

Analytical Methods

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6 **Comment on “Simple fluorescence-based detection of Cr(III) and Cr(VI)**
7 **using unmodified gold nanoparticles” by M. Elavarasi, S. A. Alex, N.**
8 **Chandrasekaran and A. Mukherjee, *Anal. Methods*, 2014, 6, 9554**
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4 Recently,¹ Mukherjee et al. presented a fluorescence-based method for the
5 determination of both Cr(III) and Cr(VI) in aqueous samples using 31.2 nm sized
6 citrate coated gold nanoparticles (AuNPs) that were synthesized based on Frens or
7 Turkevich method.² They claimed that the complexation of AuNPs by Cr(III) leads
8 to the quenching of the fluorescence intensity of AuNPs, which is directly
9 proportional to the concentration of Cr(III).
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13 Gold nanoparticles exhibit a high order of magnitude extinction coefficients ($\sim 3 \times$
14 $10^{11} \text{ mol L}^{-1} \text{ cm}^{-1}$) when the incident photon frequency is in resonance with the
15 collective excitation of the conduction electrons. This phenomena is known as
16 surface plasmon resonance (SPR) and depends on the size, shape, and inter-particle
17 spacing of gold nanoparticle as well as its own dielectric properties and those of its
18 local environment.^{3,4} When the size of AuNPs is reduced to around 2 nm or less,
19 the continuous band structure of AuNPs breaks into discrete energy states,⁵ similar
20 to the energy levels of molecules. These molecular quantum clusters of AuNPs do
21 not show plasmonic properties anymore, but exhibit strong luminescence
22 emission.⁵ Since the particle size of the AuNPs synthesized in is around 31 nm, it
23 seems that the major problem of the work done by Mukherjee et al.¹ is: “*The*
24 *Rayleigh scattering peak of Au NPs that appeared around 580 nm was introduced*
25 *as the fluorescence peak of Au NPs*”, which is a clear mistake. In addition, the
26 authors could also confirm the presence of this Rayleigh scattering peak by
27 reporting different excitation wavelengths in their work (which was not reported).
28 As Mukherjee and coworkers believed, multiply charged aggregants such as
29 Cr (III) ions can act as cross-linking agents that bind nanoparticles into dense
30 aggregates.⁶ So, by increasing Cr(III) concentration, unstable aggregated AuNPs
31 will precipitate, leading to a decrease in the intensity of their corresponding
32 Rayleigh scattering peak.
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