

Study of Palladium–Analyte Binary System in the Graphite Furnace by Surface Analytical Techniques

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The mechanisms of the stabilization of Pb, Zn and As by a palladium modifier were investigated by scanning electron microscopy, X-ray diffraction spectrometry and X-ray photoelectron spectrometry. All three elements were found to form an intermetallic solid solution with excess of Pd. The concentration ratio of Pd to analyte varies with the surface depth of Pd–analyte species. Chemical shifts measured in the binding energy of Pd and analyte are insignificant. The monophase of the Pd lattice in which some Pd atoms are displaced by the analyte atoms has been identified as being dominant. It is suggested that the reduced Pd and analyte form a stable intermetallic solid solution during the ashing stage and the analyte atoms remain in the Pd lattice until the temperature is high enough to break down the lattice.

Keywords: Palladium modifier; electrothermal atomic absorption spectrometry; surface analysis; atomization mechanism

Since Shan and Ni¹ first reported the use of Pd as a stabilizer for Hg in 1979, Pd has been widely employed as a matrix modifier for many volatile elements in electrothermal atomic absorption spectrometry (ETAAS).^{1–10} Recently, this modifier has been demonstrated to be also a very effective adsorbent for trapping hydrides.^{10,11} However, the mechanism of the Pd modification is still not well understood.

Early investigations on the formation of Pd–Pb and other binary systems were carried out by Shun¹² in 1981. Later, Shan and Wang¹³ reported that the formation of Pb–Pd and Bi–Pd bonds could be determined from the shift of binding energies by X-ray photoelectron spectrometry (XPS). More recently, Wendl and Muller-Vogt¹⁴ reported some interesting results of X-ray diffraction (XRD) spectrometry, showing the presence of Pd₃Pb and Pd₃Pb₂ intermetallic compounds in the graphite furnace, but no further data were available.

The reduction of Pd has been testified as a necessary step by several workers. Voth-Beach and Shrader¹⁵ applied an additional reducing agent to the Pd modifier such that Pd is reduced to the metallic form early in the temperature programme, resulting in a high ashing temperature for analytes. A similar observation was reported by Teague-Nishimura *et al.*,¹⁶ who observed that Se can be stabilized by Pd effectively in the presence of ascorbic acid. Recently, Rettberg and Beach¹⁷ employed 5% hydrogen as a sheath gas during the Pd pre-treatment step, and found that the Pb signal recovery was nearly consistent from 200 to 1000 °C.

In order to clarify the mechanism of the stabilization of analytes by a Pd modifier, many fundamental studies need to be pursued, especially those related to the surface chemistry of Pd. In this work, the surface interaction between Pd and analytes on the graphite platform was investigated. Three surface analytical techniques, XPS, XRD spectrometry and scanning electron microscopy (SEM), were applied to determine the species generated on the graphite platform. Possible mechanisms are proposed and discussed.

Experimental

Instrumentation

The sample pre-treatment was performed on a Perkin-Elmer 3030 atomic absorption spectrometer fitted with an

HGA-500 graphite furnace. In all experiments, pyrolytic graphite platforms (Perkin-Elmer, part No. B010-9324) were utilized to hold the samples.

The XRD spectra were obtained by a Rigaku/New X-ray diffraction system (Rotaflex D/max-c Series), equipped with a copper target source. The samples were scanned over 20–120° diffraction angles at a scanning rate of 6° min⁻¹. Computerized data acquisition and data processing systems were employed to collect the data and analyse the results.

Scanning electron micrographs of sample surfaces were accomplished using a Hitachi S-520 instrument, associated with an EDAX-9100 X-ray energy dispersion analyser.

The XPS was applied to characterize the surface compounds of the Pd–analyte system on the graphite platform. The instrument used was an Escalab MK II (VG Analytical) equipped with a magnesium target (K α) and fitted with an argon ion gun (5 kV) for sputtering the surface layer. The erosion rate was approximately 1 nm min⁻¹ at 30 μ A current with a beam diameter of \approx 8 mm. The instrument is also capable of performing measurements of accompanied Auger electron spectra (AES).

Reagents and Solutions

Analytical-reagent grade chemicals were used. A Pd stock solution was prepared by dissolution of Pd powder (99.999%) in a minimum amount of concentrated HNO₃–HCl, diluted to a final concentration of 4 g l⁻¹. Stock solutions (1 g l⁻¹) of Pb and Zn were prepared from the chlorides and of As from the arsenite. The sheath gas was pure argon (99.99%).

Procedure

In the general procedure, the sample solution was placed on the platform and dried at 100 °C for 1–2 min, and this process was repeated until the required amount of sample had accumulated. The sample was then ashed at a designated temperature for more than 2 min. Particularly when the sample was prepared as a Pd–analyte system, an ashing temperature of 1000 °C was applied and, when an analyte-only sample (Pb, As and Zn) was ashed as a reference system in the absence of Pd, a temperature of 300 or 400 °C was used to avoid losses of the analyte due to overheating. After cooling, the graphite platform was carefully removed

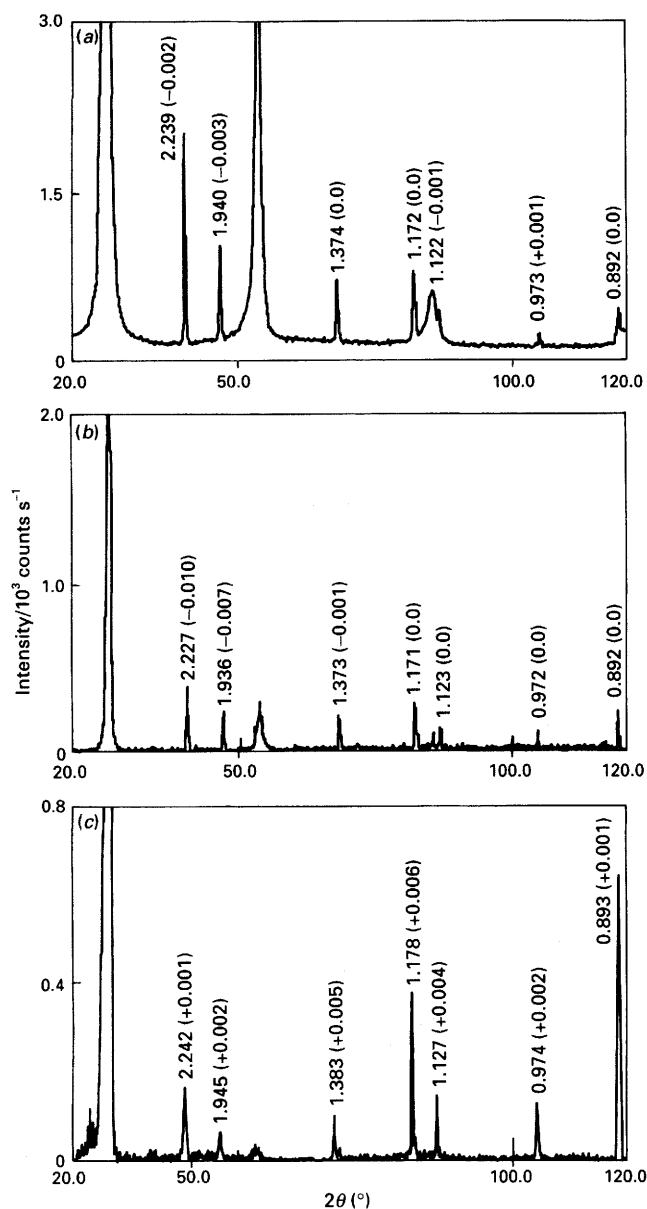


Fig. 1 XRD of Pd-analyte system: (a) Pd-Pb species; (b) Pd-As species; and (c) Pd-Zn species with surface sputtered by a 5 keV, 30 μ A argon ion beam for 30 min. The sample was ashed on the graphite platform at 1000 $^{\circ}$ C for 4 min prior to obtaining the spectra. (This sample treatment also applies to the spectra shown in Figs. 2–5 unless specified otherwise.) For the marked values above the identified peaks, the first number is the experimental d -parameter of the Pd-analyte system, and the second number in parentheses is the deviation of this d -parameter relative to the experimental d -parameter for a pure Pd system. The three unmarked, wide peaks refer to graphite carbon

from the graphite tube and stored in a sealed glass tube purged with argon gas. No further sample treatment was carried out before using the sample for surface testing. The waiting time between sample preparation and testing could last from a few minutes to several hours depending on the instrument loading. No on-line experimental measurements were considered owing to difficulties with the required instrumentation.

The amount of analytes and Pd were usually 1000–10 000 times greater than those applied in a normal routine analysis, mainly owing to the less sensitive detection capabilities of the surface analytical instruments employed. The amount of samples were 4 mg for Pd, 0.07 mg for As,

0.05 mg for Pb and 0.05 mg for Zn in the Pd-As, Pd-Pb and Pd-Zn systems tested, respectively.

In XRD analysis, the XRD spectrum for the pure Pd sample was obtained first, and served as a reference standard prior to the subsequent identification of other spectra.

Results and Discussion

XRD Results

Palladium can form a number of binary systems (or alloys) with many volatile elements exhibiting some similar feature in their phase diagrams.¹⁸ The solubility of a volatile element in Pd is about 10–20% in a Pd monophase, and the binary system formed is called an intermetallic solid solution. An intermediate phase would appear only when a large amount of the doped volatile element is present, and an intermetallic compound could result. The formation of an intermetallic solid solution or compound can be identified by the XRD technique.

Fig. 1(a) shows the XRD spectrum of the Pd-Pb binary system. All peaks were carefully identified against the standard powder diffraction d -values for Pd.¹⁹ It was surmised that some major peaks of a Pd_xPb_y ($x, y = 1-3$) compound would appear¹⁴ in an intermediate phase. Unfortunately, the major peaks illustrated in Fig. 1(a) virtually correspond to a Pd monophase with a corresponding peak sequence and intensity order. Hence no peak for a Pd_xPb_y intermetallic compound was observed with the sensitivity of the XRD instrument used in this work. The amount of Pb was purposely increased to 0.3 mg to increase the ratio of Pb to Pd, but the peaks of Pd_xPb_y and of Pb were barely visible.

It was evident that the XRD spectrum for the Pd-As binary system also does not exhibit peaks for Pd_xAs_y and As, as depicted in Fig. 1(b). In Fig. 1(b) all peaks are identified as being for the Pd α -monophase. The XRD spectra were also taken for both the surface and inner layer of the Pd-Zn system and the spectrum for the inner layer is illustrated in Fig. 1(c). Again, no peak other than for a Pd monophase can be seen.

Small shifts in the powder diffraction d -values between the pure Pd and Pd-analyte systems were observed and the order of peak intensities also differs from that for pure Pd, as indicated in Fig. 1(a)–(c). For instance, the corresponding shift in the d -value for the Pd-As system is about 0.01.

As is known from the phase diagram, the presence of an intermediate phase (e.g., a Pd_3Pb_2 phase) is hardly possible on the basis of the solubility of Pb in Pd metal when the ratios of Pd to analytes are greater than 10:1. The experimental results are essentially in good agreement with the phase diagrams of Pd-Pb,²⁰ Pd-Zn²¹ and Pd-As.²²

SEM Results

The displacement energy spectrum of the Pd-As system was scanned by the SEM X-ray microanalyser. The As species, which could not be directly identified in the XRD spectrum, exhibits a strong peak in the spectrum obtained. From the data acquired by the X-ray microanalyser, the surface mole ratio of Pd to As was roughly obtained from several speckles on the sample surface, having a value close to 3:1 analogous to that reported previously.¹¹ Because the electron beam can penetrate 1–3 μ m below the surface, caution should be exercised when SEM results are applied to interpret surface chemical phenomena.

Particular consideration was given to acquiring an image map of species on the surface such as those reported in a similar experiment on a Pd-Se system.¹⁶ The image maps of As and Pd $L\alpha$ emission, scanned ten times over a surface

speckle of the sample by the X-ray microanalyser, were obtained. The developed micrographic films displayed no bright spots for either Pd or As.

XPS Results

Fig. 2 illustrates the binding energy for Pb species in the absence and presence of Pd. The spectra were analysed against the reference value.²³ When the Pb species (added as PbCl₂ solution) exists in the absence of Pd, the XPS peak corresponds to that of PbCl₂ and/or PbO (curve A, the 0.7 eV gap in binding energy between PbCl₂ and PbO is not readily distinguishable). In the presence of Pd, double peaks appear in the spectrum. The peak of 138.5 eV was identified as a mixture of PbCl₂ and/or PbO and the other peak of 136.8 eV was Pb metal, when the added amount of Pb is large (curve B) or small (curve C). The presence of surface oxygen and chlorine was examined by XPS scanning around 284.7 eV for oxygen and 198.8 eV for chlorine. The peak height for Pb is much greater than that for PbCl₂ and PbO, indicating that the reduction of PbO seems to be sufficient in the presence of Pd.²⁴

An argon ion beam was utilized to sputter the surface layer to determine the variation of the amount of Pb with increasing surface depth. The spectra obtained are also displayed in Fig. 2. Curves C (without sputtering), D (3 min sputtering) and E (6 min sputtering) have similar profiles, indicating that the distribution of Pb atoms is nearly uniform in the tested layer. The mole ratio of Pd to Pb was calculated to be about 14:1 using Wagner's approach.²⁵

The measured shift of Pb binding energy in the Pd-Pb system was found to be relatively small, within -0.25 eV, and the shift of the Pd binding energy is only about 0.1 eV. This small shift is as expected. As is well known empirically in XPS,²³ intermetallic species usually exhibit smaller shifts in binding energy than those of chemical compounds,

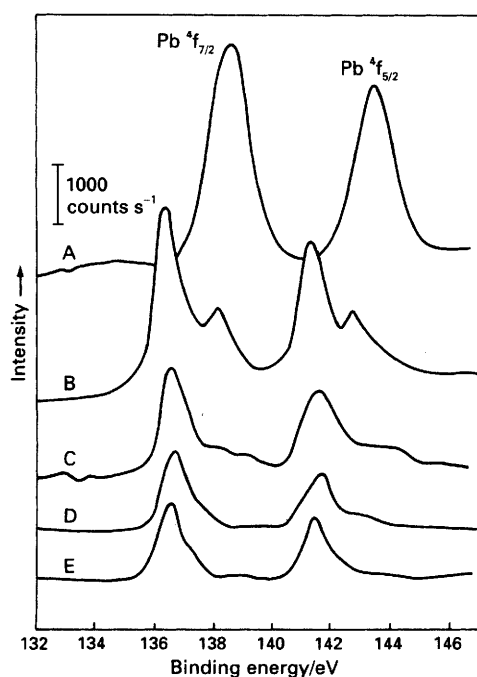


Fig. 2 XPS of Pb species for the Pd-Pb binary system. The standard binding energies are Pb 136.8, PbO 138.2 and PbCl₂ 138.9 eV. A, Surface spectra of PbCl₂ (ashed at 300 °C); B, surface spectra of Pd-Pb system with a ratio of 13:1; C, surface spectra of Pd-Pb system with a ratio of 80:1; D, inner-layer spectra of Pd-Pb after sputtering by a 5 keV, 30 μ A argon ion beam for 3 min; and E, inner-layer spectra of Pd-Pb after sputtering for 6 min

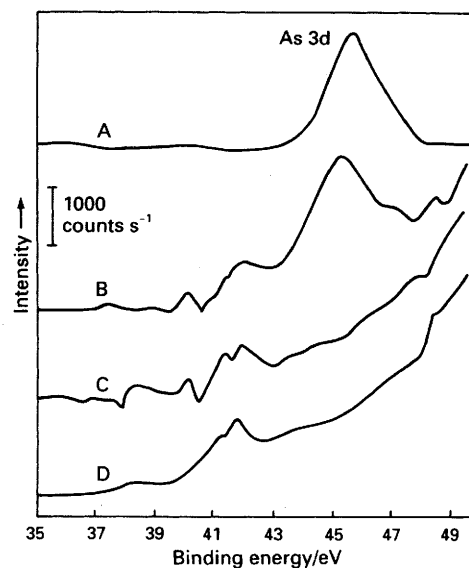


Fig. 3 XPS of As species for the Pd-As binary system. The standard binding energies are As 41.3 and 41.9 and As₂O₃ 44.2 and 44.8 eV. A, Surface spectra of As (As₂O₃ ashed at 300 °C); B, surface spectra of Pd-As system; C, inner-layer spectra of Pd-As after sputtering by a 5 keV, 30 μ A argon ion beam for 5 min; and D, inner-layer spectra of Pd-As after sputtering for 10 min

probably owing to the free electron mobility in the intermetallic binding.

The Pd-As system was investigated in a similar manner and the spectra are illustrated in Fig. 3 for As₂O₃ in the absence of Pd (curve A), and the Pd-As system on the surface (curve B) and on the inner layers after 5 min (curve C) and 10 min (curve D) sputtering by the argon ion beam. The surface As peaks for the Pd-As system (curve B) were identified as being that of As₂O₃ (large peak at 44.2 eV, oxygen was checked by XPS but its source was not identified) and that of As (small peaks at 41.3 and 41.9 eV). However, no As₂O₃ peak appeared on the inner layers (curves C and D).

It can be deduced from Fig. 3 that a large amount of As₂O₃ is present on the surface layer, and that the amount of As species gradually decreases as the surface depth increases. The mole ratio of Pd to As on the surface is about 2:1 compared with 3:1 calculated from the SEM experiment. It is not clear why As₂O₃ could remain on the surface, resisting a 1000 °C ashing. It is possible that the reduction in surface As₂O₃ on the graphite is incomplete even in the presence of Pd. It seems that if As₂O₃ could be reduced completely at an earlier time in the ashing stage, As would be stabilized by Pd more effectively.¹⁶

A shift of 0.1 eV in the Pd binding energy was indicated in the XPS of Pd in the absence and presence of As. A relatively large shift about -0.6 eV in the binding energy of As₂O₃ can be seen in the As spectra in the absence and presence of Pd. However, these shifts do not support the suggestion that the Pd-As system is close to a chemical compound.

It was found that the behaviour of Zn in the Pd-Zn system exhibits a different trend to that of the Pd-Pb system. Fig. 4 shows the Zn spectra on the surface of the Pd-Zn system (curve A) and on the inner layers after sputtering by the argon ion beam for 20 min (curve B), 35 min (curve C), 45 min (curve D), 65 min (curve E) and 85 min (curve F). In contrast to the species in the Pd-As system, surface Zn or ZnO could barely be detected (curve A). As the surface depth increases, the Zn peaks become more and more intense (curves B-D) and finally level off (curves D-F). The absence of ZnO was inferred by XPS owing to blank oxygen signals.

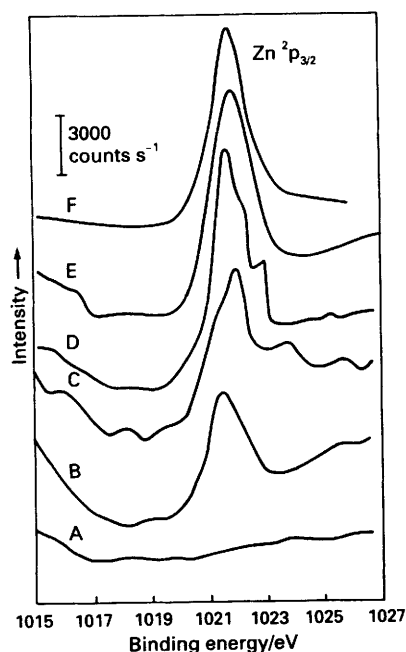


Fig. 4 XPS of Zn species for the Pd-Zn binary system. The standard binding energy for Zn is 1021.45 eV. A, Surface spectra of Pd-Zn system; B, inner-layer spectra of Pd-Zn system after sputtering by a 5 keV, 30 μ A argon ion beam for 20 min; C, inner-layer spectra after sputtering for 35 min; D, inner-layer spectra after sputtering for 45 min; E, inner-layer spectra of Pd-Zn after sputtering for 65 min; and F, inner-layer spectra of Pd-Zn after sputtering for 85 min

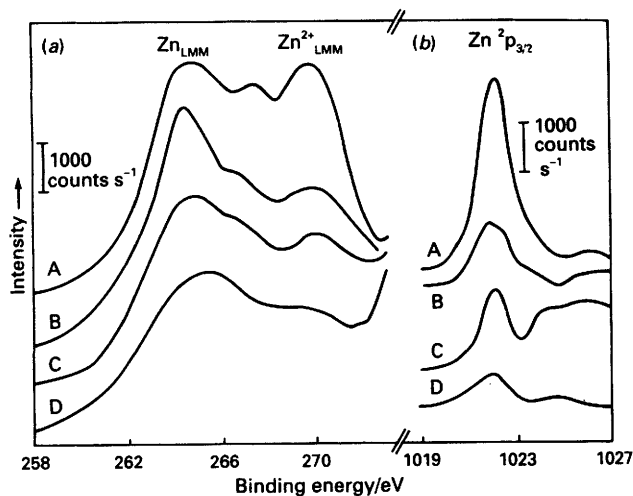


Fig. 5 X-ray photoelectron and accompanying Auger electron spectra of Zn species in the absence of Pd. (a) Auger electron spectrum; the standard binding energies are 264.6 eV for Zn and 269.4 eV for Zn²⁺; and (b) X-ray photoelectron spectrum; the standard binding energy is 1021.45 eV. The ZnCl₂ solution was injected and dried several times to accumulate a total Zn mass of 1 mg; the sample was then ashed at 300 °C for 4 min. A, Spectra for the surface Zn sample; B, inner-layer spectra after sputtering by a 5 eV 30 μ A argon ion beam for 60 s; C, inner-layer spectra after sputtering for 180 s; and D, inner-layer spectra after sputtering for 360 s

The results showed that the shift of Pd binding energy in the Pd-Zn system is again as small as 0.1 eV, and the shift of Zn binding energy is about -0.25 eV. This small shift is in agreement with that explicitly depicted in the Pd-Zn XRD spectrum in which only the Pd monophase is present.

In the absence of Pd, the X-ray photoelectron spectra [Fig. 5(b)] and accompanying Auger electron spectra [Fig. 5(a)] were recorded for Zn, which was added as ZnCl₂ and subjected to a 400 °C ashing temperature. Auger electron spectrometry was used because of its much larger chemical shift in binding energy (4.6 eV) for Zn²⁺ in Auger electron spectrometry than that in XPS (0.6 eV).²⁶ It can be seen from Fig. 5 that the Zn²⁺ (as ZnCl₂ or ZnO) species is dominant on the surface layer [curve A in Fig. 5(a) and (b)]. In the tested inner layer, the proportion of Zn²⁺ is notably smaller and the reduction of ZnO seems to be the major process [e.g., curve D Fig. 5(a)], Zn⁰ was confirmed from a Zn-only Auger electron spectrum). Apparently, most of the surface Zn species are unreduced ZnO species, and would suffer from being lost at a high temperature even in the presence of Pd, as can be seen from comparison of the curves A-D in Fig. 5(b) with curves A-F in Fig. 4.

It seems that Zn, for which the atomization process could be dominated by ZnO dissociation in the gas phase,²⁷ should preferably be reduced early during the ashing stage in order to prevent ZnO from being lost even in the presence of Pd modifier.²⁸

Bond Formation Between Pd and Analyte

Although SEM and XPS indicate the co-existence of analyte and Pd, XRD showed only the Pd monophase. The lack of an intermediate phase for an intermetallic compound confirmed that Pd and the analyte form an intermetallic solid solution. Both the intermetallic solid solution and compound have the features of an intermetallic bond but they are different in structure. In the Pd-analyte solid solution, analyte atoms replace Pd atoms remaining in the monophase rather than forming an intermetallic compound in a new crystal lattice.¹⁸ However, the intermetallic bond between Pd and the analyte is probably the major force in retarding the analyte vaporization to a relatively high ashing temperature.

Weak shifts in the binding energies for the analyte and Pd in their binary system were observed in XPS. These observations provide further support for the above deduction. The intermetallic bond between Pd and the analyte resembles that between Pd atoms in the Pd monophase such that the binding energy shift due to substituted analyte atoms is expected to be small in a Pd-analyte solid solution.

Unfortunately, the formation of an intermetallic bond cannot account for some of the results observed. The amount of Zn atoms increases with increase in surface depth of the Pd-analyte species; in contrast, that of As atoms decreases with increase in depth and that of Pb atoms remains almost constant in different layers. In fact, a large amount of As₂O₃ exists on the surface of the Pd-As system, and a small amount of PbO on that of the Pd-Pb system, but no ZnO exists on the surface of the Pd-Zn system. A possible alternative explanation is that, in addition to the intermetallic bond between Pd and the analyte, the formation of a chemisorbed bond between Pd and Pb or As oxide species might also be chemically feasible,¹¹ attributable to an additional spare electron pair in the electron orbital of As or Pb, which can also form a bond with the Pd d-orbital.²⁹

Conclusion

This study explored the possible mechanisms of Pd as a stabilizing modifier for some volatile elements. It is concluded that the reduced Pd and analyte probably form an intermetallic solid solution in a Pd monophase during the ashing and pre-atomization stages. Hence the analyte atoms can remain in the Pd lattice until the temperature is high enough to break down the Pd lattice.

The shifts of binding energies for the studied system were found to be small. The mole ratio of analyte to Pd varies with the surface depth, depending on the element investigated. It is still unclear why, at a relatively high temperature, As₂O₃ and PbO can exist stably on the surface of the Pd-analyte system but ZnO cannot.

The sample preparation employed in this study suffers from cooling and being exposed to air in addition to the large excess of sample, hence caution should be exercised when the proposed reaction mechanism is applied to real analytical situations.

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