



SELECTIVE CONJUGATION OF CHARGED AND NEUTRAL LIGANDS TO GOLD NANOPARTICLES

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BACKGROUND

Gold nanoparticles have been around since ancient times, and one of the oldest recorded uses was to stain glass. Probably the most famous example is the Lycurgus Cup¹, which is green in daylight but turns red when lit from the inside. Nowadays, gold nanoparticles are used for more sophisticated things, such as tumor detection, gene therapy, and optical biosensors². An interesting feature of gold nanoparticles is their size dependent color. This can be used to determine their stability and aggregation state.



In my experiment, the nanoparticles were around 20-30nm in size, and started out as a deep red color as shown on the left. If they turned purple like on the right, this meant that the particles were bigger, usually because they are unstable and starting to stick together.

STATEMENT OF RESEARCH PROBLEM

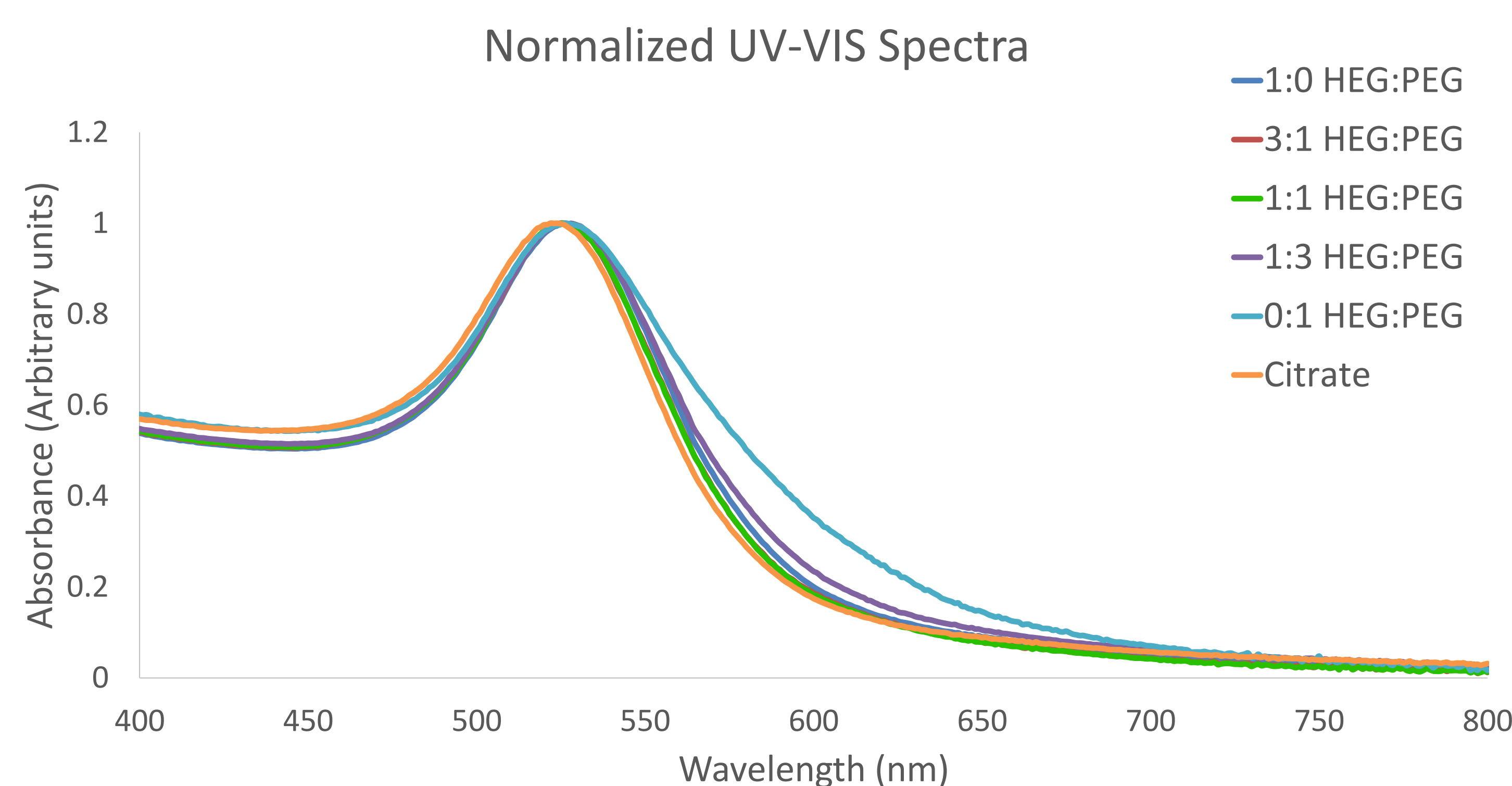
My research investigates how negatively charged and neutral ligands conjugated to gold nanoparticles affect the stability of the nanoparticles in aqueous solution. The goal of the study is to determine and control the number of carboxyl-terminate ligands on the surface of gold nanoparticles. This is directly relevant to nanoparticles-based drug delivery applications where the density drug molecules, which are often carboxylated, must be carefully controlled to maximize drug delivery efficiency and treatment success.

PROCEDURE

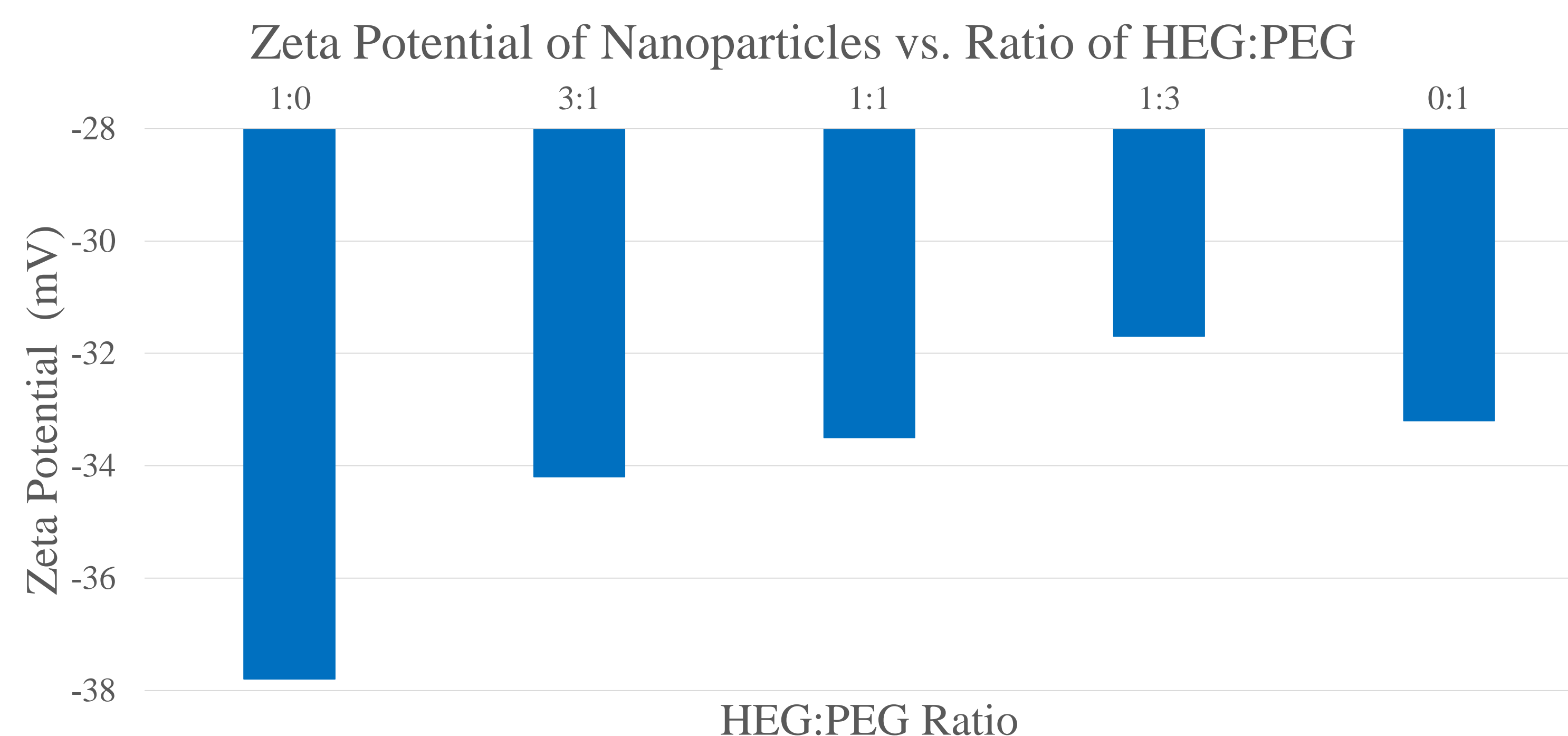
25 nm gold nanoparticles were synthesized using the Turkevich-style (Citrate Reduction) method³. In our experiments we attempted to vary the density of carboxyl groups on the surface, and the overall negative charge density, by modifying the surface of negatively charged citrate-coated gold nanoparticles with either a negatively charged ligand (carboxyl terminated polyethylene glycol; HEG) or a neutral ligand (methoxy terminated poly ethylene glycol; PEG). The ratio between the negatively charged and neutral PEG ligands was varied from 0:1, 1:1, 1:3, 3:1, and 1:0 (HEG:PEG). Gold nanoparticles with citrate on their surface was functionalized with the different HEG:PEG ratios.

DATA

When a UV-VIS spectrum is taken of gold nanoparticles, a very distinct peak is seen. The peak is due to surface plasmon resonance², which means that the electrons in the outer shell of the nanoparticles are vibrating because of an electrical field (in this case, the light from the UV-VIS). This peak can tell us how concentrated our sample of nanoparticles are, their size, and their quality. Shown below is a UV-VIS spectra of gold nanoparticles with citrate on the surface, and the same nanoparticles after being functionalized with different ratios of HEG and PEG.



After functionalization, the spectra shifts to the right due to a change in the dielectric constant at the surface. Furthermore, the peak broadens a little because the particles got bigger, causing them to scatter more light². From this UV-VIS, most of the samples look stable, except for 0:1 HEG:PEG. When the peak broadens, it indicates that the particles are unstable. Below is a graph of the surface charge for each ratio.



The surface charge of the nanoparticles decreased with increasing ratio of PEG. When the nanoparticles were functionalized with only PEG, the zeta potential decreased even more, which was not expected because PEG has a neutral charge. These numbers suggest that the functionalization reaction has not gone to completion, and that the citrate used to create the particles is still in solution.

RESULTS

Initial results show that the surface charge of HEG/PEG conjugated gold nanoparticles as measured by zeta potential did not represent the HEG/PEG ratios used. The gold nanoparticles had a negative zeta potential even after the negatively charged citrate ligands were exchanged with neutral PEG ligands.

CONCLUSION

This suggests an incomplete ligand exchange reaction. We are modifying the ligand exchange reaction condition to realize the goal of the project.

REFERENCES

- Freestone, I.; Meeks, N.; Sax, M.; Higgitt, C. The Lycurgus Cup – A Roman Nanotechnology. *Gold Bullentin*. [Online]. 2007, 40/4, 270-277 <http://master-mcn.u-strasbg.fr/wp-content/uploads/2015/09/lycurgus.pdf>
- Sigma Aldrich. Gold Nanoparticles: Properties and Applications. <https://www.sigmaaldrich.com/technical-documents/articles/material-science/nanomaterials/gold-nanoparticles.html> (accessed August 1, 2018)
- Zheng et al. Structure-Property Relationships of Amine-rich and Membrane-Disruptive Poly(oxonorborene)-Coated Gold Nanoparticles. *Langmuir*. 34 (15) 2018, 4614-4625 <https://pubs.acs.org/doi/10.1021/acs.langmuir.7b04285>