# Evaluating the dispersion of $TiO_2$ nanoparticles via sp-ICP-MS for sunscreen powder analysis

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## Introduction

Titanium dioxide ($TiO_2$) nanoparticles (NPs) are widely used in everyday consumer products such as toothpaste, sunscreens and cosmetics. Because of its high surface area-to-volume ratio, $TiO_2$ NPs are easy to aggregate due to the high surface activity and changes in surface charge in aqueous solution. Measurement of "real" particle size distribution of the commercial produced in liquid dispersions is not easy and still going on research. Therefore, in this work, we mainly focus on the stability and separation phenomena of $TiO_2$ NPs of standard material and sunscreens powder in different surfactants, organic or alkaline solution with single particle ICP-MS (spICP-MS).

## Experimental

### Different diluent

There are 6 different solutions including 1% IPA, 1%FL-70, 1%Triton X-100, 1% 1-butanol(NBA), 1%$NH_4OH$, and the mix solution with 1%$NH_4OH$ and Triton X-100 are chose to be $TiO_2$ diluents.

### Reference Material (RM)

The titanium dioxide ($TiO_2$) nanoparticles were from US Research Nanomaterials(USRN), Inc. The particle size is 30~50nm provided by USRN.

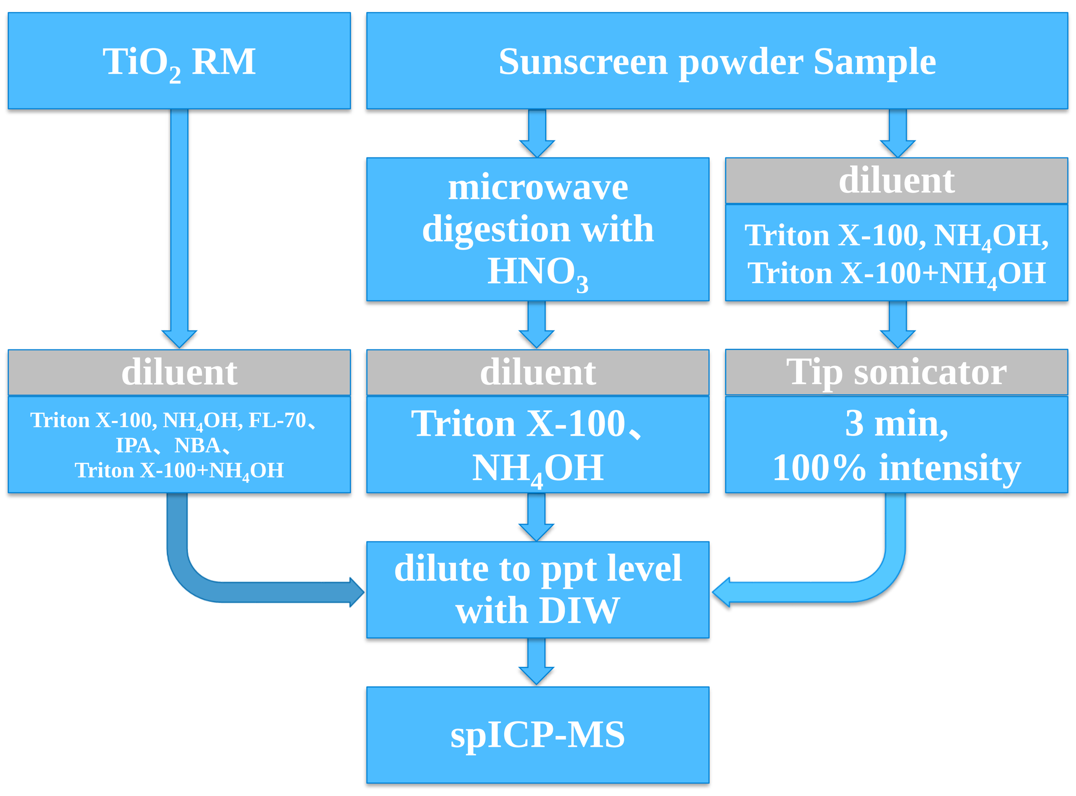
A silver NP Reference Material (Sigma-Aldrich) with a nominal particle size of 40 nm was used to measure the nebulization efficiency of the ICP-MS.

### Sunscreen Powder Sample

There are 5 commercial sunscreen powders bought in Taiwan normal pharmacy. Two kinds of sample preparation methods were tested: (1) microwave digestion and (2) direct dilution.

### Sample Preparation

All NP RMs and sample solutions were diluted followed by the steps below:




### Instrument and Condition

Agilent 7900 ICP-MS and MassHunter's Single Particle Application Module were used for data collecting and analysis. Standard quartz sample introduction systems were used with a 1.5mm injector diameter torch. $TiO_2$ NPs were measured in no gas mode.

## Results and Discussion

### $TiO_2$ RM in different diluents

Dilute $TiO_2$ RM (Anatase) in 1% FL-70, 1%Triton X-100, 1% IPA, 1% NBA and 1% $NH_4OH$ in 1st step, then using DIW to dilute to 30ppt.

From the analyzing data of $TiO_2$ RM, the particle concentration from Triton X-100 and $NH_4OH$ diluent are more than other diluents. Therefore, we chose Triton X-100 and $NH_4OH$ for the following test.

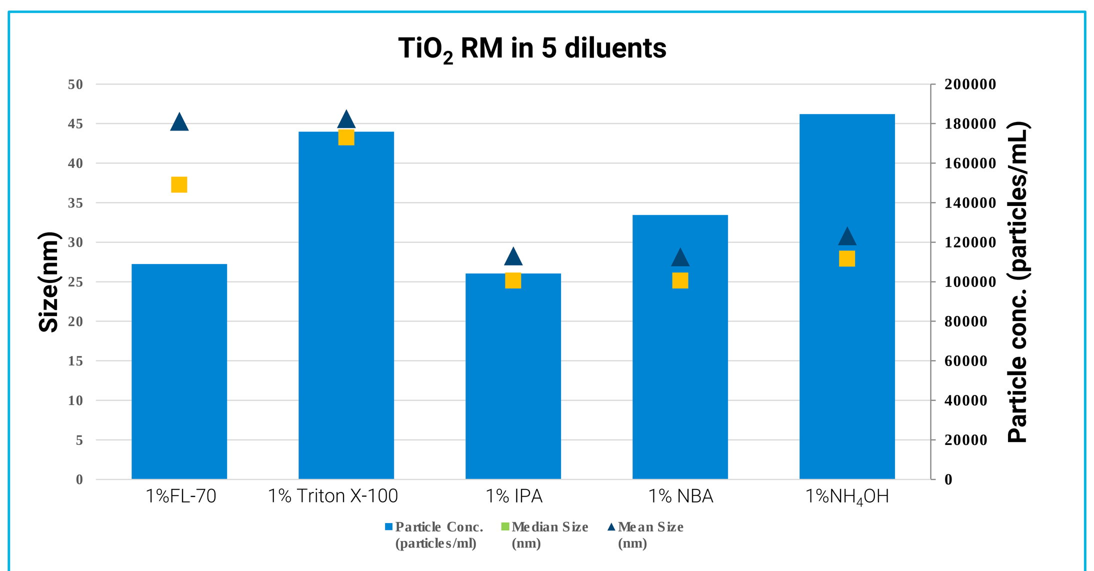



Fig. Effect of different diluents on mean particle size and particle concentration .

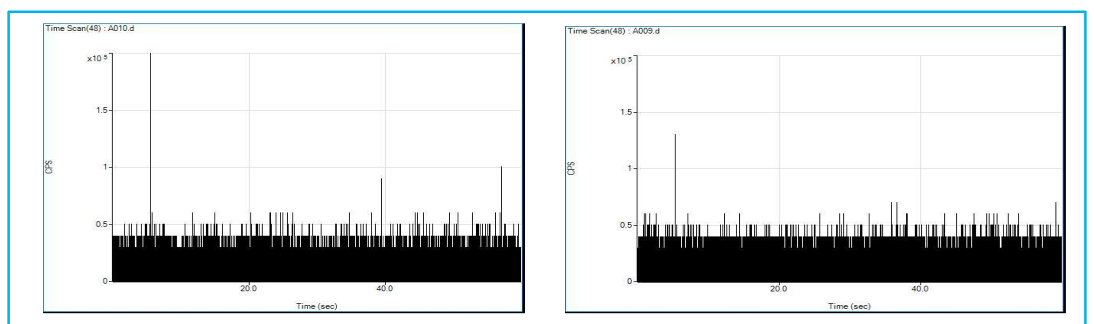


Fig. Time scan graph of blank solution from $NH_4OH$ diluent (right) and from Triton X-100 diluent (left).

## Results and Discussion

### $TiO_2$ RM in different diluents

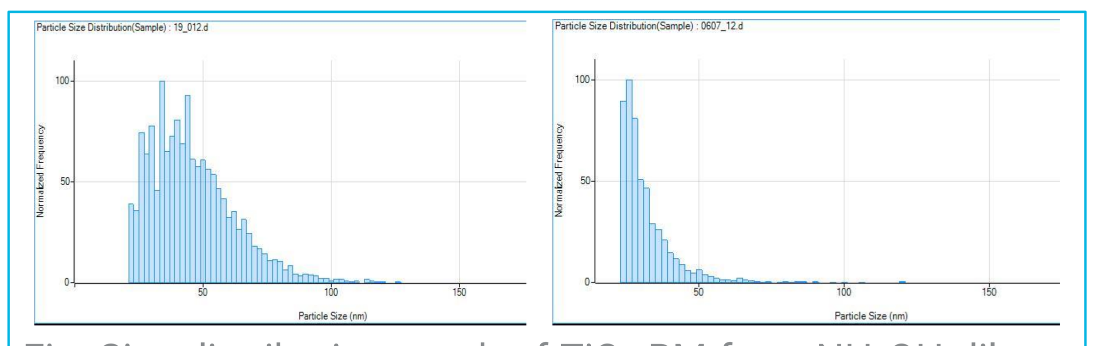


Fig. Size distribution graph of $TiO_2$ RM from $NH_4OH$ diluent (right) and from Triton X-100 diluent (left).

### Short-term stability of $TiO_2$ RM (Rutile)

Analyzing $TiO_2$ RM (Rutile) from Triton X-100 diluent for 8 hours, the RSD(%) of particle concentration, median size, mean size, and most frequent size are < 5%.

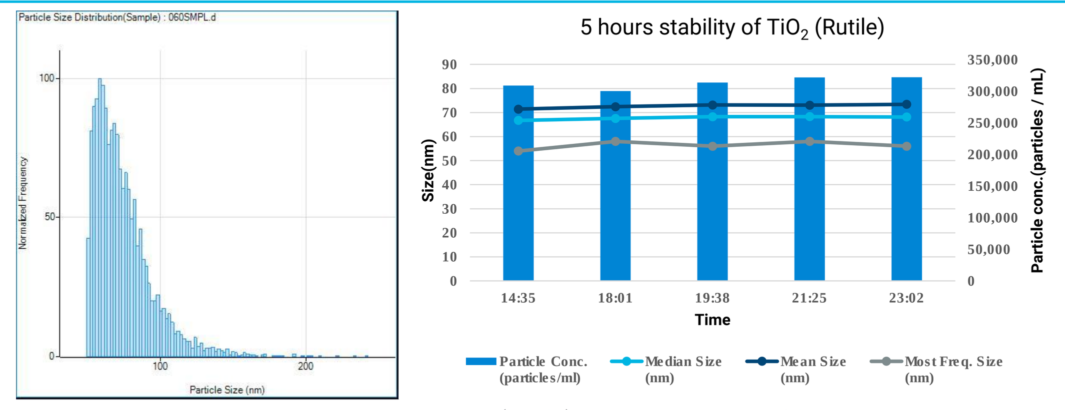



Fig. Size distribution graph (left) and time effect comparison results of size/particle conc. (right) of $TiO_2$ RM from Triton X-100 diluent.

### Commercial Sunscreen powder Sample: Microwave digestion

Then using 2 solutions, Triton X-100 and $NH_4OH$, to dilute digested sunscreen powder solution. When $NH_4OH$ was used to dilute the digested samples, better particle distributions were obtained, and the number of particles was more. However, when the same digested sample solution was diluted with Triton X-100, the number of particles was few and the size distribution was also poor then $NH_4OH$.

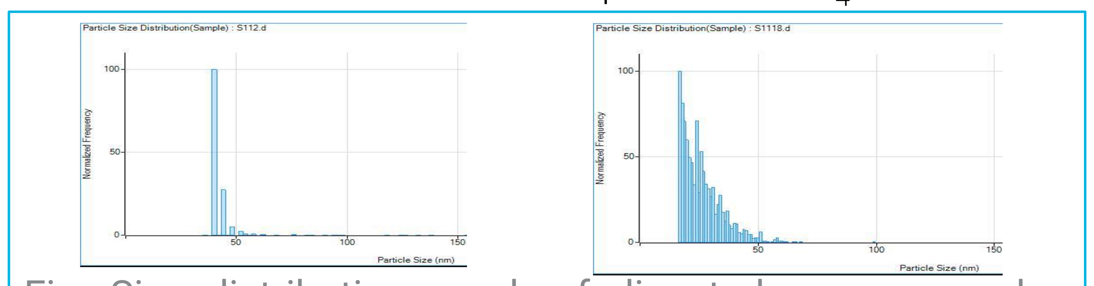


Fig. Size distribution graph of digested screen powder solution from $NH_4OH$ diluent (right) and from Triton X-100 (left).

So choose $NH_4OH$ to dilute 5 sunscreen powder digested sample. After dilute to ppt level, the results of particle size, particle concentration of 5 samples is in the following table:

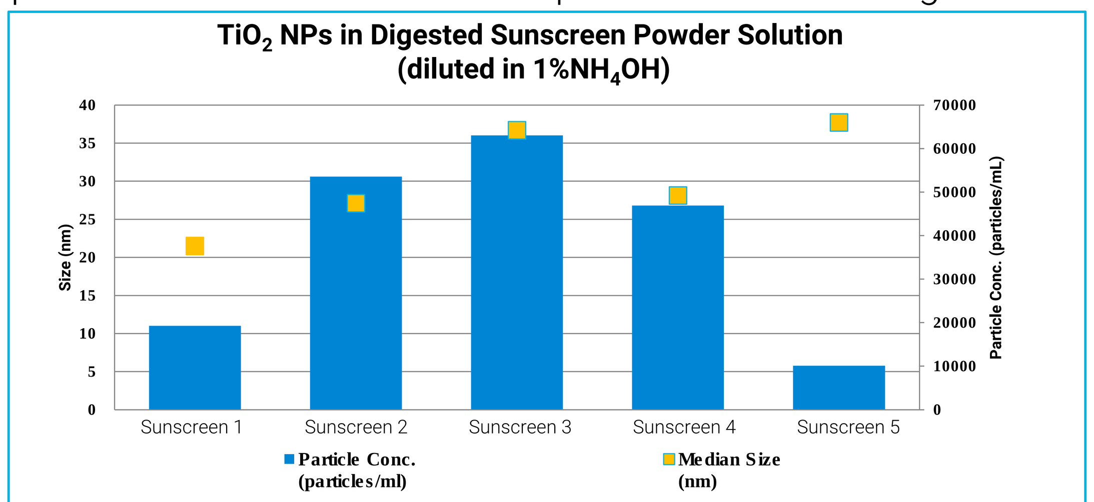



Fig. Comparison of particle size and particle concentration for 5 sunscreen powders with microwave acid digestion .

### Commercial Sunscreen powder Sample: Directly dilution-1

Then using 2 solutions, Triton X-100 and $NH_4OH$, to dilute sunscreen powder directly. Better dispersion were obtained when Triton X-100 to be diluent, including size and particle numbers .

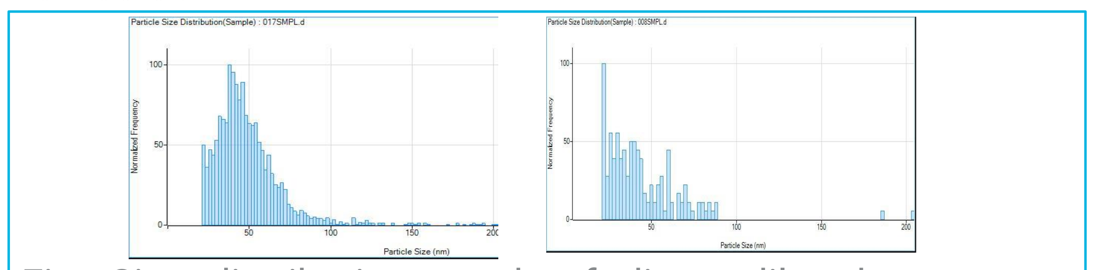


Fig. Size distribution graph of direct diluted sunscreen powders from $NH_4OH$ diluent (right) and from Triton X-100 (left).

### Mixture diluent: Triton X-100 and $NH_4OH$

Furthermore, because pH of 1%Triton X-100 is 3.97, for consider with polarity and zeta-potential(F. Loosli,, 2013), we try to dispersed the $TiO_2$ NPs in a mixed Triton X-100 and $NH_4OH$ solution.

The $TiO_2$ RM diluted with a mixture of 1% Triton X-100+ $NH_4OH$ was similar with diluted with only 1% Triton X-100:

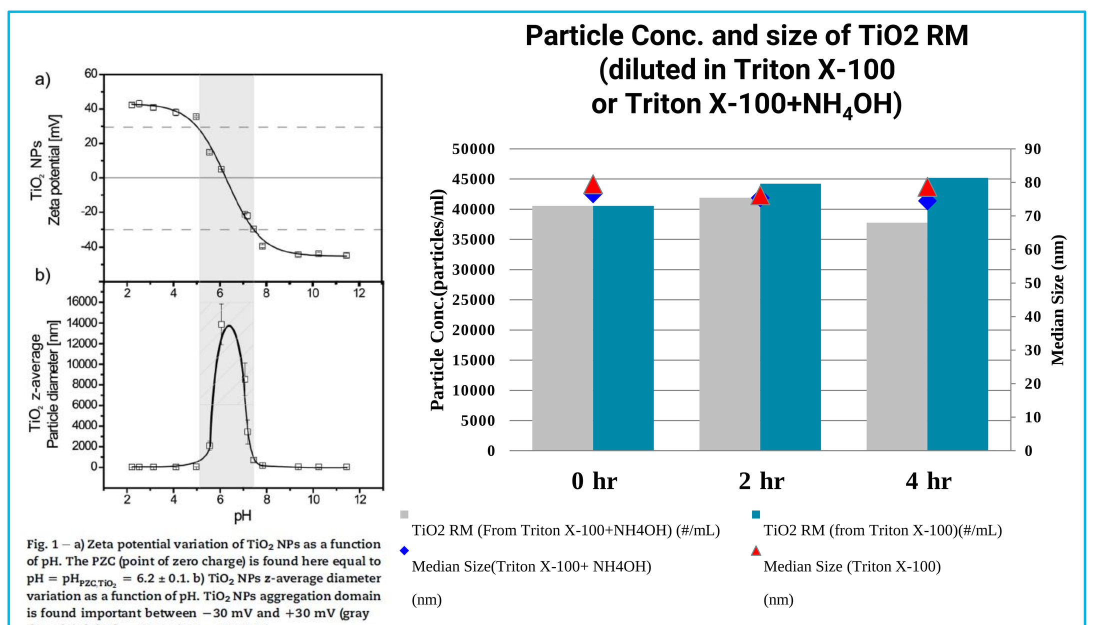



Fig. Effect of diluents on particle size and particle concentration of $TiO_2$ RM.

## Results and Discussion

### Commercial Sunscreen powder Sample: Directly dilution-2

Compared with the powder samples diluted directly with 1% Triton X-100 and Triton X-100+$NH_4OH$ mixture, because the particle size is smaller and the particle concentration are more, it shows that the dispersion of the mixture solution on the actual sample is better.

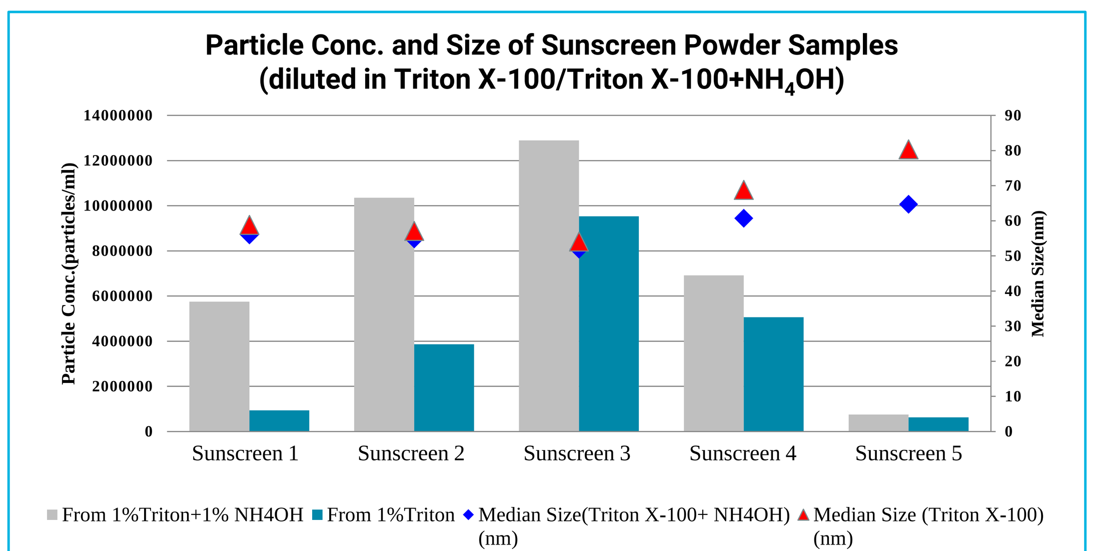



Fig. Comparison of particle size and particle concentration for 5 powder samples diluted directly with diluents.

### Calculate suitable dilution factor for real Sample: quantitative by ICP-MS

Due to the different concentrations of $TiO_2$ between commercially products , a basis is needed to help determine the appropriate dilution rate. Therefore, although the concentration of Ti ionic concentration can not completely represent the concentration of the $TiO_2$ NPs, still using ICP-MS to quantify Ti ionic concentration of 5 sunscreen powder samples help to decide the dilution ratio for $TiO_2$ spICP-MS analysis.

After analyzing 50 ug/L of each sample, the results are shown in the following table. It shows that the Ti ionic concentration isn't related with the labeled concentration. And it also shows different ionic concentration in Triton X-100 only and Triton X-100+$NH_4OH$ diluents.

| (unit) | Original labeled $TiO_2$ conc. (%, w/w) | Diluted $TiO_2$ conc. calculated by labeled conc. (ug/L) | Ti ionic conc.by ICP-MS (diluent:1% Triton X-100) (ppb) | Ti ionic conc.by ICP-MS (diluent: 1% Triton X-100 + $NH_4OH$ (ppb) |
|---|---|---|---|---|
| Sunscreen 1 | 13 | 50 | 1.2 | 4.9 |
| Sunscreen 2 | 15 | 50 | 6.9 | 13 |
| Sunscreen 3 | 14 | 50 | 9.1 | 13.3 |
| Sunscreen 4 | 14 | 50 | 7.1 | 8.3 |
| Sunscreen 5 | 14 | 50 | 2.6 | 0.97 |

Then dilute the sunscreen sample solution to 100ppt by the new Ti ionic concentration results. The result shows NPs concentration are most within $10^7$ ~ $10^8$ Particles/L (10,000~100,000 particles/mL) and suitable be analyzed by spICP-MS.

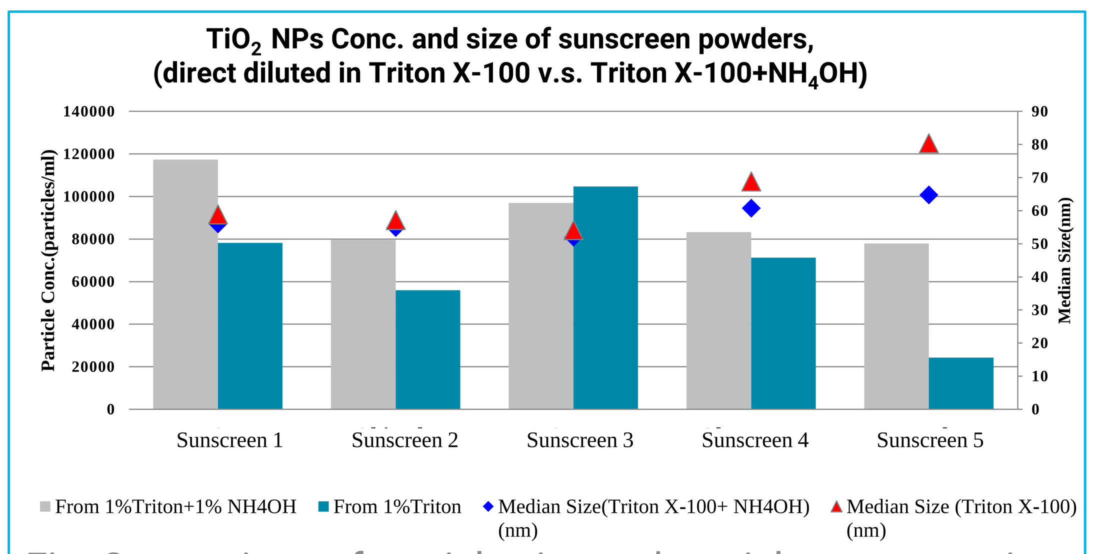



Fig. Comparison of particle size and particle concentration for 5 powder samples diluted directly with diluents.

In theory, the ionic concentration is not equal to NP concentration, however, it shows the ICP-MS quantitative result could help to determine the suitable dilution rate for NP analysis of real sample in the future.

## Conclusions

In this work, we have established a test method of spICP-MS for $TiO_2$ nanoparticles on commercially sunscreen powders, including two methods of microwave digestion and direct dilution, and found suitable diluent for $TiO_2$ nanoparticle analysis.

When the sample was pre-treated by microwave digestion, $NH_4OH$ as a diluent can get a better dispersion of $TiO_2$ NPs. In the case of the pretreatment using the direct dilution method, compared to the method of directly diluting with Triton X-100, the best result is obtained as the mixture of $NH_4OH$ and Triton X-100 because $NH_4OH$ makes the alkaline diluent.

In the future, in the actual sample analysis, ICP-MS can be used for ion concentration analysis to obtain a more suitable dilution ratio for each sample, making the SOP of $TiO_2$ NP of spICP-MS more feasible.

## References

1. S. Wilbur, M. Yamanaka and S. Sannac, *Agilent publication*, **2015**, 5991-5516EN.
2. F. Loosli, P. L. Coustumer, S. Stoll, *Water Research*, **2013**, 6052-6063.