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# 용량분석법을 이용한 화장품 중 티타늄옥사이드의 정량

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# A Novel Volumetric Method for Quantitation of Titanium Dioxide in Cosmetics

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요 약: 자외선차단용 화장품은 기능성화장품으로 분류되어 있으며 매년 다양한 종류의 유기 또는 무기 자외선 차단제를 함유하는 제품이 출시되고 있다. 높은 SPF 수치를 요구하는 제품과 유아 및 민감성 피부를 위한 자외선차단제품에 무기자외선 차단제가 많이 사용되고 있으며 대표적인 것으로 티타늄옥사이드가 있다. 티타늄옥사이드는 피부를 하얗게 표현하는 특성 때문에 착색제로 오랜 기간 사용되어 왔으나 이러한 특성이 자외선 차단제로서의 응용을 제한하여 왔다. 그러나 최근 마이크로화 기술의 발달로 하얗게 보이는 현상 없이 티타늄옥사이드를 높은 농도로 함유할 수 있게 됨에 따라 티타늄옥사이드의 자외선차단제로서의 응용 연구가 활발히 진행되고 있다. 그러나, 자외선차단 화장품 중 티타늄옥사이드의 함량분석에 대한 연구는 거의 전무한 상황이다. 본 연구에서는 산화환원적정법을 이용한 자외선차단 화장품 중 티타늄옥사이드 함량분석법을 개발하였으며, 대표적인 자외선차단제품인 크림, 메이크업베이스, 파운데이션 및 파우더에 일정량의 티타늄옥사이드를 포함시킨 다음 분석하여 시험법의 회수율이 96 ~ 105%임을 확인하였다. 또한, 본 연구의 방법으로 분석한 시판되는 자외선차단제품 7 종의 티타늄옥사이드 함량 분석결과를 ICP-AES (Inductively Coupled Plasma-Mass Spectrometry)를 이용한 기기분석결과와 비교하는 방법으로 시험법을 재검증하였다. 비록 최신 분석기기인 ICP-AES로 정확한 티타늄분석이 가능하지만 고도의 기술이 필요하고 모든 화장품사가 품질관리를 위하여 구비하기에는 분석장비가 고가인 만큼 현실적인 방법이라고는 할 수 없을 것이다. 본 연구의 티타늄옥사이드 정량법은 일반적인 초자기구 만으로 수행할 수 있으므로 현장에서 자외선차단 기능성화장품의 품질관리에 널리 활용될 수 있을 것이다.

**Abstract**: Nowadays there are many sun protection cosmetics including organic or inorganic UV filter as an active ingredient. Chemically stable inorganic sunscreen agents, usually metal oxides, are widely employed in high SPF products. Titanium dioxide is one of the most frequently used inorganic UV filters. It has been used as pigments for a long period of cosmetic history. With the development of micronization techniques, it becomes possible to incorporate titanium dioxide in sunscreen formulations without whitening effect and it becomes an important research topic. However, there are very few works related to quantitations of titanium dioxide in sunscreen products. In this research, we analyzed amounts of titanium dioxide in sunscreen cosmetics by adapting redox titration, reduction of Ti(IV) to Ti(III) and reoxidation to Ti(IV). After calcification of other organic ingredients of cosmetics, titanium dioxide is dissolved by hot sulfuric acid. The dissolved Ti(IV) is reduced to the Ti(III) by adding aluminum metals. The reduced Ti(III) is titrated against a standard oxidizing agent, Fe(III) (ammonium iron(III) sulfate), with potassium thiocyanate as an indicator. In order to test accuracy and applicability of the proposed method, we analyzed the amounts of titanium dioxide in four types of sunscreen cosmetics, such as cream, make-up base, foundation and powder, after adding known amounts of titanium dioxide (1 ~ 25 w/w%). The percent recoveries of the titanium dioxide in four types of formulations were in the range between 96 and 105%. We also analyzed 7 commercial cosmetic products labeled titanium dioxide as an ingredient and compared the results with those of obtained from ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry), one of the most powerful atomic analysis techniques. The results showed that the titrated amounts were well coincided with the analyzed amounts of titanium dioxide by ICP-AES. Although instrumental analytical methods, ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and ICP-AES, are the best for the analysis of titanium, it is hard to adopt because of their high prices for

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small cosmetic companies. It was found that the volumetric method presented here gave quantitative and reliable results with routine lab-wares and chemicals.

***Keywords:*** *titanium dioxide, sunscreens, redox titration, volumetric titration*

## 1. Introduction

The sun is a source of energy in every living organism on the earth. Since it has very high electromagnetic energy, especially UV radiations, too much exposure to them can be harmful. UV radiations are known to be responsible for skin thickening, skin aging, immediate tanning, photosensitizing and sometimes erythema [1]. For these reasons, sun protection has been one of main categories for beauty care products. There are many commercial sun protection cosmetics containing organic or inorganic sunscreen agents.

Organic sunscreen agents are conjugated aromatic chromophores, such as octyl methoxycinnamate, *p*-amino benzoic, octyl salicylate, homosalate, methoxydibenzylmethanes, benzophenone derivaties, menthyl anthranilates and camphor derivatives, etc. These molecules go to excited state by absorbing high energy UV rays and return to ground state by emitting longer wavelength low energy rays [2]. Each Organic UV absorbers have specific wavelength range for the protection.

Chemically stable and inert inorganic sunscreens, usually metal oxides, are widely employed in high SPF products [3]. They protect skin from the sun by reflecting, diffracting and sometimes absorbing UV radiations [4]. These metal oxides have many advantages. They can protect both UVA (320 ~ 400 nm) and UVB (290 ~ 320 nm) effectively and can impart high SPF (sun protection factor) value at relatively low concentration levels. Most of all, they are less allergenic than organic sunscreens. One of the most frequently used inorganic UV filters is titanium dioxide. Titanium dioxide has been used as pigments for a long period of cosmetic history. With the development of micronization techniques, it becomes possible to incorporate the titanium dioxide in sunscreen formulations without whitening effect and it becomes an important research topic [5,6].

However, in point of analytical research, there are very few works related to quantitations of titanium dioxide in sunscreen products. In this article, we investigated ways to quantify titanium dioxide in cosmetics by a titration. To examine the feasibility of the proposed method, we compared the results with data from instrumental analysis, ICP-AES.

## 2. Materials and Methods

### 2.1. Samples & Reagents

Cosmetics (cream, make-up base, foundation and powder) containing 1, 5, 10 and 25% of titanium dioxide, were separately prepared. Commercial cosmetics were purchased from market. All chemicals used here were analytical reagent grade. Two parts of experimental procedures are addressed here. They are described as following.

### 2.2. Titration

This is a modified protocol to detect titanium dioxide based on the method suggested in Japanese Standards Cosmetic Ingredient. Accurately weighted an amount of the product, equivalent to about 0.2 g of titanium dioxide according to the labeled amount, was dried and ignited carefully. After it was transferred to a 500 mL erlenmeyer flask, 3 ~ 4 mL of water, 30 mL of sulfuric acid and 12 g of ammonium sulfate were added. It was heated gradually at first, then strongly to be dissolved. After cooled, 120 mL of water and 40 mL of hydrochloric acid were added while the temperature of the solution was kept not to exceed 50℃. After it had been cooled, 3 g of aluminum was added. The generated hydrogen gas was absorbed into saturated sodium bicarbonate solution through a U-shaped glass tube which was adapted to the 500 mL erlenmeyer flask with a rubber stopper, as illustrated in the Figure 1. After aluminum became soluble, the solution turned to violet color. After cooled, the U-shaped glass tube was removed. The violet solution in the erlenmeyer flask was titrated with 0.1 N ferric ammonium sulfate (indicator: 3 mL of potassium thiocyanate solution (1→

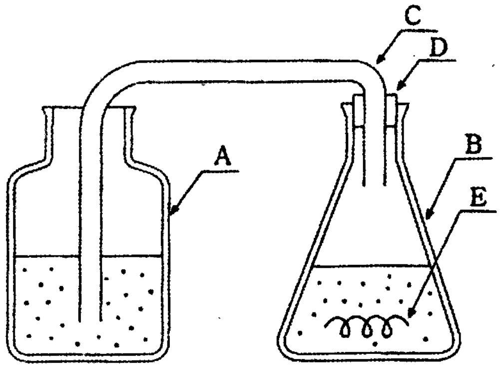


**Figure 1.** Schematic diagram of the reducing apparatus: (A) Wide neck bottle with saturated sodium bicarbonate solution; (B) 500-mL Erlenmeyer flask; (C) U-shaped glass tube; (D) Rubber stopper; (E) Aluminum wire.

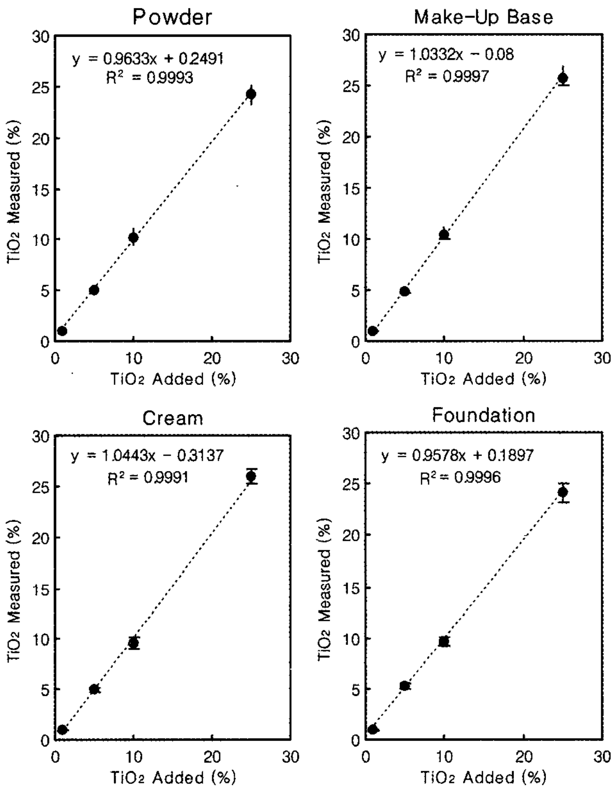


**Figure 2.** $R^2$ values of the titrations in diverse cosmetic formulations.

10)). Each mL of 0.1 N ferric ammonium sulfate was equal to 7.988 mg of titanium dioxide.

### 2.3. ICP-AES

Accurately weighted about 0.05 g samples were mixed with 3 mL of nitric acid, 1 mL of hydrochloric acid, 2 mL of hydrofluoric acid and 1 mL of sulfuric acid in PTFE vessels (XP1500, CEM) and were digested with Microwave Digestion (Mars 5, CEM) for 15 min at 400 W. The digested solutions were analyzed with ICP-AES (OPTIMA 3300DV). The following operation conditions were set for ICP-AES: incident power 2000 W; cross flow nebulizer; plasma gas flow rate 13 L/min; auxiliary gas flow rate 0.5 L/min; nebulizer gas flow rate 0.5 L/min; sample uptake rate 1.8m L/min; wavelength 323.45 nm.

**Table 1.** Recovery Tests for the Titanium Dioxide in Four Types of Cosmetic Formulations

| | Recovery (%) in each cosmetic formulations | | | |
|---|---|---|---|---|
| Added Amounts (%) | Cream | Make-Up Base | Foundation | Powder |
| 1 | 98.0 | 103.0 | 96.0 | 97.0 |
| 5 | 99.2 | 96.6 | 104.8 | 101.6 |
| 10 | 96.6 | 104.7 | 97.2 | 102.5 |
| 25 | 103.8 | 102.8 | 96.4 | 96.8 |

**Table 2.** Comparison of the Results from the Volumetric Titration to the ICP-AES

| No. | Cosmetic Type | Measured $TiO_2$ (%) | |
|---|---|---|---|
| | | Titration | ICP-AES[a] |
| 1 | Cream | 2.9 ± 0.12 | 2.8 |
| 2 | Lotion | 5.4 ± 0.21 | 5.1 |
| 3 | Cream | 4.7 ± 0.19 | 4.9 |
| 4 | Make-up Base 1 | 4.8 ± 0.17 | 4.7 |
| 5 | Make-up Base 2 | 4.8 ± 0.14 | 4.5 |
| 6 | Foundation | 10.6 ± 0.26 | 10.8 |
| 7 | Powder | 12.4 ± 0.34 | 12.9 |

[a] ICP-AES was performed by Anapex Research Inc.(Yusung, Korea)

## 3. Result and Discussion

Titanium has two different oxidation states, titanium(Ⅲ) and titanium(Ⅳ). The redox reaction between them is the basis of quatitation of titanium dioxide in our investigation.

After calcification of other organic ingredients of cosmetics, titanium dioxide was dissolved by hot concentrated $H_2SO_4$ (boiling points of $H_2SO_4$ cān be elevated by ammonium sulfate up to 500℃). The dissolved titanium(Ⅳ) was reduced to titanium(Ⅲ) by aluminum. Solid zinc amalgam or chromium(Ⅱ) chloride solution also can be used as reducing agent for titanium(Ⅳ) [7]. The reduced titanium(Ⅲ) was titrated against a standard oxidizing agent, Fe(Ⅲ) (ammonium iron(Ⅲ) sulfate), with potassium thiocyanate as an indicator.

Cosmetics are very complex products. More than 20 kinds of organic and inorganic materials are mixed up. Although organic ingredients are eliminated by calcination, remaining inorganic materials could be matrix interferences. In addition to, many kinds of inorganic metals, such as zinc oxide, silica, talc and iron oxides, are remained after calcination. In order to test accuracy and applicability of the proposed method in the presence of other cosmetic ingredients, we quantified known amounts of titanium dioxide from 1 to 25% in four types of sunscreen cosmetics. Since the SCCNFP proposed the maximum concentration of titanium dioxide as 25%, we didn't test over 25%.

As shown in Figure 2, $R^2$ values were acceptable. It seems that the linearity was established in the test range. Accuracy was evaluated *via* percent recovery. The percent recovery for the accuracy was calculated as follow :

$$\text{Recovery (\%)} = (\text{Measured amounts (\%)} / \text{Added amounts (\%)}) \times 100$$

The results are summarized in Table 1. The percent recoveries of the four types of fourmulation were in the range between 96 and 105%. These results reflect that the accuracy of the developed method was also good.

We also analyzed 7 commercial cosmetics labeled titanium dioxide. We made a comparison between the proposed method and ICP-AES, one of the most powerful atomic analysis tools. The results, given in Table 2, show that the titrated amounts accord well with the data from ICP-AES. It seems the studied method in this article is adequate for quantifying titanium dioxide in diverse commercial cosmetics.

There are many other analytical methods used for quantitative determination of titanium. But, few of them can be applied to cosmetics. One of them is colorimetric measurement using UV-VIS Spectrophotometer. Mineral acid solution of Ti(IV) produce yellow-orange colored acidic cationic species, 'pertitanic acid' such as $[Ti(OH)_2(H_2O_2)(H_2O_2)]_2^+$ or $(TiO_2.aq)_2^+$, with hydrogen peroxide [8]. This method is good for trace level analysis of titanium, up to 50 ppm [9]. However, some metals, such as Cr, V or Mo, interfere the analysis by forming coloring material with hydrogen peroxide. Ferric ions also interfere by producing yellow-orange colored solutions in acidic media. Since many of sunscreen cosmetics contain chromium oxides or iron oxides as coloring agents, it is difficult to adapt this colorimetric method to cosmetics.

Gravimetric determination is a traditional analytical technique for titanium measurement. This involves a production of a yellow flocculent precipitate, $Ti(C_6H_5O_2N_2)_4$, of cupferron and titanium in acidic solution [10]. Since other metals can be co-precipitated in this procedure, it is necessary to use some selective precipitating agent. This method is not so good for everyday routine work, since it requires some manipulative analytical skills and is time-consuming procedure.

Nowadays, analytical instruments have been powerful research tools for analytical research. There are many techniques including flame or electrothermal atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Because of poor activation efficacy of titanium in the flame, it is difficult to exploit flame AAS. Electrothermal AAS is not also widely employed, since many other elements make stable titanium complex in the furnace. Since ICP has sufficient energy for the atomization of titanium, ICP-MS and ICP-AES can effectively determine the titanium. They are the best for trace level measurements. The detection limits are in the range of 1 to 10 ppt for ICP-MS [7]. Although instrumental techniques, ICP-MS or ICP-AES, are the best for the analysis of titanium, only a minority of cosmetic companies could be able to afford them because of their high cost.

## 4. Conclusion

In this research, we analyzed amounts of titanium dioxide in sunscreen cosmetics by employing the novel volumetric method based on redox titration. On the basis of the results of this study, we found that the method gives quantitative and reliable data with routine lab-wares and chemicals.

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