Is Palladium or Palladium–Ascorbic Acid or Palladium–Magnesium Nitrate a More Universal Chemical Modifier for Electrothermal Atomic Absorption Spectrometry?

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A comprehensive comparison was made between the performances of Pd, Pd–ascorbic acid and Pd–Mg(NO₃)₂ for the determination of Ag, As, Au, Bi, Cd, Ga, Ge, Hg, In, Mn, Pb, Sb, Se, Sn, Te and Tl in terms of charring temperatures available, characteristic mass values, background absorption, permissible interference range, capability of improving the atomization signal shapes and relative standard deviations of the determinations of trace elements in real samples. Generally, the performances of Pd, Pd–ascorbic acid and Pd–Mg are similar, except that the background absorption of the Pd–Mg modifier is 1–2 orders of magnitude greater than that of the Pd and Pd–ascorbic acid modifiers. Therefore, the need for the addition of ascorbic acid appears to be matrix-dependent, while the addition of Mg(NO₃)₂ is not recommended.

Keywords: Performance comparison; palladium modifier; palladium–ascorbic acid modifier; palladium–magnesium modifier; determination of trace elements in real samples

Since the introduction of Pd as a chemical modifier for electrothermal atomic absorption spectrometry (ETAAS) in the late 1970s by Shan and Ni,¹ this element, either alone or combined with ascorbic acid or Mg(NO₃)₂, has been widely used for the determination of Hg,^{1–3} Pb,^{4–6} As,^{7,8} Se,^{9–12} Tl,^{13,14} Bi,¹⁵ Te,¹⁶ In,¹⁷ Sb¹⁸ and Co.¹⁹ Ni and Shan²⁰ reviewed the application of chemical modifiers in ETAAS with the emphasis on the research work carried out in the authors' laboratory. Tsalev and Slaveykova²¹ comprehensively examined and reviewed about 700 publications on chemical modification in ETAAS. The reviewers attempted to organize and classify a large amount of empirical information. Various theoretical and experimental approaches were used; a rather general and abstract classification of chemical modifiers was achieved. However, the authors admitted that the practical applications of the approach were limited.

Owing to the extensive use of chemical modification in ETAAS, many attempts have been made to elucidate the mechanisms by which the modifier stabilizes the elements to be determined, thus allowing the use of higher charring temperatures or delaying atomization until the electrothermal atomizer temperature is higher. The most thorough studies have been carried out on Pd as a modifier and have mainly investigated its chemical reactions with analytes. Styris *et al.*²² used mass spectrometry to study the stabilization of As by Pd and found that Pd formed a mixed oxide with As in the condensed phase. In a study of Se,²³ they found that a thermally reduced Pd modifier prevented the formation of several poly-atomic species and formed a thermally stable stoichiometric compound with Se. Other workers have suggested the catalytic

reduction of the analyte to the atomic state,²⁴ the formation of intermetallic species between Pd and various elements²⁵ or solid solution formation with Pd.²⁶ Majidi and Robertson²⁷ showed that Rutherford backscattering spectrometry was an extremely useful technique for monitoring surface reactions in ETAAS, and concluded that Pd formed a stoichiometric compound with Se. However, Qiao and Jackson^{28,29} suggested that the physical mechanism was predominant although both chemical and physical effects occurred when Pd and mixtures containing Pd were used as modifiers in ETAAS.

Although many researchers claim that Pd is effective as a modifier, some workers have preferred the use of Pd with the addition of a reducing agent.³⁰ These workers found that reducing agents prevented the low recoveries that otherwise occurred in the presence of strong oxidizing agents when Pd alone was used.³¹ Shan *et al.*¹⁴ reported that the absorbance of Tl was suppressed in the presence of HClO₄ if Pd alone was used as a modifier. Ascorbic acid has also been used with Pd for the determination of Se^{32–34} and In.¹⁷ However, Welz *et al.*³⁵ found that the addition of ascorbic acid to Pd did not reduce the interference by chloride in the determination of Tl. Qiao and Jackson²⁸ pointed out that in the dilute HNO₃ matrix used in ETAAS there was no evidence that a reducing agent such as ascorbic acid was needed. Recently, Welz *et al.*³⁶ investigated the performance of a Pd–Mg modifier in terms of charring temperature and interferences, stabilizing power and characteristic mass, and application to the determination of 21 elements. They concluded that Pd–Mg was a fairly universally applicable modifier in ETAAS and that the performance of the Pd–Mg modifier was at least equal to, but in most instances better than, that of the previously recommended individual modifiers. Since the study of Welz *et al.*, numerous applications of the Pd–Mg modifier have been reported for the determination of various trace elements in a variety of samples. The Pd–Mg modifier has been found to have both advantages and disadvantages over other modifiers, particularly when compared with Pd alone. In the determination of Pb, the presence of Mg was essential in order to avoid a low analytical recovery.³⁷ Bozsai *et al.*³⁸ found that large amounts of added Mg improved the peak shape. Qiao and Jackson²⁸ indicated that a sharper absorbance peak, and in many instances a higher recovery, were obtained when Mg was also present. Johannessen *et al.*,³⁹ while recognizing that a chemical modifier consisting of 7.5 µg of Pd and 5 µg of Mg(NO₃)₂ was the best choice from among other chemical modifiers such as Cu, Ni, Cu plus Mg, and Pd, noted that a white layer accumulated at the end of the graphite tube during the analysis of serum and urine using a chemical modifier with a high concentration of Mg(NO₃)₂. In the determination of Pb in clinical and environ-

mental materials, the addition of $\text{Mg}(\text{NO}_3)_2$ gave no significant improvement in the sensitivity; therefore, $\text{Mg}(\text{NO}_3)_2$ was not considered further.⁴⁰

Because no comprehensive comparison has been made between Pd, Pd-ascorbic acid and Pd-Mg modifiers it is difficult to judge whether the Pd-Mg or Pd-ascorbic acid modifier is better than Pd alone or whether they are equal to each other, and whether the addition of $\text{Mg}(\text{NO}_3)_2$ or ascorbic acid is essential. The main aim of this work was to compare the performances of the Pd, Pd-ascorbic acid and Pd-Mg modifiers in terms of charring temperature available, characteristic masses, background absorption, interferences, effect on the atomization profiles and application to the determination of typical trace elements in environmental samples either by decomposition of the samples with a mixture of HNO_3 - HClO_4 -HF or by slurry sampling. This would allow a conclusion to be drawn as to whether the addition of ascorbic acid or $\text{Mg}(\text{NO}_3)_2$ is essential or not.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 3030 or 4000 atomic absorption spectrometer with an HGA 400 graphite furnace atomizer was used. The deuterium arc background correction facility was employed throughout this work. Time-resolved atomization pulses were copied from the screen of the 3030 atomic absorption spectrometer. Pyrolytic graphite coated graphite tubes were used. Sample solutions and slurries were injected into the tube atomizer manually. A typical temperature programme for the determination of a variety of elements using Pd, Pd-ascorbic acid and Pd-Mg modifiers is given in Table 1.

All other instrumental parameters including lamp current, wavelength and slit-width setting were chosen according to the manufacturer's recommendations.

Reagents

The reagents used were of Specpure or at least analytical-reagent grade. The stock solutions of the elements were prepared by dissolving appropriate amounts of the metals or nitrates in suitable media. All the working solutions were prepared daily from these stock solutions by further dilution with $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$.

Palladium solution was prepared by dissolving PdCl_2 [BDH (now Merck)] in a suitable concentration of HNO_3 with heating. The concentration of Pd for the modification studies was $200 \mu\text{g cm}^{-3}$. The ascorbic acid solution (1% m/v) was prepared by dissolving the appropriate amount of ascorbic acid (analytical-reagent grade; Beijing Chemicals) in de-ionized water daily before use. The Pd-Mg modifier was prepared by mixing equal volumes of a $400 \mu\text{g cm}^{-3}$ solution of Pd and a $2000 \mu\text{g cm}^{-3}$ solution of $\text{Mg}(\text{NO}_3)_2$.

Table 1 Typical temperature programme for the determination of a variety of elements using Pd and Pd-Mg modifiers

Step	Temperature/ $^{\circ}\text{C}$	Time/s		Internal gas flow rate/ $\text{cm}^3 \text{ min}^{-1}$
		Ramp	Hold	
1	110	30	30	300
2	Various charring temperatures	30	30	300
3	Various atomization temperatures	0	5	0
4	2650	1	4	300

Slurry Preparation

Amounts of 20–50 mg of coal fly ash, depending on the concentration of analytes in the samples, were weighed into a 20 cm^3 beaker and 10 cm^3 of ethanol-water (2+8) were added. The contents of each beaker were stirred with a magnetic stirrer during sample analysis.

Decomposition of Samples

A portion (0.100–0.200 g) of the sample was accurately weighed into a 30 cm^3 Teflon container, and 0.5 cm^3 of $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$ was added to moisten the sample thoroughly, followed by 1.5 cm^3 of concentrated HNO_3 (67%). The mixture was allowed to stand overnight after which 1 cm^3 of concentrated HClO_4 (72%) and 3 cm^3 of HF (40%) were added and the container was sealed with a Teflon cover. The Teflon container was placed in a bomb in an oven; the temperature was increased to 170°C over a period of 0.5 h and then maintained at 170°C for about 6 h. The bomb was removed from the oven and cooled to room temperature before opening. The Teflon container was then removed from the bomb and the Teflon cover was carefully removed. The interior surface of the cover was washed with 0.5 cm^3 of concentrated HNO_3 and the washings were added to the container, which was then heated on a hot-plate at about 120°C until the appearance of HClO_4 fumes, at which point the temperature was increased to 160°C until the sample was nearly dry. A sufficient volume of $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$ was then added to dissolve the residue with gentle heating and the resulting solution was transferred into a 25 cm^3 calibrated flask. The procedure was repeated several times. The final solution was diluted to the mark with $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$.

General Procedure

A portion (0.01 cm^3) of the standard solution or slurry and 0.01 cm^3 of Pd or 0.01 cm^3 of Pd plus 0.01 cm^3 of ascorbic acid or 0.01 cm^3 of Pd-Mg modifier solution were injected into the pyrolytic graphite coated graphite tube and the temperature programme was initiated; the integrated absorbances were measured at the resonance wavelengths of the elements under study. In the interference study, 0.01 cm^3 portions of the standard, modifier and interference solutions were successively injected.

RESULTS AND DISCUSSION

Charring Temperature

The main purpose of using chemical modification in ETAAS is to stabilize the elements to a charring temperature as high as possible in order to remove the sample matrix efficiently in the thermal pre-treatment stage; hence less interferences are encountered in the final atomization process. Of course, the control of the chemical environment is also an equally important action of chemical modification. However, chemical modification is more frequently applied to the stabilization of elements of high and medium volatility; therefore, the emphasis of this study is on these elements. A comparison was made between the maximum charring temperatures for thermal pre-treatment without loss of elements in the absence of chemical modifier or in the presence of Pd, Pd-ascorbic acid and Pd-Mg modifiers. The results are given in Table 2.

As can be seen, the tolerated charring temperatures of the elements studied were 300 – 700°C higher in the presence of Pd and Pd-ascorbic acid modifiers than those obtained with no modifier. A $2 \mu\text{g}$ amount of Pd was found to be sufficient to stabilize all the elements except for Cd, for which a larger

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Table 2 Maximum pyrolysis temperatures for thermal pre-treatment without analyte loss, in the absence of modifier and in the presence of Pd, Pd–ascorbic acid and Pd–Mg modifiers

Element	Pyrolysis temperature/°C				
	No modifier	Pd	Pd–ascorbic acid	Pd–Mg	
				This work	Welz <i>et al.</i> *
Ag	700	1000	1000	1000	1000
As	300	1300	1300	1300	1400
Au	900	1200	1200	1100	1000
Bi	600	1100	1100	1200	1200
Cd	400	900†	900†	900†	900
Ga	800	1200	1200	1300	1300
Ge	800	1200	1200	1400	1500
Hg	—	400	400	400	400
In	600	1200	1200	1300	1500
Mn	1100	1400	1400	1400	1400
Pb	600	1000	1000	1100	1200
Sb	900	1300	1300	1200	1200
Se	600	1000	1000	1000	1000
Sn	800	1100	1100	1200	1200
Te	500	1200	1200	1100	1200
Tl	600	900	900	1000	1000

*Ref. 36.
†Amount of Pd modifier: 400 µg.

amount of Pd was required. It should be pointed out that there were no differences between the maximum charring temperatures obtained with Pd or Pd–ascorbic acid. When the Pd–Mg modifier was used the maximum charring temperatures were the same as those obtained with Pd and Pd–ascorbic acid for Ag, As, Cd, Hg, Mn and Se. However, the permissible charring temperatures were 100 °C higher for Bi, Ga, In, Pb, Sn and Tl and 100 °C lower for Au, Sb and Te.

However, temperature differences of 100 °C were not significant because a charring temperature of greater than 1000 °C could be used. In addition, the temperature differences were partly due to the change in the physico-chemical nature of the graphite tube during the experiments.

It is worth mentioning that the charring temperatures of the elements investigated in this work with the Pd–Mg modifier were also similar to those reported by Welz *et al.*³⁶ The reason for the 100 °C difference for some of the elements

was ascribed to the particular instrument and different batch of tubes used.

Characteristic Mass

As noted earlier, the main role of chemical modifiers in ETAAS is their stabilizing effect, which enables higher charring temperatures to be used. As a result, more of the sample matrix is efficiently removed during the thermal pre-treatment step and less interferences are encountered in the atomization step. In some instances the sensitivities for the determination of analytes are improved by the addition of modifiers when the peak height absorbance mode is used. However, this enhancement rarely occurs if the integrated absorbance mode is employed.

The characteristic mass, m_0 , is an important parameter in the L'vov concept of absolute analysis by ETAAS⁴¹ and might be influenced by lamp current, line voltage, temperature setting and other instrumental parameters.⁴² Because the Pd modifier not only increases the maximum charring temperature but also shifts the signal to a later appearance time, analyte is released into a hotter gas environment which has already reached its final atomization temperature; hence the atomization efficiency is improved and a lower m_0 is expected. In some instances the optimum atomization temperature also increases in the presence of a modifier. At higher atomization temperatures, diffusion losses of elements are higher so that lower integrated absorbances are obtained; hence, the m_0 values are higher than those obtained in the absence of modifiers. Considering the above properties of the modifiers a comparison was made of the m_0 values obtained with various modifiers. The results are given in Table 3, from which it can be seen that identical m_0 values were obtained with Pd and Pd–ascorbic acid. In fact similar m_0 values were obtained with Pd, Pd–ascorbic acid and Pd–Mg modifiers in this study, and the m_0 values for most elements in the absence of a modifier were also similar to those obtained with Pd alone or with Pd combined with ascorbic acid or Mg(NO₃)₂. Considering the Zeeman-factor, the differences between the m_0 values obtained by the authors and those obtained by Welz *et al.*³⁶ were negligible. The reasons for the slight inconsistency for some elements were ascribed to the particular instrument and operating conditions used by the two research groups. Based on the above comparison, it can be concluded that the addition

Table 3 Comparison of the characteristic mass (m_0) values obtained without a modifier and with Pd either alone or in combination with ascorbic acid or Mg(NO₃)₂

Element	Atomization temperature /°C	M ₀ /pg					
		No modifier		Pd	Pd–ascorbic acid	Pd–Mg	
		This work	Welz <i>et al.</i> *			This work	Welz <i>et al.</i> *
Ag	1600	1.9	1.4	1.8	1.8	1.4	1.4
As	2200	14	14	14	14	14	15
Au	1800	6.5	6.7	6.5	6.5	8.4	9.2
Bi	1900	22	18	22	22	22	28
Cd	1700	0.5	—	0.4	0.4	0.4	0.4
Ga	2200	16	15	18	18	18	20
Ge	2550	24	28	28	28	28	30
Hg	1000	—	—	110	110	105	95
In	2300	20	19	17	17	17	19
Mn	2300	3.4	2.4	2.9	2.9	1.9	3.0
Pb	2000	10	11	14	14	14	16
Sb	1900	19	19	19	19	19	19
Se	2100	28	25	25	25	25	25
Sn	2400	38	35	28	28	30	28
Te	2250	18	12	16	16	17	18
Tl	1650	16	18	16	16	18	19

*Ref. 36.

of $\text{Mg}(\text{NO}_3)_2$ to Pd does not improve the sensitivity for the determination of the elements examined.

Background Absorption

Under the optimum charring and atomization conditions for each element the background absorption values of various modifiers were compared, and the results are summarized in Table 4. Generally, the background absorption of the Pd modifier was close to that of the tube firing. In the presence of Pd-ascorbic acid the background absorption was still low for most of the elements, although a slightly higher background absorption was observed for As, Cd, Se and Tl. For most of the elements tested the background absorption of the Pd-Mg modifier was 1–2 orders of magnitude greater than that of the Pd or Pd-ascorbic acid modifier.

The large background absorption caused by Pd-Mg at the resonance lines of Ga, Pb, Mn and Sn is probably due to atomic absorption by Mg atoms in the wings of the 285.2 nm resonance line.⁴³ However, a very large background absorption was also observed at the resonance lines of Au, Bi, Cd, Ge, In and Sb, even though their resonance lines are far removed from the Mg resonance line at 285.2 nm. In this instance, the observed background absorption could, at least in part, be ascribed to molecular absorption.

Interference

A comparison was made between the maximum concentrations of interferences achievable with various chemical modifiers under the optimum ETAAS operating conditions. NaCl, CaCl_2 and Na_2SO_4 were chosen as representatives of the interferences. The reasons for this choice were as follows: (1) A particular feature of the absorption spectra of halides is the comparative sharpness of the peaks, particularly at wavelengths below 240 nm. It is clear that any background correction methods devised for measuring molecular absorption must take account of its possible rapid variation with wavelength. (2) When molecules with more than two atoms are vaporized, dissociation through various steps is observed.

The results for the permissible maximum concentrations of NaCl, CaCl_2 and Na_2SO_4 obtained with the various modifiers are listed in Table 5. The abilities of the three modifiers to remove the interferences from NaCl, CaCl_2 and Na_2SO_4 were similar for Ag, Mn, Pb and Te. For As, the Pd modifier was less efficient than the Pd-ascorbic and Pd-Mg modifiers in

Table 5 Comparison of the maximum permissible concentrations of NaCl, CaCl_2 and SO_4^{2-} as Na_2SO_4 in the presence of modifiers

Element	Concentration of element/ $\mu\text{g dm}^{-3}$	Modifier	Maximum concentration of interferent/ g dm^{-3}		
			NaCl	CaCl_2	SO_4^{2-}
Ag	0.1	Pd	5	0.1	0.5
		Pd-ascorbic acid	5	0.1	0.5
		Pd-Mg	10	0.1	0.5
As	1	Pd	10	2	2
		Pd-ascorbic acid	30	5	1
		Pd-Mg	30	5	2
Au	1	Pd	10	5	0.1
		Pd-ascorbic acid	0.5	0.3	0.1
		Pd-Mg	0.5	0.3	0.1
Bi	1	Pd	2	1	2
		Pd-ascorbic acid	1	1	2
		Pd-Mg	1	1	5
Cd	0.1	Pd	0.3	0.2	1
		Pd-ascorbic acid	0.3	0.3	0.2
		Pd-Mg	0.3	0.2	0.1
Ga	1	Pd	2	1	2
		Pd-ascorbic acid	5	3	2
		Pd-Mg	2	0.3	1
Ge	2	Pd	50	2	0.1
		Pd-ascorbic acid	10	3	0.1
		Pd-Mg	5	1	0.1
Hg	4	Pd	1	0.1	30
		Pd-ascorbic acid	2	0.3	30
		Pd-Mg	0.5	0.2	30
In	1	Pd	5	1	5
		Pd-ascorbic acid	5	5	5
		Pd-Mg	20	3	5
Mn	0.1	Pd	30	3	20
		Pd-ascorbic acid	30	3	20
		Pd-Mg	30	3	10
Pb	1	Pd	20	5	0.1
		Pd-ascorbic acid	20	5	0.1
		Pd-Mg	20	5	0.2
Sb	1	Pd	30	10	30
		Pd-ascorbic acid	50	20	50
		Pd-Mg	20	10	5
Se	1	Pd	1	0.5	0.05
		Pd-ascorbic acid	1	1	0.05
		Pd-Mg	1	0.5	0.05
Sn	1	Pd	1	0.5	1
		Pd-ascorbic acid	50	3	1
		Pd-Mg	2	1	1
Te	1	Pd	30	5	1
		Pd-ascorbic acid	30	5	1
		Pd-Mg	30	3	1
Tl	1	Pd	5	2	3
		Pd-ascorbic acid	20	5	3
		Pd-Mg	10	5	2

Table 4 Comparison of background absorption obtained with Pd, Pd-ascorbic acid and Pd-Mg($\text{NO}_3)_2$

Element	Wavelength/ nm	Background absorption at the maximum thermal pre-treatment temperature/s		
		Pd	Pd-ascorbic acid	Pd-Mg
Ag	328.1	0.004	0.007	0.072
As	193.7	0.003	0.012	0.043
Au	242.8	0.001	0.003	0.272
Bi	223.0	0.014	0.013	0.176
Cd	228.8	0.002	0.024	0.243
Ga	287.4	0.003	0.001	0.137
Ge	265.1	0.014	0.010	0.243
Hg	253.7	0.008	0.025	0.061
In	303.9	0.006	0.005	0.152
Mn	279.5	0.002	0.002	0.458
Pb	283.3	0.011	0.010	0.217
Sb	217.6	0.003	0.006	0.297
Se	196.0	0.000	0.011	0.038
Sn	224.6	0.001	0.006	0.240
Te	214.3	0.008	0.013	0.294
Tl	276.8	0.005	0.024	0.232

removing the interferences from NaCl and CaCl_2 . However, a contrary situation was observed for the determination of Au. Although differences existed among the three modifiers for the elements and interferences studied, no definite conclusion could be drawn as to which modifier was superior to the other two.

Effect of Modifiers on the Atomization Profiles of Elements by Solution and Slurry Sampling

One advantage of chemical modification is that the atomization signals become fairly symmetrical and are shifted to higher atomization temperatures. Welz *et al.*³⁶ demonstrated this

behaviour by comparing the shapes of the atomization signals of various elements in both the absence and presence of a Pd–Mg modifier. In order to demonstrate how the Pd, Pd–ascorbic acid and Pd–Mg modifiers affect the atomization profiles of elements, a comparative study was conducted. The atomization profiles of Pb, Mn and Bi in river sediment after decomposition of the samples with a mixture of HNO_3 , HClO_4 and HF both in the absence and presence of Pd, Pd–ascorbic acid and Pd–Mg modifiers are shown in Figs. 1–3, respectively. In Figs. 4 and 5 the atomization profiles of Ga and Pb in coal fly ash with slurry sampling when Pd, Pd–ascorbic acid and Pd–Mg modifiers are used are also shown. In each instance the atomization profiles of the analytes in the sample were also compared with those of the elements in the aqueous standards.

For all the figures, (a) refers to the atomization profiles obtained when no chemical modifiers were used. In (b), (c) and (d), Pd, Pd–ascorbic acid and Pd–Mg modifiers were applied, respectively. Although similar symmetrical atomization signal shapes were obtained for Pb, Mn and Bi after decomposition of the samples, both in the absence and presence of the chemical modifiers (Figs. 1–3), the atomic signals appeared at an earlier time in the absence of a modifier than in its presence. The appearance times for all the elements were identical when

Fig. 1 Atomization profile of Pb (0.5 ng) in GSD-5 River Sediment after sample decomposition with HNO_3 – HClO_4 –HF, where A1, sample; A2, standard (0.5 ng Pb); B1 and B2, background absorbance for sample and standard, respectively; and $A1_{\text{int}}$ and $A2_{\text{int}}$, integrated absorbance. (a) No modifier: $A1_{\text{int}}$, 0.129 s; B1, 0.110 s; $A2_{\text{int}}$, 0.131 s; and B2, 0.006 s. (b) Pd modifier: $A1_{\text{int}}$, 0.115 s; B1, 0.134 s; $A2_{\text{int}}$, 0.113 s; and B2, 0.013 s. (c) Pd–ascorbic acid modifier: $A1_{\text{int}}$, 0.113 s; B1, 0.132 s; $A2_{\text{int}}$, 0.113 s; and B2, 0.013 s. (d) Pd–Mg modifier: $A1_{\text{int}}$, 0.110 s; B1, 0.270 s; $A2_{\text{int}}$, 0.113 s; and B2, 0.200 s

Fig. 2 Atomization profile of Mn (0.5 ng) in GSD-5 River Sediment after sample decomposition with HNO_3 – HClO_4 –HF, where A1, sample; A2, standard (0.5 ng Mn); B1 and B2, background absorbance for sample and standard, respectively; and $A1_{\text{int}}$ and $A2_{\text{int}}$, integrated absorbance. (a) No modifier: $A1_{\text{int}}$, 0.128 s; B1, 0.010 s; $A2_{\text{int}}$, 0.131 s; and B2, 0.006 s. (b) Pd modifier: $A1_{\text{int}}$, 0.160 s; B1, 0.016 s; $A2_{\text{int}}$, 0.163 s; and B2, 0.013 s. (c) Pd–ascorbic acid modifier: $A1_{\text{int}}$, 0.158 s; B1, 0.012 s; $A2_{\text{int}}$, 0.163 s; and B2, 0.013 s. (d) Pd–Mg modifier: $A1_{\text{int}}$, 0.191 s; B1, 0.243 s; $A2_{\text{int}}$, 0.187 s; and B2, 0.179 s

comparing the elements in the samples and in the aqueous standards; however, the peak times for the elements in the samples were slightly later than those in the aqueous standards. Very similar atomization signal shapes and absorbances were obtained for Pb, Mn and Bi when Pd and Pd–ascorbic acid were applied. The reason for this is that ascorbic acid reduces Pd compounds to the free metal at charring temperatures of less than 650 °C, while Pd compounds are thermally decomposed to the metal at higher temperatures; therefore, the stabilizing effect of Pd and Pd–ascorbic acid is due to the Pd metal. When the Pd–Mg modifier was used for the determination of Pb, Mn and Bi, larger backgrounds were observed, the reason for which has already been discussed under Background Absorption. Higher absorbances were obtained for the determination of Mn with the Pd–Mg modifier than with the Pd or Pd–ascorbic acid modifiers because a lower m_0 value for Mn could be achieved with Pd–Mg.

Because the concentration of Bi in the river sediment was low, a larger amount of sample was taken; hence, a large background was observed for the determination of Bi.

As far as slurry sampling was concerned, very different atomization signal shapes were observed when no modifier was used, whereas very similar atomization profiles were obtained when Pd, Pd–ascorbic acid and Pd–Mg were used.

Fig. 3 Atomization profile of Bi (0.5 ng) in GSD-5 River Sediment after sample decomposition with $\text{HNO}_3\text{--HClO}_4\text{--HF}$, where A1, sample; A2, standard (0.5 ng Bi); B1 and B2, background absorbance for sample and standard, respectively; and A1_{int} and A2_{int}, integrated absorbance. (a) No modifier: A1_{int}, 0.045 s; B1, 0.437 s; A2_{int}, 0.043 s; and B2, 0.012 s. (b) Pd modifier: A1_{int}, 0.061 s; B1, 0.434 s; A2_{int}, 0.058 s; and B2, 0.034 s. (c) Pd-ascorbic acid modifier: A1_{int}, 0.057 s; B1, 0.441 s; A2_{int}, 0.060 s; and B2, 0.013 s. (d) Pd-Mg modifier: A1_{int}, 0.067 s; B1, 0.674 s; A2_{int}, 0.069 s; and B2, 0.481 s

With no modifier, a small absorbance was obtained for Ga in the aqueous standard and a two-fold increase in the absorbance was achieved. This was due to the enhancement effect caused by sample matrices such as Co, Mo, Mn, Al and Ni.⁴⁴ When no modifier was used, the atomic signal appeared at an earlier time for Pb in the aqueous standard than that with a modifier. With regard to slurry sampling, Pb is adsorbed on the surface of the slurry and incorporated in the bulk of the slurry, so that the appearance time for Pb in the slurry was later than that in the aqueous standard.

A detailed discussion of the modification mechanism by Pd in ETAAS is beyond the scope of this paper. Most research has suggested that the formation of intermetallic compounds between Pd and As and Pd and Se or the formation of a solid solution are the major mechanisms in retarding analyte vaporization.⁴⁵ There is increasing evidence that physical processes play a predominant role in the modifying action of metals such as Pd.^{28,29} The mechanism of the action of Pd was also discussed earlier in the Introduction. When Pd, Pd-ascorbic acid and Pd-Mg were used, the absorbance signals for Pb, Mn, Bi and Ga were shifted to a later time regardless of whether the samples were decomposed or not; the above-described mechanisms may indeed be responsible for the modifying effect of Pd.

Fig. 4 Atomization profile of Ga (0.8 ng) in GBW 08401 Coal Fly Ash with slurry sampling, where A1, sample; A2, standard (0.8 ng Ga); B1 and B2, background absorbance for sample and standard, respectively; and A1_{int} and A2_{int}, integrated absorbance. (a) No modifier: A1_{int}, 0.107 s; B1, 0.207 s; A2_{int}, 0.047 s; and B2, 0.002 s. (b) Pd modifier: A1_{int}, 0.164 s; B1, 0.343 s; A2_{int}, 0.165 s; and B2, 0.024 s. (c) Pd-ascorbic acid modifier: A1_{int}, 0.162 s; B1, 0.341 s; A2_{int}, 0.160 s; and B2, 0.013 s. (d) Pd-Mg modifier: A1_{int}, 0.140 s; B1, 0.544 s; A2_{int}, 0.140 s; and B2, 0.240 s

Determination of Trace Elements in Certified Reference Materials

In order to compare the chemical performance of the Pd, Pd-ascorbic acid and Pd-Mg modifiers, the determination of trace elements in several certified reference materials was carried out and the precision achievable with each of the chemical modifiers was compared. The results are summarized in Table 6. Good agreement was obtained between the data obtained by the proposed method and the certified values. The relative standard deviations for all the determinations were in the same range regardless of which of the three modifiers was used.

CONCLUSION

The work described here has shown that the performance of a Pd modifier is similar to that of Pd-ascorbic acid and Pd-Mg modifiers in terms of charring temperature available, characteristic mass values, permissible interference range, capability of improving atomization profiles and relative standard deviations for the determination of trace elements in real samples. However, the background absorption of the Pd and Pd-ascorbic acid modifiers is much smaller than that of the

Table 6 Comparison of the precision for the determination of Bi, Mn, Pb and Ga, in environmental samples using Pd, Pd-ascorbic acid and Pd-Mg(NO₃)₂ after acid decomposition of the samples and by slurry sampling

Sample	Element	Concentration of the elements/ $\mu\text{g g}^{-1}$			Certified value
		This work			
		Pd	Pd-ascorbic acid	Pd-Mg	
<i>After acid decomposition</i>					
GSD-6	Pd	28.3±1.2	28.3±1.3	28.3±1.3	28.5±1.9
River	Mn	964±16	981±15	986±17	976±16
Sediment	Bi	5.3±0.4	5.0±0.3	4.6±0.5	5.0±0.4
(NRC CRM, [†] China)					
GSD-5	Pb	110±5	111±5	111±3	113±4
River	Mn	1158±20	1183±23	1187±20	1170±20
Sediment	Bi	2.3±0.4	2.3±0.3	2.6±0.3	2.4±0.2
(NRC CRM, [†] China)					
<i>Slurry sampling—</i>					
GBW 08401	Ga	28.3±0.8	29.0±1.0	28.4±1.0	28.3±0.6
Coal Fly	Pb	34.8±0.4	34.1±0.6	34.2±0.4	33.8±0.4
Ash (NRC CRM, [†] China)					
NIST SRM*	Ga	59±1.8	58.2±2.1	58.7±2.0	58
1633a Coal	Pb	72.0±0.6	72.8±0.8	71.8±0.5	72.4±0.4
Fly Ash					

*NIST SRM = National Institute of Standards and Technology, Standard Reference Material.

[†]NRC CRM = National Research Centre for Certified Reference Materials. **Fig. 5** Atomization profile of Pb (0.5 ng) in GBW 08401 Coal Fly Ash with slurry sampling, where A1, sample, A2, standard (0.5 ng Pb); B1 and B2, background absorbance for sample and standard, respectively; and A1_{int} and A2_{int}, integrated absorbance. (a) No modifier: A1_{int}, 0.129 s; B1, 0.161 s; A2_{int}, 0.130 s; and B2, 0.012 s. (b) Pd modifier: A1_{int}, 0.117 s; B1, 0.176 s; A2_{int}, 0.115 s; and B2, 0.004 s. (c) Pd-ascorbic acid modifier: A1_{int}, 0.117 s; B1, 0.161 s; A2_{int}, 0.115 s; and B2, 0.013 s. (d) Pd-Mg modifier: A1_{int}, 0.117 s; B1, 0.503 s; A2_{int}, 0.114 s; and B2, 0.260 s

Pd-Mg modifier. Therefore, Pd is a universal modifier and has been widely applied in atomic spectrometry. The need for the addition of ascorbic acid to Pd appears to be matrix-dependent, while the addition of Mg(NO₃)₂ is not essential, although this compound is sometimes used as an ashing aid in dry-ashing procedures for biological samples.

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