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Biosynthesis, Characterization and Determination of Sun Protection Factor (SPF) of Iron Nanoparticles With Bee Bread

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Abstract: Bee bread is a food product obtained by fermenting bee pollen with honey and storing it in honeycomb cells. In this fermentation, phenolic compounds remain unaffected and unchanged. Bee bread contains approximately; 35% sugar, 24-35% carbohydrate, 20-22% protein, 3.5% lactic acid, 2.43% mineral, 1.6% lipid and 1.6% fat. Within the scope of the study, biocompatible iron nanoparticles were synthesized (BB@FeNPs) by utilizing the potential reducing powers of these components contained in bee bread. The characterization of obtained bee bread-based nanoparticles; was performed using spectroscopic techniques such as ultraviolet-visible light spectrophotometer, fourier transform infrared spectrophotometer, and x-ray diffraction spectrometry. Scanning electron microscopy was used as a microscopic method in the characterization of nanoparticles. In addition, the sun protection factor (SPF) of the synthesized nanoparticles was determined by ultraviolet spectrophotometry. Although the studies in recent years tend to search for bioactive molecules of natural origin, no nanoparticle synthesis with bee bread has been encountered in the literature. This study is important as it is a first in the synthesis of metal nanoparticles with bee bread.

Arı Ekmeği ile Demir Nanopartiküllerinin Biyosentezi, Karakterizasyonu ve Güneş Koruma Faktörünün (SPF) Belirlenmesi

Anahtar Kelimeler
Yeşil sentez,
Metal nanopartiküller,
Arı ekmeği,
Güneş koruma faktörü (SPF)

Öz: Arı ekmeği, arı poleninin bal ile fermente edilmesi ve petek gözlerine depolanmasıyla elde edilen bir gıda maddesidir. Bu fermantasyonda fenolik bileşikler etkilenmeden ve değişmeden kalmaktadır. Arı ekmeği içeriğinde yaklaşık olarak; %35 şeker, %24-35 karbonhidrat, %20-22 protein, %3,5 laktik asit, %2,43 mineral, %1,6 lipid ve %1,6 yağ bulunmaktadır. Çalışma kapsamında, arı ekmeğinin içermiş olduğu bu bileşenlerin potansiyel indirgeme güçlerinden yararlanılarak biyouyumlu demir nanopartiküller sentezlenmiştir (BB@FeNPs). Elde edilen arı ekmeği temelli nanopartiküllerin karakterizasyonu; ultraviyole-görünür ışık spektrofotometresi, fourier dönüşümlü kızılötesi spektrofotometresi ve x-ışını kırınım spektrometresi gibi spektroskopik teknikler kullanılarak gerçekleştirilmiştir. Nanopartiküllerin karakterizasyonunda mikroskobik yöntem olarak ise taramalı elektron mikroskobu kullanılmıştır. Ayrıca sentezlenen nanopartiküllerin güneş koruma faktörü (SPF) ultraviyole spektrofotometri ile belirlenmiştir. Son yıllardaki çalışmaların doğal kaynaklı biyoaktif molekülleri araştırma eğiliminde olmasıyla birlikte, literatürde arı ekmeği ile nanopartikül sentezine rastlanılmamıştır. Bu çalışma arı ekmeği ile metal nanopartikül sentezinde bir ilk olması açısından önemlidir.

1. INTRODUCTION

It is known that the term nanotechnology was first mentioned by Richard Feynman at the meeting of the American Physical Society (APS) in 1959 [1]. Nanotechnology on the other hand is the science that allows studies such as measurement, modeling, design, processing and arrangement that can be carried out on materials at 1-100 nm dimensions [2]. Although the word nano basically means one billionth of any unit, it is used as a technical unit of measurement [3]. In this respect, nanoparticles constitute the basic building blocks of nanotechnology [4]. Although the usage area of nanoparticles is quite wide, a few of these areas are as follows; the food, health, aerospace and pharmaceutical and cosmetic industries [5].

There are 3 different synthesis methods for the synthesis of nanoparticles; physical, chemical and biological. The negative effects of physical and chemical synthesis methods are replaced left to the biological synthesis method, which is a less costly and environmentally friendly method [5]. With biological green synthesis, it is possible to synthesize nanoparticles in an environmentally friendly and easy way without the need for toxic chemicals, high temperature, high pressure and high energy [6]. In the green synthesis method, nanoparticles with different content, shape, size and physicochemical properties are synthesized. In this method, nanoparticle synthesis is carried out by using phenolic compounds, amines, proteins, enzymes, pigments, alkaloids and microorganisms in plants as reducing agents [7]. Biological (fungi, plants, algae, bacteria, etc.) natural resources are used for the green synthesis of nanoparticles [5]. Nanoparticles prepared with natural product extracts generally show promising bioactivity as they contain phytocomponents as stabilizing ligands on their surface. In the synthesis of biocompatible nanomaterials, bee products such as honey, pollen, royal jelly, bee venom and beeswax are thought to be a potential product source to prevent nanoparticle aggregation [8].

With the increase in health awareness and interest in functional foods in today's world, bee products bring new perspectives to future productions. In this context, bee bread, which is a bee product, contributes to human health and nutritional values due to its unique chemical content and also having microbial fermentation effect. The abundant presence of compounds such as polyphenols and flavonoids, which are important for the human body, reduces the formation of reactive oxygen species (ROS). All bee products, including bee bread; it has many biological properties such as biodegradation, non-toxic structure and biocompatibility. All these properties pave the way for the use of bee bread as a complementary ingredient in traditional medicines or nanoparticle production. In addition to the prediction that bee bread can be used in the production of nanoparticles, from bee products nanoparticles; it has been stated that it can be used in advanced imaging, probing and cancer treatment [9]. Figure 1 shows a section of the bee bread sample used in the study.

Figure 1. Bee bread samples

Metal oxide nanoparticles are used in many different areas from food packaging to drug delivery systems, from solar cells to cosmetics [10]. The most preferred basic metal oxide nanoparticles are iron oxides (FeO, Fe_2O_3, Fe_3O_4 etc.), zinc oxide (ZnO), titanium dioxide (TiO_2), aluminum oxide (AlO), and cerium oxide (CeO_2) nanoparticles [10, 11]. Thanks to the physicochemical properties of iron oxide nanoparticles, which are among metal oxide nanoparticles, they are frequently used in in vitro and in vivo research [12, 13]. Iron oxides are either naturally found or synthesized under laboratory conditions [14].

Based on all this information, within the scope of the study, green synthesized iron nanoparticles were produced with bee bread. The sun protection factor (SPF) of the synthesized nanoparticles was determined by in vitro method, providing an idea for future studies. Although green synthesis through bee products such as honey, pollen, and propolis has been performed before, no studies using bee bread have been conducted to date. For this reason, the study reveals a first in the literature with metal nanoparticle synthesis using bee bread.

2. EXPERIMENTAL METHODS

2.1. Materials

Bee bread samples were obtained from local beekeepers at Bingöl, Turkey, in 2021. Iron (II) chloride ($FeCl_2$), iron (III) chloride ($FeCl_3$), sodium hydroxide (NaOH), nitric acid (HNO_3) and sodium nitrate ($NaNO_3$) reagents used in nanoparticle synthesis and characterization were of analytical purity.

2.2. Methods

2.2.1. Preparation of bee bread extract

The bee bread obtained from the Bingöl (Turkey) region was weighed approximately 10 g and ground into powder with the help of a grinder. Powdered bee bread samples were added into 100 mL of distilled water brought to 100 ˚C. The resulting mixture was homogenized at 100 ˚C in a heated magnetic stirrer for 30 minutes. The homogeneous mixture was filtered through filter paper and purified water was added on it so that the final volume was 100 mL. The pH value of bee bread extract was measured as 1.5 and stored in a glass bottle at -18 ˚C to be used in the studies.

2.2.2. Synthesis of BB@Fe nanoparticles

0.01 M $FeCl_2$ solution and 0.02 M $FeCl_3$ solution were prepared in 50 mL distilled water separately and on a magnetic stirrer. Then, the two solutions were combined and mixed in a heated magnetic stirrer until the temperature reached 60˚C. On the other hand, the prepared bee bread extract was diluted with distilled water at a ratio of 1:10. While the pH value of the diluted bee bread extract was 7 at the beginning, 1 M NaOH was added to ensure the final pH value was 10. When the temperature of the mixture prepared with $FeCl_2$ and $FeCl_3$ solutions reached 60˚C, 30 mL of diluted bee bread extract was added. Until the pH value of the whole mixture reached 12, 2 M NaOH was added dropwise, and it was mixed in a heated magnetic stirrer until the temperature reached 60˚C. As a result of the precipitation of magnetic nanoparticles, the separation of the supernatant was achieved. Nanoparticles were taken into a petri dish and left to dry in an oven at 40˚C.

2.2.3. Determination of isoelectric point of BB@Fe nanoparticles

It was prepared with 100 mL of 0.1 M $NaNO_3$ distilled water on a magnetic stirrer. 100 mL of $NaNO_3$ solution was divided into 10 beakers in equal amounts. The pH values of the solutions in the beakers were adjusted between 3-12 ($pH_{initial}$). 0.1 M HNO_3 and 0.1 M NaOH solutions were used to adjust the pH values. 10 mg of BB@Fe nanoparticles were added to each of the pH-adjusted solutions. The nanoparticle added solutions were allowed to mix at room temperature for 1 day. At the end of the waiting period, the pH value (pH_{end}) of each solution was measured again and the isoelectric point of the nanoparticles was determined.

2.2.4. Characterization of BB@Fe nanoparticles

Biosynthesis of BB@Fe nanoparticles was observed using Ultraviolet-Visible Light Spectrophotometer, UV-VIS-NIR (SHMADZU UV-3600). Related functional groups in biosynthesis and stabilization of bee bread extract, $FeCl_2$, $FeCl_3$ and BB@FE nanoparticles used in the study were screened using Fourier Transform Infrared Spectrophotometer, FT-IR (Perkin Elmer Spectrum 100). The size and shape of the BB@Fe nanoparticles were determined using X-Ray Diffraction Spectrometer, XRD (RIGAKU ULTIMA IV), and the morphology was determined using Scanning Electron Microscopy, SEM (JEOL JSM 6510).

2.2.5. Determination of sun protection factor (SPF) of BB@Fe nanoparticles

The term sun protection factor (SPF), which is used to evaluate the effectiveness of sunscreens against the UVB effect, is defined as the ratio of the UV dose required to create a minimal erythema reaction after the sunscreen is applied to the skin, to the UV dose required to produce the same erythema in unprotected skin. In short, the SPF value expresses how many times the sunscreen prolongs the time to reach the minimal erythema dose [15]. The equation used in this study to determine the SPF value of nanoparticles biosynthesized with bee bread is given below (1).

$$\text{SPF spectrophotometric} = CF \times \Sigma EE(\lambda) \times I(\lambda) \times Abs(\lambda) \quad (1)$$

EE= erythemal effect spectrum
I= sun intensity spectrum
CF= confirmation factor
Abs= absorbance

To determine the SPF value of BB@FeNPs; The nanoparticles were weighed 10 mg and dissolved in 10 mL DMSO. Absorption spectra of the samples prepared at 100-1000 ppm concentrations were measured in the range of 290-320 nm against DMSO. The results were calculated according to the Mansur equation and the SPF values of the nanoparticles were determined [16, 17]. The EE x I values determined by Sayre et al. [18], are constant and are given in Table 1.

3. RESULTS AND DISCUSSION

3.1. Isoelectric Point of BB@FeNPs

Similar charged particles in the same liquid repel each other, while differently charged particles attract each other. These push-pull forces of the particle are defined as the zeta potential [19]. The zeta potential value takes different values according to the pH value of the solution in which the particle is located. The pH value, where these values intersect with the zero axis, is defined as the "isoelectric point". Amino acids and proteins are cationic at low pH values, anionic at high pH values, and neutral at isoelectric points [20]. At the isoelectric point, the positive (+) and negative (–) charges being equal to each other result in the formation of attraction instead of electrostatic repulsion between the same molecules and the collapse of proteins [21]. Measurements of the pH value to detect the surface charge of BB@FeNPs are given in Figure 2. According to this figure, the isoelectric point of BB@Fe nanoparticles was found to be 7.8.

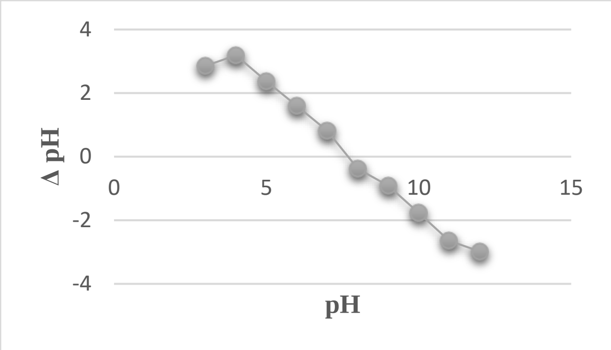

Figure 2. Graph of BB@FeNPs isoelectric point

Considering the acidic nature of bee bread samples, it is expected that the isoelectric point of BB@FeNPs is close to neutral compared to iron nanoparticles in the literature [22, 23].

3.2. UV-VIS-NIR Spectrophotometer

UV-VIS-NIR absorption spectrum of iron nanoparticles synthesized with bee bread showed a peak around 242 and 273 nm (Figure 3). According to Mirza et al. [24], reported that iron oxide nanoparticles peaked at 248 and 278 nm through extracts of *Agrewia optiva* and *Prunus persica*, similar to our study.

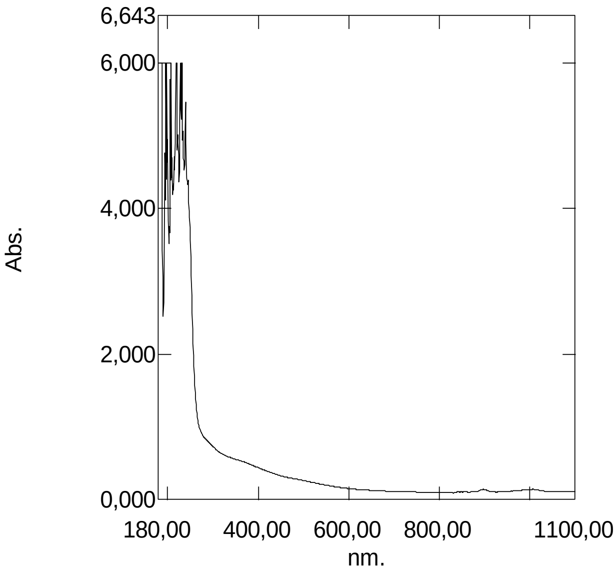

Figure 3. UV-VIS-NIR spectra of BB@FeNPs

3.3. FT-IR Spectrophotometer

FT-IR analysis was performed to determine the bond relationship and functional groups in BB@FeNPs with bee bread sample. FT-IR spectra of bee bread, BB@FeNP, $FeCl_3$ and $FeCl_2$ samples are given in Figure 4.

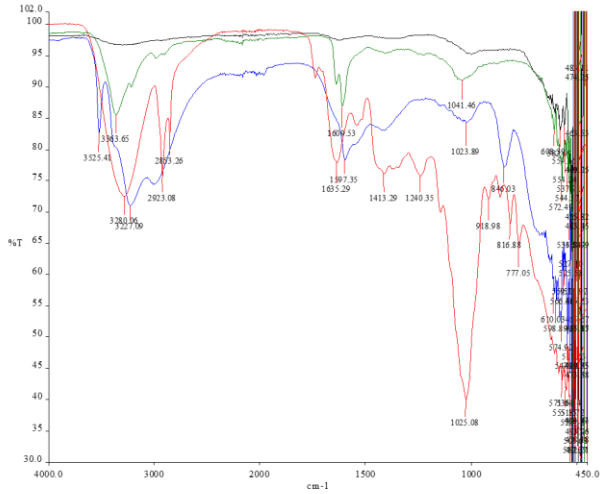
Figure 4. FT-IR spectra of bee bread (red), BB@FeNP (black), $FeCl_3$ (blue) and $FeCl_2$ (green)

Spectra of bee bread sample showed strong bands at 3655.17, 3280.06, 3000.00, 2923.08, 2853.26, 1733.42, 1635.29, 1488.34, 1413.29, 1297.01, 1240.35, 1127.18, 1025.08, 918.98, 816.88, 777.05 cm^{-1}; BB@FeNPs showed strong bands at 3659.48, 3340.51, 2969.82, 2159.48, 1926.90, 1737.72, 1634.53, 1402.35, 1174.47, 1004.64, 815.46, 660.67 cm^{-1}. The peak at about 3300 cm^{-1} is due to the O\H stretching vibrations of phenolic groups, while the peak at 1600 cm^{-1} is thought to be due to the C=O stretching vibrations of carboxylic acids. This situation is also observed in similar studies [24, 25]. In addition, C\H stretching vibrations of the aromatic compound of the samples were observed at around 2900 cm^{-1}, C\O stretching vibrations were observed at 1000-1100 cm^{-1} and C\O\C stretching vibrations at 1400 cm^{-1} peaks [26]. Apart from the defined bands, there are a few more bands in both bee bread and iron nanoparticles synthesized with bee bread. Finding these specific peaks may vary depending on the type of bee bread and the extraction method. Multiple peaks appearing in BB@Fe nanoparticles indicate the presence of Fe in accordance with the literature [24, 25]. According to the FT-IR analysis results, it can be assumed that the phenolic compounds in bee bread can provide closure and stabilization of BB@FeNPs.

3.4. XRD Spectrophotometer

The estimation of the crystal sizes of iron nanoparticles synthesized using bee bread characterized by XRD is shown in Figure 5. The main diffraction peaks of BB@FeNPs are 32°(220), 36°(311), 45°(422), 57°(511) and 63°(440). These peaks are standard JCPDS NO. The 85-1436 data can be compared with the standard XRD model of Fe_3O_4 NPs in the database.

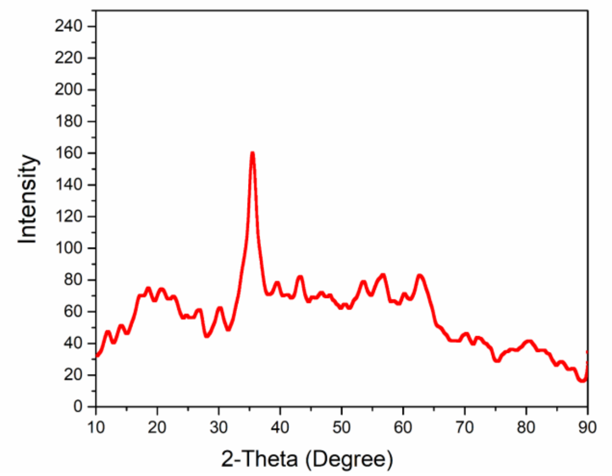

Figure 5. XRD spectra of BB@FeNPs

In the literature, Fe_3O_4 nanoparticles used for magnetic resonance imaging and hyperthermia [27], Fe_3O_4 nanoparticles coated with fucan polysaccharides [28], and aqueous extracts of food processing wastes Fe_3O_4 nanoparticles [29] XRD spectra are similar to our study.

3.5. SEM and EDX Analysis

In the characterization of BB@FeNPs, nanoparticles were observed under scanning electron microscopy (SEM) and the morphological analysis results are shown in Figure 6. In addition, energy dispersive X-ray (EDX) spectroscopy, shown in Figure 6, confirmed that the synthesized nanoparticles contained Fe [29].

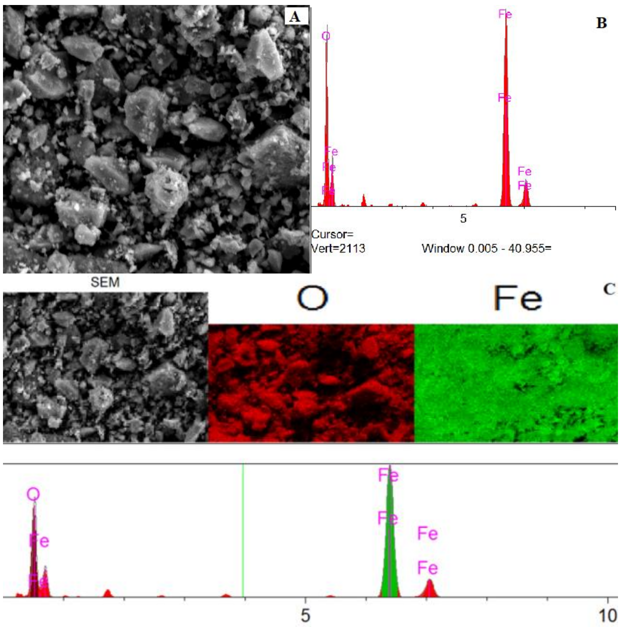

Figure 6. SEM image of BB@FeNPs (A), EDX spectra of BB@FeNPs (B), elemental mapping of BB@FeNPs (C)

3.6. Sun Protection Factor (SPF) of BB@Fe Nanoparticles

UV radiation from the sun can cause skin burning, inflammation, and other serious side effects such as skin cancer [30]. For this reason, various sunscreen formulations have been developed to protect the skin from harmful UV rays from the sun. The effectiveness of sunscreen formulations is universally evaluated for sun protection factor (SPF) [31]. Nanoparticles are known to be carriers that enhance the protective effects of various natural sunscreen agents [32]. Permission for the use of nanoparticles in sunscreens has been granted by the Food and Drug Administration (FDA) [33]. Therefore, nanoparticles based on titanium dioxide (TiO_2) and zinc oxide (ZnO) are widely used as SPF enhancers in sunscreen formulation [34]. However, studies have shown that ZnO nanoparticles form free radicals and cause oxidative stress and cytotoxicity [35-37]. In addition, the Scientific Committee for Consumer Safety (SCCS) recommended avoiding the use of photocatalytically active TiO_2 in sunscreen and cosmetic products [38]. Among the materials examined as an alternative; there are metal oxide nanoparticles containing ceria (CeO_2) [39-45], tin oxide (SnO_2) [46], iron oxide (Fe_2O_3) [47-48]. Iron oxides are used in cosmetic products, especially foundations and eye shadows. It has even been known to be added to sunscreens to give them a brown tint [49]. Iron oxide nanoparticles have more commercialization potential in this field due to their low cost and high volume. In this study, the SPF value of metal nanoparticles biosynthesized with bee bread for sunscreen formulations was determined in vitro (Table 1). Determination of the SPF value by the in vitro method is now universally accepted due to the simplicity of the analysis and the reproducibility of the results [16].

According to the findings given in Table 1, SPF values of BB@FeNPs were evaluated between 100-1000 ppm. It is observed that the SPF value of BB@FeNPs increases with increasing concentrations. The highest SPF value was found at the highest concentration with 18.82. This value encourages the use of safer and environmentally friendly materials to be used in commercial sunscreen formulations on the market.

4. CONCLUSIONS

Bee bread is a bee product obtained by an anaerobic fermentation process by storing bee pollen in honeycombs with the help of honey and digestive enzymes. The high nutritional value of bee bread and its richness in bioactive substances enabled the production of nanoparticles by the green synthesis method. The characterization of the synthesized nanoparticles was carried out and the sun protection factor was determined.

Sun rays have negative effects on skin aging. Sunscreens positively affect the formation of photo-aging and sunburn, especially in the melanoma layer. The reason for the increase in skin cancer cases in recent years is seen as unprotected sun exposure. People with light skin color and people who blush quickly in the sun are at a higher risk of developing skin cancer. With this study, it has been demonstrated that iron nanoparticles are an alternative to sunscreen instead of dangerous titanium dioxide and zinc oxide nanoparticles.

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Appendices

Table 1. SPF values of BB@FeNPs at different concentrations

Compound	Concentration	Wavelength	CF	EE*I	Abs	SPF
BB@FeNP	1000 ppm	290	10	0,0015	1,955	18,81973
		295	10	0,0817	1,906	
		300	10	0,2874	1,888	
		305	10	0,3278	1,878	
		310	10	0,1864	1,872	
		315	10	0,0839	1,863	
		320	10	0,0180	1,859	
	500 ppm	290	10	0,0015	0.981	9,732117
		295	10	0,0817	0.974	
		300	10	0,2874	0.971	
		305	10	0,3278	0.973	
		310	10	0,1864	0.974	
		315	10	0,0839	0.975	
		320	10	0,0180	0.975	
	200 ppm	290	10	0,0015	0.654	6,516159
		295	10	0,0817	0.650	
		300	10	0,2874	0.648	
		305	10	0,3278	0.652	
		310	10	0,1864	0.654	
		315	10	0,0839	0.655	
		320	10	0,0180	0.660	
	100 ppm	290	10	0,0015	0.490	4,920233
		295	10	0,0817	0.486	
		300	10	0,2874	0.491	
		305	10	0,3278	0.492	
		310	10	0,1864	0.494	
		315	10	0,0839	0.495	
		320	10	0,0180	0.498	