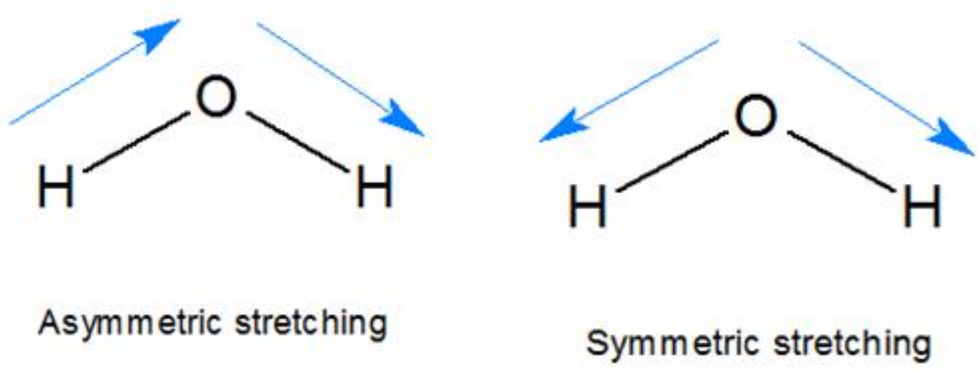


Figure 10. Asymmetric and symmetric stretching of water, both shows in IR-spectrum

However, with the carbon dioxide molecule, symmetric stretching does not causes any rhythmic change like asymmetric stretching does, thus, cannot be detected. [9, 12]

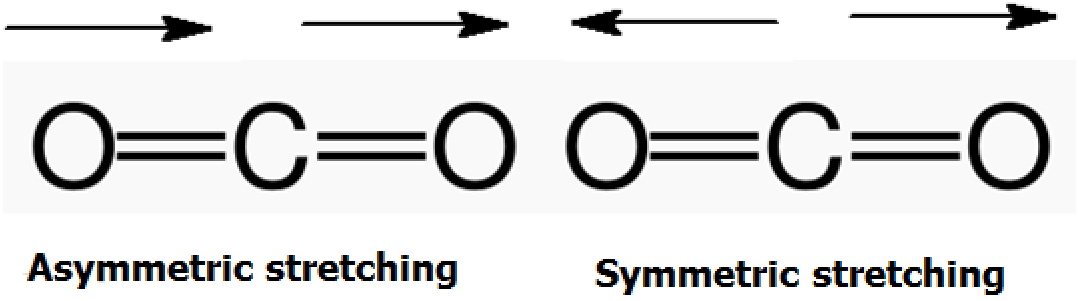


Figure 11. Asymmetric and symmetric stretching of carbon dioxide

The intensity of absorption has to be strong enough to be detected with a FTIR spectrometer and the absorption must happen in the registration range (4000 – 400). Therefore, it is impossible to detect all transmission minimums, especially with more complex compounds.  Also some stronger signals can hide some other weaker signals. [9, 11, 12]

### 3.2.2 Overtone Bands

Normally, the molecule travels from the ground state (E=0) to the first state (E=1) and shows the vibrational spectrum (Figure 12). The overtone band occurs when the molecule makes a transition to the second excited state (E=2) from the ground state (E=0). This behavior leads to overtone bands that is normally occur at a wavenumber, which is almost twice the wavenumber to the "main" peak. These peaks are also rather small to combine the main peaks. [13, 14]

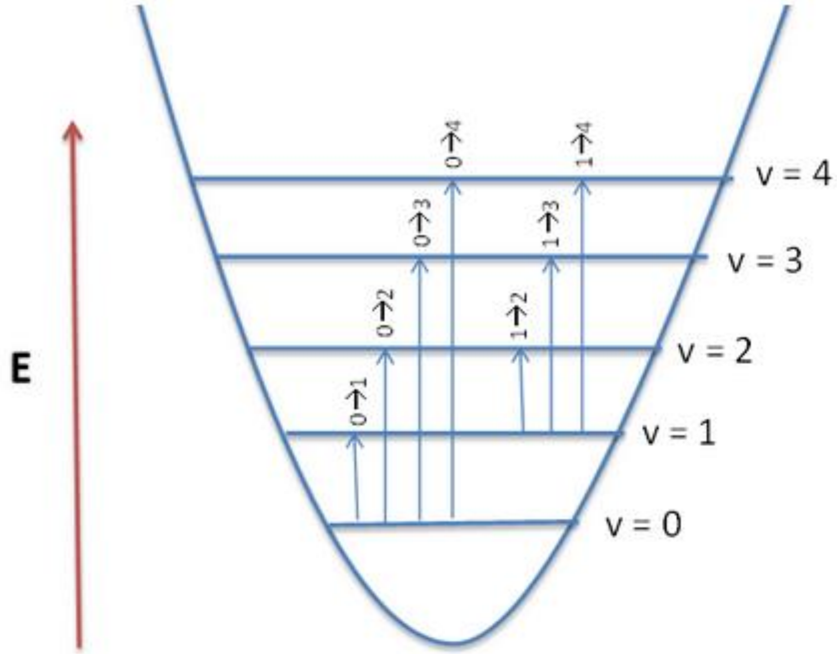


**Figure 12. Molecules transition**

E (vibrational quantum number) can be determined after solving the Schrödinger equation (Figure 13). [14]

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E - V)\psi=0$$

**Figure 13. Schrödinger eguation**

### 3.2.3 Combination Bands

Combination bands could show when more than one fundamental vibrations excited simultaneously. One explanation for the occurrence of a combination band could be that there are symmetrical vibrations that do not show in the spectrum. This "invisible" vibration could lead to an addition of frequencies, but it is also possible to have a difference band where the frequencies are subtracted. [13, 14]

## 3.3 FTIR Spectrometer

The FTIR spectrometer includes the Michelson interferometer, which splits one light beam into two. After a beam splitter (A), two mirrors, one stationary (B) and one movable mirror (C) reflect beams to travel different paths before recombining. Utilizing a moving mirror, beams also travel different distances; therefore, one is out of phase from the other and as beams recombine they produce an interference pattern of all wavelengths in the beam. After recombining the beam travels into the detector through the sample. [9, 11, 12]

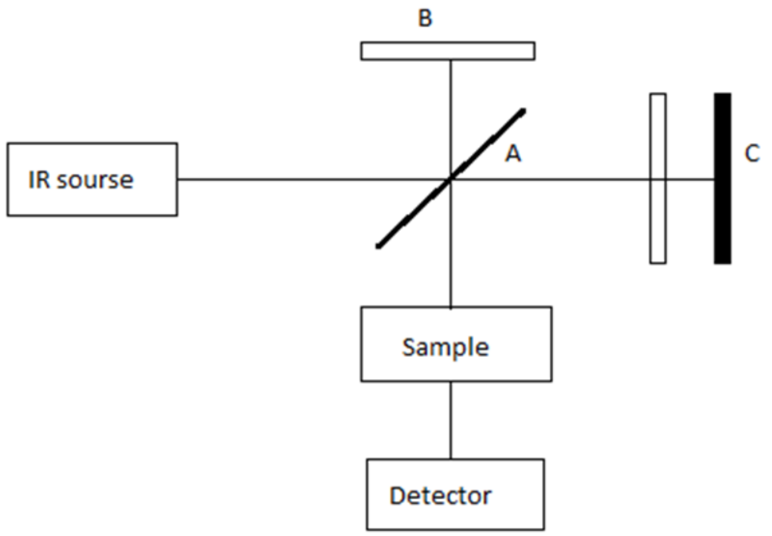


Figure 14. Operation principle FTIR spectrometer

Using an analog-to-digital converter (ADC) the analog signal is converted to a digital form and transferred to the computer. [9, 11, 12]

As the movable mirror is moving, the interface pattern changes and the result of absorption is an interferogram (sine wave), a spectrum in the time domain. This is converted via a mathematical equation, called a Fourier transform, into the frequency domain and a conventional infrared spectrum. [9, 11, 12, 14]

$$F(k) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i k x}\, dx$$

The spectrometer uses polychromatic light as an IR source, but the Lambert-Beer`s law works only with monochromatic light. Therefore, when the light passes the sample and reaches the detector, the detector has to sort all different light altitudes and calculate those as their own. This method leads to rather small errors when the Lambert-Beer`s law is applied, and these errors can be ignored. [11; p. 422-430, 14]

## 3.4 Spectrum

Result from the spectrometer is a spectrum (Figure 15). Normally it is displayed on a linear frequency scale or wavelength scale at the x-axis, and transmittance is shown at the y-axis. Spectrum gives information on which frequency or wavelength the sample absorbs. When there is a peak, it means that the transmittance of light through sample is less and it gives a clue that there might be some molecule bonds. [9, 11, 13]

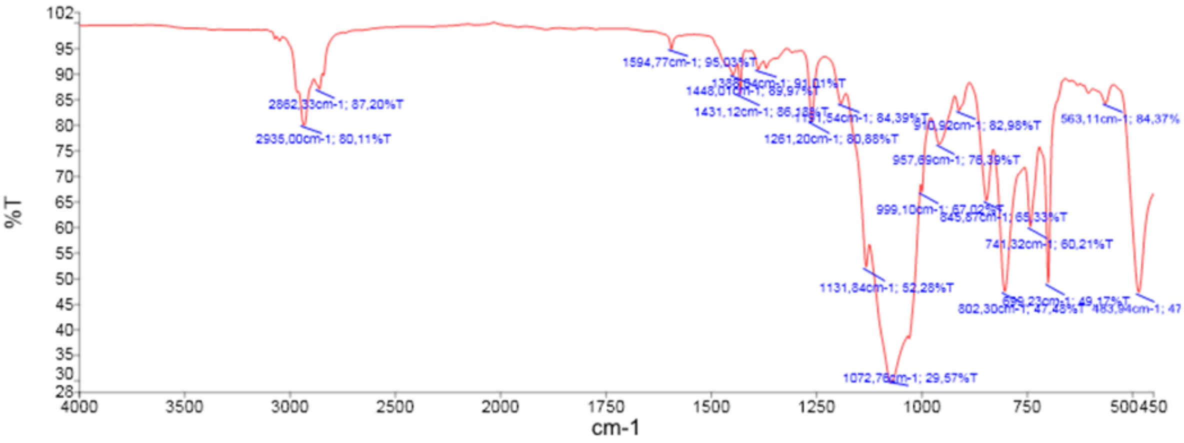


Figure 15. Spectrum from FTIR spectrometer

Transmittance gives information about the relative number of bonds (or functional groups), and sometimes it is changed to absorbance. In this case, the spectrum shows also more realistic numbers of bonds or functional groups. Peaks are growing when the absorbancies are growing like in Figure 14. In this sense, it is reciprocal to the spectrum with transmittance (formula 3). [9, 11, 13]

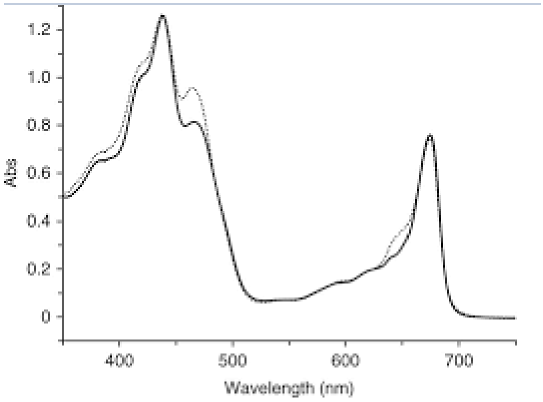


**Figure 16. Spectrum, when transmittanse is replaced with absorbace**

Because every bond has its specific area, where shows a peak or peaks in the spectrum, it can be identified. But when the sample is more complex or shows several bonds in the same area, the task is quite hard. [9, 11, 13]

# 4 Experiment

## 4.1 Arrangement

The experiment started with the preparation of a test batch by mixing 20 g of resin and 4.6 g of the hardener-catalysis mixture together. The hardener-catalysis mixture contains 5 % of TIB KAT 318, 30 % of Deolink Amino TM 100, and the rest is Deolink Amino TE 100. Additives or pigments were not added to get better spectrum form reactions between the resin and the hardener.

The prepared resin-hardener mixture was spread on a clean Teflon layer as small 1-ml drops using a pipette. There were on average 20 drops on a layer, which was put in a climate chamber. Settings in the climate chamber were 25 °C and 50 % of relative humidity.

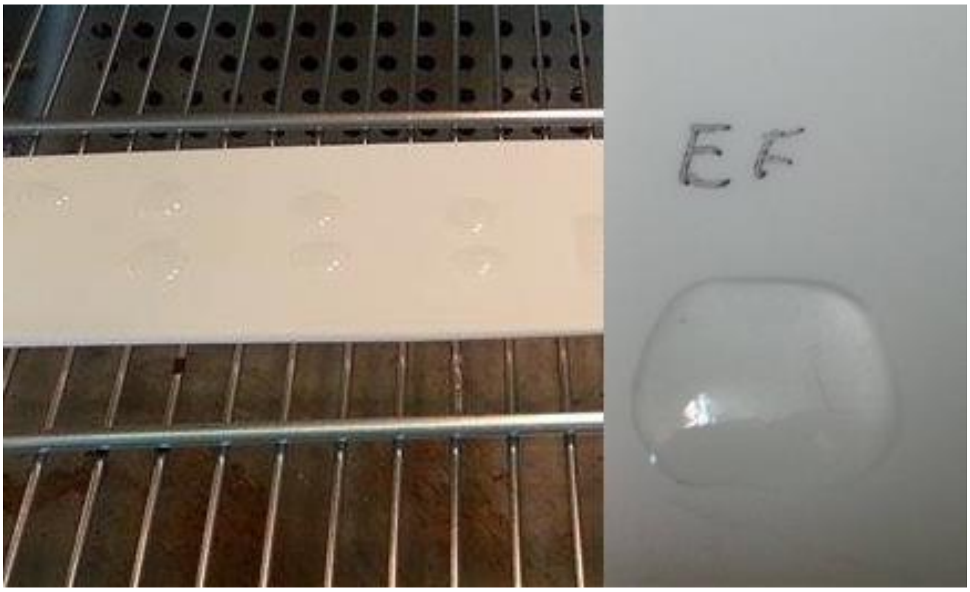


Figure 17. Experimental settings

## 4.2 Experimental Procedure

The first sample was taken immediately after the mixture was done and the following 7 samples every 30min. Samples 9 to 18 were taken every 24 hours and the last one after 2 weeks.  Background measurements were taken before every sample.

Table 2. Experiment-time table

| Experiment (number) | Time (h) |
|---|---|
| 1 | 0 |
| 2 | 0,5 |
| 3 | 1 |
| 4 | 1,5 |
| 5 | 2 |
| 6 | 2,5 |
| 7 | 3 |
| 8 | 3,5 |
| 9 | 24 |
| 10 | 48 |
| 11 | 72 |
| 12 | 96 |
| 13 | 168 |
| 14 | 192 |
| 15 | 216 |
| 16 | 240 |
| 17 | 264 |
| 18 | 336 |
|  |  |
| Both sides of the drops |  |

When the samples were hard enough, the spectra were taken from the top and from the bottom of the drop. This was made because most of the water (from the air) is on top of the drop; therefore, there might be differences in reaction and kinetics in different layers of the drop.

Spectra were taken with PerkinElmer`s Spectrum Two FTIR Spectrometer and the solvent for cleaning after analyzed sample was ethyl acetat. The used method was the attenuated total reflectance or ATR method [15, 16]

## 5 Calculations

The crosslinking reaction rate between the resin and the hardener should not be 100 % or over because the epoxy helps against humidity, while the aimino group absorb water. A preferable crosslinking ratio is between 92 % - 98 %.

**Table 3. Used amounts of the resin and the hardener**

| | Deilink Amonio TM 100 | Deilink Amonio TE 100 | Silikopon EF |
|---|---|---|---|
| M(g/mol) | 179,26 | 221,37 | 450 |
| m % | 30 | 0,65 | |
| m(g) | 1,38 | 2,99 | 20 |
| n(mol) | 0,0077 | 0,014 | 0,044 |

The mole of hardeners together is calculated as follows:

$$\sum n = 0{,}021 mol$$

The hardener can react two times; thus, the mole of hardener required for the reaction doubles.

$$n_{hardeners} = 0{,}042 mol$$

The crosslinking rate is as follows:

$$\frac{n_{hardener}}{n_{resin}} = \frac{0{,}042 mol}{0{,}044 mol} = 0{,}9545 \approx 95{,}5\%$$

# 6 Results

The results of the experiment are spectra, which are compared. Reactions are observed from the decreases and increases of the peaks. The evaluation was based on the hypotheses of reaction mechanisms; therefore, comparison of peaks was made at certain peaks.

The hypotheses were as follows:

- Silicone resin`s condensation reaction
  - Observed peaks:
    - Si-O bond 800 $cm^{-1}$ - 900 $cm^{-1}$
    - Si-O-Si bond 1000 $cm^{-1}$ - 1100 $cm^{-1}$
    - Si-OH bond 1000 $cm^{-1}$ -1110 $cm^{-1}$
- Oxide ring`s epoxy reaction
  - Observed peaks:
    - N-H bond 2800 $cm^{-1}$ - 3000 $cm^{-1}$
    - C-N bond 3310 $cm^{-1}$ - 3350 $cm^{-1}$ and ~700 $cm^{-1}$
    - O-H bond 1020 $cm^{-1}$ - 1250 $cm^{-1}$

## 6.1 Spectra

The results 1 to 8 were obtained when samples were in liquid form. The biggest changes are at the wavelengths 1072 $cm^{-1}$, 1030 $cm^{-1}$ and 802 $cm^{-1}$. Si-OH bound shows a strong peak around 800 to 900 $cm^{-1}$ and the decrease of the peak could be a result from the condensation reaction of the silicone resin (figure 4). Because of the reaction, the aliphatic Si-O bond which shows a strong peak at around 1000 to 1110 $cm^{-1}$ is also decreasing. While the reaction goes further, Si-O-Si complexes are developing. These can cause a strong peaks around 1000 to 1100 $cm^{-1}$. From the results, it seems that the condensation reaction has started in the first 3.5 hours while there is no evidence for other reactions. [17, 18]

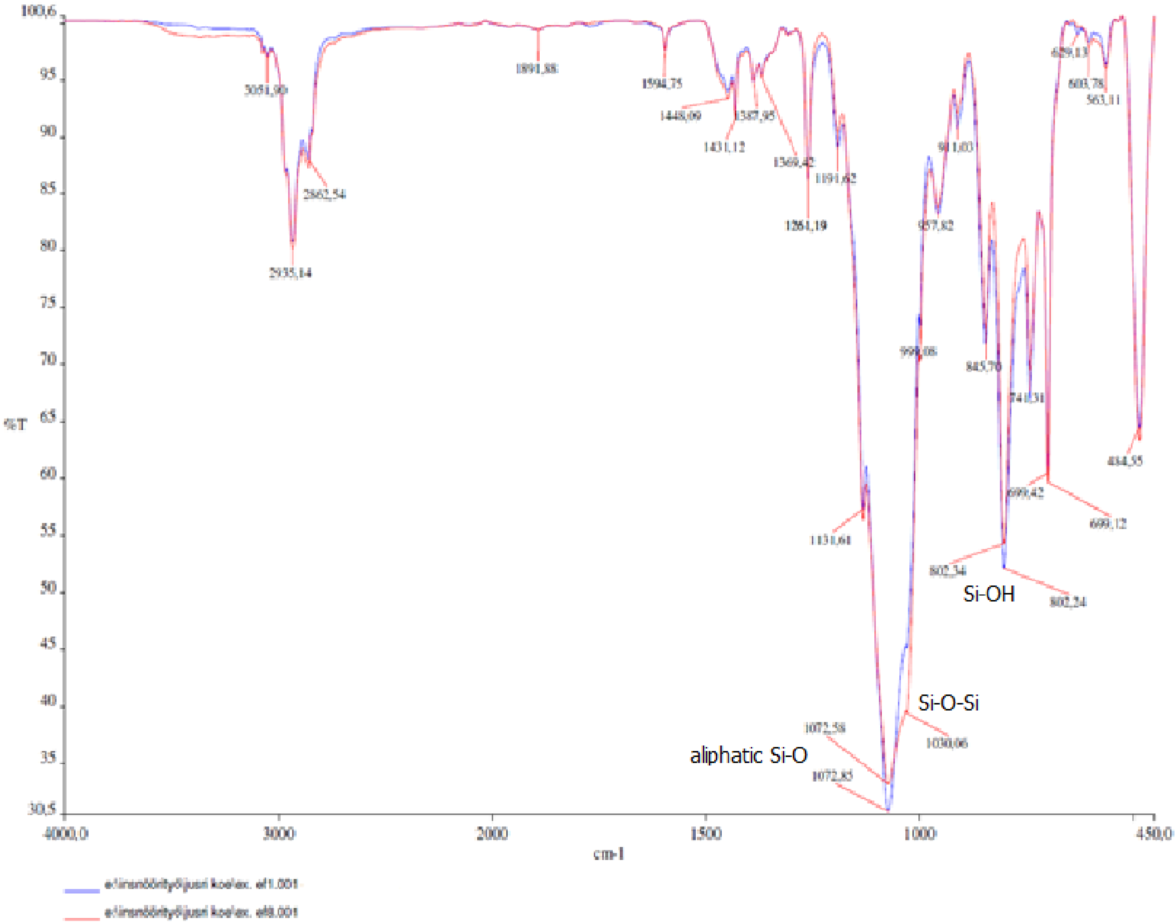


Figure 18. Results 1 and 8

After 24 hours the samples were in solid form and spectra were taken from the top and from the bottom of the drop. The results from 8 to 13 were taken from the bottom of the drops. The results show that the condensation reaction is still going on, but there are other peaks showing up (figure 19). A wide peak at the wavelength of 3375 cm$^{-1}$ could be caused by the hydrogen bond (O-H bond). O-H bonds also have two, sharp peaks. This might be water from the condensation reaction. [18, 19]

Normally, water has also a clear peak at around 2000 cm$^{-1}$ and because this peak is missing, it may lead to the conclusion that the O-H band is from an alcohol group. Also FTIR spectrometer has water- compensation on default, so the peak is more likely from the alcohol. [17, 18]

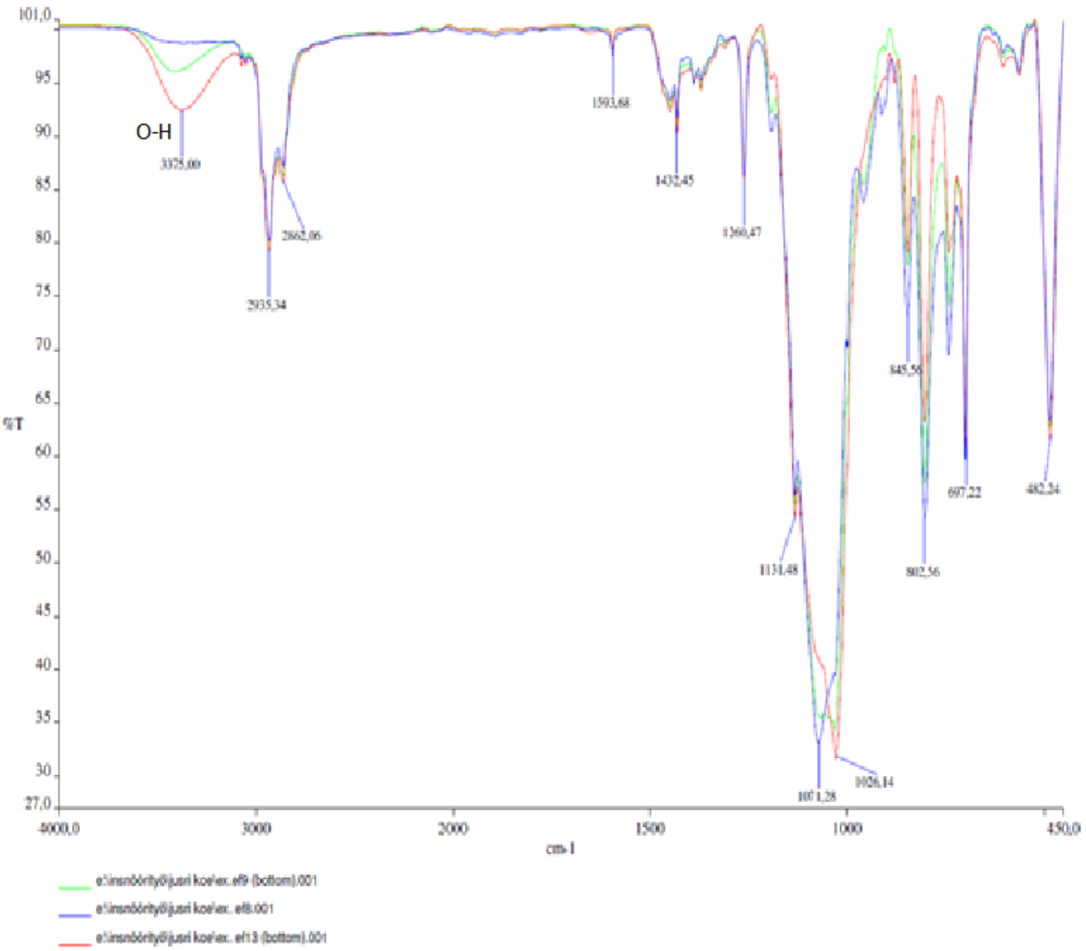


**Figure 19. The Results 8, 9 and 13 obtained from the bottom of the drops: blue curve 3,5 hours, green 24 hours and red curve 168 hours**

The results from 13 to 16 obtained from the bottom of the drops are shown in Figure 19. The results show that the reactions rate dropped rapidly, and there is no evidence for the reactions going further.

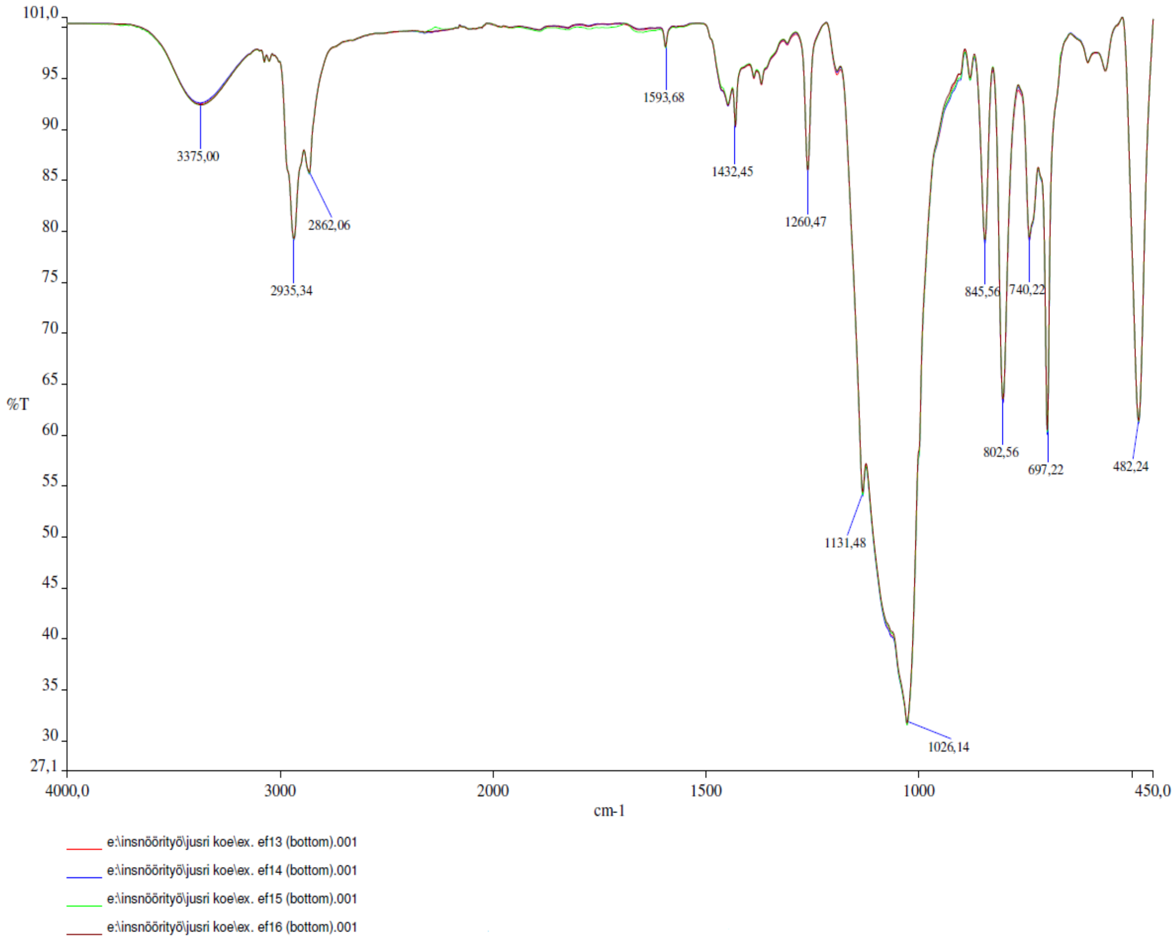


**Figure 20. The Results 13 to 16 obtained from the bottom of the drops**

The results from 16 to 18 obtained from the bottom of the drops are shown in the Figure 20. The condensation reaction is once again going further. There is also a slight increase of the secondary amine's N-H bonds, which is illustrated by two sharp growing peaks around 2800 cm$^{-1}$ -3000 cm$^{-1}$. This could be an evidence of the beginning of epoxy reaction. [17, 18]

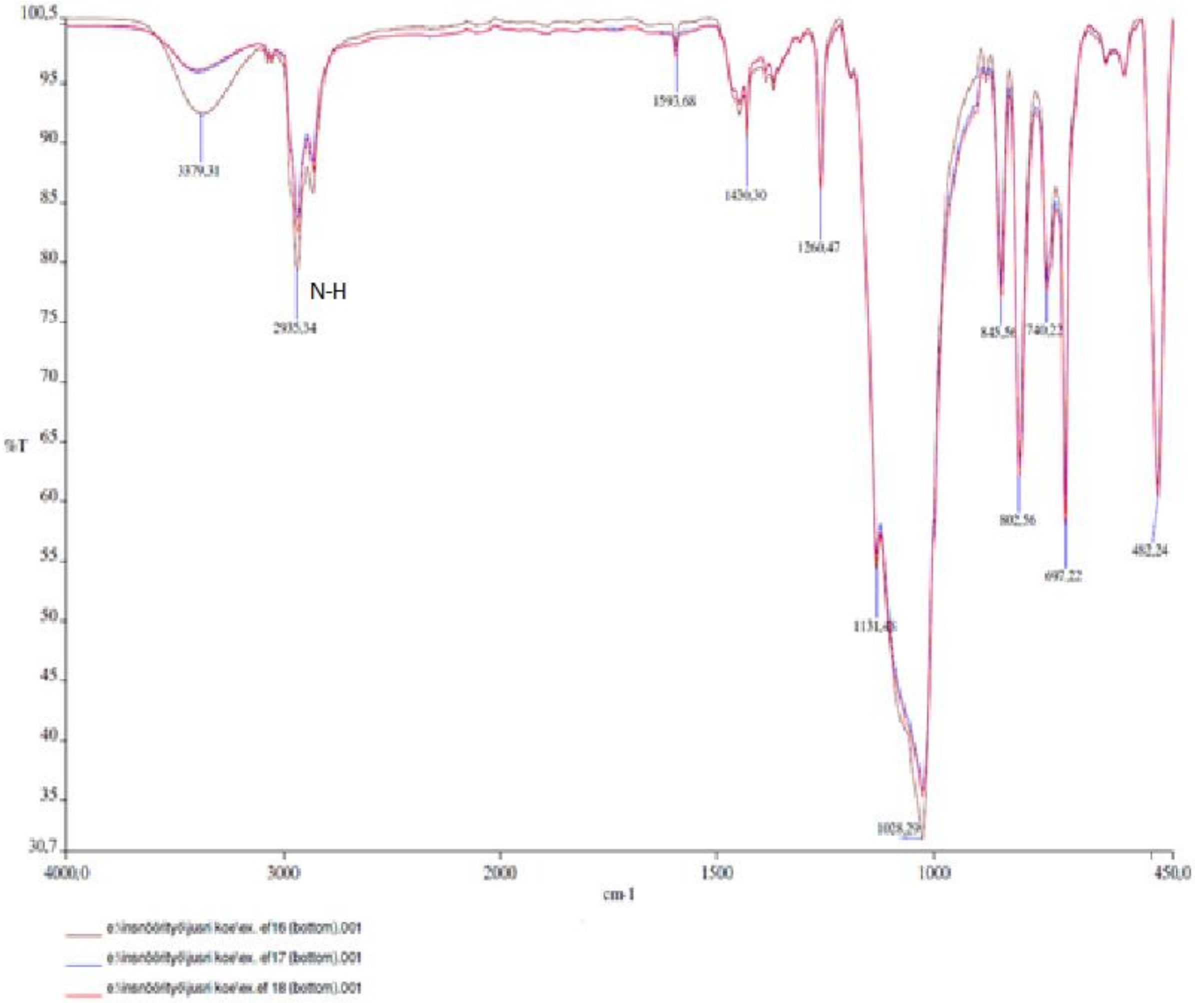


**Figure 21. The Results 16 to 18 obtained from the bottom of the drops**

The results from 8 to 10 obtained from the top of the drops are shown in Figure 21. There is an even stronger condensation reaction but also an epoxy reaction where the product is a secondary amine. The amine has one, wide signal at 3310 cm$^{-1}$ - 3350 cm$^{-1}$ caused by stretching vibration of the N-H bond. Wagging vibration can be seen at around 700 cm$^{-1}$. The amine could also have a C-N bond twisting vibration at 1020 cm$^{-1}$ - 1250 cm$^{-1}$. The results show that there is an epoxy reaction at the same time with the condensation reaction. [17, 18]

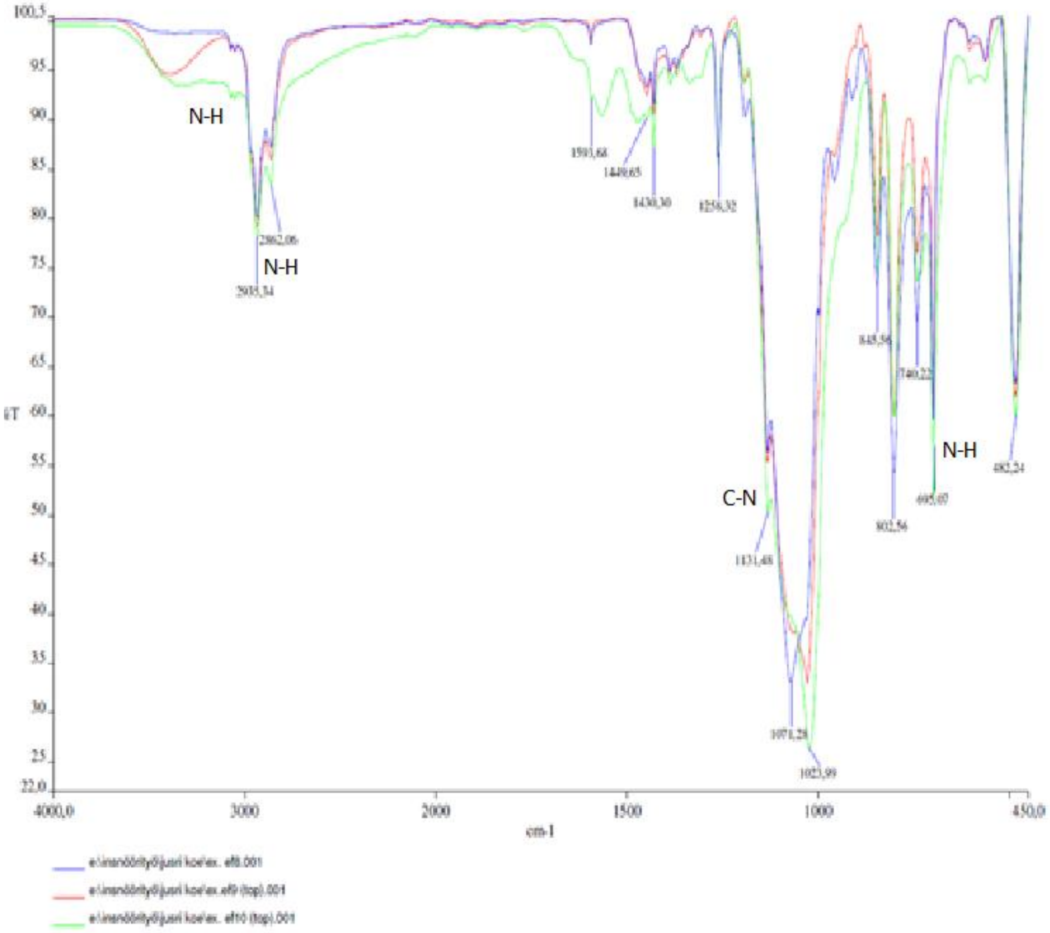


Figure 22. The Results 8 to 10 obtained from the top of the drops

The results from 10 to 18 obtained from the top of the drops are presented in Figure 22. There are no rapid reactions going on.

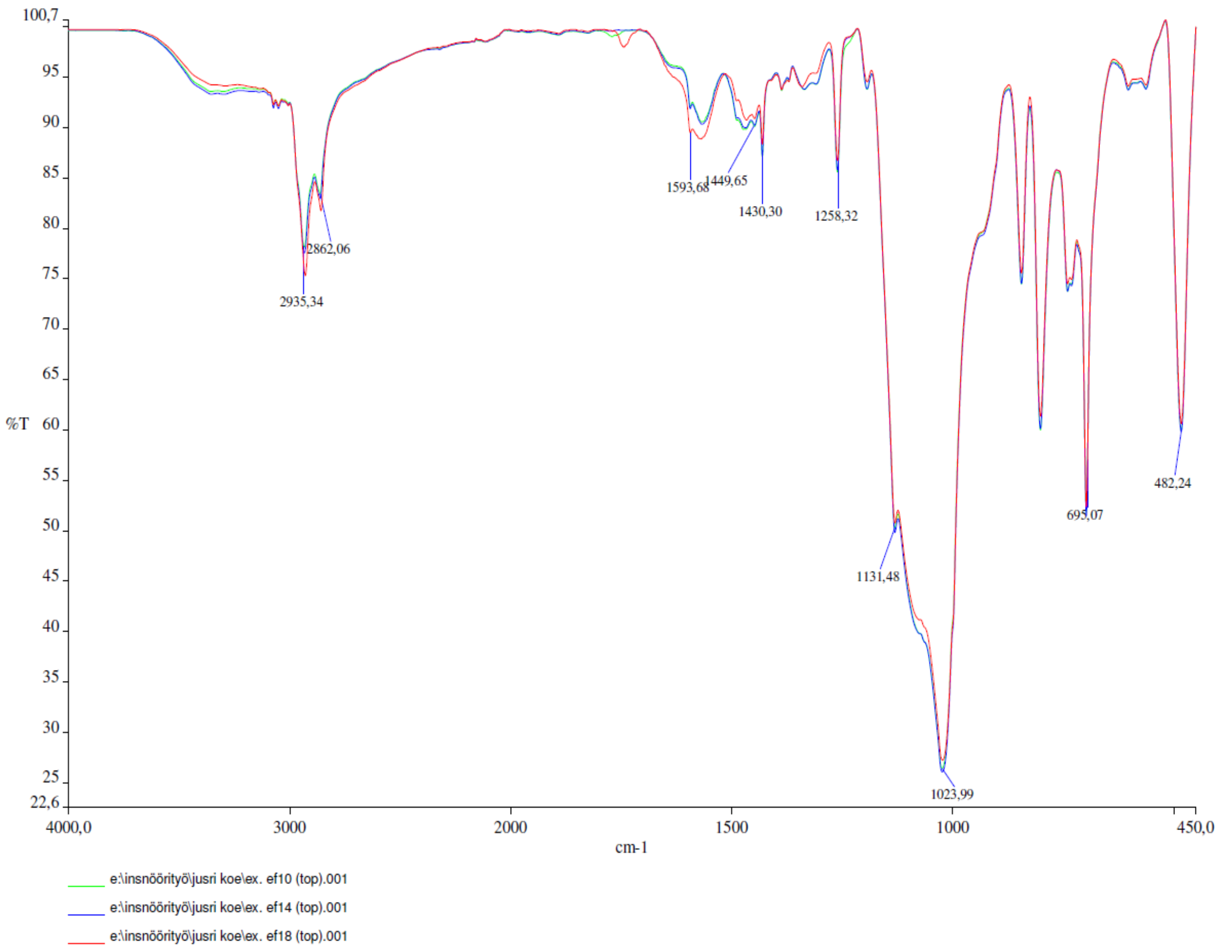


**Figure 23. The Results 10, 14 and 18 obtained from the top of the drops: green curve 48 hours, blue curve 192 hours and red curve 336 hours**

The bottom and top results 9, 14 and 18 were compared to each other (Figure 24, 25and 26). Differences between the top and bottom of the drop may have been caused by water, which also work as a catalyst.

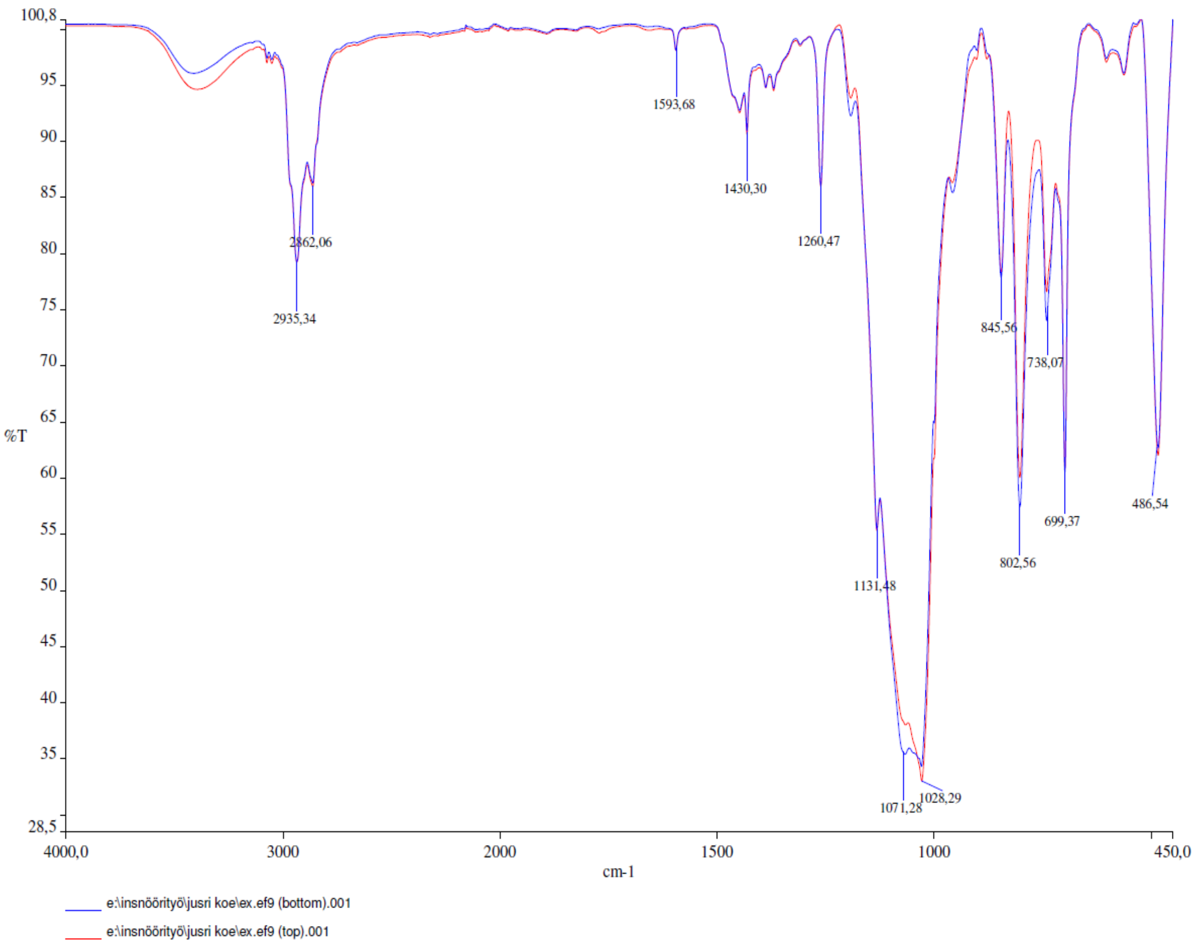


Figure 24. Comparing bottom and top results 9

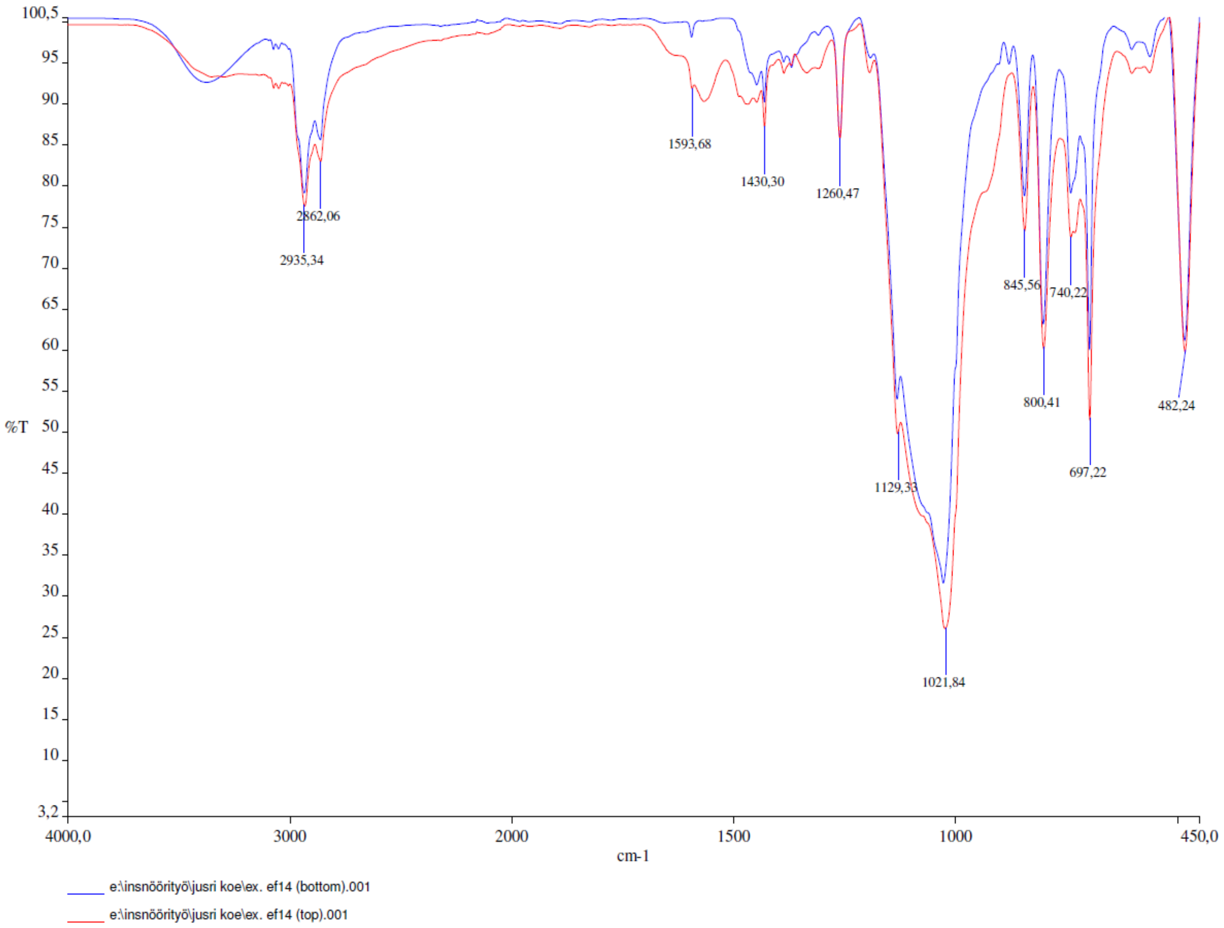


**Figure 25. Comparing bottom and top results 14**

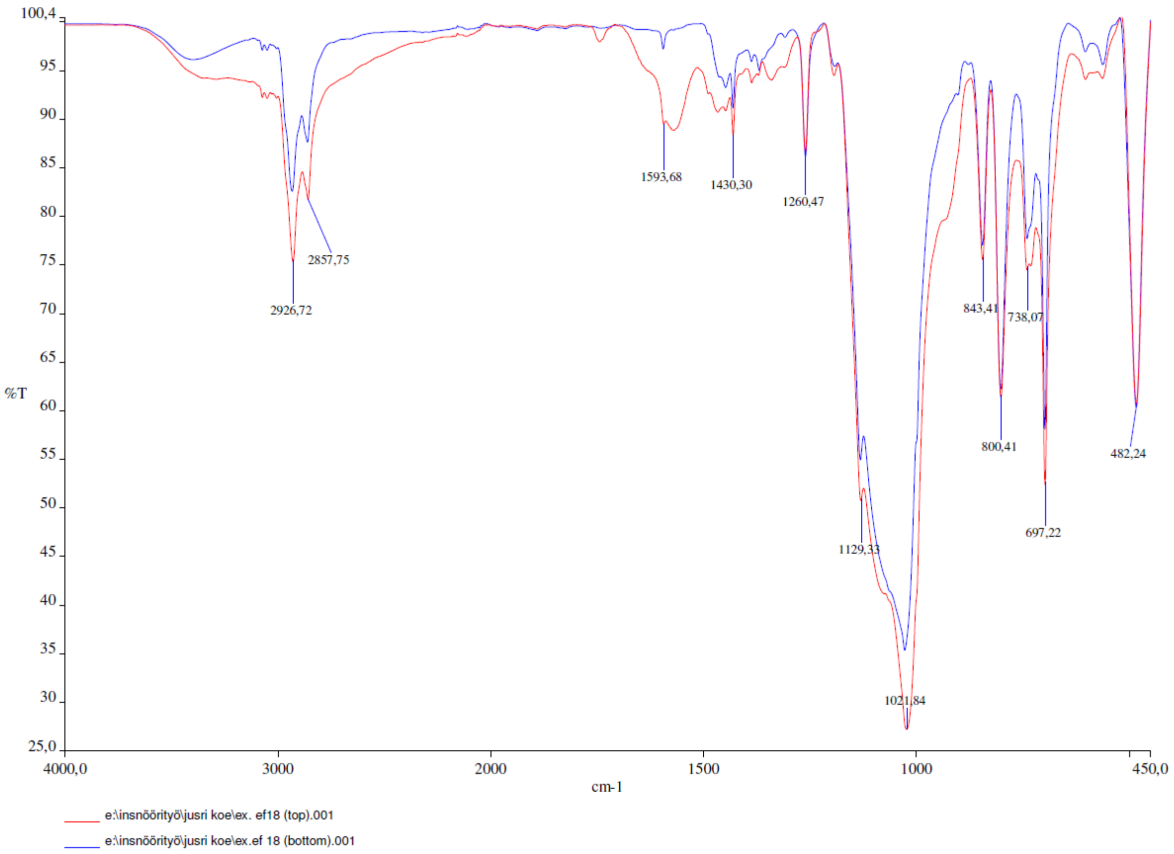


**Figure 26. Comparing bottom and top results 18**

In some samples there are small signals around the wavelength 1700 $cm^{-1}$ -1800 $cm^{-1}$. It could be caused by C=O bounds and can be evidence of catalysis reactions. Other signals from carboxyl acid are so weak that they are covered by the stronger signals. [17, 18] There is also a possibility of an overtone band (Figure 20).

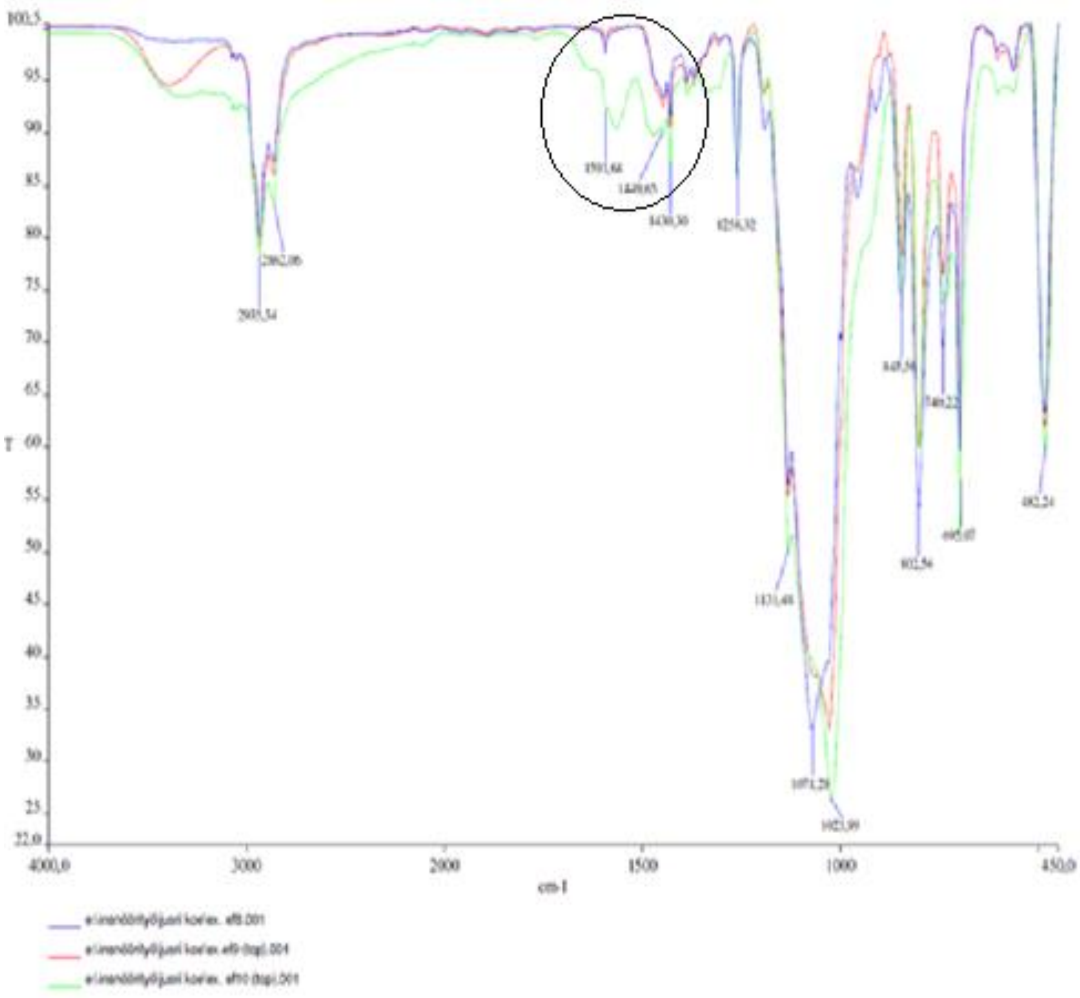


Figure 27. Possible overtones bands

Overtone peaks show at the wavenumber that is a slightly less than the main peak, in this case the overtone peaks are at around 1450 cm$^{-1}$. These overtone bands could be caused by the Si-OH bond, which main peak is at around 800 cm$^{-1}$ or by the N-H bond, which shows a peak at around 700 cm$^{-1}$. There is also a possibility of a combination band. There could be symmetrical vibrations that do not shows in the spectrum and creates combination bands with either the N-H bond or the Si-OH bond (or even with both). [15]

## 6.2 Kinetics

It is hard to compare the kinetics of epoxy, since there are not many reactions going on the bottom layer in this experiment period. On the other hand, the condensation reaction can be compared. Figure 21 shows that the reaction time is almost the same at the bottom and at the top, but the reaction itself is more radical on the top. At the wave-length 1024 cm$^{-1}$ a Si-O-Si bond can be observe. From the beginning till around 50 hours, the reaction is most rapid, and, around 150 hours, it is already over.

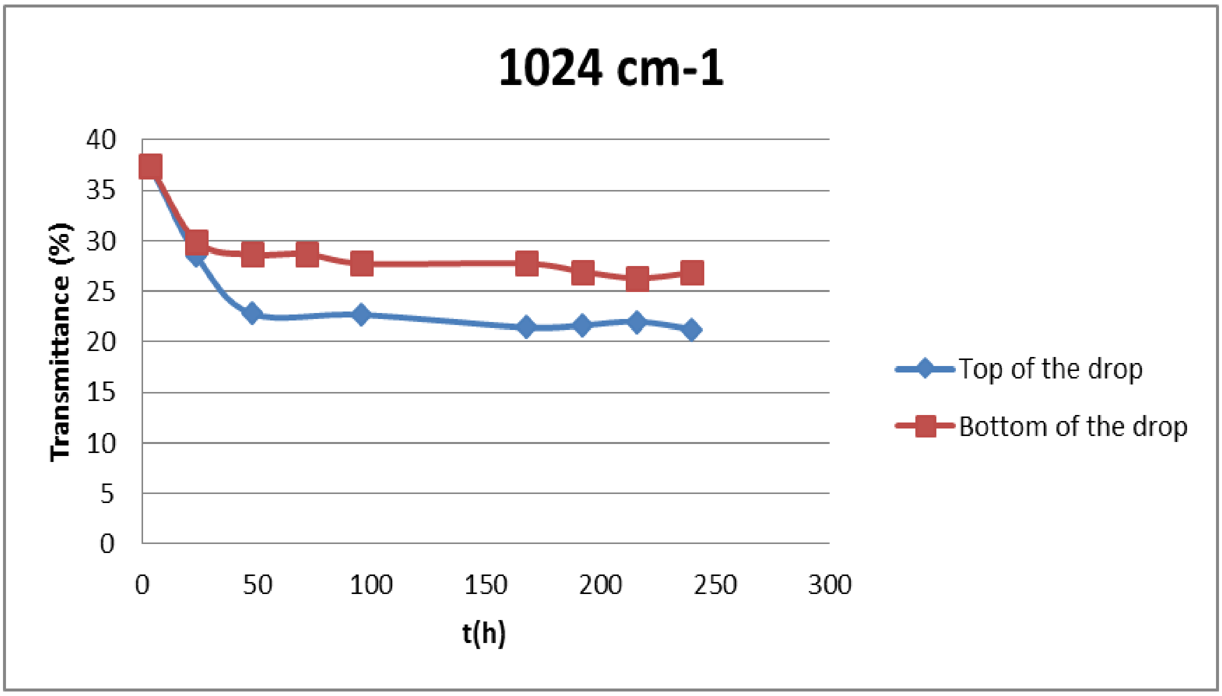


Figure 28. Kinetics of the silicone resin reaction; Si-O-Si bond

Then again, the condensation reaction leads to a decrease of aliphatic Si-O bonds (Figure 22).

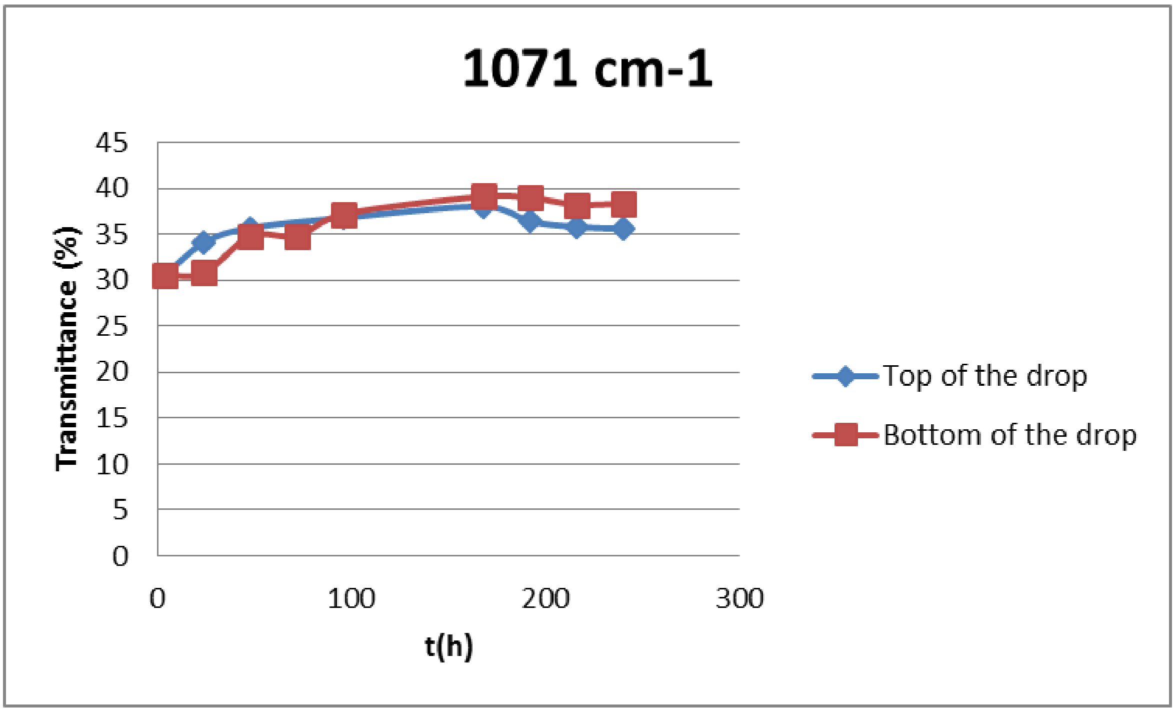


**Figure 29. Kinetics of the silicone resin reaction; aliphatic SI-O bond**

The reaction kinetics is the same: the first 50 hours are the most rapid reaction time, and after 150 hours there is not much going on.

# 7 Conclusions

The results show that the epoxy reaction started at the top layer where more water is available. Therefore, the epoxy reaction does not shows at the bottom of the drop but at the very end when water reaches the bottom layer. On the other hand the condensation reaction is going further in every layer of the drop; thus, the silicon resin reactions are ready before the epoxy reaction. It takes about a week for the condensation reactions and around one month for the epoxy reactions. Providing water to the bottom layer may help the epoxy reaction, but, at the same time, it could cause some other problems with the application of the paint itself.

The condensation reaction goes further in every layer of the drop almost at the same reaction rate. After one week, the reactions do not go further anymore and it could be assumed that there are only epoxy reactions left. As a coating solidify by drying, the reactive functional groups cannot move freely anymore, which slow down the reactions.

The epoxy reaction goes further rapidly at the top of the drop and after two days, there are reactions only in the lower layers. In this experiment it is impossible to say when all the epoxy reactions are completed, but it takes more than two weeks.

Even though the volumes of the drops were the same, the shapes were different and that could have some effects on the results. Drops were taken from the same batch which was blended quickly by hand, and that is why there could be some differences in the mixing rations between the drops.

The results were rather clear but because of the method of this study and the use of the FTIR spectrometer, anything specific cannot be found. Nonetheless, results of this thesis prove assumed reactions and brought some information about reactions kinetics and chemical behavior of the resin. This information can be used in R&D work and even for marketing and selling purposes.

# 8 Literature

1 Regulations of glycol-ethers [Internet], [cited 2015 March 14] Available from: http://www.glycol-ethers.eu/regulations

2 Teknos Oy [Internet], [cited 2015 March 28] Available from: http://www.teknos.fi/

3 Shin-Etsu Silicone: Silane Coupling Agents 2002.2/2010 Japan

4 Paints & coatings resource center [Internet], [cited 2015 March 26] Available from: http://www.paintcenter.org/ctc/Coatmatl.cfm

5 Hare CH Protective Coatings Fundamentals of chemistry and composition, Pittsburgh: Technology Publ. Co; 1994

6 Kirchner M Katalyse der Vernetzungsreaktionen von Epoxi-Siloxan-Hybridbeschichtungen unter toxikologischen Aspekten und der Anwendbarkeit im schweren Korro-sionsschutz. : at Niederrhein university of applied sciences; 2011

7 Evonik Industries Comparative Study: Life Cycle Assessment of Corrosion Protection Coating Systems; July 2014

8 TIB chemicals [Internet], [cited 2015 March 28] Available from: http://www.tib-chemicals.com/fileadmin/uploads/PDF/Broschueren_englisch/IS_Catalysts.pdf

9 Atkins P & De Paula J Atkins' Physical Chemistry. 10th ed. Oxford University Press; 2014

10 Laboratorioanalyysit, Opetushallitus [Internet], [cited 2015 March 16] Available from: http://www03.edu.fi/oppimateriaalit/laboratorio/analyysimenetelmat_5-4_infrapunaspektrometria.html

11 Christian GD Analytical Chemistry. 5th ed. John Wiley & Sons; 1993

12 Koivisto J ORGAANINEN RAKENNEANALYTIIKKA. lecture materials: 2013

13 Jaarinen S & Niiranen J Laboratorion analytiikka. Helsinki: Edita Publishing Oy; 2005.

14 Chemwiki, UC Davis [Internet], [cited 2015 March 18] Available from: http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Combination_Bands,_Overtones_and_Fermi_Resonances

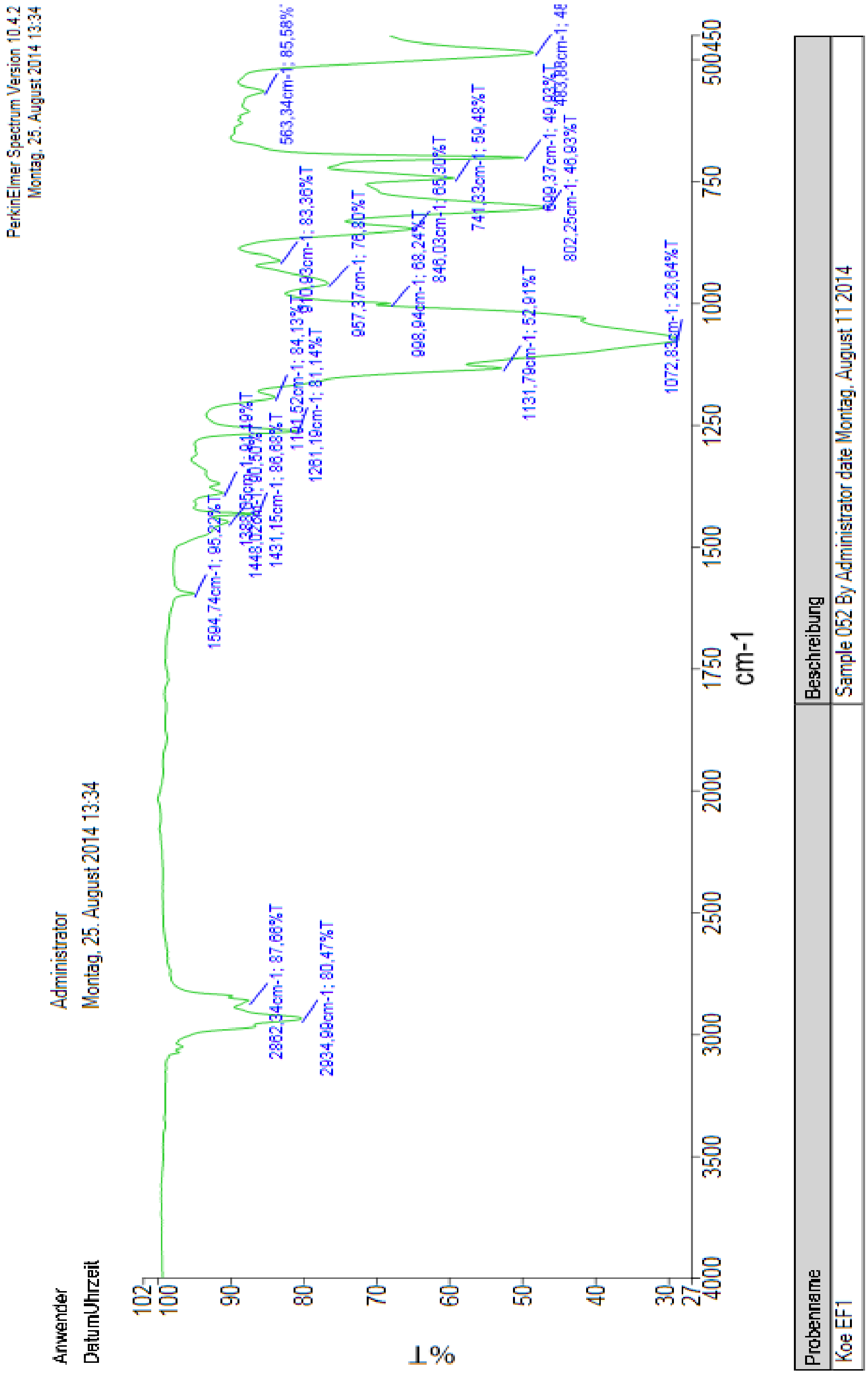
15 Infrared Spectroscopy [Internet], [cited 2015 March 28] Available from: http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared

16 Perkin Elmer [Internet], [cited 2015 March 18] Available from: http://www.perkinelmer.com/catalog/family/id/spectrum%20two

17 Hase T Sperktrometriset taulukot. 3rd ed. Espoo: Otakustantamo; 1984

18 Vandeberg, J. T Infrared Spectroscopy Atlas for the Coatings Industry. Federation of Societies for; 1980

## Appendix 1. Spectra from the experiment



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PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:34

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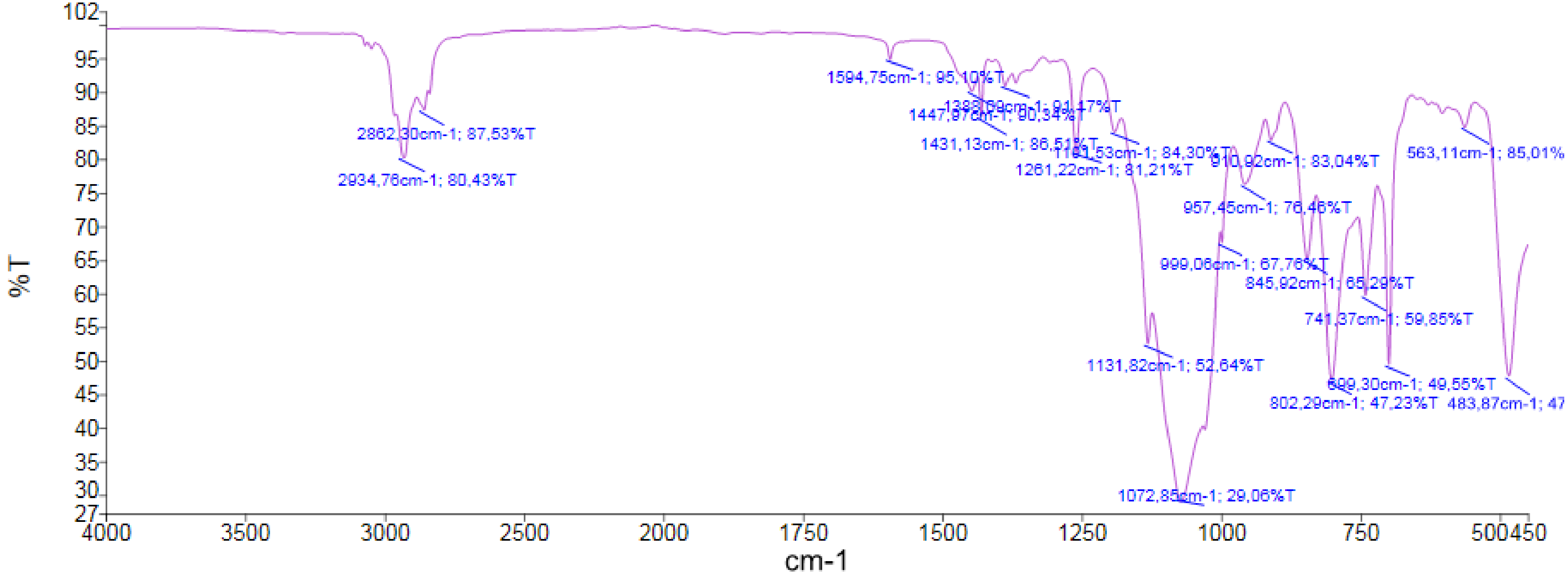

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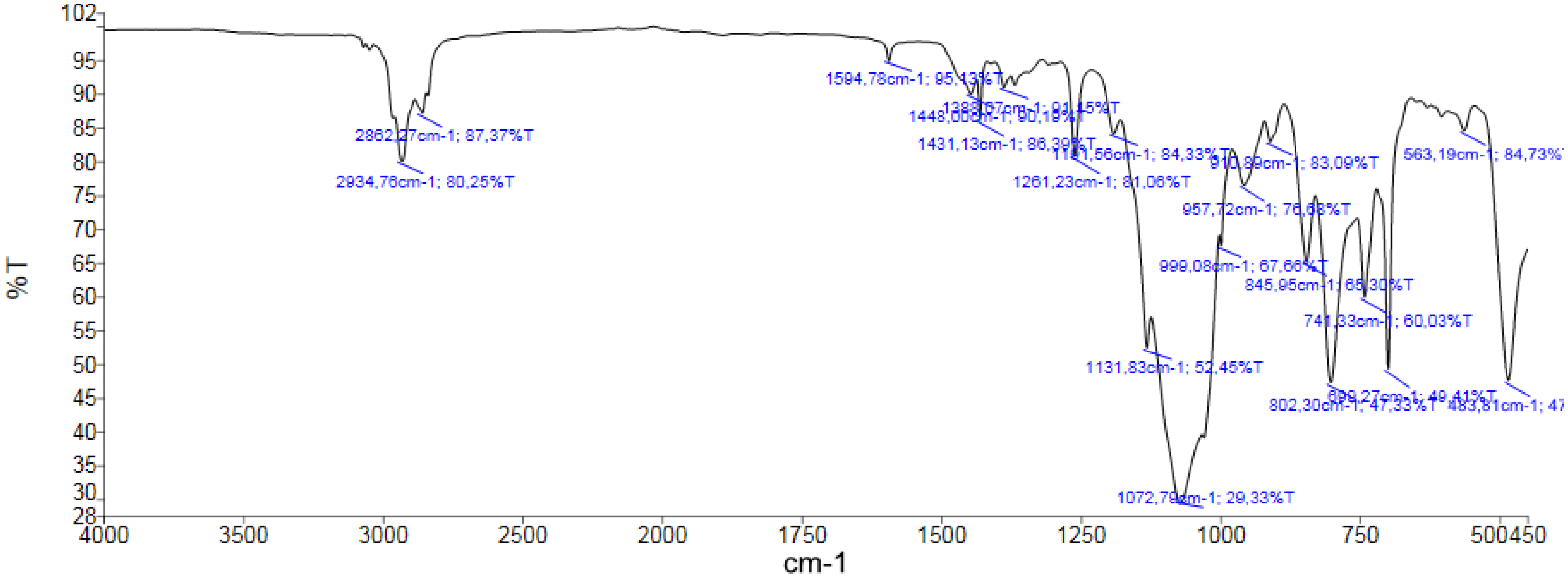

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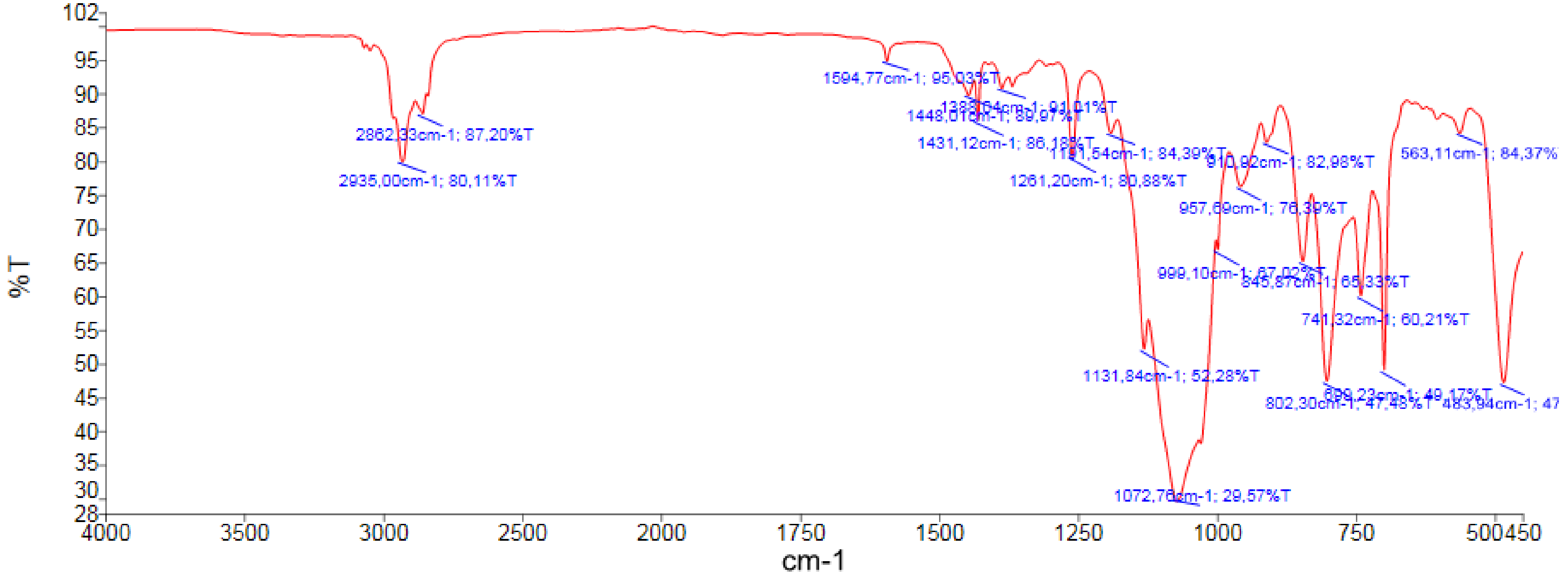

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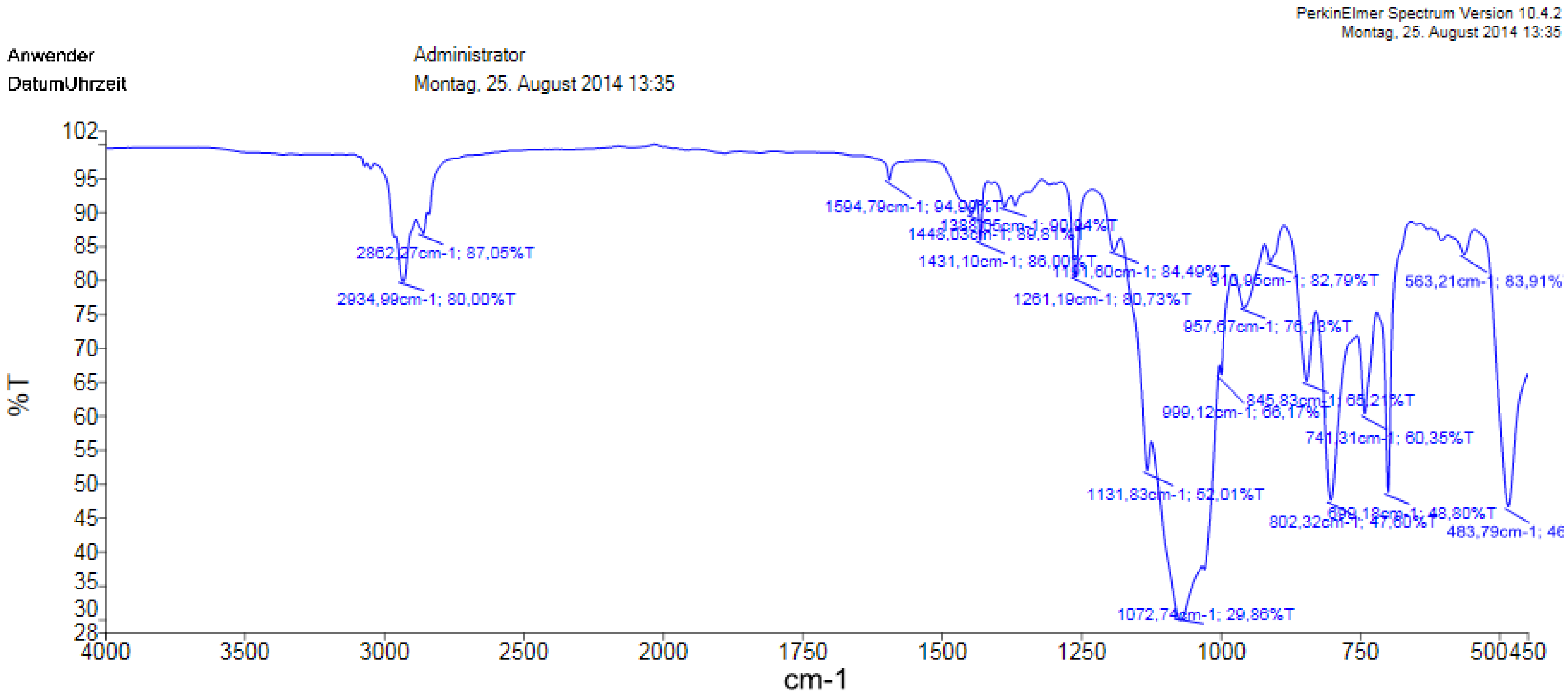

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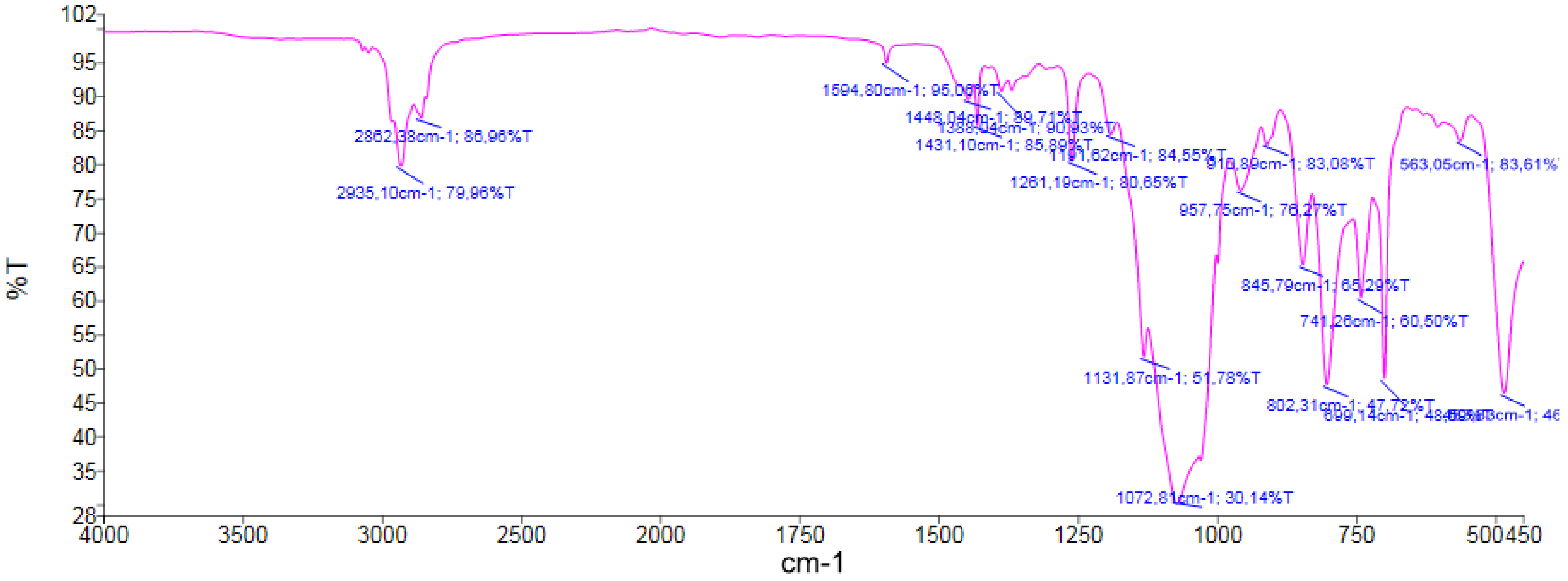

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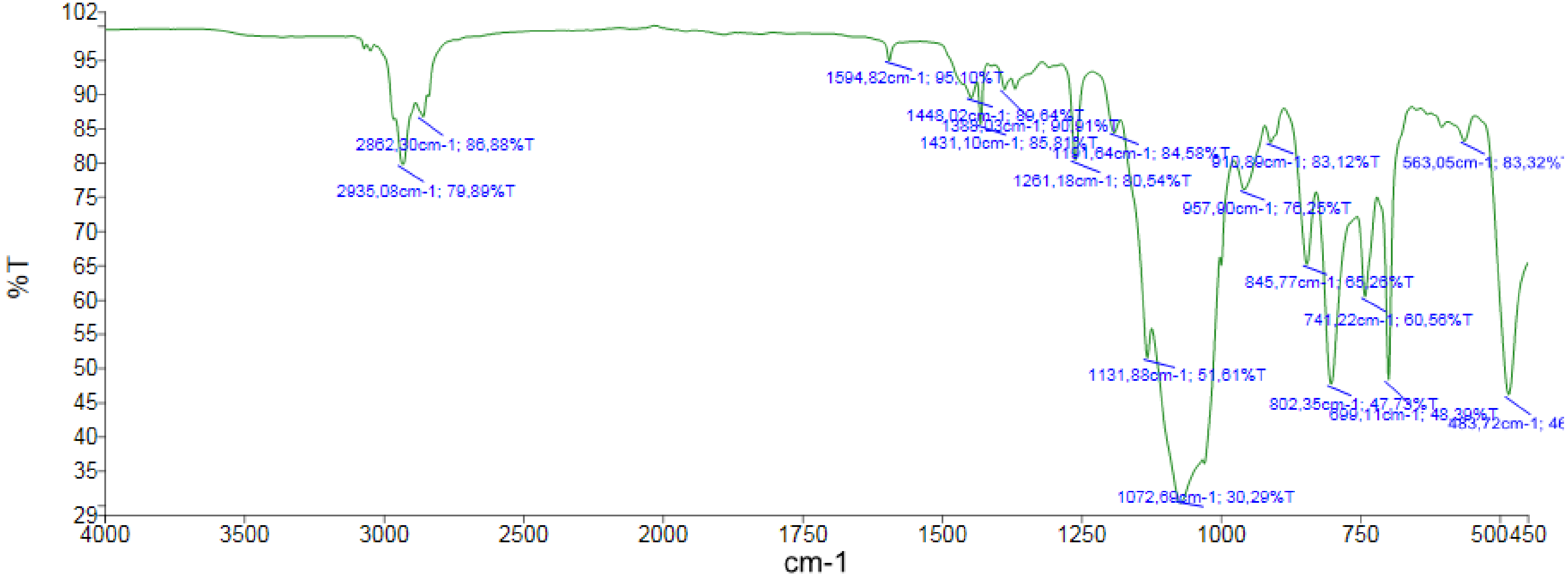

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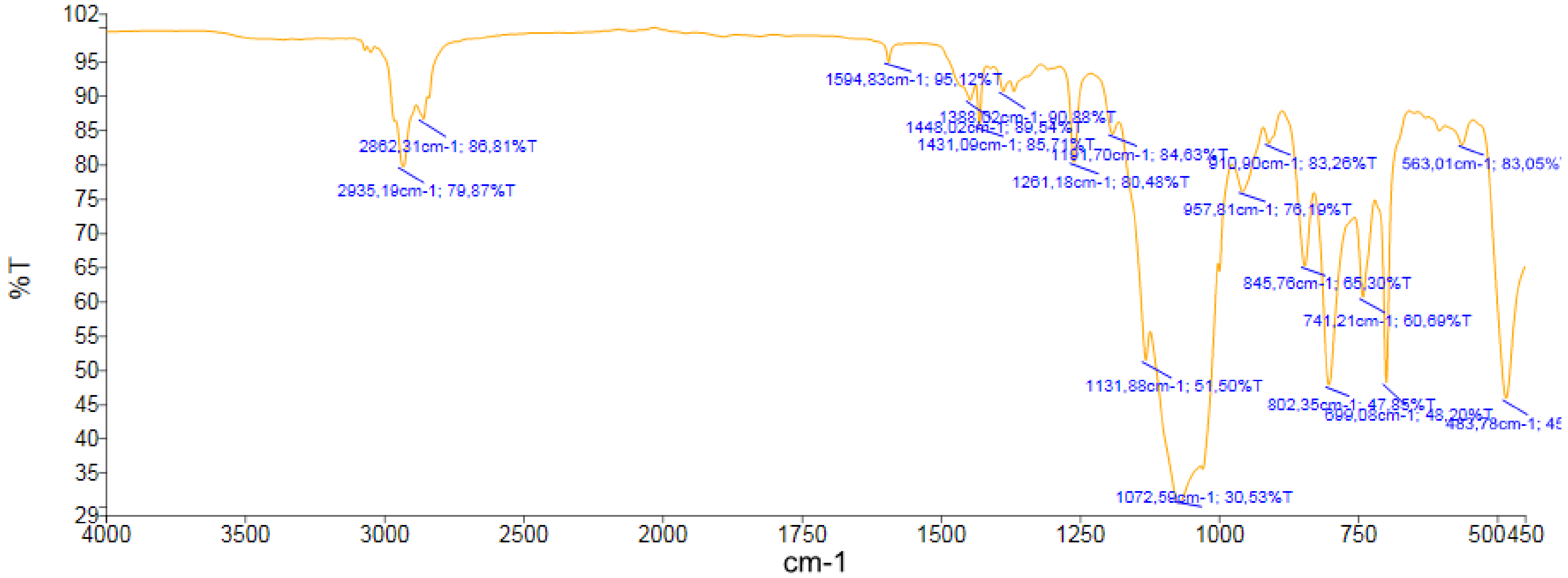

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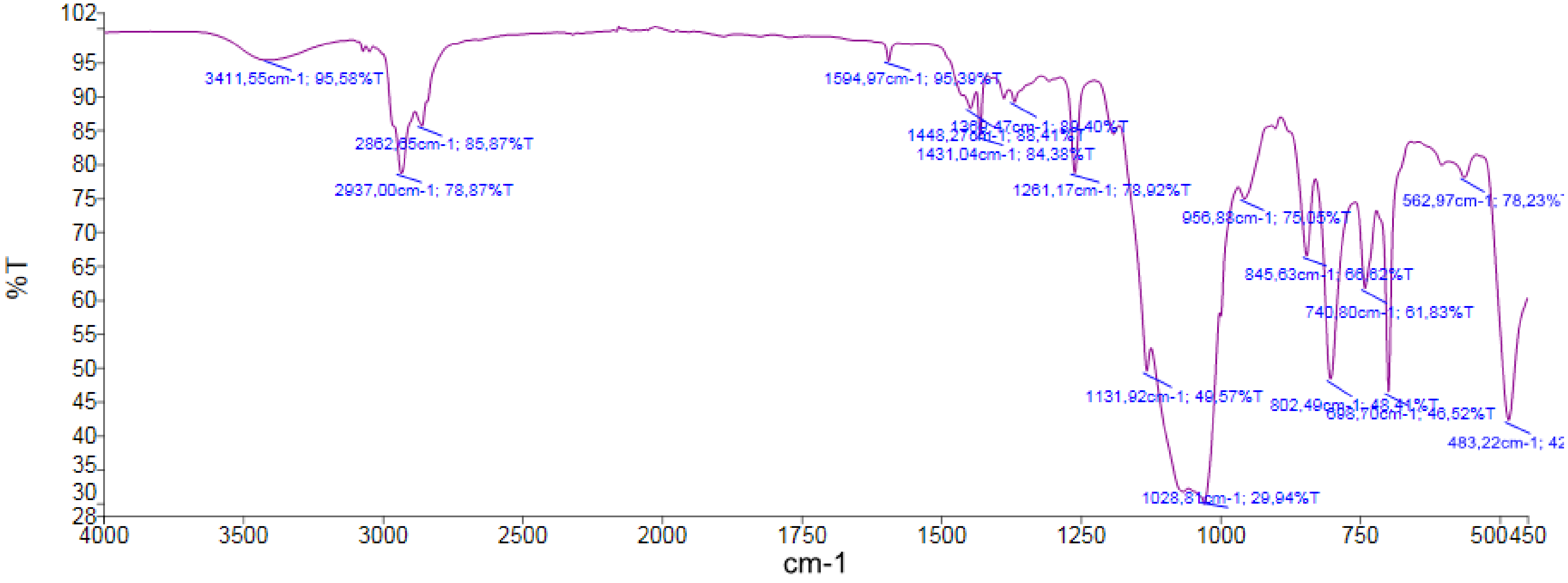

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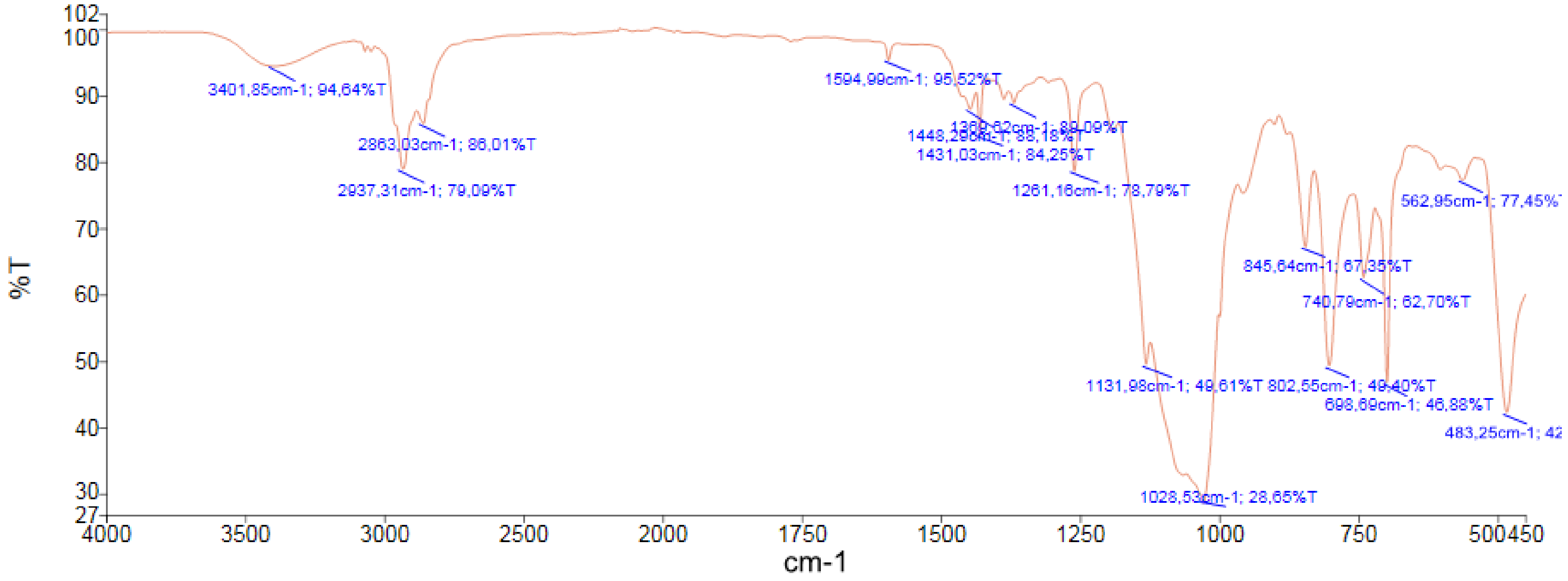

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PerkinElmer Spectrum Version 10.4.2
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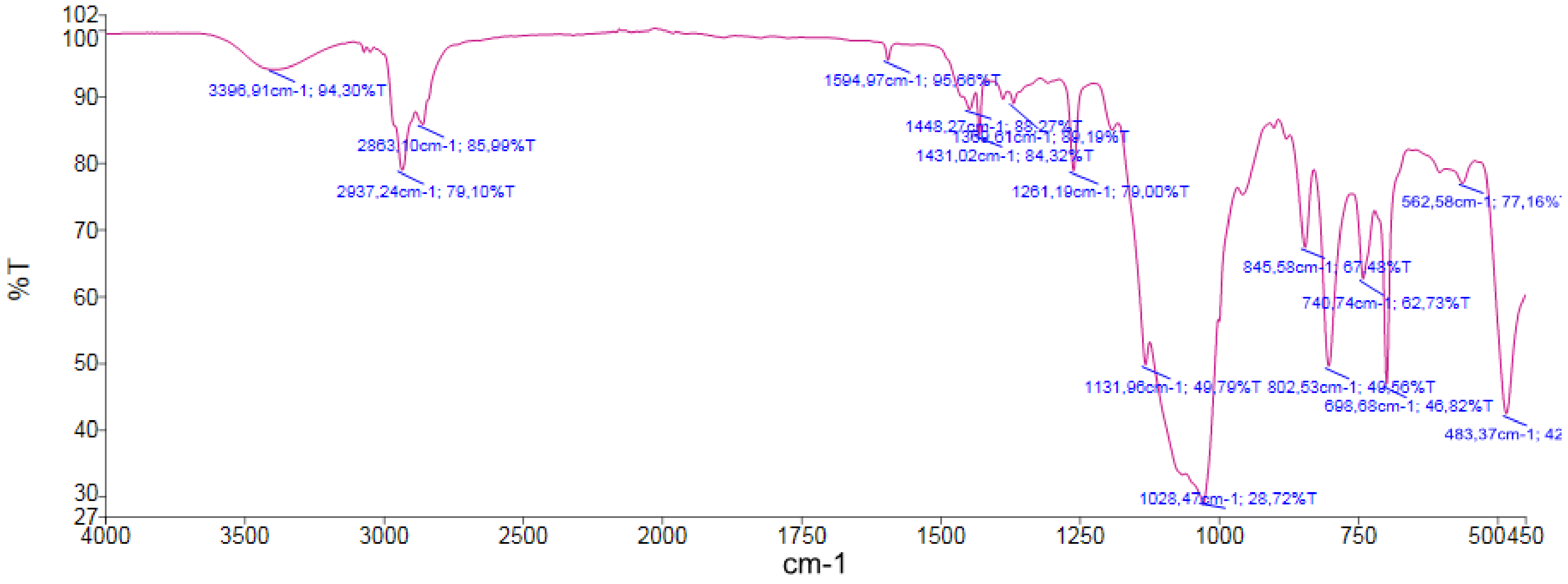

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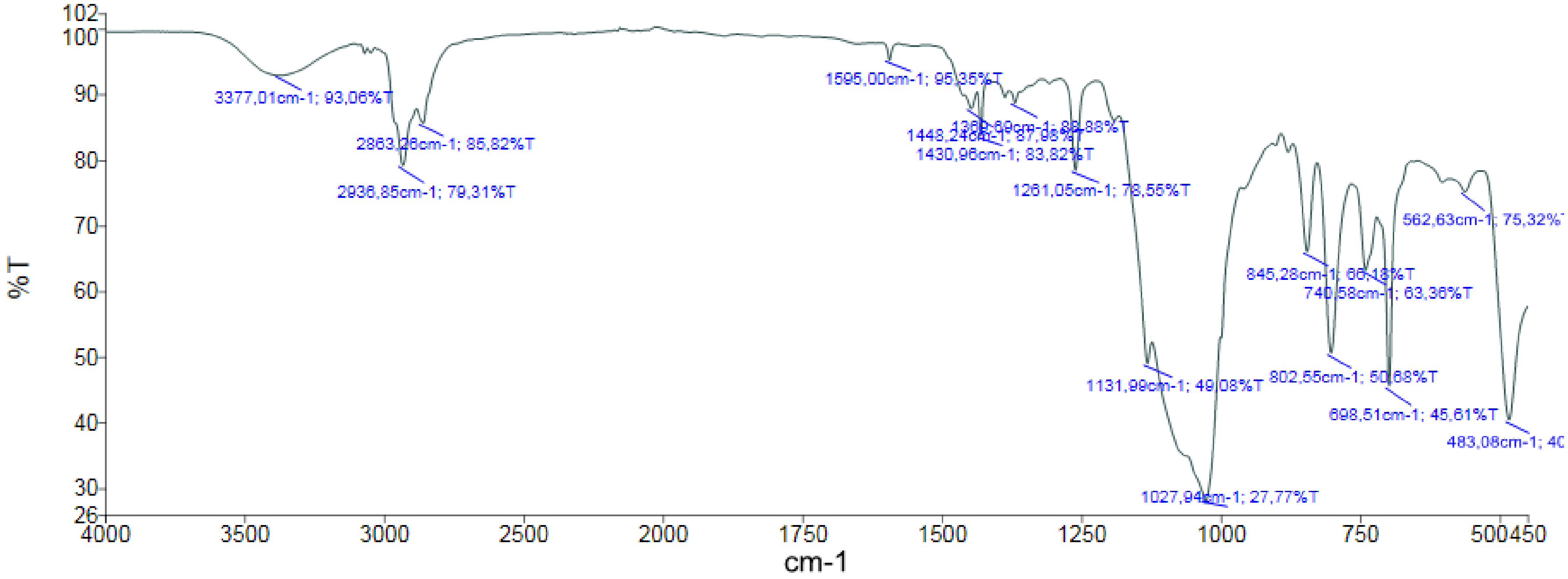

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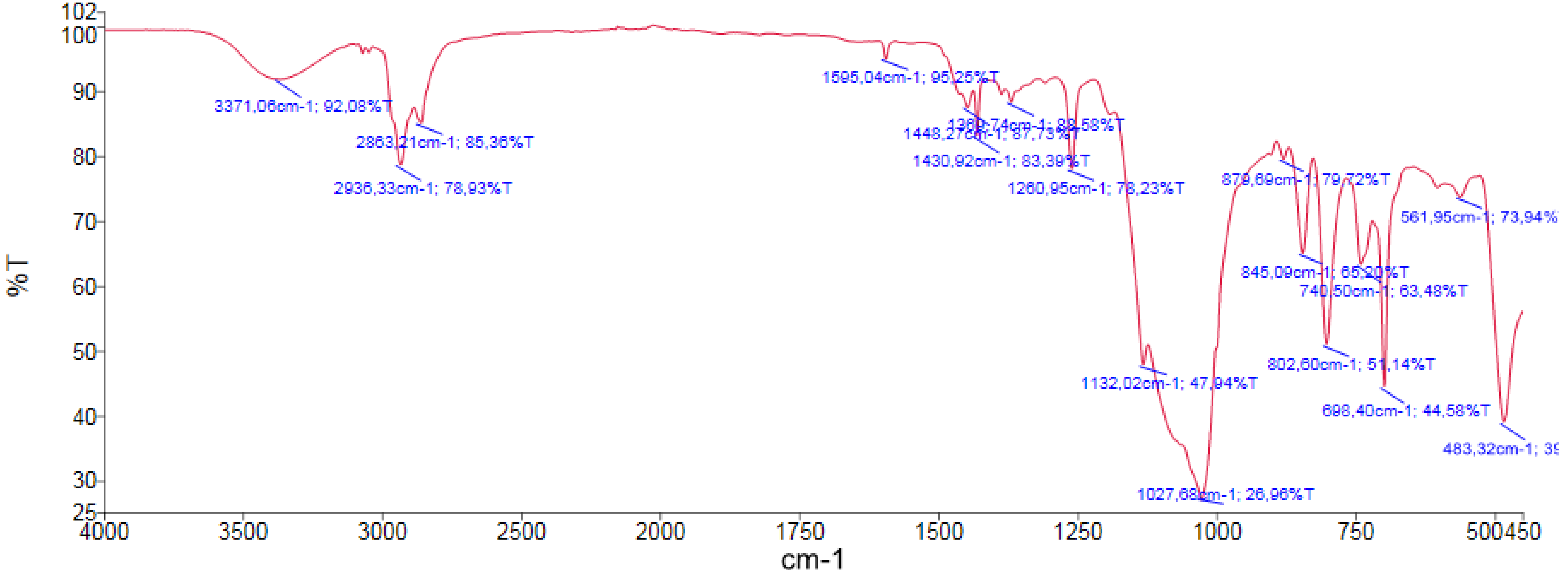

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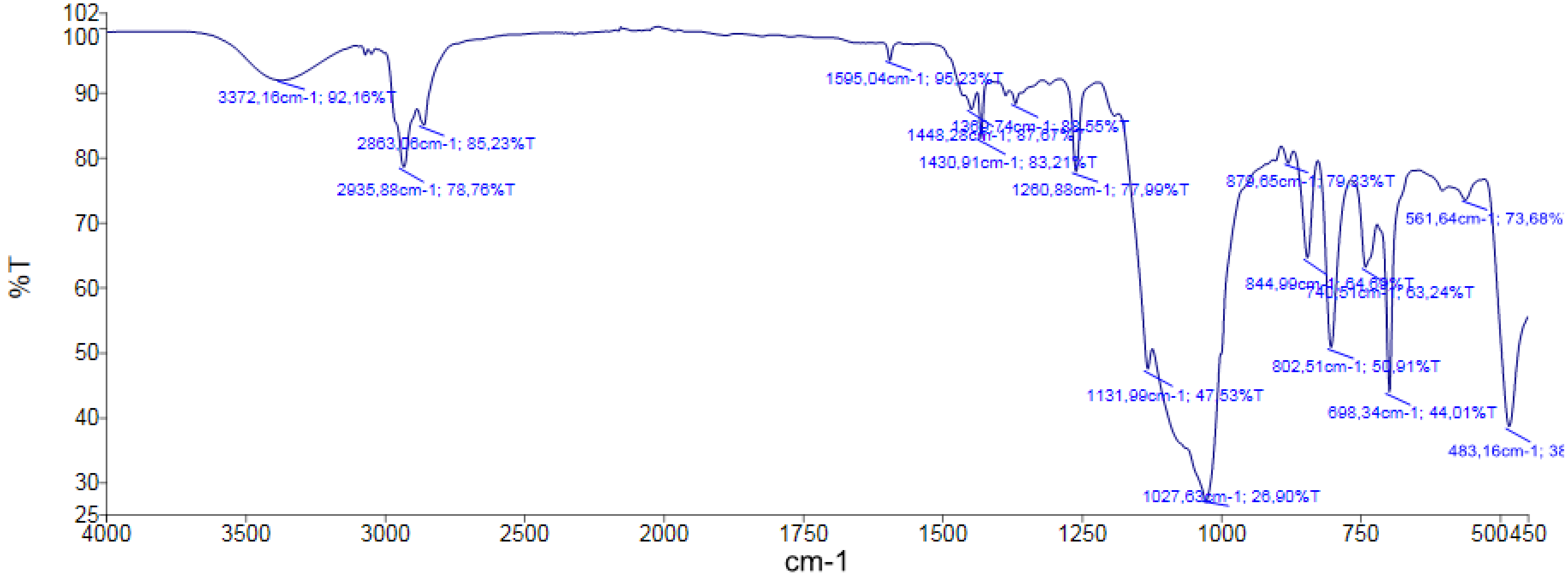

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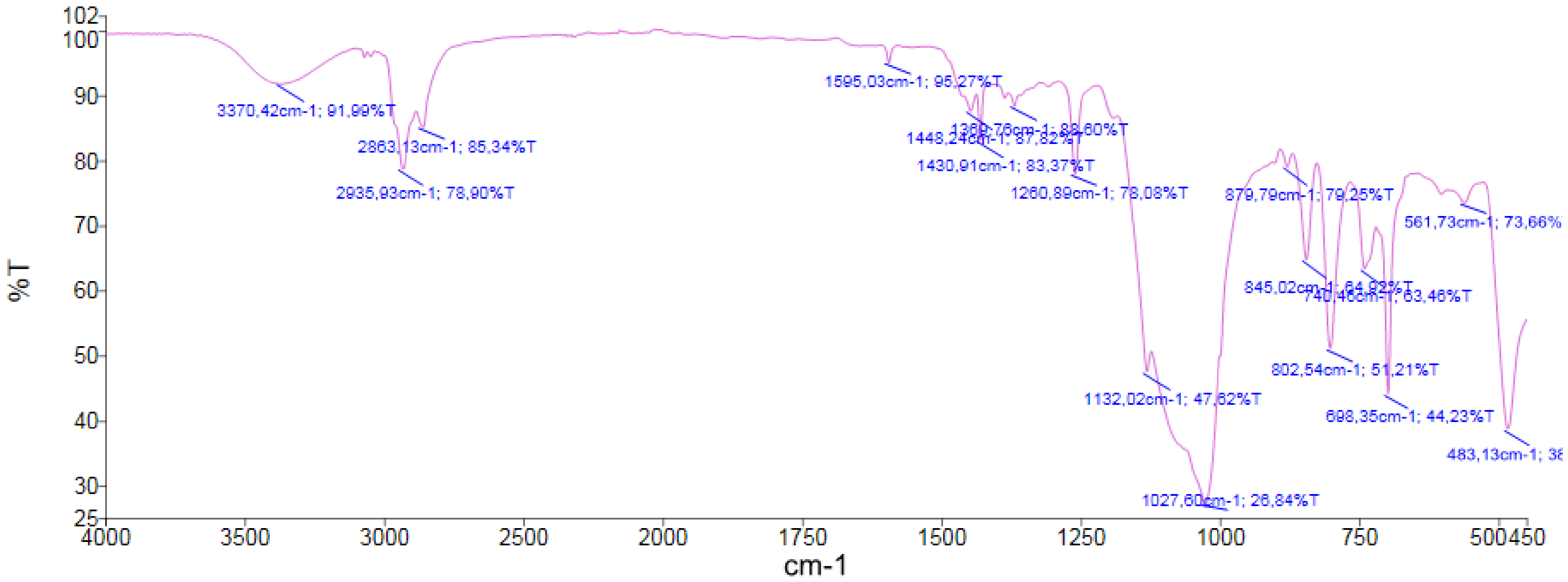

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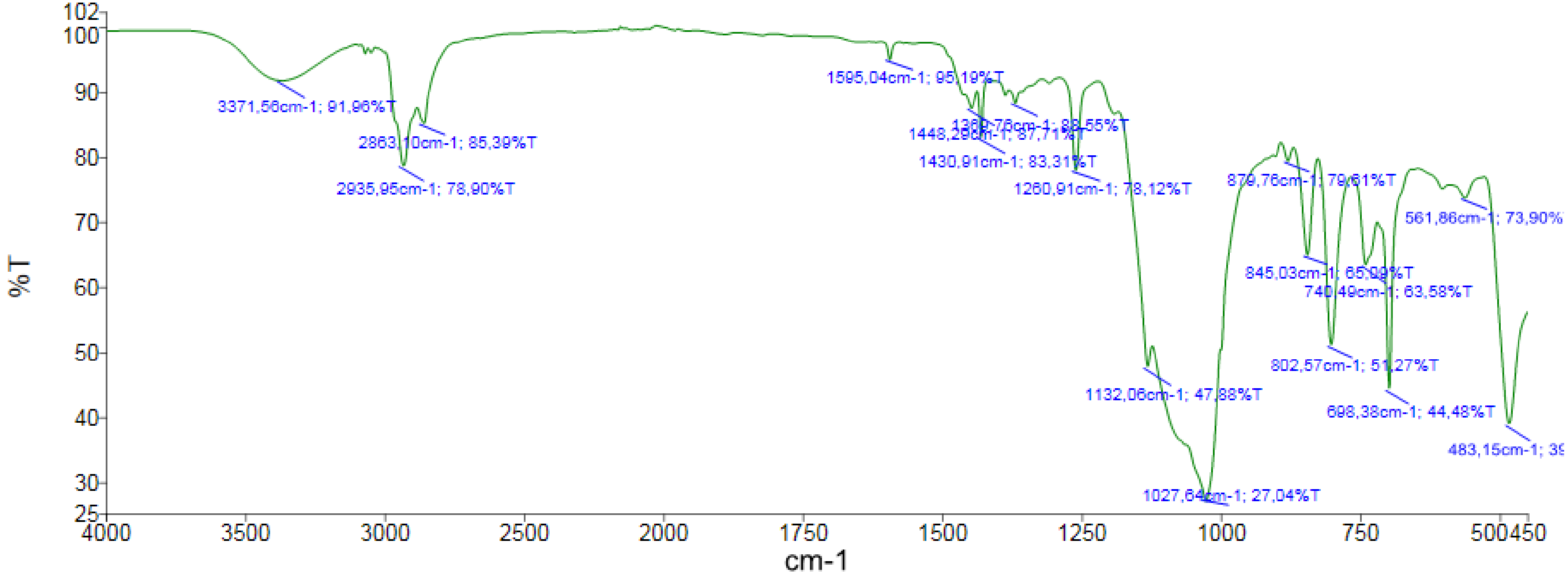

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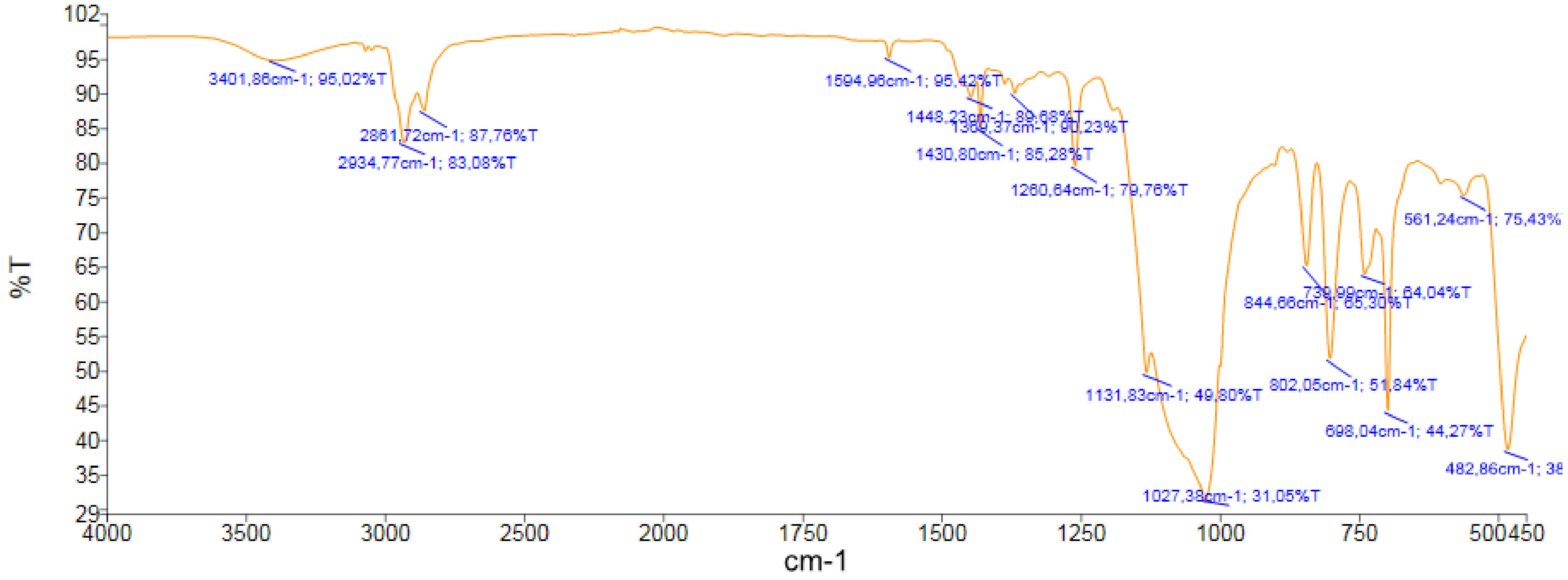

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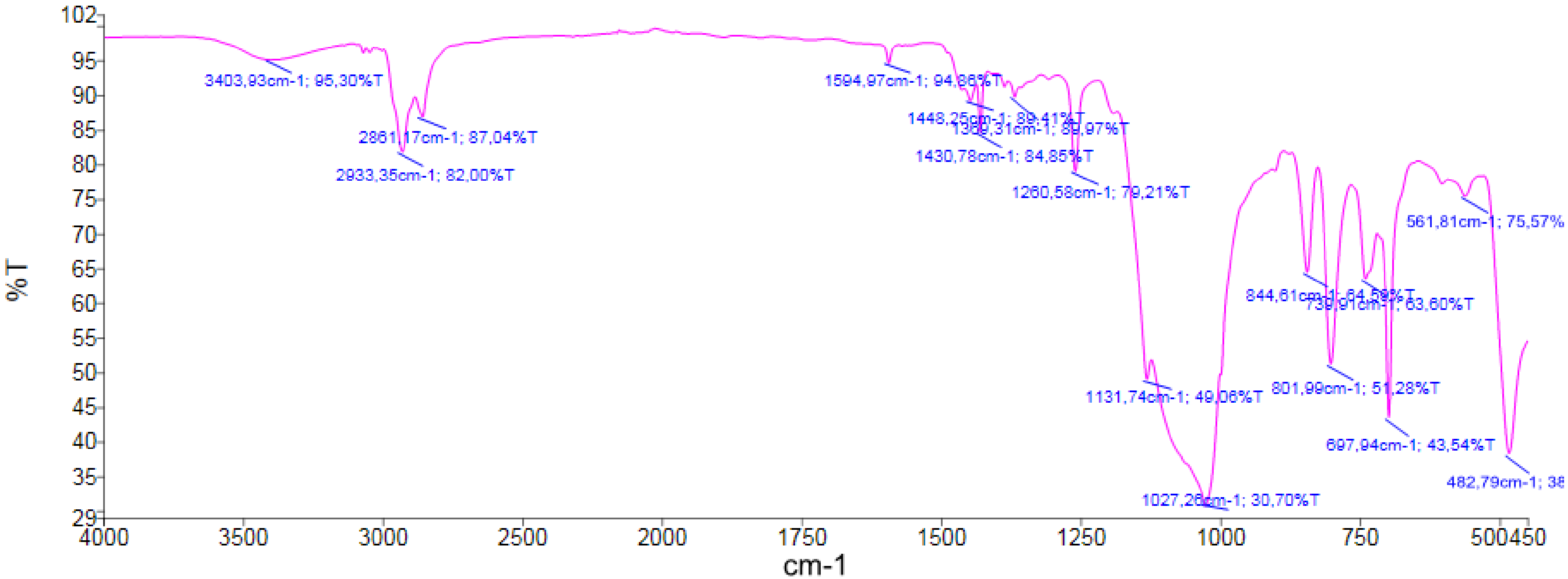

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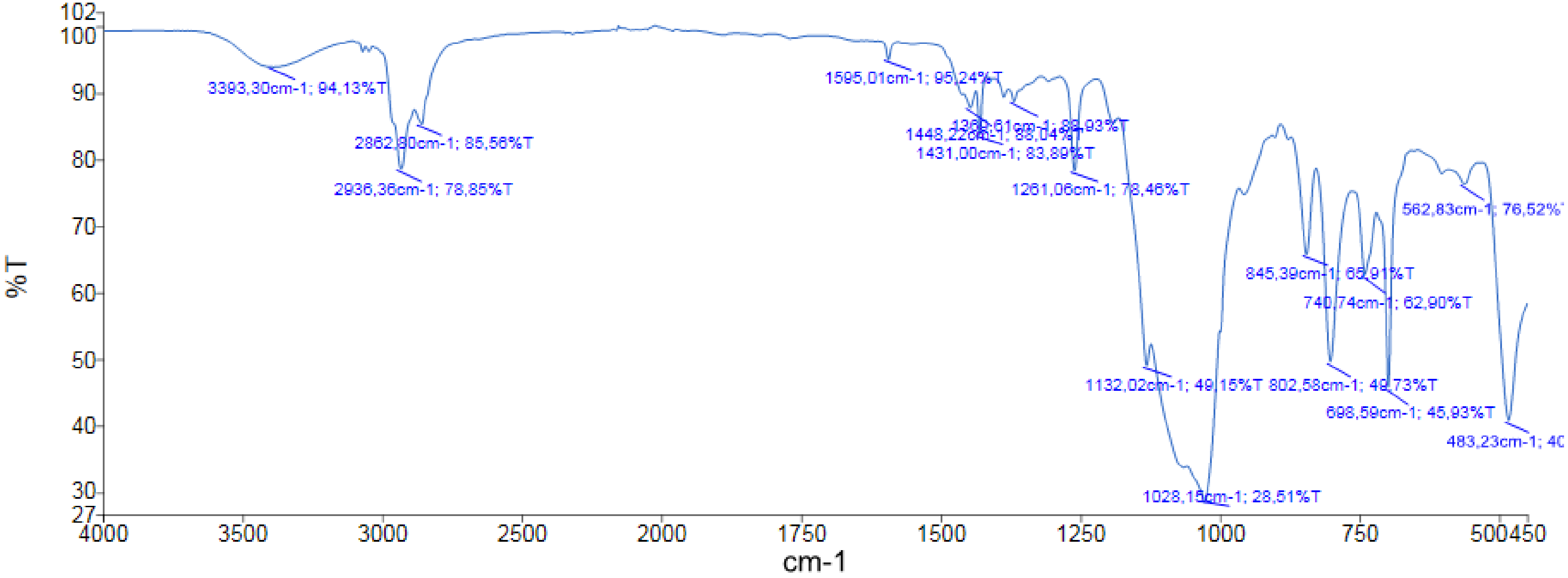

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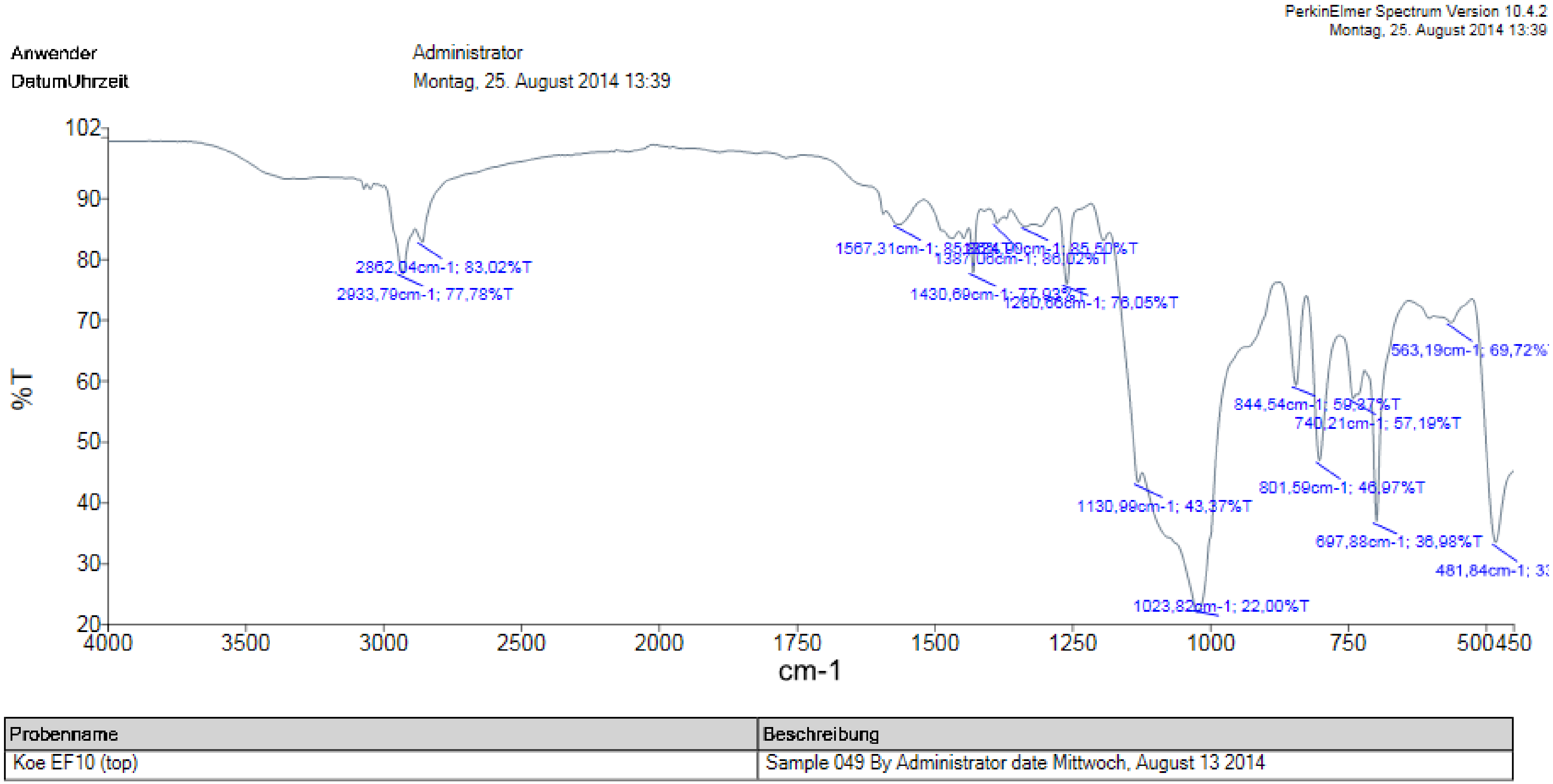

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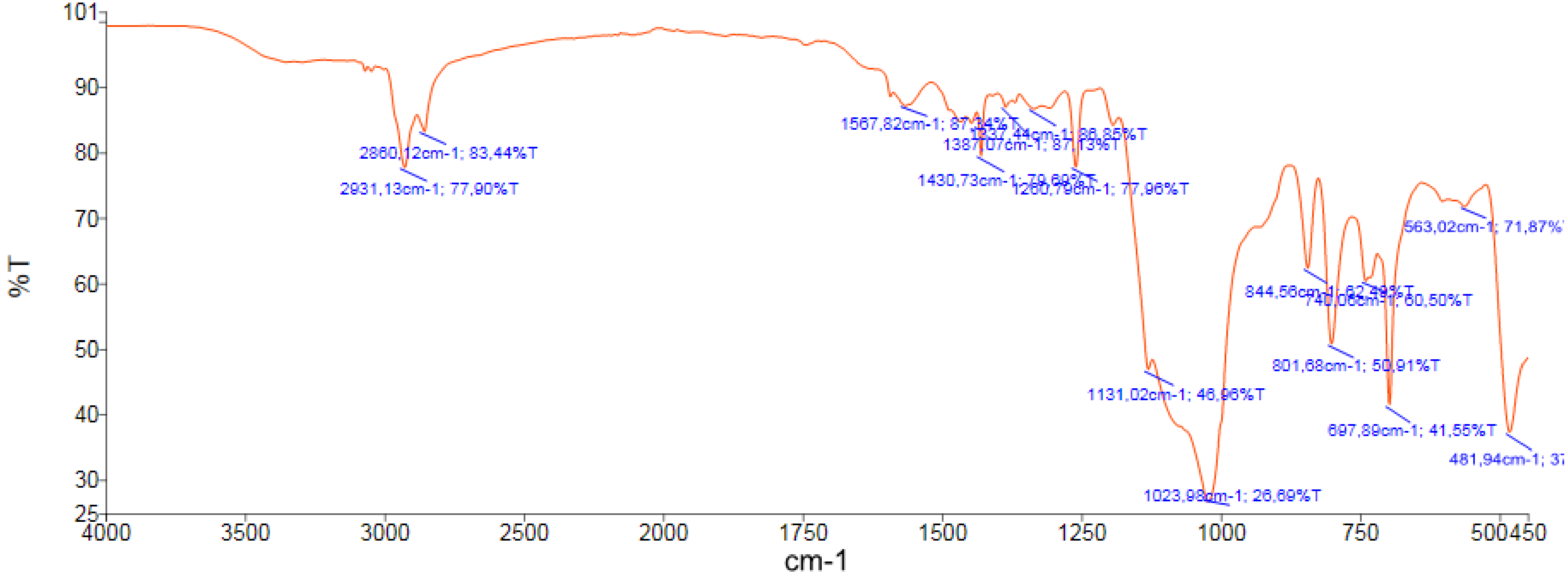
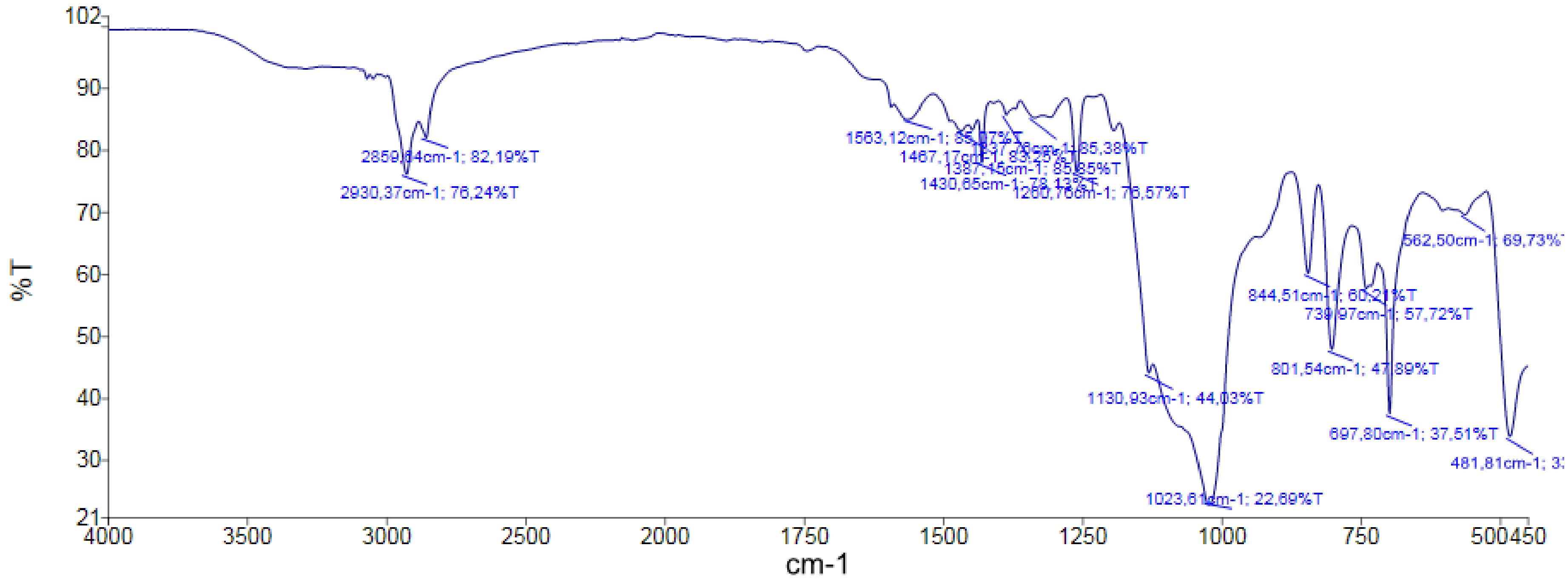


| Probenname | Beschreibung |
|---|---|
| Koe EF11 (top) | Sample 056 By Administrator date Donnerstag, August 14 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

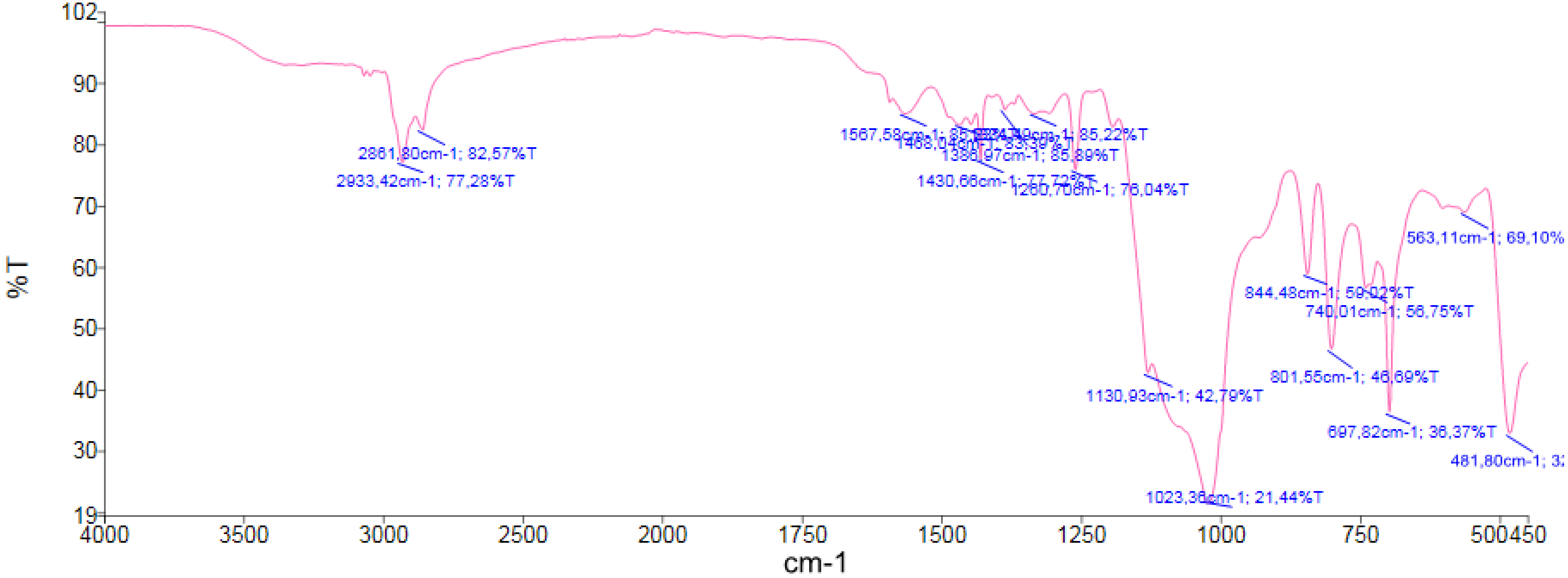
Anwender Administrator
DatumUhrzeit Montag, 25. August 2014 13:40



| Probenname | Beschreibung |
|---|---|
| Koe EF12 (top) | Sample 069 By Administrator date Freitag, August 15 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

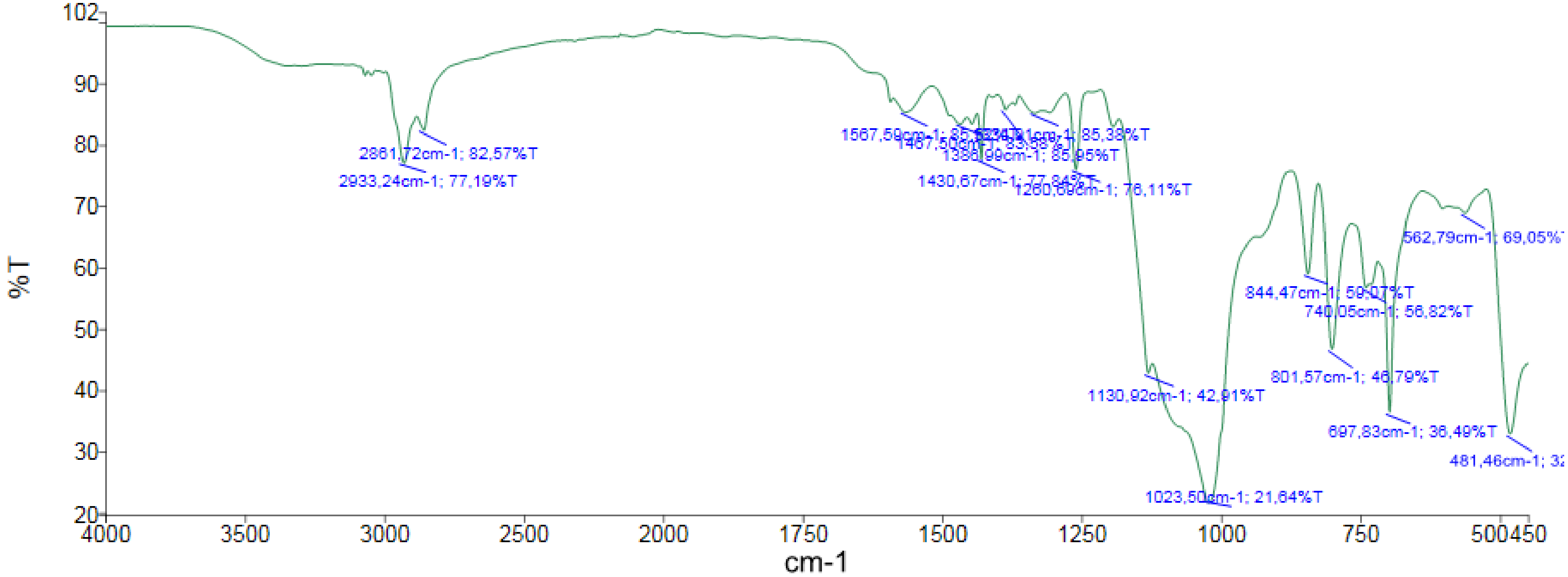
| | |
|---|---|
| Anwender | Administrator |
| DatumUhrzeit | Montag, 25. August 2014 13:40 |



| Probenname | Beschreibung |
|---|---|
| Koe EF13 (top) | Sample 073 By Administrator date Montag, August 18 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

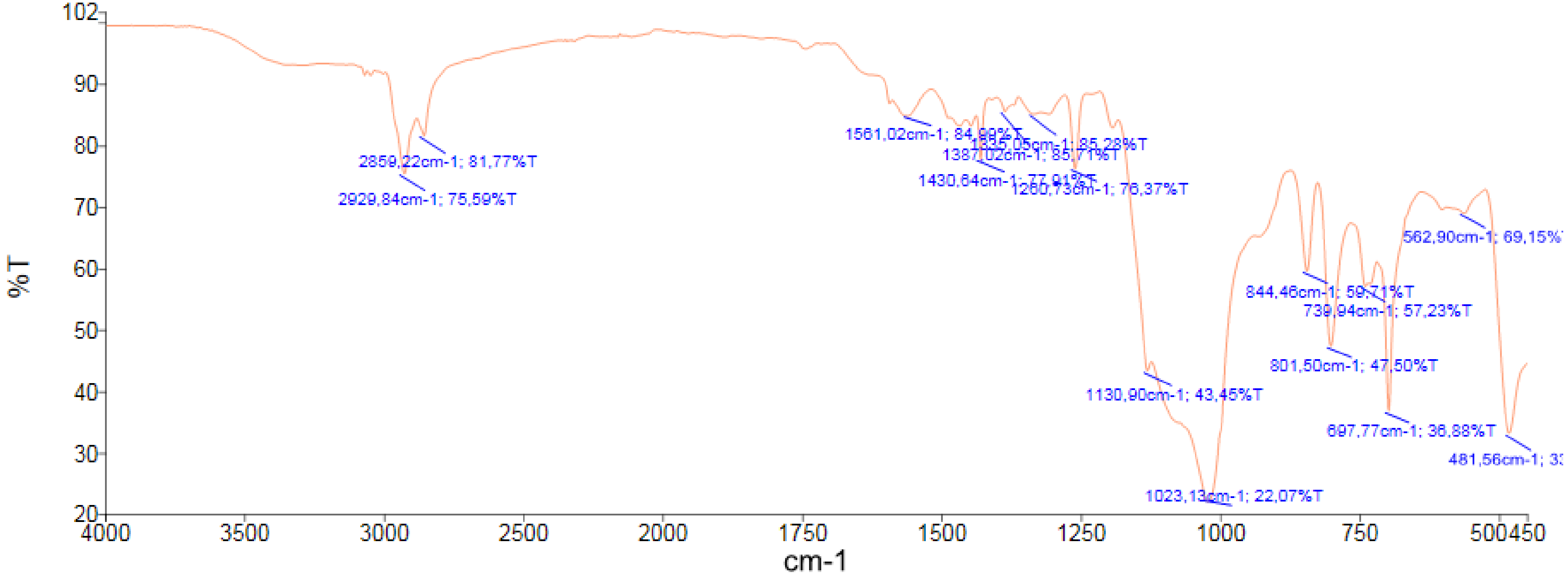
| | |
|---|---|
| Anwender | Administrator |
| DatumUhrzeit | Montag, 25. August 2014 13:40 |



| Probenname | Beschreibung |
|---|---|
| Koe EF14 (top) | Sample 049 By Administrator date Dienstag, August 19 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

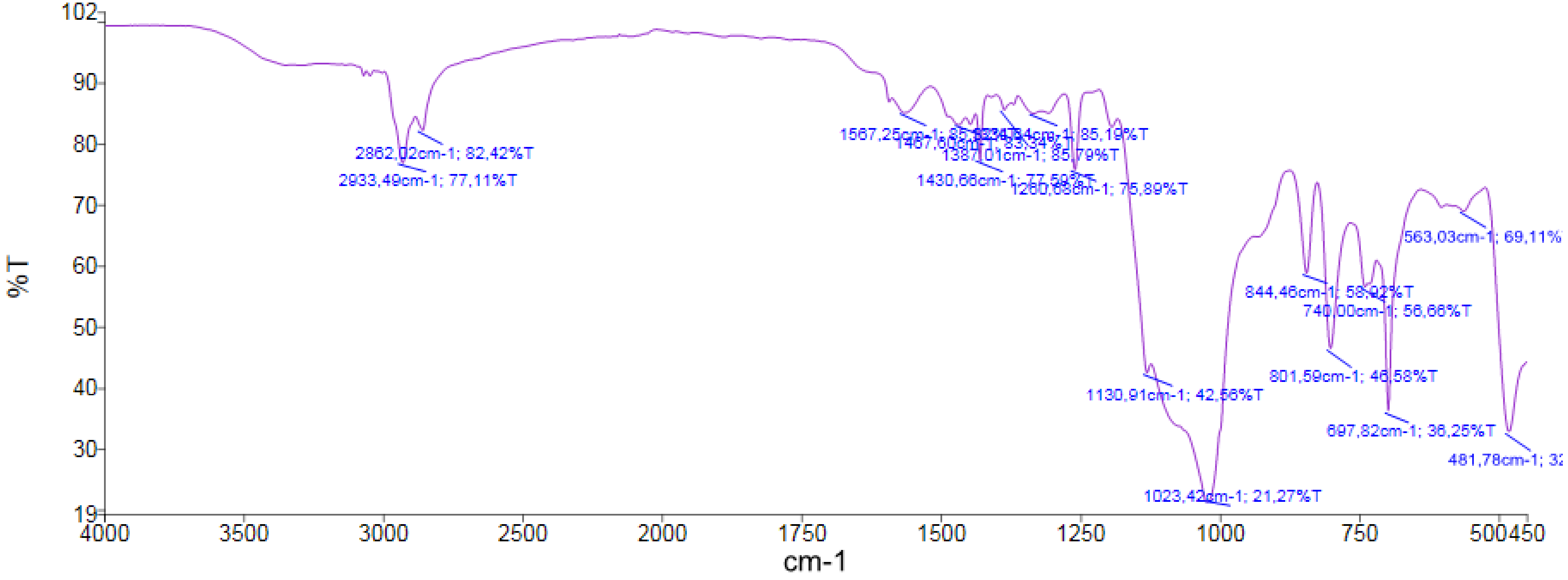
| | |
|---|---|
| Anwender | Administrator |
| DatumUhrzeit | Montag, 25. August 2014 13:40 |



| Probenname | Beschreibung |
|---|---|
| Koe EF15 (top) | Sample 054 By Administrator date Mittwoch, August 20 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

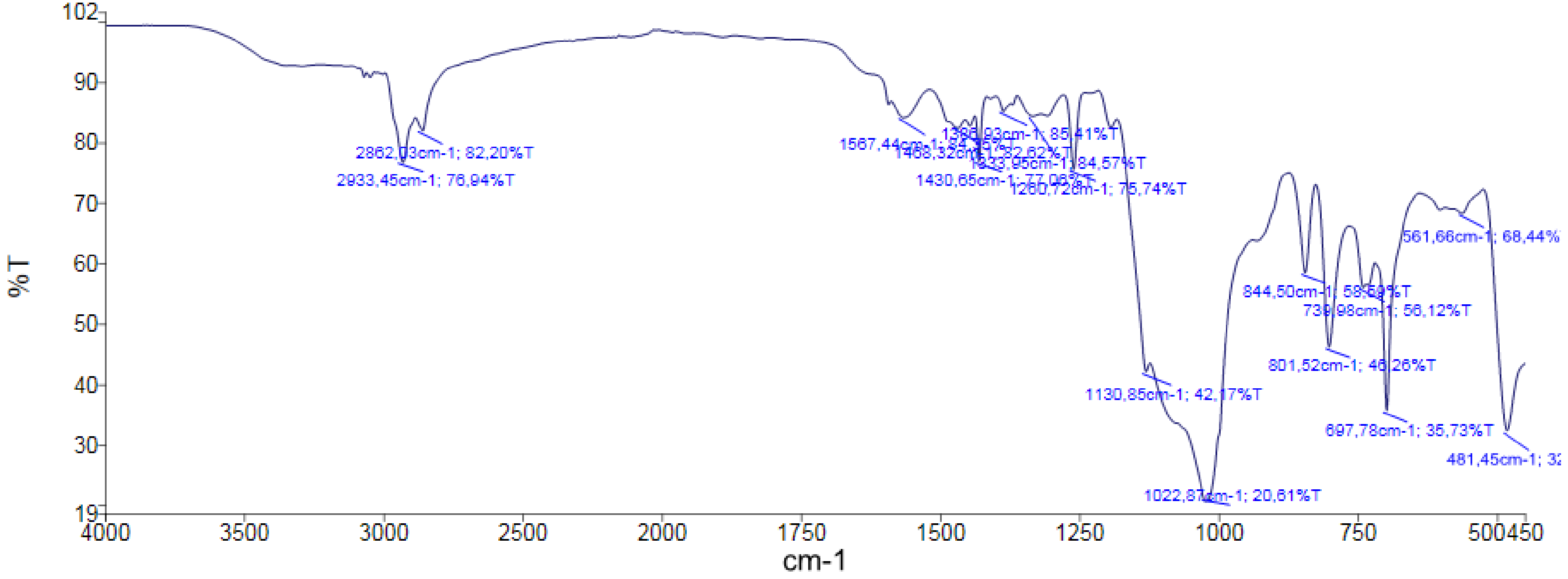
Anwender Administrator
DatumUhrzeit Montag, 25. August 2014 13:40



| Probenname | Beschreibung |
|---|---|
| Koe EF16 (top) | Sample 052 By Administrator date Donnerstag, August 21 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:40

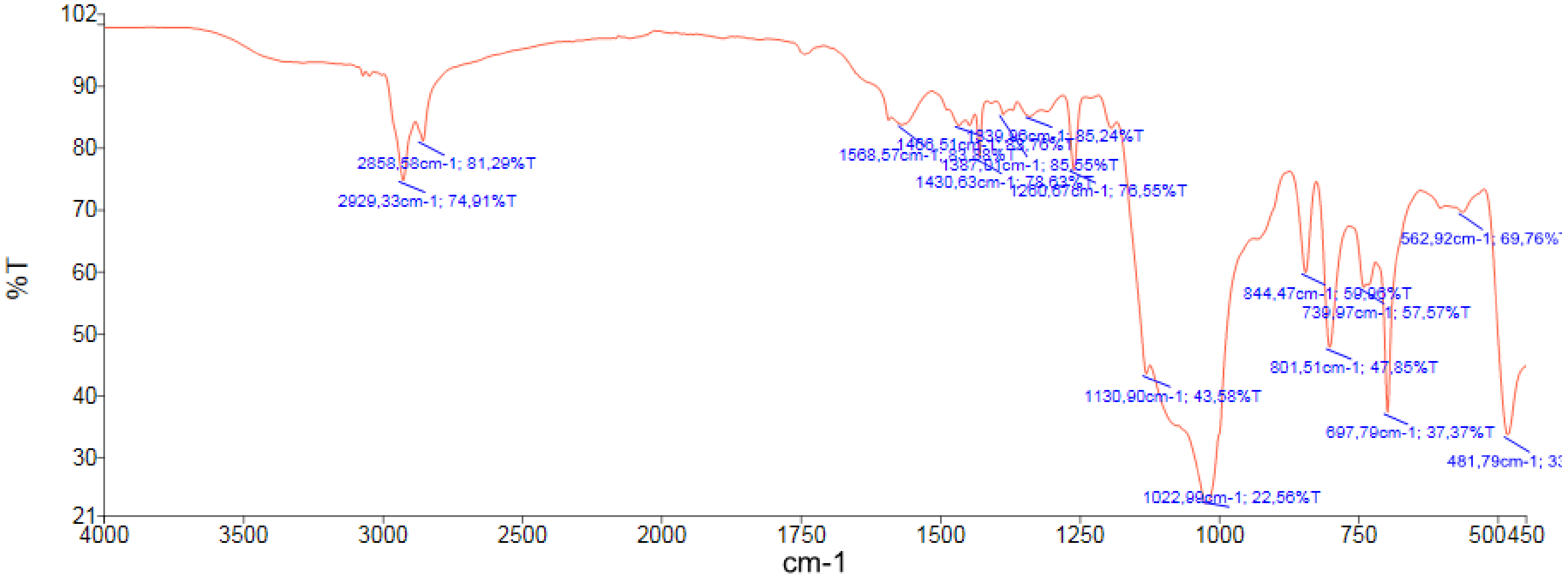
Anwender Administrator
DatumUhrzeit Montag, 25. August 2014 13:40



| Probenname | Beschreibung |
|---|---|
| Koe EF17 (top) | Sample 050 By Administrator date Freitag, August 22 2014 |

PerkinElmer Spectrum Version 10.4.2
Montag, 25. August 2014 13:41

Anwender Administrator
DatumUhrzeit Montag, 25. August 2014 13:41



| Probenname | Beschreibung |
|---|---|
| Koe EF18 (top) | Sample 052 By Administrator date Montag, August 25 2014 |