

10<sup>th</sup> World Congress on **Pharmacology**

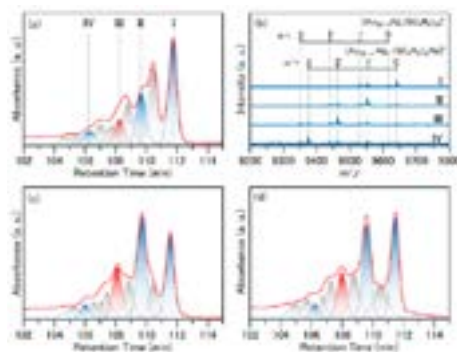
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6<sup>th</sup> International Conference and Exhibition on**Advances in Chromatography & HPLC Techniques**

August 02-03, 2018 | Barcelona, Spain

**Atomic and isomeric high-resolution separation of thiolate-protected alloy clusters by reversed-phase high-performance liquid chromatography****Sayaka Hashimoto and Yuichi Negishi**  
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By doping heteroatoms to thiolate-protected gold clusters, we can add more functionality to the cluster depending on the number of doped heteroatoms and the difference in doping positions. However, in the synthesis of alloy clusters, the mixture of clusters with a different number of heteroatoms is produced. Therefore, a precise separation of each cluster is required to understand their properties. In this study, we attempted to separate gold-silver alloy clusters precisely, furthermore investigated isomer change by reversed-phase high-performance liquid chromatography (RP-HPLC).  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  was used as a sample. This cluster was synthesized by two methods, (1) by adding  $[\text{Ag}(\text{SC}_4\text{H}_9)]$  complex to  $\text{Au}_{38}(\text{SC}_4\text{H}_9)_{24}$  (metal exchange) and gold and silver ions were reduced in the presence of butanethiol in solution (co-reduction). The mixture of alloy clusters was separated by RP-HPLC using gradient program for controlling mobile phase, and core-shell type column. The peaks obtained from the chromatogram were evaluated by electrospray ionization (ESI) mass spectrometry connected to RP-HPLC directly. Figure.1 (a) shows the chromatogram of  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  obtained by the metal exchange. Some clear peaks were observed in chromatogram. Each peak was attributed to the cluster having a precise number of silver atoms (Figure. 1(b)). These results indicate that the mixture of  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  was precisely separated according to the number of silver atom. Furthermore, the shape of chromatogram of  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  prepared by the metal exchange changed by leaving this cluster in toluene for 6 days (Figure. 1(c)). Interestingly, the shape was similar to that of  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  prepared by the co-reduction (Figure. 1 (d)). These results suggest that  $\text{Au}_{38-n}\text{Ag}_n(\text{SC}_4\text{H}_9)_{24}$  prepared by the metal exchange contains metastable clusters, these are transformed to the stable clusters by leaving in toluene. In conclusion, we have succeeded in the high-resolution separation of alloy clusters according to each chemical composition, and observation of isomer transformation.



**Figure 1:** (a) Chromatograms obtained by metal exchange, (b) ESI spectrum of each peak in chromatogram, (c) Chromatograms obtained by metal exchange after 6 days, and (d) Chromatograms obtained by co-reduction.

**Recent Publications**

1. Y Negishi, et al. (2016) Precise synthesis, functionalization and application of thiolate-protected gold clusters. *Coord. Chem. Rev.*, 320-321:238-250.
2. Y Negishi, et al. (2016) High-resolution separation of thiolate-protected gold clusters by reversed-phase high-performance liquid chromatography. *Phys. Chem. Chem. Phys. (Perspective)* 18:4251-4265.
3. Y Negishi, et al. (2015) Understanding ligand-exchange reactions on thiolate-protected gold clusters by probing isomer distributions using reversed-phase high-performance liquid chromatography. *ACS Nano* 9: 9347-9356.

4. Y. Negishi, et al. (2015) A critical size for emergence of nonbulk electronic and geometric structures in dodecanethiolate-protected Au clusters. *J. Am. Chem. Soc.* 137:1206-1212.
5. Y. Negishi, et al. (2013) Separation of precise compositions of noble metal clusters protected with mixed ligands. *J. Am. Chem. Soc.* 135:4946-4949.

### **Biography**

Sayaka Hashimoto received her BSc in Applied Chemistry at Tokyo University of Science, Japan, in 2018. Her main research interest and work includes "Establishment of high resolution-separation technique of reversed-phase high-performance liquid chromatography (RP-HPLC)". She has recently succeeded in separating gold-silver alloy cluster by improving the resolution of RP-HPLC.

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