

Literature Review: Measuring Titanium Dioxide Particles Size in Sunscreen and Its Effectiveness as UV Radiation Absorber

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ABSTRACT

The purpose of this study was to use the ICP-MS method to examine the particle size of TiO₂ in various forms of sunscreen, with a focus on the effectiveness of UV radiation absorption. Research methods are employed to support this research by reviewing many sources as references. ICP-MS was used to measure the size of TiO₂ nanoparticles in sunscreens in various forms such as powder, cream, and spray. The particle size of TiO₂ in powder form is 41.17nm, in cream form is 42nm, and in spray form is 94.5nm, according to the studies. Sunscreen in the form of a spray has the biggest particle size in terms of particle size. Absorption and scattering can be increased by using larger particles.

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Introduction

Sunscreen is a product containing chemical compounds that has the ability to absorb, scatter, or reflect UV rays that hits our skin. Sunscreen is used to protect the function and structure of the human's skin. It is also used to protect the skin from UV damage [1] Sunscreen can be made from natural compounds and synthetic compounds, such as titanium dioxide (TiO₂) and zinc oxide (ZnO). The safety and effectiveness of the use of sunscreen is guaranteed, but it needs to be known that the use of sunscreen in several countries are being limited by the rules now. This is because products containing SPF or sunscreen are now regulated as medicine, so that makes sunscreen a high priority product. Sunscreen is a protective cosmetic that can filter and protect the skin from the sun. There are various forms of cosmetics sunscreen that can be adapted to skin type and activity. The cosmetics sunscreen form are lotion, cream, gel, spray, stick.

UV rays is one of the lights that is emitted by the sun in the wavelength range of 200-400 nm. UV rays consist of UV A (320-400 nm), UV B (290-320 nm), and UV C (200-290 nm) The most UV rays that hit the earth surface are

UV A for about 90-99% and UV B for about 1-10%. Meanwhile, UV C has the biggest energy therefore couldn't hit the earth surface because it was absorbed by the ozone layer

Titanium dioxide (TiO₂) has three crystal forms in nature, which is rutile, anatase, and brookite. TiO₂ is an inorganic solid compound that is unstable, insoluble in water, non-volatile chemically, and is passive biologically. TiO₂ has a strong ability to absorb the UV light and a high refractive index. [2]. With the ability to reflect the UVA and UVB light at the same time, TiO₂ can be used as a UV protection. With said functions, TiO₂ is used as a sunscreen and also used as cosmetic material [3]. TiO₂ is usually found as a powder and is used as products such as paint, coating, paper, ink, food, medicine (pill and tablet), and toothpaste; as a whitening pigment for skimmed milk [3].

ICP-MS can also be used to analyze a solid sample if it uses an electrothermal vaporization (ETV) or laser ablation (LA) as an ion-forming medium that enter the mass spectrometer to be sorted and chopped. A solid sample that analyzed with ICP-MS, whether using ETV or LA has to be standardized. Precise and thorough analysis result only possible after

optimization for each type of solid sample. Generally, the ICP-MS method is used for element determination in solution .

Previous research has investigated the size of TiO₂ in powder [4], liquid [5] , and spray sunscreens [6]. The researchers analyzed the size of TiO₂ nanoparticles found in various sunscreens. However, no study has investigated which TiO₂ nanoparticles are more effective for use on the skin to block UV rays based on the size of various types of sunscreen. Therefore, the aim this study was to compare the size of TiO₂ nanoparticles in various types of sunscreens to see how effective they are at absorbing UV rays. Previous research about sunscreen were listed in the following Table 1. At this time a lot of research on the role and importance of sunscreen in everyday life. The many forms of sunscreen on the market raise the question of which form of sunscreen is the most effective in scattering UV rays. Therefore, this article review aims to determine the most effective form of sunscreen in preventing UV rays by comparing the size of TiO₂ nanoparticles. The method used in this study uses the ICP-MS method. In this study, the results of the comparison of TiO₂ particle size in various forms of sunscreen (powder, spray, and cream) on the effectiveness of UV radiation absorption using the ICP-MS method was obtained.

Method

The literature review study approach was used to help the development of this article. The literature used is from a peer-reviewed international publication published within the last five years and indexed by Scopus. The terms TiO₂ nanoparticles, nanoparticle measurement, ICP-MS, and UV absorption were used in the literature search. Science Direct, Google Scholar, and ACS Publications are all used in the literature search.

Result and Discussion

In general, there are several forms of sunscreen such as cream, powder and spray. These three forms of sunscreen were measured for TiO₂ nanoparticles using SP ICP-MS. Where the principle of SP-ICP-MS is atomizing elements so that they can emit light of a certain

wavelength which can then be measured. Table 1 show the size of several TiO₂ nanoparticle in different form.

Table 1. The size of several TiO₂ nanoparticles

No	Type Sunscreen	Method	Particle	
			Size (nm)	Reference
1	Powder	Determined by SP ICP-MS	41,14	[12]
2	Spray	Determined by ICP-MS	89-100	[14]
3	Cream	Determined by SP ICP-MS	42-49	[13]
4	Cream	Determined ICP-MS	45	[15]
5	Powder	Determined by XRPD (rutile size)	58,8	[16]
6	Spray	Determined by TEM	27,9	[17]
7	Cream	Determined by TEM	45	[18]

1. Measurement of TiO₂ nanoparticles on sunscreen in the form of spray

1.1 Sunscreen spray sample

Two samples of commercial sunscreen spray were selected based on a label claiming that the sunscreen contained metal oxides nano-forms in its formulation. The selected sunscreen has a different sun protection factor (SPF), namely 30 and 50+. The standard solution TiO₂ was used NM-100, where a nominal size of 228.6 nm and a particle size of 27.1% less than 100nm was used as the reference material as obtained by DLS [7]

Type of sunscreen, SPF claimed on the label, ingredients claimed by the label. Sunscreen characteristics by their claim at the labels are listed in the Table 2.

Table 2. Sunscreen characteristics by their claim at the labels

Sunscreen	Application	Sun	Claimed
		Protection Factor (SPF)	Ingredients
A	Spray	50+	TiO ₂ (nano)
B	Spray	30	TiO ₂

1.2 SP ICP-MS Analysis

The standard used for TiO₂ nanoparticles was dissolved in 1% Triton X-100 (Alfa Aesar, Ward Hill, MA, USA). The sunscreen of each sample was weighed (ca. 0.1g) and diluted with 1% Triton X-100 (aq) 1:25,000 v/v solution for TiO₂ detection [7]. Standard suspensions and samples were extracted using the sonication method in an ultrasonic bath for 20 minutes. This is useful to prevent particle build-up or continuous agglomeration.

Before starting, the ICP-MS must be tested for sensitivity by calibration testing using a calibration stock solution of Ti dissolved in the ionic form. (CPAChem, C.P.A. Ltd., Stara Zagora, Bulgaria). Sensitivity testing is useful for the transport efficiency of the ICP-MS sample recognition system, it can be measured from a nominal size Au NP standard solution of 60nm [7]. ICP-MS based sensitivity test can be seen in Table 2 [6]. In SP ICP-MS, the mass of Ti is measured first, then 60% mass fraction is used to convert the mass of Ti into mass of TiO₂, this happens because the ratio of Ti/TiO₂ is 60% of the actual weight. The mass of TiO₂ (m) converted into the diameter of the TiO₂ particle size (D). According to the SP ICP-MS theory, the known particle size density of TiO₂ is 4.23 g/cm³ and assuming the TiO₂ particles are spherical. [7]. SP-ICP-MS sensitivity testing are showed in the following Table 3.

Table 3. SP-ICP-MS sensitivity testing

Instrument	iCAP-Q (Thermo Fisher)
Nebulizer; flow	PFA-ST; 0.33 mL/min
Masses (m/z)	⁴⁸ Ti
Acquisition mode and time	Q-Cell in KED (4.8 mL/min He), 60 s
Nebulization efficiency	4%
Dwell time	5 msec
Density	TiO ₂ 4,23 g/cm ³

1.3 Result

1.3.1 SP ICP-MS Performances

The NM-100 TiO₂ nano dispersion served as a reference for the SP ICP-MS study, the average size measured was 232 ± 25nm, this size corresponds to the size stated by the manufacturers. The particle size measured from the small size is ca 60nm and represents 27.5% of the total number of TiO₂ particles in the material, this corresponds to the percentage of TiO₂ particles <100nm claimed by the manufacturer.

To calculate recovery, a spike of NM-100 TiO₂ at 128g/L was added to the sunscreen blank, with a recovery of 98%. Calculations were carried out with three repetitions and measured by the relative standard deviation (RSD) at a mean value of 1.6% for TiO₂ which resulted in a TiO₂ size of ca 25nm [6].

1.3.2 TiO₂ Shape in Sunscreen

The concentration of the number of particles in the two sunscreens from the SP ICP-MS analysis is shown in Table 3. The mean D value is from 89nm ~ 100nm. To support measurement, there is an increase in reliable methodologies, namely by particle measurement. Particle measurement based on ICP-MS detection is not only based on particle size, but also can provide metal concentrations that depend on the size of the species. The high detection capability of the SP ICP-MS provides specific results that make it possible to read the average diameter of the particles [8], [9], [10], [11].

This method shows good results, especially with the addition of the standard SP ICP-MS method, which makes it easy to approach the

concentration of TiO₂ NPs and the range of nanoparticle sizes in sunscreens.

The results show that the two sunscreens analyzed with an average D value of 89nm ~ 100nm, the higher the concentration of TiO₂ particle count obtained When the SPF is increased, this result is consistent with the higher weight concentration of TiO₂ observed in the SPF 50% sunscreen [6]. Size, number and weight concentration of TiO₂ in sunscreen by SP-ICP-MS are shown in the following Table 4.

Table 4. Size, number and weight concentration of TiO₂ in sunscreen by SP-ICP-MS

Sunscreen	TiO ₂		
	Mean	Particle/mL	%Weight
	Diameter (nm)		
A	89±18	156,151	6.00
B	100±15	86.086	3.30

2. Measurement of TiO₂ nanoparticles in powdered sunscreen

To detect TiO₂ nanoparticles in sunscreen powder, 0.04 g or more of the sunscreen powder sample is dispersed in a 1 percent Triton X-100 aqueous solution to homogenize the nanoparticle suspension. The suspension sample was then sonicated for 30 minutes to homogenize the mixed solution. Finally, prior to SP-ICPMS analysis, the combined solution was properly diluted with DI-water. This procedure was used to examine eight samples of powder sunscreens from diverse brands [12] . Table 5 shows the results of the SP-ICP MS analytical measurements on numerous sunscreen powder samples.

Tabel 5. SP-ICP MS analytical measurements on numerous sunscreen powder samples.

Sample	Mean Size(nm)
Com 1	53.29
Com 2	38.17
Com 3	46.57
Com 4	39.48
Com 5	45.68
Com 6	38.71

Com 7	31.04
Com 8	40.00
Com 9	37.67
Average	41.17

*Com : commercial sunscreen powder

The average size of TiO₂ nanoparticles in sunscreens from the eight samples evaluated is 41.17 nm, as shown in Table 5.

3. Measurement of TiO₂ nanoparticles in cream-form sunscreen

The SP ICP-MS measures diameter (d) on a mass basis. In SP ICP-MS it cannot be used to distinguish between constituent particles and agglomerated particles. The following in figure 1 and figure 2, assumptions regarding the NP shape, composition, and density have been taken into account with respect to the experimental parameters applied.

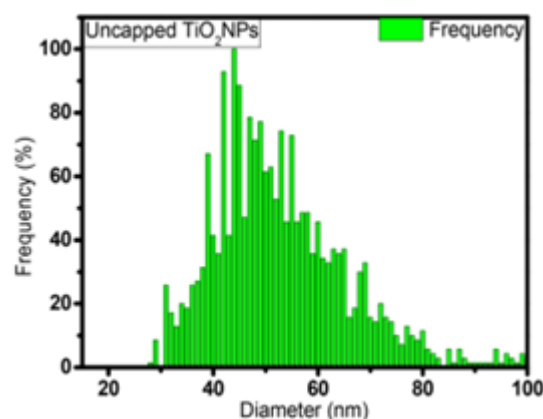


Figure 1. SP ICP-MS PSD for uncapped TiO₂NPs.

Thus, it can be observed that after coating the uncovered TiO₂NPs with PEG, SP ICP-MS revealed a reduced size in the PEGylated particles indicating increased separation and highlighting the polymer stabilizing properties of the TiO₂NPs. The following is an image that shows the measurement data for nano-TiO₂ particles using SP ICP-MS.

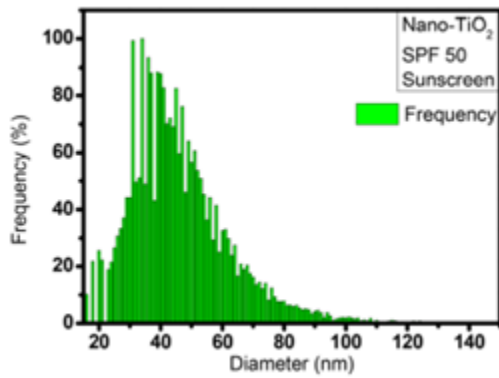


Figure 2. SP ICP-MS PSD for nano-TiO₂ SPF 50 sunscreen.

The following in table 6 is the result of the measurement of nano-TiO₂ particle size data using SP ICP-MS.

Table 6. Results of TiO₂ nanoparticle size data using SP ICP-MS.

Sample	SP ICP-MS mass-based mean diameter (nm)
Nano-TiO ₂ SPF sunscreen, tR 17-20 min	42
Unspecified SPF 50 sunscreen (population 2), tR 16-24 min	49

SP ICP-MS analysis Figure. 2 revealed diameter-based measures ($d = 42$ nm, Table. 6) Sample recovery was evaluated to be $94 \pm 4\%$.

4. The correlation between particle size and UV absorption

The relationship between Particle size and UV absorption is shown in Figure 3.

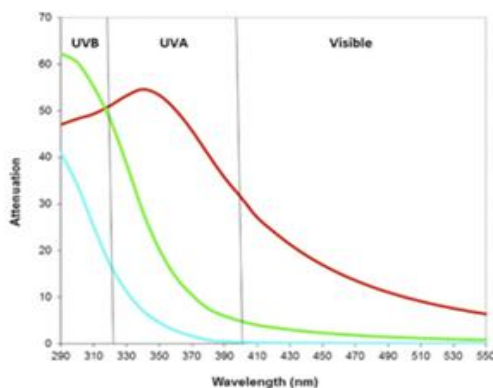


Figure 3. Graph of UVB, UVA and Visible vs. UVB wavelengths. Attenuation, for each TiO₂ nanoparticle size, a. red : 100 nm, b. Green: 50 nm, and c. blue: 20 nm. Based on the graph

Figure 3, it is known that TiO₂ nanoparticles measuring about 100 nm (red line) show their effectiveness in good UVA and UVB protection, but are less effective in protecting from visible light. Unlike the 50 nm TiO₂ nanoparticles which show their effectiveness in UVA protection and do not show their effectiveness in UVA and Visible light protection, so that the use of these nanoparticles needs to be combined with a composition that can help protect from UVA rays. Different from the two previous nanoparticles, the 20 nm nanoparticles are very different, this size is effective against UVB light protection but not as effective as 50 nm and 100 nm particle sizes, and also less effective against UVA and Visible light protection. It is concluded that the effective nanoparticle size to protect from UVA and UVB rays is the TiO₂ nanoparticle size of 100 nm.

Based on previous research on the measurement of TiO₂ nanoparticles on sunscreen in the form of powder, cream and spray. The results obtained are the size of TiO₂ nanoparticles in 41.17nm powder form, 42nm in cream form, and 94.5nm in spray form. Based on Figure 3. Among the three forms, the closest size to the effective size of protecting UVA and UVB rays is in the form of a spray.

Nanoparticles of TiO₂ have three types of shapes, namely the form of primary particles (5-20 nm), aggregates (30-150 nm), and agglomerates (1-100 microns). The absorption of TiO₂ to UV light itself is influenced by the particle size. Primary particles have strong attractive forces between crystals within them. Aggregate is a collection of primary particles that form clumps that are tightly bound together. Agglomerate is a collection of aggregates that form lumps that are larger than aggregates.

TiO₂ particles in powder sunscreen are 41.17 nm, so they can be classified as aggregates based on their size. TiO₂ particles in cream sunscreens are 42 nm, so they are classified as aggregates, and TiO₂ particles in spray sunscreens are 94.5 nm, so they are also classified as aggregates. Based on these results, it is known that the TiO₂ particles of 94.5 nm in the spray form of sunscreen are the particles with the most effective size as an antidote to UV rays, both UV A and UV B. This is because the

particle size greatly affects the level of absorption and scattering of TiO₂ in the UV region, i.e. the larger the particle size, the better the scattering of UV rays it can do. However, if the TiO₂ particle size in the sunscreen exceeds 100 nm or around 220-250 nm, it can leave a white cast on the skin. One way to overcome white cast is to reduce the particle size to about 20 nm, but this has its own drawbacks, namely causing sunscreen to be radical and harmful to the skin because it is unstable. Another way to get a sunscreen that is safe for the skin and effective at scattering UV rays is to make it in the form of a transparent gel.

Conclusion

From a study that aims to review the particle size of TiO₂ in various forms of sunscreen, focusing on the effectiveness of UV radiation absorption, using the ICP-MS method. The results show that the particle size of TiO₂ in powder form is 41.17 nm, in cream form is 42nm and in spray form is 94.5nm. Based on particle size, spray sunscreen has the largest particle size. The larger the particles, the higher the absorption and scattering of UV rays. So that the sunscreen in the form of a spray is a sunscreen that is more effective in scattering / blocking UV rays.

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