

XPS Characterization of Bi and Mn Collected on Atom-Trapping Silica for AAS

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The chemical state of analyte species collected on a water-cooled silica tube during atom-trapping atomic absorption spectrometric determination is investigated with the use of X-ray photoelectron spectroscopy (XPS) for Bi and Mn. Analysis of the Bi 4f_{7/2} peak reveals that the chemical state of Bi is +3 during initial trapping (before the atomization stage), but an additional 0-valence state of Bi is also observed after the atomization stage. With the use of the measured Mn 2p_{3/2} binding energy together with the observed 3s multiplet splitting, the chemical state of Mn is determined as +2 in all stages. Together with our previous determination of 0 valence for Au, it is now postulated that the stability of certain valence states of the three elements (Au, Bi, and Mn) on the silica matrix can be correlated to their electrochemical reduction potentials.

Index Headings: XPS; Valence state determination of Bi and Mn; Multiplet splitting in XPS; Atom-trapping silica; AAS.

INTRODUCTION

The technique called atom trapping is known to enhance the sensitivity of conventional flame atomic absorption spectrometry (AAS).¹⁻⁶ *In situ* preconcentration of analyte atoms is the goal in flame atom-trapping AAS. The flame is used as a medium for both generating and preconcentrating the atoms before the measurement. A silica tube that is water cooled is mounted in the center and parallel to the burner axis to condense the analyte atoms from the flame after the initial aspiration of the sample solution for the time required to build up a measurable concentration. The condensed species are released back into the gas phase 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. The behavior and optimum conditions for application of the *in situ* preconcentration technique of atomic absorption spectrometry were investigated for 12 elements by using an atom-trapping silica tube and were compared to those of conventional AAS; 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 deviation is only slightly less favorable even at these low levels.⁴

Not only is the mechanism of the collection and atomization at the surface of the silica atom trap an important issue with respect to the atom-trapping technique; it is also thought to have some relevance to atomization by electrothermal techniques. 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.³ 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 other thermodynamic variables such as heat of fusion and vaporization.⁶ Their conclusion was that appearance times were related to the melting point and ΔH 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 key crucial issue. Lau et al., by trapping concentrated solutions (500 ppm) for a minute or two, observed the formation of mechanically strong coatings of metals such as Ag, Cu, Fe, etc., except for Cr, which gave a green deposit suggesting oxide formation on the silica tube.¹ By physical examination of deposits after spraying strong solutions of Au, Ag, Cd, Co, Cu, Pb, Se, and Zn it was determined that these elements accumulated as metals, and this determination was confirmed by X-ray crystallographic and electron microscopy measurements.⁴ However, Ca, Cr, K, Li, Mg, Mn, Al, V, and Na were trapped as silicates or oxides.^{3,4} In all previous investigations, very concentrated solutions of analyte were used; however, no techniques that were sensitive to the surface and/or chemical state have been employed for the chemical state of analyte species. In a previous study we reported the first XPS investigation of the silica surfaces used for atom trapping of Au after preconcentration and also atomization steps.⁷ We now extend our analysis to include Bi and Mn.

EXPERIMENTAL

Silica collector tubes, 6.0 mm o.d. and 4.0 mm i.d. (Quartz Scientific Inc.), were used as trapping surfaces. The 10 cm slot burner of a Perkin-Elmer Model 305B 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 described in our previous publication.⁷ Collection (trapping) conditions of elements from the aspirated standard solution on silica were optimized for obtaining the maximum AAS signal. Analyte solutions containing 10–100 mg/L of Bi or Mn solution were aspirated for 10 min with a 5 mL/min aspiration rate. XPS measurements were performed on a Kratos ES300 spectrometer with MgK α X-rays (1253.6 eV). The base pressure in the spectrometer was kept below 10⁻⁹ mbar during measurement. Drops of solutions containing

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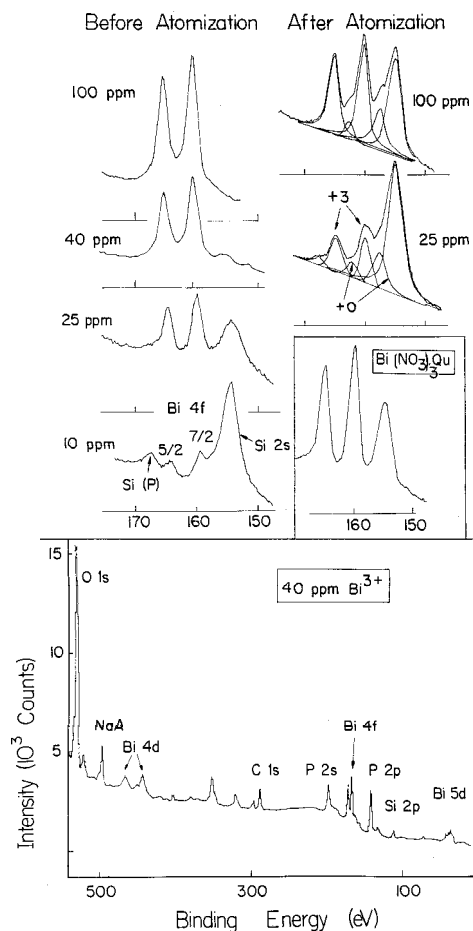


FIG. 1. XPS spectra (using MgK α X-rays) of Bi deposited on atom-trapping silica from a 40.0 mg/L of Bi stock solution that was aspirated for 10 min with a 5 mL/min aspiration rate. In the upper part of the diagram the Bi 4f region (which overlaps with the Si 2s peak) is shown in detail for different solutions used before and after atomization stages. The spectrum of Bi(NO₃)₃ deposited on quartz is also given for comparison. After atomization, a new set of doublets (assigned to 0-valence Bi) can also be observed.

100 ppm stock solutions of Bi and Mn were deposited on quartz plates and were analyzed after allowing for evaporation of the solvent and drying steps. Spectra of reference compounds such as Bi(NO₃)₃, Mn(NO₃)₂, and MnO₂ in their powdered forms were also recorded for comparison.

RESULTS

Bismuth. In Fig. 1, XPS spectra of 40 ppm Bi collected on the atom-trapping silica are shown in full detail. In addition to Bi and Si peaks, O 1s, C 1s, P 2s and 2p, and Na_{KLL} Auger peaks are the other prominent features. The strong Bi 4f region and Si 2s peak overlap, as shown on top of the figure. The Bi 4f features get stronger relative to the Si 2s peak as the concentration increases from 10 to 100 ppm. In the same figure, the Bi 4f region of Bi(NO₃)₃ deposited on quartz is also shown. The relevant data are collected in Table I. Assignment of the chemical state in the case of Bi is relatively straightforward since our measured binding for the 4f_{7/2} peak of the Bi deposited on the atom-trapping silica tube is 160.0 eV and the

TABLE I. Measured and tabulated binding energy Bi 4f levels.

	4f _{7/2} (eV)		4f _{5/2} (eV)	
	This work	Others	This work	Others
Bi (m)	...	156.9 ^a	...	162.2 ^a
Bi (on silica)	156.9, ^b 160.0 ^c	...	162.2, ^b 165.3 ^c	...
Bi(NO ₃) ₃ (powder)	159.8	...	165.1	...
Bi(NO ₃) ₃ (on quartz)	160.0	...	165.3	...
BiOCl	...	159.9 ^a	...	165.2 ^a
BiF ₃	...	160.8 ^a	...	166.1 ^a

^a Reference 8.

^b Observed only after the atomization stage and assigned to Bi(0).

^c Observed both before and after the atomization stages and assigned to Bi(III).

corresponding ones for metallic Bi (0) and Bi (+3) in Bi(NO₃)₃ are 156.9 and 160.0 eV.⁸

Figure 1 also contains spectra after the atomization stage where additional peaks appear on the lower binding energy side between the 4f_{7/2} and the Si 2s peak, which can be curve-fitted to another set of doublets at 156.9 and 162.2 eV and can also easily be assigned to the Bi 4f_{7/2} and 4f_{5/2} doublet of the 0-valence Bi by using both our measured and other tabulated values. Hence, the bismuth is initially trapped as +3 and is partially converted to 0 valence after (and/or during) the atomization stage.

Manganese. In Fig. 2 we display part of the XPS spectra of 40 ppm Mn collected on the atom-trapping silica tube together with Mn(NO₃)₂ and MnO₂ deposited on quartz for comparison. The conventional XPS analysis of Mn is usually carried out in the 2p region around 640 eV since the 2p has the highest photoionization cross section. However, assigning the chemical state is difficult, if not impossible, due to the proximity of the binding energy values. For example, 2p_{3/2} binding energies are 638.8,

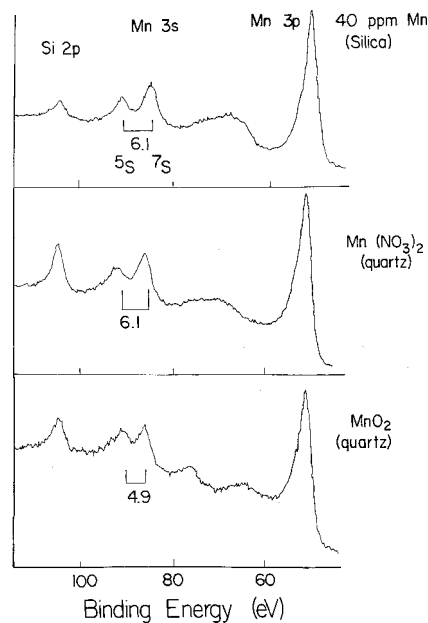


FIG. 2. The 3s-3p region of the XPS spectra (using MgK α X-rays) of Mn; (top) 40 ppm Mn collected on atom-trapping silica; (middle) Mn(NO₃)₂ deposited on quartz; and (bottom) MnO₂ deposited on quartz. The 3s region exhibits a multiplet splitting due to the coupling (parallel or antiparallel) of the remaining 3s electron with the unpaired valence electrons. The magnitude of this splitting can also be used to determine the chemical state of Mn (see text).

TABLE II. Measured and tabulated 2p binding energies and 3s splittings of Mn.

	2p _{3/2} (eV)		ΔE 3s (eV)	
	This work	Others	This work	Others
Mn (m)	...	638.8 ^a
Mn (on silica tube)	642.6	...	6.1	...
Mn(NO ₃) ₂ (powder)	642.8	...	6.0	...
Mn(NO ₃) ₂ (on quartz)	643.0	...	6.1	...
MnCl ₂	...	642.0 ^a	...	6.0 ^b
MnO	5.9 ^c
Mn ₃ O ₄	...	641.4 ^a
Mn ₂ O ₃	...	641.6 ^a	...	5.2 ^c
MnO ₂ (powder)	642.8	642.6 ^a	4.8	4.5 ^c
MnO ₂ (on quartz)	643.0	...	4.9	...

^a References 8 and 9.

^b References 9 and 10.

^c References 9 and 11.

642.0, 641.4, 641.6, and 642.6 eV for Mn, MnCl₂, Mn₃O₄, Mn₂O₃, and MnO₂, respectively (see Table II).^{8,9} Furthermore, this region is crowded by the strong shake-up satellites as well. When paramagnetic atoms or ions are present, there are additional features in the XPS spectra due to paramagnetic splitting, which could also be used to aid chemical state assignment.^{9,12} For example, the 3s peaks in Mn is split into two as a result of the coupling of the remaining 3s electron in the parallel or antiparallel spin state to the spin of the unpaired 3d electrons of the atom or ion. The observed multiplet splitting is 5.9, 5.2, and 6.0 eV for MnO, Mn₂O₃, and MnCl₂ but is around 4.5 eV for MnO₂.^{9-11,13} As shown in Fig. 2, our measured values for Mn(NO₃)₂ and MnO₂ of 6.1 and 4.9 eV, respectively, are in very good agreement with previously reported values. Accordingly, the measured 6.1 eV multiplet splitting in Mn trapped on the silica tube points to a value of +2 for the chemical state of Mn both before and after the atomization stage.

DISCUSSION

Most of the previous efforts concentrated on correlation of the appearance times to certain properties of elements, and only some physical measurements were employed for determination of the chemical species on the trap.¹⁻⁶ The question now concerns determination of the fundamental thermodynamic property of the elements/oxides affecting the stabilization of certain valence states on the silica matrix before and after the atomization stages. A somewhat related situation is encountered during XPS analysis and Ar⁺ ion etching for cleaning the surfaces and/or depth profiling. Certain elements such as Au, Bi, V, Cr, and Mo are readily reduced under X-ray and Ar⁺ bombardment, while others are stable.¹⁴ Attempts to correlate this effect to free energy in the formation of metal oxides have not been successful.^{14,15} As was also shown in our previous work, Au(III) readily undergoes partial reduction to Au(0) during simple deposition onto the silica tube and platinum foil or during XPS analysis, but no discussion relating to the various thermodynamic factors was given.⁷

We now suggest that the electrochemical reduction potential is the factor for determining the stability of certain valence states of the elements, although they are only tabulated for aqueous solutions.¹⁶ Previously discussed

TABLE III. Melting points, heats of fusion, free energy of formation of the oxides, and standard reduction potentials of Au, Bi, and Mn.⁽¹⁶⁾

Chemical state		MP (K)	ΔH _{fus} (kJ/mol)	ΔG _{for} (kJ/mol)	ε ⁰ _{red} (V)
(in analyte)	(on silica)	(of the metal)		of the oxide	in aq sol
Au ³⁺ (aq)	Au ⁰	1337	12.6	+163	+1.50
Bi ³⁺ (aq)	Bi ³⁺ , Bi ⁰	544	11.3	-494	+0.31
Mn ²⁺ (aq)	Mn ²⁺	1519	14.4	-363	-1.18

thermodynamic properties such as melting points, heat of fusion, and free energy of formation of the oxides are given together with the standard reduction potentials for the three elements—Au, Bi, and Mn—in Table III. As is evident from the table, no obvious correlation exists between melting points, heat of fusion of the metals, or free energy of the oxides. However, a surprisingly strong correlation can be found between their electrochemical reduction potentials in aqueous solutions. Gold and manganese are more stable in their metallic (0) and +2 states due to their positive (+1.50 V) and negative (-1.18 V) reduction potentials, respectively; bismuth is intermediate and is observed in both +3 and 0 valence states as reflected by its nearly 0 V reduction potential. It is not reasonable to expect that aqueous electrochemical stability can be directly related to stability on silica matrices for every element, but it can be stated that the physicochemical parameters responsible seem to follow similar trends at least for these three elements.

CONCLUSION

Processes leading to atomization into the flame, deposition 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. We believe that the roles played by each part are different for each element, as clearly demonstrated by this work together with our previous study.⁷ Understanding the roles of all or part of the constituents will not only improve our knowledge about the mechanism(s) but will also help to 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 states of the trapped Bi and Mn on silica. Together with our previous work on Au, we have demonstrated that the elements can be trapped (1) in the reduced state, (2) in a partly reduced and partly oxidized state, and (3) in the oxidized state. Furthermore, the stability of a certain valence state can be correlated with electrochemical reduction potentials.

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1. C. Lau, A. Held, and R. Stephens, *Can. J. Spectrosc.* **21**, 100 (1976).

2. J. Khalighie, A. M. Ure, and T. M. West, *Anal. Chim. Acta* **107**, 191 (1979).
3. J. Khalighie, A. M. Ure, and T. M. West, *Anal. Chim. Acta* **117**, 257 (1980).
4. T. West, *Anal. Proc.* **25**, 240 (1988).
5. S. H. Wen, Y. Li-Li, and Z. D. Ciang, *J. Anal. At. Spectrom.* **11**, 265 (1996).
6. L. A. Ellis and D. J. Roberts, *J. Anal. At. Spectrom.* **11**, 259 (1996).
7. Ş. Suzer, N. Ertaş, S. Kumser, and O. Y. Ataman, *Appl. Spectrosc.* **51**, 1537 (1997).
8. D. Briggs and M. P. Seah, *Practical Surface Analysis*, Vol. 1, *Auger and X-Ray Photoelectron Spectroscopy* (Wiley, Chichester, 1996), 2nd ed.
9. J. S. Foord, R. B. Jackman, and G. C. Allen, *Philosophical Magazine A* **49**, 657 (1984).
10. J. C. Carver, T. A. Carlson, L. C. Cain, and G. K. Schweitzer, in *Electron Spectroscopy*, D. A. Shirley, Ed. (North-Holland, Amsterdam, 1972), pp. 803–812.
11. L. Z. Zhao and V. Young, *J. Electron. Spect. Relat. Phenom.* **34**, 45 (1984).
12. M. Kantcheva, M. U. Kucukkal, and Ş. Suzer, *J. Mol. Structure*, paper to appear in 1999.
13. C. S. Fadley, in *Electron Spectroscopy: Theory, Techniques and Applications*, C. R. Brudle and A. D. Baker, Eds. (Academic Press, London, 1978), Vol. 2, pp. 781–801.
14. K. S. Kim, W. E. Baitinger, J. W. Amy, and N. Winograd, *J. Electron. Spect. Relat. Phenom.* **5**, 351 (1974).
15. S. Storp, *Spectrochim. Acta* **40B**, 745 (1985).
16. *Handbook of Physics and Chemistry* (CRC Press, Boca Raton, Florida, 1995), 75th ed.