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# X-ray Photoelectron Spectroscopic Characterization of Au Collected with Atom Trapping on Silica for Atomic Absorption Spectrometry

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The nature of analyte species collected on a cooled silica tube for atom-trapping atomic absorption spectrometric determination was investigated with the use of X-ray photoelectron spectroscopy (XPS). An XPS spectrum of gold deposited on atom-trapping silica tubes reveals a Au 4f<sub>7/2</sub> 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<sub>4</sub><sup>-</sup> solution on silica results in two different Au 4f<sub>7/2</sub> peaks with binding energies of 84.8 and 87.3 eV corresponding, respectively, to Au(0) and Au(III). Deposition of the same AuCl<sub>4</sub><sup>-</sup> solution on platinum metal again gives 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<sub>7/2</sub> Hg<sub>2</sub><sup>2+</sup> measured in Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O powder and that deposited on silica.

Index Headings: Atom trapping of Au on silica; XPS; Matrix shifts in binding energies.

## INTRODUCTION

Sensitivity of a conventional flame atomic absorption spectrometer (AAS) can be enhanced by using a technique known as *atom trapping*.<sup>1-6</sup> In flame atom-trapping AAS, the main idea is *in situ* preconcentration of analyte atoms. The flame is used as a medium for generating and preconcentrating the atoms before the usual measurement stage. A water-cooled silica tube is mounted in the center and parallel to the burner axis. Upon aspiration of sample solution, analyte atoms condense on the tube for the time required to build up a measurable concentration and are released by shutting off the water and allowing the silica tube to heat up in the flame so that the temperature of the surface of the silica tube rises sufficiently to release the atomic species for detection. In an effort to further increase the sensitivity, the silica tubes were coated by alumina and/or iron oxide. The behavior and optimum conditions for application of the *in situ* preconcentration technique of atomic absorption spectrometry were investigated for 12 elements with the use of an atom-trapping silica tube and compared with those of conventional AAS.<sup>4</sup> From the data collected, it was concluded that the technique was more sensitive than conventional flame AAS by one or two orders of magnitude in the characteristic concentration following *in situ* collection for 2-3 min for most metals and that the relative standard devi-

ation is only slightly less favorable even at these low levels.<sup>4</sup>

Understanding the mechanism of the collection and atomization at the surface of the silica atom trap has been a key issue not only with respect to the atom-trapping technique but also in connection to atomization by electrothermal techniques. Work by Khalighie et al. suggested that there was a linear relationship between appearance time (defined as the time elapsed between the appearance of the absorption signal and the start of the atomization cycle) and the melting point of the metal under study.<sup>3</sup> In a recent study, Ellis and Roberts used a multivariate approach in an attempt to improve the model relating appearance times to elemental physical properties such as melting and boiling points and enthalpies of fusion and vaporization.<sup>6</sup> Their conclusion was that appearance times were related to the melting point and  $\Delta H$  of fusion of the element, suggesting that the elements were removed from the tube surface in a liquid form by the scouring action of the flame gases.

The chemical nature of the trapped species has also been a central issue. With the use of the studies based on the relation between the melting points and appearance times, it was suggested that Au, Ag, Cd, Co, Cu, Pb, Se, and Zn were accumulated as metals, while K, Li, Na, Cr, Mg and Mn were trapped as silicates or oxides. In order to improve sensitivity, the collector tube was coated by aspirating 500 mg/L ammonium metavanadate solution; the yellow stain was investigated by XRD to show the presence of vanadium(III) oxide on the surface.<sup>3</sup> No surface and/or chemical state-sensitive techniques, however, have been employed for the chemical state of analyte species. In a previous study, we reported an investigation of an alternative atomization technique for atom-trapping AAS.<sup>7</sup> In this contribution, we report an XPS investigation of the silica surfaces used for atom trapping of Au after preconcentration step. This, to our knowledge, is the first time that such a direct attempt has been reported.

## EXPERIMENTAL

Silica collector tubes, 6.0 mm o.d. and 4.0 mm i.d. (Quartz Scientific Inc., Ohio), were used as trapping surfaces. The 10-cm slot burner of a Perkin-Elmer Model 305 B atomic absorption spectrometer was used with air and acetylene flow rates regulated by the fuel regulator. Silica tubes were mounted on the flame burner assembly by a holder made from brass, as shown in Fig. 1. Collection (trapping) conditions of Au from the aspirated standard solution on silica were optimized for obtaining

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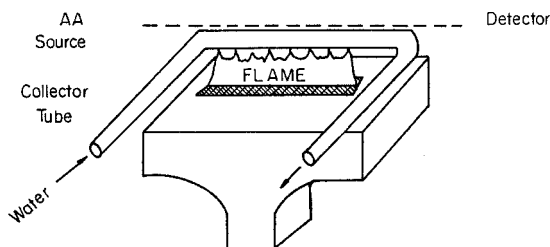


FIG. 1. A schematic diagram of the atom-trapping silica tube used in flame atomic absorption spectrometry.

maximum AAS signal. The height of the silica tube from the burner head was 7.0 mm; flow rates of air and acetylene were 5 L/min and 2.8 L/min, respectively, which corresponded to fuel-lean flame. Forty mg/L of Au solution was aspirated for 10 min with a 5-mL/min aspiration rate. The samples were kept in argon atmosphere until surface analysis.

For calibration purposes, besides the use of a gold metal strip, different samples containing 20, 40, and 100 Å vapor-deposited Au on silica in vacuum were prepared. For preparing Au calibrants with different oxidation states, several drops of 1000-mg/L standard Au solution, which was known to be  $\text{AuCl}_4^-$ , were deposited on silica tubes or on metallic gold and platinum strips that were later dried in air. A similar procedure was followed for preparing mercury calibrants. A 1000-mg/L  $\text{Hg}_2^{2+}$  standard solution was prepared by dissolving  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in water. Several drops of this solution were deposited on silica and dried in air.

XPS measurements were performed on a Kratos ES300 spectrometer with  $\text{MgK}\alpha$  X-rays (1253.6 eV). The measured resolution on the Au  $4f_{7/2}$  peak of the metallic gold was 1.4 eV [full width at half-maximum (FWHM)]. The base pressure in the spectrometer was kept below  $10^{-9}$  mbar during measurement.

## RESULTS AND DISCUSSION

In Fig. 1, a schematic diagram of the atom-trapping silica tube used in this work is shown. Figure 2 displays the XPS spectra of (a) a gold-coated silica tube after the preconcentration step and (b)  $\text{AuCl}_4^-$  solution deposited on silica. For the Au trapped on silica, in addition to the Au 4f doublet, the spectra contains additional C 1s, O 1s, P 2s and 2p, and Si 2s and 2p peaks. Carbon is always present in XPS as a result of hydrocarbon deposits in air and/or vacuum, which is commonly used as an internal energy calibrant at 285.0-eV binding energy. The photoionization cross section of Au 4f is  $17 \times$  larger when compared with that of Si 2p.<sup>8</sup> Hence, when the relative intensities are corrected with the sensitivity factors, the atomic Si/Au ratio can be determined as approximately 50. Considering the fact that the sampling depth in XPS is only 50 Å, the deposited Au can be estimated to be no more than 1–3 atomic layers. The same holds for  $\text{AuCl}_4^-$  deposited on silica.

The question arises as to the chemical nature of Au deposited. The measured binding energy of Au  $4f_{7/2}$  on atom-trapping silica is 84.8 eV with an estimated uncertainty of  $<0.2$  eV. This value falls in the middle of the tabulated binding energy of 84.0 and 85.2 for the zer-

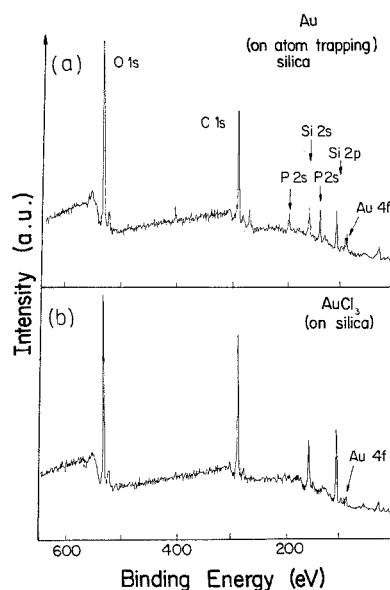


FIG. 2. Part of the XPS spectra (using  $\text{MgK}\alpha$  X-rays) of (a) Au deposited on atom-trapping silica from a 40.0-mg/L Au solution that was aspirated for 10 min with a 5-mL/min aspiration rate, and (b)  $\text{AuCl}_4^-$  solution deposited and dried on silica tube.

ovalent Au(0) and monovalent Au(I), respectively; and is farther away from the tabulated binding energy for the trivalent Au(III), which is 86.7 eV.<sup>8</sup> However, it is also well known that the binding energies shift, depending on the chemical and/or physical environment.<sup>8–10</sup> Calibration using only C 1s levels can be inaccurate, and very careful referencing is needed for more accurate measurements. Gold deposition is, ironically, one of the best methods for referencing other XPS peak energies.<sup>8–11</sup> The  $4f_{7/2}$  binding energy for the gold metal is 84.0 eV, but it is expected that this energy will be shifted on the silica matrix, even if the valency is zero.<sup>8</sup>

To assess the effect of the silica matrix, we prepared Au films with thicknesses varying from 20 to 100 Å by the well-known vacuum deposition technique. The Au 4f binding energy in these films also varies with film thickness, and for the range of 20–40 Å it exactly matches that of Au on the atom-trapping silica, i.e., 84.8 eV. The peaks, however, are broader. The question of the chemical state [whether Au(0) or Au(I)] could still not be resolved. We then deposited Au from the 1000-mg/L stock solution containing  $\text{AuCl}_4^-$  ions that consisted mainly of Au(III) in the solution. The presence of Au(III) in the solution was confirmed from its two UV absorption bands at 324 and 232 nm.<sup>12</sup> After drying in air, the thin solid film, which was expected to be  $\text{AuCl}_3$ , was inserted into the spectrometer and its XPS spectrum was recorded. To our surprise, the Au 4f region consisted of four peaks (a doublet of doublets), as shown in Fig. 3. The very same four peaks were also observed when the  $\text{AuCl}_4^-$  solution deposition was carried out on Pt or even Au foils. These four peaks could be curve-fitted into two  $7/2$ – $5/2$  doublets with an energy separation of 2.7 eV between them. This 2.7 eV exactly matched the binding energy difference between Au(0) and Au(III), indicating that some of Au(III) on the surface of silica or platinum foil was reduced to the zerovalent metallic state. Furthermore, since Pt 4f lines were near (71.2 eV for the  $7/2$  peak in the

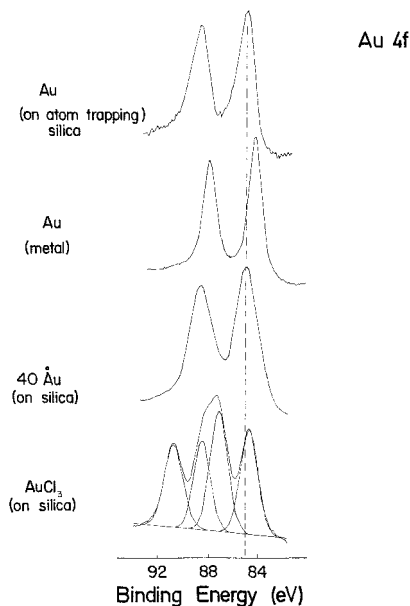


FIG. 3. Au  $4f_{7/2-5/2}$  region of the XPS spectra (using MgK $\alpha$  X-rays) of Au deposited on atom trapping silica, Au metal, 40 Å Au vacuum deposited on silica, and AuCl<sub>3</sub> deposited on silica from the reference 1000-mg/L stock solution of AuCl<sub>4</sub><sup>-</sup> after drying.

metal) to the Au 4f lines, very accurate energy calibration could be achieved.

Figure 3 displays the Au  $4f_{7/2-5/2}$  doublet regions of (1) Au deposited on atom-trapping silica, (2) the metal, (3) 40 Å Au vacuum deposited on silica, and (4) AuCl<sub>3</sub> deposited on silica from the reference 1000-mg/L stock solution of AuCl<sub>4</sub><sup>-</sup> after drying. The spectra of AuCl<sub>3</sub> deposited on Pt and Au metals were also recorded but are not reproduced here. The relevant data are collected in Table I.

The puzzle is solved backwards. AuCl<sub>4</sub><sup>-</sup> deposited on Pt metal gives two gold species, Au(0) and Au(III), with the corresponding  $4f_{7/2}$  binding energies at 84.4 and 87.3 eV, respectively. The same AuCl<sub>4</sub><sup>-</sup> deposited on silica also yields the same two gold species, the binding energies of which are now 0.8 eV higher than the corresponding ones on the Au metal. Hence, the 84.8-eV Au  $4f_{7/2}$  peak observed for the atom-trapping silica can now clearly be assigned to metallic zerovalent Au(0). The 0.8 eV difference between the binding energies on metals and on silica is attributed solely to the matrix effect.

To verify this matrix shift, we carried out similar measurements on Hg 4f levels. Hg is next to Au in the periodic table, with a similar 4f binding energy and cross section, and is also known to have variable valency. Due to the very high vapor pressure of the elemental mercury, measurements were carried out on a compound of Hg in powder form and after deposition on silica. The measured Hg  $4f_{7/2}$  binding energy of Hg<sub>2</sub><sup>2+</sup> on silica is 102.0 eV and is 0.6 eV larger than that of Hg<sub>2</sub><sup>2+</sup> measured in powders of Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O as given in Table I. The matrix shift on Hg 4f is not only in the right direction and but is also comparable in magnitude to the one on Au 4f.

The mechanism(s) of atomization into the flame, de-

TABLE I. Measured binding energies (in eV) and FWHM (shown in parentheses and in eV) of the various Au and Hg  $4f_{7/2}$  peaks using MgK $\alpha$  X-rays.

	Au(0)	Au(I)	Au(III)
Au (deposited on atom-trapping silica)	84.8(1.6)		
Au (metal)	84.0(1.4)		
40 Å Au (vacuum deposited on silica)	84.8(2.2)		
AuCl <sub>3</sub> (deposited on silica)	84.7(1.8)	...	87.4(1.9)
AuCl <sub>3</sub> (deposited on Pt)	84.4(1.9)	...	87.1(2.0)
	<u>Hg(0)</u>	<u>Hg(I)</u>	
Hg (metal)	99.9 <sup>a</sup>	...	
Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	...	101.2 <sup>a</sup>	
Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O (powder)	...	101.4(2.0)	
Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O (deposited on silica)	...	102.0(2.0)	

<sup>a</sup> From Ref. 8.

position onto the (water-cooled) silica surfaces during preconcentration, and later atomization from the surface of the reheated silica back into the flame are relatively complex and are believed to involve active participation of both flame constituents and silica surfaces. The roles played by each process, we believe, are different for each element. Elucidating the roles of all or part of the constituents will not only aid in understanding the mechanism(s) but will also help improve the sensitivity of the relatively simple, widely used, and almost interference-free analytical tool, flame atomic absorption spectrometry. In this work, our contribution has been the determination of the chemical state of the trapped Au on silica, and we are presently carrying out similar measurements on other elements.

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