The nature of analyte species collected on a cooled silica tube for atom trapping atomic absorption spectrometric determination was investigated using electron spectroscopy. XPS spectrum of gold deposited on atom trapping silica tube reveals a Au 4f\(_{7/2}\) peak with a binding energy of 84.8(±0.2) eV which falls in the middle of the binding energies corresponding to zerovalent Au(0) at 84.0 eV and that of monovalent Au(I) at 85.2 eV. The corresponding energy for Au vapor deposited on silica is also 84.8 eV. Deposition of AuCl\(_4^-\) solution on silica results in two different Au 4f\(_{7/2}\) peaks with binding energies of 84.8 and 87.3 eV corresponding respectively to Au(0) and Au(III). Deposition of the same AuCl\(_4^-\) solution on platinum metal gives again two peaks, this time at 84.4 and 87.0 eV energies corresponding again to Au(0) and Au(III). Combining all these data we conclude that gold is trapped on atom trapping silica surface as zerovalent Au(0) with a 0.8 eV matrix shift with respect to the metal surface. A similar 0.6 eV shift is also observed between the binding energy of 4f\(_{7/2}\) Hg\(_2\)\(^{2+}\) measured in Hg\(_2\)(NO\(_3\))\(_2\),2H\(_2\)O powder and that deposited on silica.