Palladium as a Matrix Modifier in Graphite-Furnace Atomic Absorption Spectrometry of Group IIIB – VIB Elements

Kazuko MATSUMOTO

Department of Chemistry, Waseda University,   Okubo, Tokyo 169, Japan

The performances of palladium as a matrix modifier for group IIIB – VIB elements in graphite-furnace atomic absorption spectrometry were compared to those of other modifiers hitherto reported.   The application of palladium and mixed modifiers containing palladium to biological, mineral sediment or natural water samples is summarized.   The addition of palladium generally makes a higher thermal pretreatment temperature possible without any sensitivity loss, thus reducing the interferences of coexisting materials.   Mass spectrometry connected to graphite-furnace atomic absorption spectrometry enabled real-time observations of the vaporized species in the furnace and revealed the vaporization and atomization process of arsenic and selenium in the presence of palladium.   Both elements form compounds $Pd_nM_mO_l$ (M=As or Se), which are then decomposed to PdM and finally to atomic vapor of M.

Keywords   Palladium, graphite-furnace atomic absorption spectrometry, matrix modifier, group IIIB – VIB elements, atomization mechanism

1   Introduction

The determination of group IIIB – VIB elements at the ultratrace level by graphite-furnace atomic absorption spectrometry (GF-AAS) has traditionally been very difficult.   Hydride generation combined with atomic absorption spectrometry is a method that is often employed, owing to its high sensitivity.   However, the method requires a tedious procedure for each analysis.   The addition of a matrix modifier to the sample solution is another method used to obtain high sensitivity and to avoid any interference.   In fact, GF-AAS is rarely attempted for volatile group IIIB – VIB elements without using matrix modifiers to reduce the analyte loss during the thermal ashing stage, and to maximize free-atom formation during the atomization stage.   Various matrix modifiers have been historically proposed: the concept and term "matrix modification" were introduced more than a decade ago by Ediger, who employed nickel as a modifier for selenium and arsenic determination.[1,2] At about the same time, molybdenum was used as a modifier for selenium determination.[3]   Since then, however, palladium has been increasingly frequently used, and has become widely acknowledged as a universal modifier for group IIIB – VIB elements.   Early reports concerning the potential utility of palladium were filed by Shan and Ni.[4–6]   Although a number of reports appeared thereafter concerning the use of palladium in combination with other modifiers, they mainly focused on practical applications of the modifiers to real samples; little was known about the chemical reactions occurring behind the sensitivity enhancement and the removal of interference.   The employment of advanced physical techniques, such as electron microscopy or mass spectrometry attached to GF-AAS, is providing a powerful tool to observe the physical state of a furnace and to detect any chemical species produced during the thermal processes.   In this article, the following points are reviewed as a recent trend in this field: (1) why palladium is superior to other modifiers for group IIIB – VIB elements; (2) to what degree the mechanism of a palladium modifier is understood; and (3) recent practical applications of palladium modifiers.   Since it has often been reported that the signal peak shape differs depending on the matrix modifier used[7], integrated absorbances are used throughout, except in Table 2.

2   Palladium as a Matrix Modifier and a Comparison with Other Modifiers

Palladium and mixed modifiers containing palladium are   summarized   in   Table 1   together   with   their

Table 1   Palladium as a matrix modifier in GF-AAS

Analyte	Modifier	Sample	Ref.
In	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2$	minerals, sediments, coal fly ash	20
Tl	$Pd(NO_3)_2$	brackish waters, soils, fish tissues	11
		waste waters	21
	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2+glycerol+H_2$		10
Sn	$Pd(NO_3)_2$		11
	$Pd(NO_3)_2+HONH_3Cl$	sediments, natural waters, biological samples	15
	$Pd(NO_3)_2+ascorbic$ acid	biological samples	14
	$Pd(NO_3)_2+(NH_4)_2SO_4$	biological samples	14
	$Pd(NO_3)_2+Mg(NO_3)_2$		12
Pb	$Pd(NO_3)_2+Mg(NO_3)_2$	sea waters	12
	$Pd(NO_3)_2+NH_3$	foods	13
As	$Pd(NO_3)_2$	soils, coal fly ash, biological samples	11, 18, 19
	$Pd(NO_3)_2+NH_3$	foods	13
	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2+ascorbic$ acid	biological samples	14
	$Pd(NO_3)_2+(NH_4)_2SO_4$	biological samples	14
Sb	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2+ascorbic$ acid		25
Bi	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2$	waste waters, sea waters, urines	17
Se	$Pd(NO_3)_2$		4-6
	$Pd(NO_3)_2+albumin$	serums	8
	$Pd(NO_3)_2+ascorbic$ acid	serums	9
	$Pd(NO_3)_2+NH_2OH$	sea waters	10, 11
	$Pd(NO_3)_2+Mg(NO_3)_2$	biological samples	12
Te	$Pd(NO_3)_2$	organically-bound Te	11, 16
	$Pd(NO_3)_2+Mg(NO_3)_2$		12
	$Pd(NO_3)_2+Mg(NO_3)_2$		11

applications to real samples. Various inorganic and organic compounds are used in addition to $Pd(NO_3)_2$. Magnesium nitrate is frequently used together with $Pd(NO_3)_2$ to reduce any interference of chloride and other metal ions, and is generally recommended for analyses of biological materials.[12,22-24] Many of the inorganic and organic modifiers, other than palladium in Table 1, are added in order to reduce $Pd(NO_3)_2$ to Pd metal; many researchers claim that reduced palladium (palladium metal) is a species which is quite effective as a matrix modifier.[10,11]

Palladium fulfills the following requirements for matrix modifiers: (1) it does not reduce the tube lifetime, (2) it does not produce any undesired background around the wavelength of the analyte elements, and (3) it allows a higher ashing temperature than when no palladium is added. For the third reason, a palladium modifier is almost always used when samples of organic matrices, such as biological or food samples, are analyzed. In such samples, group IIIB - VIB elements vaporize more easily at lower temperatures and the detection limits are worsened, compared to those for the corresponding elements in simple inorganic matrices. The addition of

palladium circumvents such vaporization loss of the analyte elements during the ashing stage. Figure 1 shows how the thermal pretreatment and atomization temperatures can be increased by adding palladium and magnesium nitrates. A comparison of the effects of various metal modifiers in selenium determination is shown in Fig. 2, which indicates that palladium is the best choice. A similar comparison of modifiers for other group IIIB - VIB elements also revealed that palladium is the best modifier.[11,12,14]

As an example of one of the severest types of interference and the removal of such interference by palladium, Niskavaara et al. examined the effects of nickel, palladium and ascorbic acid for the determination of antimony in rock samples.[25] They compared the relative sensitivities of antimony in the presence of various matrix elements whose interference to antimony is frequently encountered in rock analyses. Table 2 summarizes the results; it is clear that: (1) palladium gives slightly better results than does nickel, except when a mixed matrix of Mn, Co, Cu, Ni, Zn, Pd and Cd is present; (2) the negative interference of manganese, iron and a mixture of Fe, Mn, Co, Cu, Ni, Zn, Pd and Cd
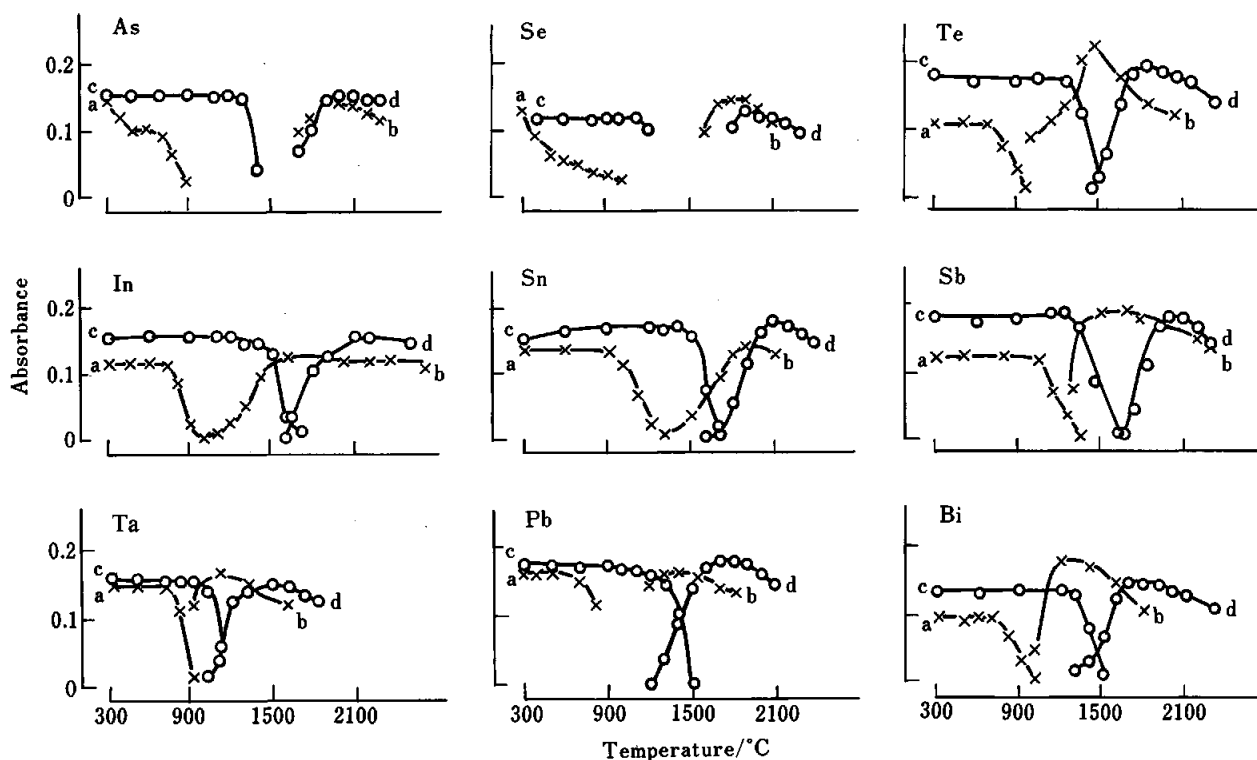
Fig. 1   Thermal pretreatment and atomization curves for nine elements without using a modifier (curves a and b) and with palladium and magnesium nitrates (curves c and d).   Ten microliters of a solution containing 3000 mg l⁻¹ of Pd and 2000 μg l⁻¹ of Mg(NO₃)₂ was added to the sample solution.   Inserted pyrolytic graphite platforms (L'vov platform) were used, and the integrated absorbance values are shown.   Reprinted from Ref. 12 with permission (© 1986, Pergamon Journals Ltd.).
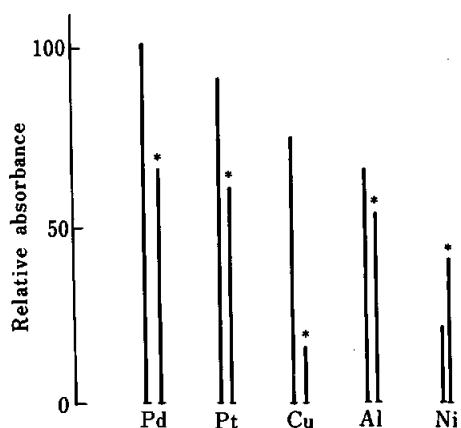

Fig. 2   Comparison of the effects of Pd, Pt, Cu, Al and Ni on the Se sensitivity.   Each solution contains 0.05 μg ml⁻¹ Se and 0.1% albumin.   The metals are present as their chlorides at 100 μg ml⁻¹.   The peaks indicated with an asterisk contained no albumin.   Integrated absorbance values are used.   Reprinted from Ref. 8 with permission (© 1987, American Chemical Society).

cannot be removed even by palladium, but can be removed by the addition of both palladium and ascorbic acid.   To give another example of interference, the

modification performances were compared for ($Pd(NO_3)_2$+glycerol+H_2 gas) and ($NH_4H_2PO_4$+$Mg(NO_3)_2$+use of a platform), in tin determination as shown in Table 3.[10]   The palladium modification is especially better when NaCl is present.

Although there have been many claims that the use of a L'vov stabilized-temperature platform furnace (STPF) practically removes matrix interference[26-36], this does not seem to be the case for group IIIB – VIB elements, as Fig. 1 and Table 2 show.

3   Organo-Palladium Compounds as Matrix Modifiers in Organic Solvents

Although only inorganic palladium has thus far been studied, since several organic materials help palladium exhibit positive effects, as Table 1 shows, the question arises whether organo-palladium compounds may also exert an effect in organic solvents.   Such an attempt was made for determining alkyltin compounds in ethyl acetate/hexane.   Organo-palladium compounds,, ($PdCl_2(CH_3CN)_2$, $PdCl_2(C_6H_5CN)_2$, $PdCl_2(C_8H_{12})$ (C_8H_{12}=cyclooctadiene), $Pd(C_4H_7N_2O_2)_2$ ($C_4H_7N_2O_2$= dimethylglyoximate), [$PdCl(C_3H_5)$]₂ and $Pd(C_5H_7O_2)_2$ ($C_5H_7O_2$=acetylacetonate)) were added to an ethyl acetate/hexane (3:2, v/v) solution containing tributyltin

Table 2   The effects of Ni or Pd chlorides and ascorbic acid on the peak height sensitivity of 2 ng of antimony[25]

Metal amount/ μg	20 μg Ni		2 μg Pd	
	Without ascorbic acid	With ascorbic acid	Without ascorbic acid	With ascorbic acid
Ni 20	95	97	98	94
Ni 10	97	96	108	98
Ni 1	103	100	100	103
Zn 20	103	105	100	102
Zn 10	102	109	107	101
Zn 1	101	104	102	104
Al 20	124	118	102	100
Al 10	115	116	99	99
Al 1	107	109	106	99
Ca 20	100	104	115	100
Ca 10	108	109	106	100
Ca 1	108	108	102	101
Mn 20	88	91	81	92
Mn 10	91	94	89	93
Mn 1	94	96	92	95
Mg 20	94	104	102	102
Mg 10	100	102	102	101
Mg 1	101	104	103	99
K 20	89	78	92	73
K 10	89	81	96	77
K 1	94	89	95	90
Cu 20	99	98	97	96
Cu 10	102	101	98	99
Cu 1	101	98	98	104
Na 20	105	98	96	94
Na 10	102	96	100	95
Na 1	98	97	98	96
*	94	92	86	95
†	91	96	82	94
‡	88	89	92	94
ξ	111	110	94	96

* 4 μg of each Fe, Mn, Co, Cu, Ni, Zn, Pd, Cd.
† 8 μg of each Fe, Mn, Co, Cu, Ni, Zn, Pd, Cd.
‡ 20 μg $Na_2(S_2O_7)$.
ξ 20 μg $Na_4(S_2O_7)$.
The volumes of sample and matrix modifer solutions were 20 μl, and the L'vov platform was used.   Signal for Sb without metal chloride is 100.

Table 3   Tin recoveries from interferent matrices[10]

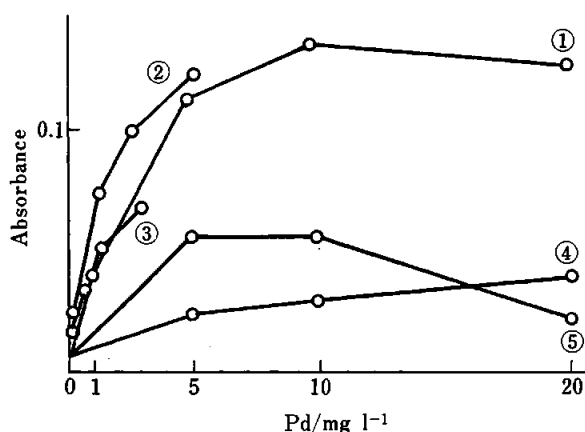| Interferent	Current method [200 μg $NH_4H_2PO_4$ 10 μg $Mg(NO_3)_2$, platform]	Palladium method [20 μg Pd 150 μg glycerol 5% hydrogen, wall]
5 μl 2.5% NaCl (125 μg)	22%[a]	91%[a]
	26%[b]	110%[b]
5 μl 5.0% NaCl (250 μg)	0	92%
	0	107%
5 μl seawater	0	87%
	0	99%
5 μl conc. HCl	97%	96%
	92%	100%
5 μl conc. HNO_3	79%	92%
	87%	93%
5 μl 20% H_2SO_4	39%	60%
	58%	79%
5 μl 0.5% Na_2SO_4 (25 μg)	87%	101%
	85%	101%
5 μl 1.0% Na_2SO_4 (50 μg)	82%	103%
	85%	100%

a. Peak height.
b. Peak area.

Fig. 3   Effect of the palladium concentration on the tin integrated absorbance.   A 400 μgSn l⁻¹ tributyltin chloride (TBTC) solution was used for the addition of each palladium complex.   (1) $PdCl_2(CH_3CN)_2$; (2) $PdCl_2(C_6H_5CN)_2$; (3) $PdCl_2(C_8H_{12})$; (4) $Pd(C_4H_7N_2O_2)_2$; (5) $[PdCl(C_3H_5)]_2$.[37]

chloride (TBTC) at 400 μgSn l⁻¹; the relative sensitivities were then compared.   The results are summarized in Fig. 3 and Table 4.[37]   The most effective modifier [(PdCl₂(CH₃CN)₂ exhibits an identical effect to TBTC, dibutyltin dichloride (DBTC) and triphenyltin chloride (TPTC); an identical calibration curve is obtained for these compounds.   The detection limit is 0.11 ng of tin. The method was successfully applied to the determination of total alkyltin leached from ship paints.

Although the utility of the method is still limited to the determination of alkyltin compounds, it should be possible to extend its application to organic solutions of the liquid-liquid extraction systems used for the preconcentration in GF-AAS.   With organo-palladium compounds and the direct analysis of the extract organic solution, neither back extraction of the analyte element into an aqueous solution nor acid decomposition of the organic solution is necessary.

Table 4   Enhancement ratio and optimum concentration of each palladium complex[37]

Pd complex	Solubility/ mgPd l⁻¹	Optimum concentration/ mgPd l⁻¹	Enhancement ratio
$PdCl_2(CH_3CN)_2$	50	10	19.1
$PdCl_2(C_6H_5CN)_2$	13	5	18.2
$PdCl_2(C_8H_{12})$	7	3	9.6
$Pd(C_4H_7N_2O_2)_2$	50	20	5.7
$[PdCl(C_3H_5)]_2$	1035	5	8.0
$Pd(C_5H_7O_2)_2$	630	—	—

4 Mechanism of a Palladium Matrix Modifier

Despite the long history concerning the practical aspects of palladium as a matrix modifier, little is known about the mechanism behind the observed phenomena. Many researchers speculated that palladium and the analyte element would form compound whose boiling point is higher than that of the simple analyte element. This leads to a suppression of the volatilization loss of the analyte during the thermal-pretreatment stage. However, no physical evidence for this hypothesis was obtained until the first physical examination targetting the reaction mechanism of a palladium modifier was recently carried out for selenium determination. Surface observations of a graphite furnace with electron microscopy and EPMA semi-quantitative analysis, which located the surface distribution of palladium and selenium, revealed that palladium and selenium exist in many small particles as palladium selenide (PdSe) during the ashing stage.[8] A similar electron microscopic method was also employed to observe that reduced palladium metal is produced on a graphite surface at an early stage of the temperature program by the addition of 5% hydrogen gas in 95% argon and ascorbic acid or hydroxylamine hydrochloride to palladium nitrate. It was concluded that reduced palladium is the actual acting modifier.[11] The electron microscopic technique also showed that, in lead determination, thermal pyrolyzing of ascorbic acid in the absence of palladium produces a pyrographite-coated graphite tube; for this reason the appearance temperature of the lead signal is lowered when ascorbic acid is added.[38] Ascorbic acid is widely used as a matrix modifier, as Table 1 shows; its reducing property was believed to produce a sensitivity enhancement. Although many researchers have suggested that the oxide of the analyte element is reduced by ascorbic acid, this now seems to be rather improbable, since other organic materials, such as albumin or active carbon, are effective to the same extent for group IIIB – VIB elements as well;[8,39] it thus seems more probable that ascorbic acid works as a source material for pyrographite, which then acts physically to enhance the sensitivity. Albumin in the determination of selenium was found to form a new graphite layer on the original tube surface, which is effective for a sensitivity enhancement.[8]

Another technique recently introduced for studying the mechanism is mass spectrometry. Holcombe *et al.* devised a GF-AAS system connected to a mass analyzer (Fig. 4).[40] The chemical species vaporized from the graphite furnace (shown as an atomizer in Fig. 4) are detected both by AAS and concurrently by ion monitoring *via* a mass spectrometer. The vaporization process as a function of time can be observed in real time, as shown in Fig. 5 for lead measurements. The connected AAS-MS system was employed in order to elucidate the mechanisms that controls the atomization of arsenic and its stabilization by palladium.[41] Various
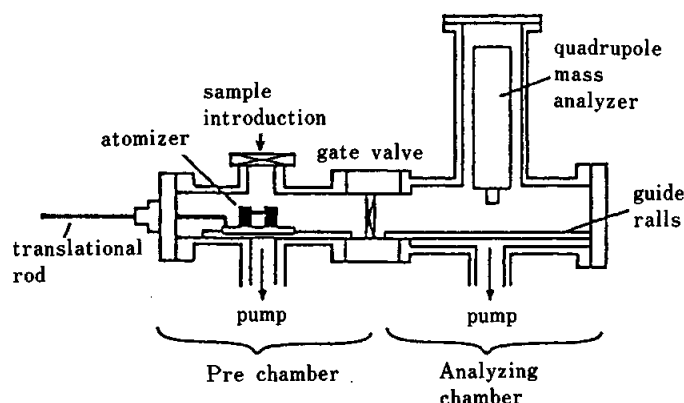

Fig. 4 Atomic absorption/mass spectrometer vacuum system (AA optics not shown). Reprinted from Ref. 40 with permission (© 1987, American Chemical Society).
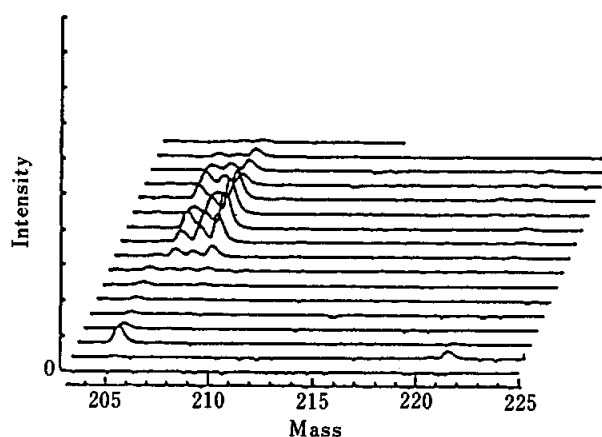

Fig. 5 Mass spectrograms for Pb in excess $NH_4H_2PO_4$. The major isotopes of Pb (206, 207, 208) are shown. Each scan represents 74 ms during the firing of the atomizer. A total time of 1.2 s is displayed. Reprinted from Ref. 40 with permission (© 1987, American Chemical Society).

species such as AsO^+, As^+, As_2^+, AsC^+ and Pd^+ were detected. Composite figures concerning the appearance of each species, as detected by MS and AAS, are shown in Figs. 6, 7 and 8 for arsenic only, arsenic+PdO, and arsenic+reduced Pd, respectively. It is clear from these figures that the addition of PdO removes any vaporization loss of As during the early lower temperatures (<1000 K) significantly, whereas reduced Pd completely removes any loss at lower temperatures. The overall thermal process concluded from the MS analyses is as follows: As_2O_3 thermally decomposes (*ca.* 500 K) forming arsenic monoxide, higher arsenic oxides, and condensed-phase arsenic, which polymerizes and then sublimates as the dimer (*ca.* 800 K). Atomization occurs by dissociative adsorption of the oxide and desorption of the resulting arsenic (*ca.* 1500 K). Palladium oxide stabilizes arsenic atomization by reacting with the condensed-phase arsenic (*ca.* 500 K), thus preventing the evolution of the dimer by forming a $[Pd_xAs_yO_m]$ com-
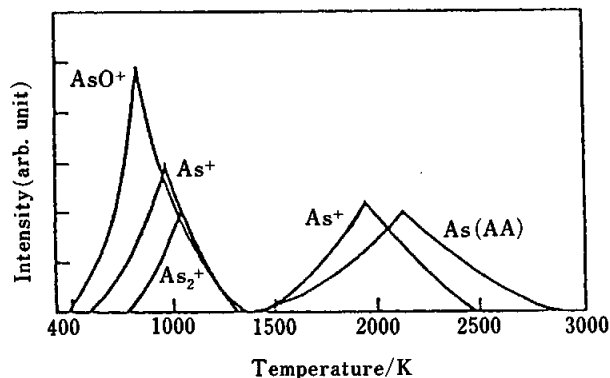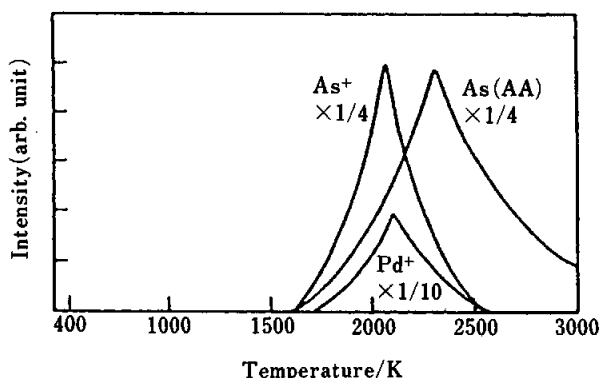
Fig. 6   Normalized composite temperature profiles of atomic absorption and mass spectroscopic signals for atmospheric pressure vaporization of 20 ng of As. The ionizer electron energy was 40 eV. As⁺ and AsO⁺ are monitored concurrently during a given experiment. Reprinted from Ref. 41 with permission (© 1991, American Chemical Society).

Fig. 8   Normalized composite temperature profiles of atomic absorption and mass spectroscopic signals for atmospheric pressure vaporization of 20 ng of As with 115 ng of reduced Pd. The ionizer electron energy is 40 eV. Reprinted from Ref. 41 with permission (© 1991, American Chemical Society).
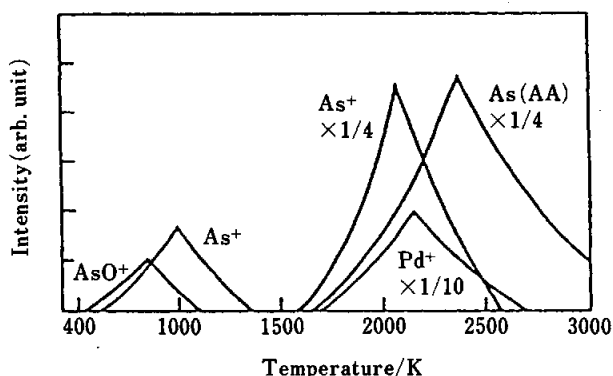

Fig. 7   Normalized composite temperature profiles of atomic absorption and mass spectroscopic signals for atmospheric pressure vaporization of 20 ng of As with 115 ng of PdO. The ionizer electron energy is 40 eV. As⁺ and AsO⁺ are monitored concurrently during a given experiment. Reprinted from Ref. 41 with permission (© 1991, American Chemical Society).

In the presence of Pd, $Pd^0(s)$ reacts with $SeO_2(s,l)$ at 400 K to produce a [Pd, Se, O] (ad) compound and SeO(g). The [Pd, Se, O] compound then decomposes to give Se(g), Pd(g) and a [Se-Pd] compound at 1200 K. The [Se-Pd] compound also decomposes to Se(g) and Pd(ad) at 1550 K. In the presence of PdO, it reacts with Se(s,l) and $SeO_2(s,l)$, forming [Pd, Se, O], which then decomposes at 1200 K to produce Se(g), Pd(g) and [Se-Pd](ad). The [Se-Pd](ad) finally decomposes to Se(g) and Pd(ad) at 1700 K.

5   Conclusion

Palladium is certainly a universal modifier for group IIIB – VIB elements; it stabilizes the analyte element to higher temperatures, thus eliminating interference due to various inorganic and organic materials. The mechanism of palladium stabilization is becoming elucidated due to the recently developed AAS-MS system. Although some of the thermal reactions and the species produced during the whole process are still ambiguous, even with MS monitoring, there is no doubt that this tool is opening up new aspects of the thermal reactions.

pound or solid solution. Elemental palladium reacts directly with the As_2O_3, probably forming the same compound and dimer; oxide losses are therefore inhibited. In a similar AAS-MS analysis of the selenium vaporization process with and without palladium, SeO_2^+, SeO^+, Se_2^+, SeC_2^+, $Se(OH)_2^+$, Se^+ and Pd^+ were detected.[42] From their appearance profile, the reaction process is deduced to be as follows: in the absence of palladium, $SeO_2(ad)$ ((ad) indicates adsorption) reacts with water to form $SeO_2(g)$, SeO(g), Se(s,1) and $Se(OH)_2$ (g) at 400 K. Selenium (s,1) thermally polymerizes to form higher selenium (400 K). Selenium oxide Se_yO_x (g, ad) is reduced by carbon to release Se(g) at 1600 K.

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