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Microanalysis of Silver and Gold Nanoparticles Used in Surface-Enhanced Raman Spectrometric Characterization of Aminobiphenyl Isomers

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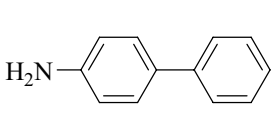
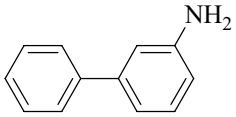
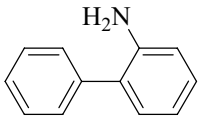
Aromatic amines such as aminobiphenyl (ABP) isomers have been studied by various research groups as putative bladder carcinogens. Among the three isomers, 4-ABP and 3-ABP are reported as human carcinogens and the carcinogenicity of 4-ABP has been shown to be greater than that of 3-ABP [1]. The current methods of detection for ABP isomers and their metabolites include high performance liquid chromatography [2], liquid chromatography/mass spectrometry [3], gas chromatography/mass spectrometry (GC/MS) [4], and electrochemical techniques [2].



4-Aminobiphenyl



3-Aminobiphenyl



2-Aminobiphenyl

Raman spectroscopy is capable of detecting ABP isomers at very low concentrations via surface–enhanced Raman scattering (SERS), in which the Raman signal is enhanced by the presence of silver nanoparticles that allow the adsorption of analytes. The shape and size of the silver nanoparticles play an important role in influencing the magnitude of the signal enhancement [5]. Silver and gold colloidal nanoparticles prepared under different synthesis and centrifugation conditions have been characterized by transmission electron microscopy (TEM) in conjunction with the "Image J" image processing software in order to correlate the physical characteristics of particles with the degree of Raman signal enhancement. It was found that nebulization of colloidal nanoparticles using either a pneumatic or ultrasonic nebulizer was suitable for preparing TEM specimen grids that gave good images with no appreciable overlap or aggregation of nanoparticles. Further analysis of the ABP isomers by Raman microscopy also showed that the SERS enhancement factor of 4-ABP is significantly larger than those of 2-ABP and 3-ABP for both gold and silver colloids. The spectral differences of the Raman spectra of the neat ABP isomers versus their SERS spectra will be described with regard to the changes in the intensities, positions, and shapes of the peaks.

Raman signal enhancement is highly dependent on the rate of 4-ABP adsorption onto the silver nanoparticles. The SERS signal was found to increase from the time of mixing the colloid and 4-ABP up to 4 hours followed by a gradual decrease over a 24-hour period. The adsorption kinetics is further studied by solid phase micro extraction in conjunction with gas chromatography-mass spectrometry (GC-MS) to provide a better understanding of the adsorption process among the three ABP isomers in order to develop an optimal method for their analysis.

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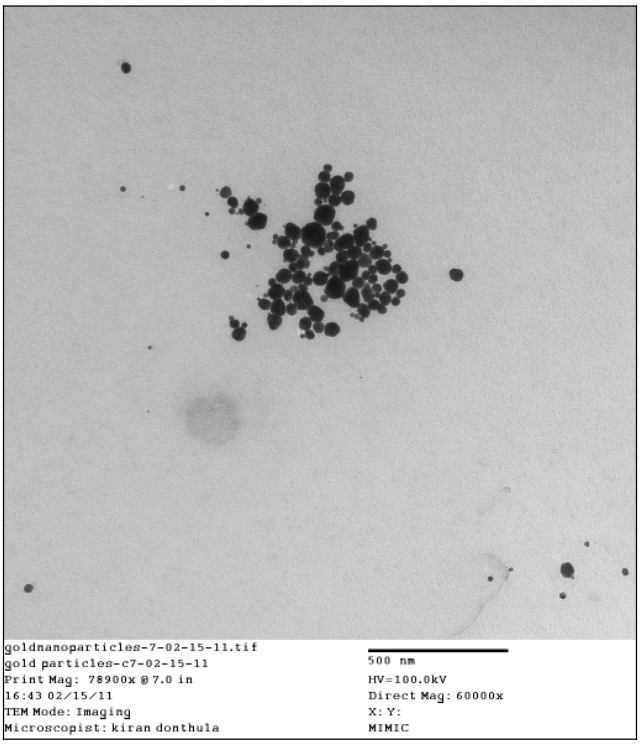

FIG. 1. TEM micrograph of gold nanoparticles prepared by reducing gold chloride solutions with using sodium citrate.

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