

Quantification of Gold Nanoparticles Using the Thermo Scientific NanoDrop 2000 Spectrophotometer

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Introduction

Metal nanoparticle (NP) colloids with diameters (d) between 1-100 nm possess a unique optical absorption that is related to the oscillation of surface electrons. This surface plasmon resonance (SPR) property is dependent on the size and shape of the NP as well as the surrounding medium.^{1,2} Since the SPR band is a characteristic of the NP composition and morphology, it is often the first property tested to judge synthesis success. Subsequently, the SPR is used to monitor a number of characteristics, such as concentration. Gold NPs (AuNPs) have extinction coefficients $>10^7 \text{ M}^{-1}\text{cm}^{-1}$, when $d > 10 \text{ nm}$, making them very strongly absorbing. It is therefore difficult to measure absorbance of highly concentrated samples using a 1 cm pathlength. In addition, since many of these AuNPs are used in self-assembly studies, in which the NPs have undergone tedious functionalization and purification,³ often only small volumes are available.

Thus, an instrument capable of measuring high AuNP concentrations at small sample volumes is ideal. The Thermo Scientific NanoDrop 2000 UV-Vis Spectrophotometer has proven to be particularly useful in this regard because of the instrument's short pathlengths (0.05 -1.0 mm) and microliter sample volume requirement. Here, we show that it is possible to accurately quantify the SPR band of two AuNPs ($d = 13 \text{ nm}$, $d = 52 \text{ nm}$) over a wide range of concentrations.

Experimental Procedures

The AuNPs used in these experiments were synthesized following two procedures. The AuNP with $d = 13 \text{ nm}$ were synthesized via a standard sodium citrate reduction of gold (III) chloride.³ The AuNP with $d = 52 \text{ nm}$ were synthesized by a seed-mediated growth approach.⁴ The NanoDropTM 2000 was first used to determine the approximate diameter by measuring the SPR band of each AuNP. For example, the AuNP with $d = 13 \text{ nm}$ had a SPR maximum of 520 nm (fig. 1a), whereas the AuNP with $d = 52 \text{ nm}$ showed SPR of 533 nm (fig. 2a), as previously reported.^{2,5}

The AuNP were then purified and concentrated using centrifugation, which allowed for systematic dilutions

when collecting the SPR. The auto-pathlength option was selected in the NanoDrop 2000 software, and each spectrum collected using a 5 μl aliquot of a known stock solution. Between measurements, the NanoDrop 2000 optical surfaces were simply cleaned using a standard laboratory tissue and distilled water.

Results

The corresponding UV-Vis results for the AuNPs with $d = 13 \text{ nm}$ and $d = 52 \text{ nm}$ are shown in Fig. 1 and Fig. 2 respectively. As shown, the SPR spectra are highly reproducible, with high signal to noise ratio. The SPR was successfully measured over a wide concentration range (1~150 nM).

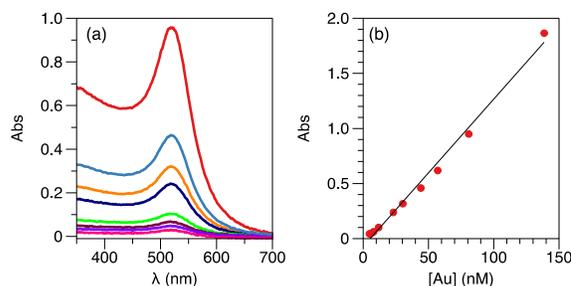


Fig. 1 (a) UV-Vis spectra for AuNP ($d = 13 \text{ nm}$) collected using 5 μl aliquots of systematic dilutions. (b) Corresponding 1 mm Abs vs [Au] plot showing the linearity over a large concentration range with a slope of $1 \times 10^8 \text{ M}^{-1}\text{cm}^{-1}$.

As can be seen from the 1 mm Abs vs. [Au] plot in Fig. 1b, the relationship is linear, with an extracted extinction coefficient of $1 \times 10^8 \text{ M}^{-1}\text{cm}^{-1}$ in agreement with literature values.^{2,5}

A similar trend was shown for the AuNP with $d = 52 \text{ nm}$ (Fig. 2), with an extracted extinction coefficient of $3 \times 10^{10} \text{ M}^{-1}\text{cm}^{-1}$, again, in agreement with literature values.^{2,5}

For a number of samples, the absorbance values were measured in triplicate, with a typical standard deviation

of 0.002 A. Thus, the spectra produced by the NanoDrop 2000 were highly reproducible even with the small sample volumes (5 μ l). Volumes as small as 2 μ l also showed consistent results.

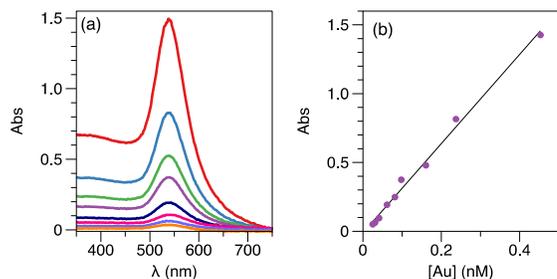


Fig. 2 (a) UV-Vis spectra for AuNP (d = 52 nm) collected using 5 μ l aliquots of systematic dilutions. (b) Corresponding 1 mm Abs vs [Au] plot showing the linearity over a large concentration range with a slope of $3 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$.

Conclusion

The NanoDrop 2000 was found to be very versatile in the analysis of AuNP SPR signatures. Given the ability to measure NP concentration over large concentration ranges, as well as the small volumes required, the NanoDrop 2000 is an ideal instrument where very small amounts of concentrated particles are produced.

References

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