

# Lead Atomisation from Soil by Slurry Introduction Electrothermal Atomisation Atomic Absorption Spectrometry

## Part 2.\* Atomisation Characteristics With Various Matrix Modifiers

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Lead atomic absorption signals were obtained from a model soil matrix (montmorillonite and humic acid) introduced into a graphite furnace as slurry particles. The effects of various matrix modifiers on the absorbance-peak characteristics were studied. This provided information on probable atomisation processes and mechanisms of matrix modification. Several soils were analysed and the modifiers Mg, phosphate, a Mg - phosphate mixture, Pd and a Mg - Pd mixture were all effective. The Mg - Pd mixture was the most suitable, because it produced similar absorbance appearance and peak maximum times for the slurries and aqueous calibration standards. Other matrix modification methods (making the slurry in 1% HNO<sub>3</sub>, O<sub>2</sub> ashing and pre-slurry ashing in a muffle furnace) were less suitable, because the Pb atomisation characteristics differed from those of aqueous standards.

**Keywords:** *Electrothermal atomisation atomic absorption spectrometry; slurry; atomisation studies; matrix modifiers; soil analysis*

In Part 1 of this series<sup>1</sup> a model was presented to describe the atomisation of Pb from soil particles introduced into a graphite furnace as a slurry. The soil matrix was simulated by the clay montmorillonite with added humic acid. Montmorillonite has Pb adsorbed on its particles, and this is similar to the manner in which Pb is incorporated in soil. Through the use of this model, adsorption on montmorillonite particles was found to delay Pb atomisation, but organic matter (humic acid) counteracted this effect by early shifting the Pb absorbance signal. Hence, soils with a high carbon concentration could suffer volatilisation loss of Pb unless a matrix modifier is used. This was demonstrated in a later publication.<sup>2</sup> The modifiers examined in Part 1<sup>1</sup> were phosphate and Mg (separately and in combination). Recently, Pd<sup>3-6</sup> and a Mg - Pd mixture<sup>7</sup> have been promoted as universal matrix modifiers. A Mg - Pd mixture was effective for the determination of Pb in soil slurries,<sup>2</sup> but smaller amounts of Pd (as PdCl<sub>2</sub>) were needed compared with previous reports.

It is evident from reviews of electrothermal atomisation atomic absorption spectrometric (ETA-AAS) methods<sup>8,9</sup> that, for each analyte and matrix, there are different recommended modifier schemes arising from mainly empirical studies. It is now appropriate for efforts to be made to understand the mechanisms by which some common modifiers act on elements of varying volatilities and in different matrices. When these situations are understood, perhaps matrix modification for other situations could be guided more by theory than by empirical study. Some work has been conducted in this vein. Czobik and Matousek<sup>10</sup> postulated that phosphate acts on the analyte to form the pyrophosphate prior to atomisation. Evidence for this was also provided by Bass and Holcombe<sup>11</sup> and Wendl and Muller-Vogt.<sup>12</sup> Slavin *et al.*<sup>13</sup> speculated that analyte atoms are embedded within particles of MgO when Mg(NO<sub>3</sub>)<sub>2</sub> is used as a modifier. Studies on Pd as a modifier indicated its reduction during the charring step<sup>6</sup> and formation of Pb-Pd bonds.<sup>4</sup> More work is needed to define clearly the mechanisms of these modification reactions. This paper presents a systematic study of the effects of some modifiers on the atomisation characteristics of Pb when it is

introduced into the ETA as a solution and as slurry particles. The measurement of absorbance-peak characteristics and activation energies has allowed an insight into likely atomisation processes. In order to simplify the complex matrix of soil,<sup>14</sup> the montmorillonite - humic acid model used in Part 1<sup>1</sup> has also been used in this work.

## Experimental

### Apparatus

The ETA-AA spectrometer was the same as in Part 1.<sup>1</sup> As described previously,<sup>15</sup> the spectrometer (Perkin-Elmer Model 2280) and optical pyrometer (Series 1100, Ircon, Niles, IL, USA) were interfaced to a 12-bit A/D board (Model DT2801, Data Translation, Marlborough, MA, USA) inside an IBM-PC microcomputer. An essential feature for this work was the accurate (within 1/60 s) correlation of absorbance, time and pyrometric temperature. Wall and platform atomisation were investigated with Perkin-Elmer pyrolytic graphite coated tubes and solid pyrolytic graphite L'vov platforms. The operating parameters are listed in Table 1. In all instances, deuterium-arc background corrected absorbances were measured.

### Samples and Reagents

The montmorillonite (Ward's Natural Science, Mississauga, Ontario, Canada) used in this study was described in the American Petroleum Institute Research Report No. 49.<sup>16</sup> It was ground to <20- $\mu$ m particle diameter using a miniature ball mill (Retsch Model MM2, Brinkman Instruments, Rexdale, Ontario, Canada). Within this size range, analyte atomisation efficiency is unaffected by changes in particle diameter.<sup>17</sup> Soils used were certified reference materials prepared by Energy, Mines and Resources, Canada.<sup>18,19</sup> They did not require further grinding. Soils were oven dried at 105 °C for 24 h prior to use.

All water was glass distilled and had no measurable Pb concentration. Analytical-reagent grade chemicals were used throughout. The following stock solutions were prepared in 1% HNO<sub>3</sub>: 1000 mg l<sup>-1</sup> Pb prepared from Pb(NO<sub>3</sub>)<sub>2</sub>

\* For Part 1 of this series, see reference 1.

(Analchemia Chemicals, Mississauga, Ontario, Canada), 10% *m/V* Mg from Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (BDH Chemicals, Toronto, Ontario, Canada), 10% *m/V* (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (BDH) and 5000 mg l<sup>-1</sup> Pd prepared from PdCl<sub>2</sub> (BDH). A humic acid slurry was prepared from its sodium salt (Aldrich Chemicals, Milwaukee, WI, USA) by stirring 0.12 g of the acidified material overnight in 80 ml of water.

Solution and Slurry Preparation

Aqueous solutions

Dilution of the Pb stock solution with 1% HNO<sub>3</sub> allowed appropriate amounts to be injected into the ET atomiser using a 10-μl micropipette (Socorex ISBA SA, 1020 Renens, Switzerland). Matrix modifier solutions (10-μl aliquots) were added to the ETA after partially drying the sample aliquot. With platform atomisation, this ensured that the platform cavity was not overfilled. Amounts of Pb and modifier used in wall and platform atomisation are given in Table 2.

Slurries

Slurries were prepared by adding 30 mg of montmorillonite or 45 mg of soil to exactly 20 ml of distilled water in a beaker. After stirring magnetically for a minimum of 5 min, appropriate amounts of humic acid slurry (to the montmorillonite) and matrix modifiers (from the stock solutions) were added. The amounts were small, so dilution effects were negligible. For platform atomisation, 10 μl of montmorillonite or 20 μl of soil slurry (*i.e.*, 45 μg of soil) were micropipetted (Socorex) into the ETA. For wall atomisation, 20 μl of montmorillonite slurry were used. The amounts of Pb and modifier added to the ETA per aliquot of montmorillonite slurry were the same as those used for aqueous solutions. These, together with the amounts of montmorillonite and humic acid used, are given in Table 2.

Measurement of Wall Atomisation Parameters

The ETA-AA spectrometer provides a print-out of time, background-corrected absorbance and temperature at 1/60-s intervals.<sup>15</sup> From this, appearance temperatures (*T*<sub>app</sub>) were measured accurately as the temperature when the background-corrected absorbance became consistently greater than 0.010 (*i.e.*, the analytical signal was clearly above the base-line noise). Arrhenius activation energies (*E*<sub>a</sub>) were determined from the data print-outs. A simple algorithm<sup>15</sup> allowed automatic calculation of *E*<sub>a</sub> by Smets' method,<sup>20</sup> which uses the rising edge of the absorbance profile. At least

five data points were used in calculating *E*<sub>a</sub> values. A new graphite tube was used with each modifier.

Measurement of Platform Atomisation Parameters

Appearance times (*τ*<sub>app</sub>) were measured from the beginning of the atomisation stage to the point where the analytical signal became consistently greater than 0.010 A. The peak maximum time (*τ*<sub>peak</sub>) was the time from the beginning of the atomisation stage to the time of maximum background-corrected absorbance. For quantitative determinations of Pb in soil, aqueous calibration standards were prepared in 1% HNO<sub>3</sub> from the Pb stock solution. Matrix modifiers were added in the same amounts to standards and soil slurries alike. Integrated absorbances were measured. A new tube and platform were used for each modifier. In light of the recent paper by Shuttler and Delves,<sup>21</sup> the Pb signal was checked whenever a tube or platform was replaced. This was carried out by atomising a Pb standard solution and comparing the absorbance *versus* time signal profile obtained with that of a reference tube and platform. Specifically, the tube - platform combination was rejected if *τ*<sub>app</sub>, *τ*<sub>peak</sub> or the peak absorbance had changed significantly.

Results and Discussion

Wall atomisation measurements (*T*<sub>app</sub> and *E*<sub>a</sub>) were used to follow changes in atomisation processes when different modifiers were used. Aqueous Pb solutions and montmorillonite slurries (with and without humic acid) were studied. Results of *T*<sub>app</sub> measurements are reproducible [Fig. 1(a)] and they can indicate the temperatures at which compounds on the graphite surface vaporise or dissociate. Results of *E*<sub>a</sub> measurements (Table 3) must be interpreted with care. Frech *et al.*<sup>22</sup> noted that uncertainty in these measurements could arise with changing tube surface effects and with several mechanisms occurring during atomisation. The presence of large amounts of solid material during slurry atomisation would probably incur both of these effects. In this paper, changes in *E*<sub>a</sub> values are interpreted as indicating probable changes in the atomisation mechanism. Previously,<sup>23</sup> an inner gas flow (Ar at 50–100 ml min<sup>-1</sup>) through the graphite tube was maintained during *E*<sub>a</sub> measurements to ensure that the rate of removal was greater than the rate of atom formation. However, the associated loss in sensitivity necessitated large sample masses, and bulk mass transfer effects might then influence atomisation. In order to permit the use of stopped gas flow conditions, a slow heating rate was used as an alternative way of keeping the rate of formation less than the rate of removal. This allowed the use of 1.26-ng amounts of analyte, *i.e.*, only double those used for platform atomisation. It was then possible to use the same amounts of modifiers in wall and platform atomisation measurements. The *E*<sub>a</sub> obtained for Pb solutions under these conditions (196 ± 6 kJ mol<sup>-1</sup>) is in agreement with the result from Karwowska and Jackson<sup>23</sup> (188 ± 26 kJ mol<sup>-1</sup>) who used an inner gas flow and a heating rate of 250 °C s<sup>-1</sup>.

Platform atomisation results (*τ*<sub>app</sub> and *τ*<sub>peak</sub>) are given in Fig. 1(b). These parameters depend on instrumental conditions, particularly the tube heating rate, and on the mass and heat conducting properties of the platforms. Hence, they are not exact measurements that can be related to atomisation processes. However, they show the behaviour of samples under real analytical conditions, and trends in peak characteristics can be studied. In particular, the signal delaying

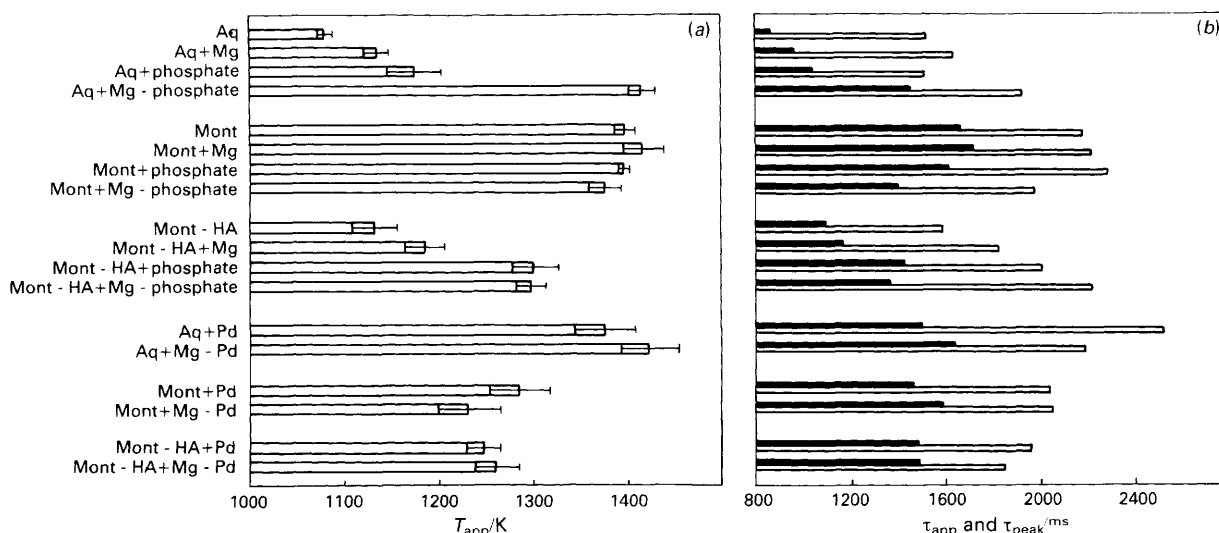
Table 1. Instrumental operating parameters

Parameter	ETA stage				
	Dry	Char	Cool*	Atomise	Clean
Temperature/°C	130	900	200	1900*/2000†	2700
Ramp time/s	10	20	10	0*/2†	1
Hold time/s	60	30	20	5	5
Wavelength/nm	..	..	..	283.3	..
Spectral band width/nm	..	..	..	0.7	..
Lamp current/mA	..	..	..	8	..
Purge gas	..	..	..	Ar (flow stopped during the atomise stage)	..

\* Platform atomisation.  
† Wall atomisation.

Table 2. Amounts of analyte, matrix and matrix modifier per aliquot of aqueous solution or montmorillonite slurry

Atomisation mode	Pb/ng	Montmoril-lonite/μg	Humic acid/μg	Mg/μg	Phosphate/μg	Pd/μg
Wall .. ..	1.26	30	4.5	1.0	14	0.6
Platform .. ..	0.63	15	2.3	1.0	14	0.6



**Fig. 1.** Absorbance-peak characteristics for: (a) wall atomisation; and (b) platform atomisation. Appearance temperature ( $T_{app}$ ) shows precision limits ( $\pm 1$  standard deviation). Precision limits (1 standard deviation) for the characteristic times [ $\tau_{app}$  (shaded area) and  $\tau_{peak}$  (unshaded area)] are  $\pm 65$  ms. Aq = aqueous Pb solution; Mont = montmorillonite (added as a slurry); Mont - HA = montmorillonite containing 15% humic acid (added as a slurry). For amounts of Mg, phosphate and Pd, see Table 2

**Table 3.** Experimental activation energies for Pb

Sample*	$E_a$ †/kJ mol <sup>-1</sup>
Aq . . . . .	196 ± 6
Aq + Mg . . . . .	215 ± 37
Aq + phosphate . . . . .	348 ± 37
Aq + Mg - phosphate . . . . .	636 ± 46
Mont . . . . .	266 ± 26
Mont + Mg . . . . .	394 ± 31
Mont + phosphate . . . . .	231 ± 15
Mont + Mg - phosphate . . . . .	286 ± 46
Mont - HA . . . . .	219 ± 20
Mont - HA + Mg . . . . .	158 ± 19
Mont - HA + phosphate . . . . .	248 ± 19
Mont - HA + Mg - phosphate . . . . .	234 ± 22
Aq + Pd . . . . .	248 ± 13
Aq + Mg - Pd . . . . .	240 ± 40
Mont + Pd . . . . .	268 ± 58
Mont + Mg - Pd . . . . .	219 ± 43
Mont - HA + Pd . . . . .	317 ± 27
Mont - HA + Mg - Pd . . . . .	413 ± 34

\* Aq = aqueous Pb solution; Mont = montmorillonite (added as a slurry); Mont - HA = montmorillonite containing 15% humic acid (added as a slurry). For amounts of Mg, phosphate and Pd, see Table 2.

† Error limits are one standard deviation.

capabilities of modifiers can be compared from  $\tau_{app}$  results, and their effects on the duration of the atomisation signal (temporal peak widths) can be compared using  $\tau_{app}$  and  $\tau_{peak}$  measurements. In the results presented below there is no attempt to compare directly platform and wall parameters.

### Magnesium and Phosphate Matrix Modifiers

#### Effect on aqueous Pb solutions

Previous work<sup>2</sup> showed that 14  $\mu$ g of phosphate and 1  $\mu$ g of Mg would have a strong delaying effect on the atomisation of 0.6 ng of Pb from soil slurries. These amounts were used first to examine the effect of the modifiers on aqueous Pb solutions. The trends (Fig. 1), in both wall and platform atomisation, were as expected.

Magnesium alone delays atomisation. Slavin *et al.*<sup>13</sup> suggested that this delay is caused by analyte atoms becoming embedded in the MgO remaining after  $Mg(NO_3)_2$  is charred. It would be expected that Pb atomisation would then be delayed until MgO vaporised. Sturgeon *et al.*<sup>24</sup> determined

that MgO dissociated at 1510 K on vaporisation (for 0.4 ng of Mg). In the present work, an AA measurement on 1  $\mu$ g of Mg gave a  $T_{app}$  of 1411 K. However, Fig. 1(a) shows that Pb atoms were released at 1135 K in the presence of Mg, so the suggestion of Pb occlusion within MgO may be misleading (unless vaporisation of MgO occurs at a much lower temperature than its dissociation). Possibly Pb atoms are adsorbed either physically or chemically on MgO particles. The similarity in  $E_a$  values for the atomisation of Pb with and without Mg (Table 3) suggests that Mg may not change the atomisation mechanism of Pb. Also, the peak profile ( $\tau_{peak} - \tau_{app}$ ) is similar with and without added Mg.

Phosphate had a slightly greater delaying action than Mg on Pb atomisation, and produced sharper peaks (indicated by  $\tau_{peak}$ ). An increase in  $E_a$  over the aqueous Pb result indicates that phosphate changes the atomisation mechanism. Czobik and Matousek<sup>10</sup> concluded that  $Pb_2P_2O_7$  was formed through the heterogeneous reaction between  $PbO(s)$  and  $P_4O_{10}(g)$ . Formation of this pyrophosphate has been supported by Bass and Holcombe<sup>11</sup> from combined mass spectrometry - AAS studies. They postulated the formation of a short-lived  $PbO$  - graphite species upon decomposition of the pyrophosphate. Their  $T_{app}$  (1150 K) was in close agreement with our value (1176 K in Fig. 1). This temperature is reasonably close to the melting-point of  $Pb_2P_2O_7$  at 1097 K<sup>25</sup> and its probable decomposition temperature of 1208 K.<sup>26</sup> Neither Czobik and Matousek<sup>10</sup> nor Bass and Holcombe<sup>11</sup> used a charring step in their furnace heating cycle, but charring appears to influence the type of Pb - phosphate compounds produced. After charring at 1100 K, Wendl and Muller-Vogt<sup>12</sup> observed that phosphate modification left species such as  $Pb_3(PO_4)_2$ ,  $PbO$  and Pb on the graphite surface. However, they observed  $Pb_3(PO_4)_2$  and  $Pb_8P_2O_{13}$  after charring at 500 and 700 K.

The combination of Mg and phosphate is a recommended matrix modifier<sup>27,28</sup> and it resulted in a large delay in Pb atomisation. As with phosphate alone, platform atomisation peaks are narrower than without modifier. The much higher  $E_a$  (compared with either Mg or phosphate alone) indicates a different atomisation mechanism. Perhaps Pb is embedded in particles of  $Mg_3(PO_4)_2$  and is released when this compound melts at 1457 K.<sup>25</sup> This temperature is close to the  $T_{app}$  of 1415 K in Fig. 1.

#### Effect on Pb adsorbed on montmorillonite

The two major matrix components of soil are clay and organic matter. Previously<sup>1</sup> the clay matrix was shown to delay Pb



atomisation, because Pb is adsorbed on the clay particles. This was consistent with atomisation studies on Pb adsorbed on alumina particles.<sup>23,29</sup> Fig. 1 shows this delay in both wall ( $T_{app}$ ) and platform ( $\tau_{app}$ ) atomisation, compared with the aqueous solution. The  $E_a$  (Table 3) is not much higher than the value for aqueous Pb solutions, suggesting that the Pb - clay interaction is weak. When montmorillonite is slurried with distilled water, no detectable amounts of Pb are displaced into solution, *i.e.*, the solid material in the furnace remains as clay particles with adsorbed Pb. On heating to atomisation temperature, it is likely that Pb or PbO is released from the particle surface and then undergoes multiple collisions with the graphite wall. At the elevated temperatures ( $\geq 1400$  K) of Pb release, the dissociation of any PbO should be rapid. Also, Pb - graphite interactions are weak, so Pb atoms will tend not to stick to the graphite tube wall. Therefore, the rate-limiting process should be desorption from the clay particles.

On addition of Mg, no detectable amounts of Pb are displaced from the particle into solution. Addition of phosphate or the Mg - phosphate mixture displaces only about 5% of the adsorbed Pb. This is probably due to the counter ions ( $\text{NH}_4^+$  and  $\text{H}^+$ ) in solution with the phosphate. Hence, when Mg, phosphate or Mg - phosphate are added to montmorillonite, it can be assumed that, after drying in the furnace, almost all the Pb remains bound to the clay particles, and the modifier is spread on the particles and the graphite surface. It is likely, therefore, that Pb - modifier reactions do not occur prior to vaporisation. On heating to the atomisation temperature ( $\geq 1400$  K), the matrix modifiers will be mostly vaporised and the Pb atoms released from the clay particles. Interactions between Pb and the matrix modifiers may then occur as gas-, heterogeneous- or condensed-phase reactions after collision with the graphite walls. Whichever mechanism occurs, these reactions are likely to be rapid compared with the desorption of Pb from the particles. Hence, the rate-limiting step should be desorption, irrespective of the matrix modifier (Mg, phosphate or Mg - phosphate). The similarity of  $T_{app}$  values (Fig. 1) between Pb adsorbed on montmorillonite without modifier and with Mg, phosphate or Mg - phosphate supports this atomisation mechanism. Also, the  $E_a$  values are similar, except where a Mg matrix modifier is used. This high  $E_a$  value cannot be explained.

The similarity of the four  $T_{app}$  values would predict platform  $\tau_{app}$  values to be similar. However, when the Mg - phosphate mixture is added to montmorillonite,  $\tau_{app}$  is at least 200 ms shorter compared with the other montmorillonite slurries. Also, there is some indication of peak broadening (greater  $\tau_{peak}$ ). This behaviour cannot be explained, but the more reproducible conditions of wall atomisation are expected to give the more accurate prediction of atomisation behaviour.

The addition of 15% humic acid to the montmorillonite slurry has resulted in an earlier shift of the absorbance signal, *i.e.*,  $T_{app}$  is 1133 K compared with 1400 K for a montmorillonite slurry with no added humic acid. However, the signal is delayed compared with aqueous Pb ( $T_{app} = 1080$  K). This agrees with earlier studies,<sup>1</sup> when it was suggested that the humic acid acts as an oxygen scavenger to lower the partial pressure of  $\text{O}_2$  and aid the release of Pb from the particle surface.

Unlike the situation without humic acid, the addition of matrix modifiers to the slurries has changed the Pb atomisation characteristics. On adding Mg there is a small increase in  $T_{app}$  (from 1133 to 1185 K). At this temperature, MgO(s) can exist. Therefore, the atomisation process may now involve desorption of Pb from slurry particles followed by adsorption on MgO particles and subsequent desorption. This might also explain why platform peaks are now broadened somewhat (greater  $\tau_{peak}$ ). The difference in  $E_a$  values between montmorillonite - humic acid with or without Mg may not be significant. Phosphate delays atomisation for longer than Mg, and this is to be expected if atomisation proceeds via Pb

desorption from montmorillonite followed by its reaction with phosphorus-containing species. The  $E_a$  for Pb atomisation when phosphate is added to montmorillonite - humic acid is smaller than the  $E_a$  value for phosphate added to aqueous Pb. The effectiveness of phosphate may be reduced in the presence of humic acid because a colour change from dark grey to dark red - brown is observed on adding phosphate to the slurries. (A slight colour change is also seen on adding phosphate to soil slurries.) This probably results from a reaction between the phosphate ion and humic acid. No colour change was apparent when the counter ions in  $(\text{NH}_4)_2\text{HPO}_4$  were added to the montmorillonite - humic acid slurry ( $\text{NH}_4^+$  as  $\text{NH}_4\text{NO}_3$  and  $\text{H}^+$  as  $\text{HNO}_3$ ). Phosphate, in the presence of humic acid also produced substantially greater background absorbances than other modifiers. (For a Pb peak absorbance of 0.5, the background peak absorbance was 0.1-0.2). Addition of Mg to phosphate did not significantly change its effect on the atomisation of Pb from montmorillonite - humic acid. This appears to preclude the entrapment of Pb in  $\text{Mg}_3(\text{PO}_4)_2$  in this instance, because  $T_{app}$  (1300 K) is much lower than the melting-point (1457 K) of this compound.<sup>25</sup> The formation of the humic acid - phosphorus compound is presumably more favourable. In all instances, platform atomisation ( $\tau_{app}$ ) values follow the same trends as those for wall atomisation ( $T_{app}$ ) results.

### Palladium and Magnesium Matrix Modifiers

#### Effect on aqueous Pb solutions

The optimum amounts of Pd, with and without the addition of Mg, were established previously<sup>2</sup> for aqueous solutions and for soil slurries. For solutions, as little as 3  $\mu\text{g}$  of Pd produced large delays in Pb atomisation, and the amount could be reduced to 0.6  $\mu\text{g}$  of Pd if at least 1  $\mu\text{g}$  of Mg was present. In Fig. 1, 0.6  $\mu\text{g}$  of Pd delayed  $T_{app}$  to 1380 K and 0.6  $\mu\text{g}$  Pd + 1  $\mu\text{g}$  Mg delayed it further to 1425 K. The use of Pd alone produced a broad peak (large  $\tau_{peak}$ ), but the addition of Mg made it sharper (smaller  $\tau_{peak}$ ). The  $T_{app}$  value for the use of Mg - Pd is slightly lower than the 1470 K reported by Schlemmer and Welz,<sup>30</sup> but they used larger amounts of Pd and dissolved Pd in  $\text{HNO}_3$ , whereas  $\text{PdCl}_2$  was used in the present work. There seems to be agreement<sup>4,6,7</sup> that the most likely mechanism involves the formation of Pb-Pd bonds, but the role of Mg is unclear. In spite of the large atomisation delaying characteristics of Pd and Mg - Pd,  $E_a$  values (Table 3) are increased only slightly compared with aqueous Pb without matrix modifier.

#### Effect on Pb adsorbed on montmorillonite

Previously, when Pd was added to a soil slurry,<sup>2</sup> up to 20% of the adsorbed Pb was displaced into solution. With montmorillonite, the addition of Pd alone or in combination with Mg displaced approximately 70% of the Pb into solution. Clays are cation exchangers, and this difference can be attributed to the high ion-exchange capacity of pure clay (montmorillonite) compared with soil. Magnesium alone did not displace Pb, as mentioned earlier. This displacement may partly explain the reduction in  $T_{app}$ ,  $\tau_{app}$  and  $\tau_{peak}$  for Pb atomised from montmorillonite when Pd is added. However, these parameters are also smaller than for the aqueous Pb solution with added Pd, *i.e.*, on atomisation of Pb, the presence of montmorillonite inhibits the effectiveness of Pd or Mg - Pd. This effect is more pronounced with wall ( $T_{app}$ ) than platform ( $\tau_{app}$ ) atomisation. Unlike solutions, the addition of Mg to the slurry has not significantly improved the delaying effectiveness of Pd.

Adding humic acid to the montmorillonite has not significantly affected either  $T_{app}$  or  $\tau_{app}$ , although the  $E_a$  values are much higher.

### Comparison of Matrix Modification Methods

Matrix modification serves a dual purpose in ETA-AAS. It allows charring temperatures to be increased without analyte

**Table 4.** Absorbance-peak characteristic times for platform atomisation with various matrix modification methods

Modification method†	Characteristic time*/ms					
	Soil slurry (SO-4)			Aqueous solution		
	$\tau_{app}$	$\tau_{peak}$	$\Delta\tau$	$\tau_{app}$	$\tau_{peak}$	$\Delta\tau$
Pre-slurry ash . . . . .	1603	2474	871	—	—	—
Mg - Pd . . . . .	1530	1973	443	1641	2188	547
Pd . . . . .	1468	1889	421	1505	2518	1013
O <sub>2</sub> ash . . . . .	1319	1860	541	—	—	—
Mg - phosphate . . . . .	1212	1818	606	1455	1921	466
Mg . . . . .	1274	1764	490	968	1634	666
Phosphate . . . . .	1148	1599	451	1040	1513	473
1% HNO <sub>3</sub> . . . . .	1097	1480	383	—	—	—
None . . . . .	1042	1588	546	871	1525	654

\* Standard deviation is 65 ms.

† Pre-slurry ashing was at 600°C for 12 h; O<sub>2</sub> ashing used 20 ml min<sup>-1</sup> during the char stage; for amounts of Mg, phosphate and Pd, see Table 2.

loss, and it delays the atomisation signal to ensure the analyte does not vaporise until the interior of the furnace is temporally nearly isothermal. Both of these effects will be discussed.

#### Effectiveness in delaying atomisation

The above studies using a soil model (montmorillonite - humic acid) showed that organic carbon early shifted the Pb absorbance signal. All the modifiers tested (phosphate, Mg - phosphate, Pd and Mg - Pd) were able to counter this effect. Using platform atomisation, the effectiveness of these modifiers on soil slurries was examined, together with other methods to modify the release of Pb atoms. They were 1% HNO<sub>3</sub> (as a slurry medium), O<sub>2</sub> introduction during the charring step (O<sub>2</sub> ashing) and ashing the soil in a muffle furnace prior to making a slurry (pre-slurry ashing). When slurries were made in 1% HNO<sub>3</sub>, about one third of the adsorbed Pb was leached into solution (the usual distilled water slurries have no detectable amounts of Pb in the supernatant). Oxygen ashing has been used previously<sup>31-33</sup> for Pb determinations. It was implemented simply by having O<sub>2</sub> as the alternate gas flowing at 20 ml min<sup>-1</sup> during the charring stage (as outlined by Littlejohn *et al.*<sup>33</sup>). The tube and platform were not visibly degraded by this procedure, although there were insufficient firings of each tube to determine whether its lifetime was reduced. Pre-slurry ashing was performed in a muffle furnace at 600°C for 12 h. The mass losses due to ashing, determined gravimetrically, for soils SO-1, SO-3 and SO-4 were 5.2, 13.7 and 10.7%, respectively. These values were used to calculate the Pb concentrations in the original soils.

Measurement of  $\tau_{app}$  and  $\tau_{peak}$  allowed the delaying properties to be compared, and these results are given in Table 4. The difference ( $\Delta\tau$ ) between  $\tau_{peak}$  and  $\tau_{app}$  allows peak widths to be compared. The modifying methods are rank ordered with the largest signal delay for soil slurries at the top. Also in the table, results for aqueous Pb solutions are included for comparison. An important aspect in slurry - ETA-AAS is that aqueous standards can be used. The same matrix modification should then be used with sample slurries and with standards. The modifying method should cause a similar atomisation delay with soil slurries and aqueous solutions, because the temperature distribution along the length of the graphite tube has been shown to change with time,<sup>34,35</sup> *i.e.*, commercial ET atomisers are not temporally isothermal except where the temperature is measured at the tube centre (near the dosing hole). Pre-slurry ashing failed to meet this requirement,  $\tau_{app}$  being almost doubled (1603 ms) compared with an aqueous Pb solution (871 ms). The region of temporal near-isothermality starts at about 900 ms, so the aqueous Pb signal would be just in this region. Also, pre-slurry ashing is slow, inconvenient and produces broad absorption peaks (large  $\Delta\tau$ ). These peaks had similar characteristic times to Pb adsorbed on montmorillonite (Fig. 1), *i.e.*, ashing removed

the organic carbon and Pb remained adsorbed on the matrix particles. *In situ* O<sub>2</sub> ashing appears less effective than pre-slurry ashing in removing carbon, but the signal delay is satisfactory, and it is convenient to use compared with adding modifier solutions to slurries. However, it has no effect on the peak characteristics of aqueous solutions, so there is a big difference in  $\tau_{app}$  (1319 ms for the slurry and 871 ms for the solution). Of the matrix modifiers, those containing Pd are clearly the best. With slurries, the use of Mg - Pd compared with Pd alone does not give significantly different peak characteristics (considering the standard deviation of the measurements). This was found previously.<sup>2</sup> However, with solutions, the absence of Mg leads to very broad peaks (large  $\Delta\tau$ ). The Mg - Pd mixture gives similar  $\tau_{app}$  and  $\tau_{peak}$  values for slurries and solutions. The use of Mg - phosphate and phosphate alone are satisfactory, but they give smaller signal delays than the Pd modifiers. Also, background absorbance is higher when phosphate is present. Magnesium alone gives an earlier  $\tau_{app}$  and slightly broader peaks with aqueous solutions than with slurries. The addition of HNO<sub>3</sub> to the slurry did not significantly affect the peak characteristics.

#### Effectiveness in permitting higher charring temperatures

The charring temperatures are the nominal values programmed (in °C) into the ET atomiser power supply.

Matrix modifiers are probably used more for increasing permitted charring temperatures than for delaying atomisation, but charring temperatures for soils can be as low as 700°C without matrix interference.<sup>17</sup> In Part 1 of this work,<sup>1</sup> a maximum char temperature of 900°C was used without volatilisation loss of Pb. Nevertheless it was interesting to investigate the maximum charring temperatures the various modifiers would permit without Pb being lost from montmorillonite - humic acid. Table 5 shows the maximum temperature without modifier to be 900°C, *i.e.*, the same as that for typical soils, and the selected modifiers allow this to be increased to 1000 or 1100°C. As discussed earlier<sup>2</sup> our pyrometric measurements indicate the actual temperatures are somewhat lower than these programmed temperatures. This illustrates the importance of optimising the maximum permitted charring temperature on a particular instrument. It should then be found that the modifiers allow charring temperatures to be increased by at least 100–200°C.

#### Analysis of soils

Results of quantitative determinations of Pb in three certified reference soils are listed in Table 6. Recoveries are satisfactory without matrix modification. However, as discussed previously,<sup>1,2</sup> soils high in organic carbon may lose Pb unless a modifier is used. Therefore, matrix modification should always be used for soil slurry analysis. Generally, good agreement is seen between the experimental and certified

**Table 5.** Maximum permissible charring temperatures for montmorillonite - humic acid slurries\* with various matrix modifiers

Matrix modifier	Programmed temperature/°C
None . . . .	900
Mg . . . .	1000
Phosphate . . . .	1000
Mg - phosphate . . . .	1100
Pd . . . .	1100
Mg - Pd . . . .	1100

\* For amounts of matrix components and modifiers per aliquot, see Table 2.

**Table 6.** Analysis of certified reference soils SO-1, SO-3 and SO-4 by slurry - ETA-AAS

Matrix modifier†	Pb concentration*/µg g <sup>-1</sup>		
	SO-1 (21 ± 3)‡	SO-3 (14 ± 3)‡	SO-4 (16 ± 3)‡
None . . . .	20.2 ± 0.3	12.3 ± 0.2	14.5 ± 0.3
Mg . . . .	20.1 ± 1.3	11.1 ± 1.6	15.2 ± 1.0
Phosphate . . . .	18.2 ± 0.4	12.3 ± 0.8	14.0 ± 0.7
Mg - phosphate . . . .	19.1 ± 0.5	13.2 ± 0.6	14.3 ± 0.5
Pd . . . .	16.9 ± 0.2	13.1 ± 2.2	14.2 ± 0.9
Mg - Pd . . . .	21.2 ± 1.9	14.2 ± 1.6	15.4 ± 1.6
Pre-slurry ash . . . .	21.2 ± 0.4	14.3 ± 0.7	16.1 ± 0.5
O <sub>2</sub> ash . . . .	17.0 ± 0.5	11.0 ± 0.3	13.0 ± 0.5
1% HNO <sub>3</sub> . . . .	19.9 ± 0.3	13.9 ± 0.3	14.5 ± 0.6

\* Precision limits include ± one standard deviation.

† Pre-slurry ashing was at 600°C for 12 h; O<sub>2</sub> ashing used 20 ml min<sup>-1</sup> during the char stage; for amounts of Mg, phosphate and Pd, see Table 2.

‡ Certified concentrations with 95% confidence limits.

**Table 7.** Characteristic masses ( $m_0$ ) for Pb in aqueous solution

Matrix modifier*	$m_0/\text{pg}(0.0044 \text{ A s})^{-1}$
Mg . . . .	12
Phosphate . . . .	12
Mg - phosphate . . . .	12
Pd . . . .	13
Mg - Pd . . . .	14
1% HNO <sub>3</sub> . . . .	13
O <sub>2</sub> ashing . . . .	17

\* For amounts of matrix modifiers per aliquot, see Table 2.

values. However, results from Pd modification and O<sub>2</sub> ashing are on the lower edge of the confidence intervals and they should be viewed with suspicion. Of the remaining modification techniques, Mg - Pd is the best from consideration of its signal delaying characteristics discussed earlier.

Any effect these modifiers might have on the sensitivity of the aqueous standard calibration graph was investigated by measuring the characteristic masses. These are given in Table 7. Aqueous Pb standards in the normal medium (1% HNO<sub>3</sub> only) gave a value of 13 pg (0.0044 A s)<sup>-1</sup>, and all except O<sub>2</sub> ashing gave this sensitivity (within experimental error). When O<sub>2</sub> ashing is used, the significantly higher characteristic mass may be due to volatilisation losses of Pb during ashing. If so, this could explain the low results for Pb in soil when O<sub>2</sub> ashing was used (Table 6).

### Conclusions

The atomisation studies have provided some information on the probable mechanisms of matrix modification. Clearly, in terms of signal delay, adsorption of analyte on solid particles influences the effectiveness of the modifiers. For aqueous Pb, mixtures of Mg - phosphate and Mg - Pd both produced long delays. Adsorption of Pb on montmorillonite causes an atomisation delay without added modifier, and no modifier

was effective in increasing this delay. With the modifiers Mg, phosphate and Mg - phosphate, desorption from the montmorillonite particle is rate determining, whereas modifiers containing Pd cause most of the Pb to be desorbed from the particles during slurry preparation. This destroys the signal-delaying effect of analyte adsorption. Hence, there would be no advantage in adding modifiers to soil if it behaved the way montmorillonite does. However, soil contains organic carbon, and this can have a profound effect on Pb atomisation from samples introduced to the ET atomiser as slurries. All the modifiers delayed analyte atomisation when humic acid was added to montmorillonite. The analysis of soils showed that Mg - Pd is the most suitable of the modifying methods tested. This modifier mixture produced similar peak characteristic times for soil slurries and aqueous standards, and allowed quantitative recoveries of Pb from soil.

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