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

SHAN XIAO-QUAN AND WEN BEI

Research Center for Eco-Environmental Sciences, Academia Sinica, P.O. Box 2871, Beijing 100085, China

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, this element, either alone or combined with ascorbic acid or Mg(NO₃)₂, has been widely used for the determination of Hg,²⁻³ Pb,⁴⁻⁶ As,⁸⁻¹³ Se,⁷⁻¹² 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 polyatomic 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 Jackson²⁸ indicated 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.³² 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 Se³³⁻³⁴ and In.³⁵ However, 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.,³⁶ 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 Jackson³⁹ indicated that a sharper absorbance peak, and in many instances a higher recovery, were obtained when Mg was also present. Johannessen et al.,⁴⁰ 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-

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mental materials, the addition of Mg(NO₃)₂ gave no significant improvement in the sensitivity; therefore, Mg(NO₃)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 Mg(NO₃)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 HNO₃-HClO₄-HF or by slurry sampling. This would allow a conclusion to be drawn as to whether the addition of ascorbic acid or Mg(NO₃)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 mol dm⁻³ HNO₃.

Palladium solution was prepared by dissolving PdCl₂ (BDH (now Merck)) in a suitable concentration of HNO₃ with heating. The concentration of Pd for the modification studies was 200 μg cm⁻³. The ascorbic acid solution (1% m/v) was prepared daily from these stock solutions by further dilution with 0.1 mol dm⁻³ HNO₃.

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

| Step | Temperature/°C | Time/s | Internal gas flow rate/cm³ 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 cm³ beaker and 10 cm³ 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 cm³ Teflon container, and 0.5 cm³ of 0.1 mol dm⁻³ HNO₃ was added to moisten the sample thoroughly, followed by 1.5 cm³ of concentrated HNO₃ (67%). The mixture was allowed to stand overnight after which 1 cm³ of concentrated HClO₄ (72%) and 3 cm³ 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 cm³ of concentrated HNO₃ and the washings were added to the container, which was then heated on a hot-plate at about 120 °C until the appearance of HClO₄ fumes, at which point the temperature was increased to 160 °C until the sample was nearly dry. A sufficient volume of 0.1 mol dm⁻³ HNO₃ was then added to dissolve the residue with gentle heating and the resulting solution was transferred into a 25 cm³ calibrated flask. The procedure was repeated several times. The final solution was diluted to the mark with 0.1 mol dm⁻³ HNO₃.

General Procedure

A portion (0.01 cm³) of the standard solution or slurry and 0.01 cm³ of Pd or 0.01 cm³ of Pd plus 0.01 cm³ of ascorbic acid or 0.01 cm³ 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 cm³ 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 μg amount of Pd was found to be sufficient to stabilize all the elements except for Cd, for which a larger
could be used. In addition, the temperature differences were
also similar to those reported by Welz et al.* Considering the
above properties of the modifiers a comparison was made of the
maximum charring temperatures obtained with Pd or Pd-ascorbic
acid for Ag, As, Cd, Hg, Mn and Sn. However, the permissible
charring temperatures were 100°C higher for Bi, Ga, In, Pb,
and other instruments parameters. 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 atomiz-
ation efficiency is improved and a lower m0 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 m0 values
are higher than those obtained in the absence of modifiers.
Considering the above properties of the modifiers a comparison
was made of the m0 values obtained with various modifiers.
The results are given in Table 3, from which it can be seen that
identical m0 values were obtained with Pd and Pd-ascorbic
acid. In fact similar m0 values were obtained with Pd,
and Pd-Mg modifiers in this study, and the
m0 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 m0 values obtained
by the authors and those obtained by Welz et al.* were negligible.

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 tem-
peratures 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 ana-
lytes 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, m0, 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 atomiz-
ation efficiency is improved and a lower m0 is expected. In
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Zeeman-factor, the differences between the m0 values obtained
by the authors and those obtained by Welz et al.* 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 2

| Element | No modifier | Pd | Pd-ascorbic acid | Pd-Mg |
|---------|-------------|----|-----------------|-------|
| Ag      | 700         | 1000 | 1000            | 1000  |
| As      | 300         | 1300 | 1300            | 1300  |
| Au      | 900         | 1200 | 1100            | 1100  |
| Bi      | 600         | 1100 | 1100            | 1200  |
| Cd      | 400         | 900  | 900             | 900   |
| Ga      | 800         | 1200 | 1200            | 1300  |
| Ge      | 800         | 1200 | 1200            | 1400  |
| Hg      | 400         | 400  | 400             | 400   |
| In      | 600         | 1200 | 1200            | 1300  |
| Mn      | 1100        | 1400 | 1400            | 1400  |
| Pb      | 600         | 1000 | 1000            | 1200  |
| Sb      | 900         | 1300 | 1300            | 1200  |
| Se      | 600         | 1000 | 1000            | 1000  |
| Sn      | 800         | 1100 | 1100            | 1200  |
| Te      | 500         | 1200 | 1200            | 1100  |
| Ti      | 600         | 900  | 900             | 1000  |

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

### Table 3

| Element | Atomization temperature /°C | No modifier | Pd | Pd-ascorbic acid | Pd-Mg |
|---------|-----------------------------|-------------|----|-----------------|-------|
| Ag      | 1600                        | 1.9         | 1.8 | 1.8             | 1.4   |
| As      | 2200                        | 14           | 14  | 14              | 14    |
| Au      | 1800                        | 6.5          | 6.5 | 6.5             | 8.4   |
| Bi      | 1900                        | 22           | 22  | 22              | 22    |
| Cd      | 1700                        | 0.5          | 0.4 | 0.4             | 0.4   |
| Ga      | 2200                        | 16           | 18  | 18              | 18    |
| Ge      | 2550                        | 24           | 28  | 28              | 28    |
| Hg      | 1000                        | —             | 110 | 110             | 105   |
| In      | 2300                        | 20           | 17  | 17              | 17    |
| Mn      | 2300                        | 3.4          | 2.9 | 2.9             | 1.9   |
| Pb      | 2000                        | 10           | 14  | 14              | 14    |
| Sb      | 1900                        | 19           | 19  | 19              | 19    |
| Se      | 2100                        | 28           | 25  | 25              | 25    |
| Sn      | 2400                        | 38           | 28  | 28              | 30    |
| Te      | 2250                        | 18           | 16  | 16              | 17    |
| Ti      | 1650                        | 16           | 16  | 16              | 18    |

*Ref. 36.
of Mg(NO₃)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 Ti. 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. 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, CaCl₂ and Na₂SO₄ were chosen as representatives of the interferences. The results 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, CaCl₂ and Na₂SO₄ obtained with the various modifiers are listed in Table 5. The abilities of the three modifiers to remove the interferences from NaCl, CaCl₂ and Na₂SO₄ 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 removing the interferences from NaCl and CaCl₂. 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. demonstrated this

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**Table 4** Comparison of background absorption obtained with Pd, Pd-ascorbic acid and Pd-Mg(NO₃)₂

| Element | Background absorption at the maximum thermal pre-treatment temperature/s |
|---------|---------------------------------------------------------------|
|                   | Pd             | Pd-ascorbic acid | Pd-Mg             |
| Ag     | 0.004 | 0.007 | 0.072 |
| As     | 0.003 | 0.012 | 0.043 |
| Au     | 0.001 | 0.003 | 0.272 |
| Bi     | 0.014 | 0.013 | 0.176 |
| Cd     | 0.002 | 0.034 | 0.243 |
| Ge     | 0.003 | 0.001 | 0.137 |
| Hg     | 0.014 | 0.010 | 0.243 |
| In     | 0.008 | 0.025 | 0.061 |
| Mn     | 0.006 | 0.005 | 0.152 |
| Pb     | 0.002 | 0.002 | 0.458 |
| Sb     | 0.011 | 0.010 | 0.217 |
| Se     | 0.003 | 0.006 | 0.297 |
| Sn     | 0.000 | 0.011 | 0.038 |
| Te     | 0.008 | 0.013 | 0.294 |
| Ti     | 0.005 | 0.024 | 0.232 |

**Table 5** Comparison of the maximum permissible concentrations of NaCl, CaCl₂ and SO₄²⁻ as Na₂SO₄ in the presence of modifiers

| Element | Concentration of element/µg dm⁻³ | Modifier | Maximum concentration of interferent/g dm⁻³ |
|---------|---------------------------------|---------|------------------------------------------|
| Ag     | 0.1 | Pd             | 5       | 0.1 | 0.5 |
| As     | 1   | Pd             | 10      | 2   | 2   |
| Au     | 1   | Pd             | 10      | 5   | 0.1 |
| Bi     | 1   | Pd             | 2       | 1   | 1   |
| Cd     | 0.1 | Pd             | 0.3     | 0.2 | 1   |
| Ga     | 1   | Pd             | 2       | 1   | 2   |
| Ge     | 2   | Pd             | 50      | 2   | 0.1 |
| Hg     | 4   | Pd             | 10      | 0.1 | 30  |
| In     | 1   | Pd             | 5       | 5   | 5   |
| Mn     | 0.1 | Pd             | 30      | 3   | 20  |
| Pb     | 1   | Pd             | 20      | 5   | 0.5 | 0.1 |
| Sb     | 1   | Pd             | 30      | 10  | 30  |
| Se     | 1   | Pd             | 1       | 0.5 | 0.05 |
| Sn     | 1   | Pd             | 50      | 3   | 1   |
| Te     | 1   | Pd             | 30      | 5   | 1   |
| Ti     | 1   | Pd             | 20      | 5   | 3   | 2   | 0.1 |

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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 HNO₃, HClO₄ 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 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. 1 Atomization profile of Pb (0.5 ng) in GSD-5 River Sediment after sample decomposition with HNO₃–HClO₄–HF, where A₁, sample; A₂, standard (0.5 ng Pb); B₁ and B₂, background absorbance for sample and standard, respectively; and A₁int and A₂int, integrated absorbance. (a) No modifier: A₁int, 0.129 s; B₁, 0.110 s; A₂, 0.131 s; and B₂, 0.006 s. (b) Pd modifier: A₁int, 0.115 s; B₁, 0.134 s; A₂, 0.113 s; and B₂, 0.013 s. (c) Pd–ascorbic acid modifier: A₁int, 0.113 s; B₁, 0.132 s; A₂, 0.113 s; and B₂, 0.013 s. (d) Pd–Mg modifier: A₁int, 0.110 s; B₁, 0.270 s; A₂, 0.113 s; and B₂, 0.200 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. 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. There is increasing evidence that physical processes play a predominant role in the modifying action of metals such as Pd. 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.

**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(NO$_3$)$_2$ after acid decomposition of the samples and by slurry sampling

| Sample          | Element | This work | Certified value |
|-----------------|---------|-----------|-----------------|
|                 |         | Pd        | Pd-ascorbic acid| Pd-Mg |
|                 |         | 28.3±1.2  | 28.3±1.3        | 28.5±1.9 |
|                 |         | 964±16    | 981±15          | 976±16  |
| Sediment        | Bi      | 5.3±0.4   | 5.0±0.3         | 5.0±0.4 |

- **GSD-6**
- **River**
- **Sediment (NRC CRM, China)**

**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(NO$_3$)$_2$ is not essential, although this compound is sometimes used as an ashing aid in dry-ashing procedures for biological samples.

REFERENCES

1. Shan, X.-q., and Ni, Z.-m., *Hua Hsheh Hsheh Pao*, 1979, 37, 261.
2. Liu, P., Fuwa, K., and Matsumoto, K., *Anal. Chim. Acta*, 1985, 171, 279.
3. Welz, B., Schlemmer, G., and Mudakavi, J. R., *J. Anal. At. Spectrom.*, 1992, 7, 499.
4. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1983, 151, 179.
5. Fang, Y., Wuer, G., and Wei, F.-s., *J. Anal. At. Spectrom.*, 1985, 3, 125.
6. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1983, 151, 179.
7. Knowles, M. B., and Brodie, K. G., *J. Anal. At. Spectrom.*, 1988, 3, 311.
8. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1984, 31, 150.
9. Shan, X.-q., Yuan, Z.-n., and Ni, Z.-m., *Can. J. Spectrosc.*, 1986, 31, 35.
10. Jin, L.-z., and Ni, Z.-m., *Can. J. Spectrosc.*, 1985, 31, 219.
11. Shan, X.-q., Ni, Z.-m., and Yuan, Z.-n., *Anal. Chim. Acta*, 1985, 171, 269.
12. Niskavaara, H., Virtasalo, J., and Lajunen, L. H. J., *Spectrochim. Acta, Part B*, 1985, 40, 1219.
13. Sampson, B., *J. Anal. At. Spectrom.*, 1988, 3, 465.
14. Niskavaara, H., and Virtasalo, J., *Spectrochim. Acta, Part B*, 1987, 42, 917.
15. Tsalev, D. L., and Slaveykova, V. I., *J. Anal. At. Spectrom.*, 1992, 7, 147.
16. Styris, D. L., Prell, L. J., and Redfield, D. A., *Anal. Chem.*, 1991, 63, 503.
17. Styris, D. L., Prell, L. J., Redfield, D. A., Holcombe, J. A., Bass, D. A., and Majidi, Y., *Anal. Chem.*, 1991, 63, 508.
18. Arpadjan, S., Karadjoova, I., Tserovski, E., and Aneva, Z., *J. Anal. At. Spectrom.*, 1990, 5, 195.

**REFERENCES**

1. Shan, X.-q., and Ni, Z.-m., *Hua Hsheh Hsheh Pao*, 1979, 37, 261.
2. Liu, P., Fuwa, K., and Matsumoto, K., *Anal. Chim. Acta*, 1985, 171, 279.
3. Welz, B., Schlemmer, G., and Mudakavi, J. R., *J. Anal. At. Spectrom.*, 1992, 7, 499.
4. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1983, 151, 179.
5. Fang, Y., Wuer, G., and Wei, F.-s., *J. Anal. At. Spectrom.*, 1985, 3, 125.
6. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1983, 151, 179.
7. Knowles, M. B., and Brodie, K. G., *J. Anal. At. Spectrom.*, 1988, 3, 311.
8. Shan, X.-q., Ni, Z.-m., and Wang, L., *Anal. Chim. Acta*, 1984, 31, 150.
9. Shan, X.-q., Yuan, Z.-n., and Ni, Z.-m., *Can. J. Spectrosc.*, 1986, 31, 35.
10. Jin, L.-z., and Ni, Z.-m., *Can. J. Spectrosc.*, 1985, 31, 219.
11. Shan, X.-q., Ni, Z.-m., and Yuan, Z.-n., *Anal. Chim. Acta*, 1985, 171, 269.
12. Niskavaara, H., Virtasalo, J., and Lajunen, L. H. J., *Spectrochim. Acta, Part B*, 1985, 40, 1219.
13. Sampson, B., *J. Anal. At. Spectrom.*, 1988, 3, 465.
14. Niskavaara, H., and Virtasalo, J., *Spectrochim. Acta, Part B*, 1987, 42, 917.
15. Tsalev, D. L., and Slaveykova, V. I., *J. Anal. At. Spectrom.*, 1992, 7, 147.
16. Styris, D. L., Prell, L. J., and Redfield, D. A., *Anal. Chem.*, 1991, 63, 503.
17. Styris, D. L., Prell, L. J., Redfield, D. A., Holcombe, J. A., Bass, D. A., and Majidi, Y., *Anal. Chem.*, 1991, 63, 508.
18. Arpadjan, S., Karadjoova, I., Tserovski, E., and Aneva, Z., *J. Anal. At. Spectrom.*, 1990, 5, 195.
25 Zhuang, Z., Yang, P., Luo, J., Wang, X., and Huang, B., Can. J. Appl. Spectrosc., 1991, 36, 9.
26 Votynský, A., Tikhomirov, S., and Elagin, A., Analyst, 1991, 116, 145.
27 Majidi, V., and Robertson, D., Spectrochim. Acta, Part B, 1991, 46, 1723.
28 Qiao, H., and Jackson, K. W., Spectrochim. Acta, Part B, 1991, 46, 1841.
29 Qiao, H., and Jackson, K. W., Spectrochim. Acta, Part B, 1992, 47, 1267.
30 Voth-Beach, L. M., and Shadrer, D. E., Spectroscopy, 1986, 1, 49.
31 Voth-Beach, L. M., and Shadrer, D. E., J. Anal. At. Spectrom., 1987, 2, 45.
32 Jacobson, B. L., and Lockitct, G., Clin. Chem. (Winston-Salem, N.C.), 1988, 34, 709.
33 Knowles, M. B., and Brodie, K. G., J. Anal. At. Spectrom., 1988, 3, 511.
34 Pohl, B., Knowles, M., and Grund, A., Fresenius’ Z. Anal. Chem., 1987, 327, 20.
35 Welz, B., Schlemmer, G., and Mudakavi, J. R., Anal. Chem., 1988, 60, 2567.
36 Welz, B., Schlemmer, G., and Mudakavi, J. R., J. Anal. At. Spectrom., 1992, 7, 1257.
37 Hinds, M. W., and Jackson, K. W., J. Anal. At. Spectrom., 1990, 5, 199.
38 Bozal, G., Schlemmer, G., and Grobenski, Z., Talanta, 1990, 37, 545.
39 Johannessen, J. K., Gammelgaard, B., Jens, O., and Hansen, S. H., J. Anal. At. Spectrom., 1993, 8, 999.
40 Granadillo, V. A., Navarro, J. A., and Romero, R. A., J. Anal. At. Spectrom., 1993, 8, 615.
41 L'vov, B. V., Spectrochim. Acta, Part B, 1978, 33, 153.
42 Slavina, W., Mazzing, D. C., and Carnrick, G. R., Talanta, 1989, 36, 171.
43 Macdonald, L. R., O’Haver, T. C., Ottaway, B. J., and Ottaway, J. M., J. Anal. At. Spectrom., 1986, 1, 485.
44 Shan, X-q., Wang, W., and Wen, B., J. Anal. At. Spectrom., 1992, 7, 761.
45 Strys, D. L., and Redfield, D. A., Spectrochim. Acta Rev., 1993, 15, 71.

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