Palladium and Magnesium Nitrate as Modifiers for the Determination of Lead by Graphite Furnace Atomic Absorption Spectrometry

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It was found that palladium used as modifier for the determination of lead extends the range of the acceptable pyrolysis temperatures up to 1100°C. It eliminates at these temperatures the losses of lead due to evaporation in the form of chloride, intermetallic compounds with sodium or as elemental lead. It plays also an important role during the atomization phase by separation the atomization of lead from the atomization of more volatile components of the sample. Palladium in any form, however, is not able to eliminate the interference effect of chlorides, which decompose at the temperatures below 400°C and, under some conditions, it can become itself a strong interferent of similar type. The interference of easily decomposing chlorides may be eliminated only either by a strong acidification of the sample with nitric acid or by addition of an excess of magnesium nitrate or sodium nitrate.
In the recent paper [1] we have shown that the analytical signal of lead in graphite furnace atomic absorption spectrometry is strongly suppressed by thermally unstable chlorides, e.g. ferric chloride or palladium chloride, which decompose in the temperatures lower than or equal to the temperature of pyrolysis phase. The evolved free chlorine atoms form with lead volatile compounds and they can cause the losses of lead already in the temperatures above 200°C. The effect of thermally stable chlorides, e.g. sodium chloride, is relatively small and it is rather limited to the atomization phase. During pyrolysis these chlorides can exert only an indirect influence, e.g. their excess can protect lead chloride against the decomposition on the hot surface of the graphite tube. It was shown also that palladium, used as a modifier, is not only unable to save lead from losses in the presence of thermally unstable chlorides but, under some conditions it becomes itself a strong interferent. This fact explains why palladium is considered by some authors as a more effective modifier when used in a mixture with magnesium nitrate [2, 3].

All above mentioned phenomena do not disqualify palladium as a very effective modifier for the determination of lead, however, they should be taken into account to avoid serious errors which can arise in some analytical systems. In the present work we have discussed the consequences resulting from these phenomena for the application of palladium as a modifier and we have tried to establish the optimum conditions for its use.

EXPERIMENTAL

Apparatus

A Pye–Unicam (Philips) SP-9-800 atomic-absorption spectrometer equipped with a PU-9095 video programmer graphite furnace (including temperature feedback control), PU-9090 microprocessor, deuterium (D₂) lamp background correction and a lead hollow-cathode lamp (Photron–PTY,Ltd) have been used.

Uncoated graphite tubes were used for all measurements.

Reagents

All reagents used for the preparation of standards and test sample solutions were of “Suprapur” or “Specpure” (Johnson–Mathey, Merck, Koch–Light) grade.

Hydrochloric and nitric acids used to prepare the solutions were purified by sub-boiling distillation.

Water used was doubly distilled in fused-silica apparatus.

Stock standard solutions of lead, sodium and palladium (nitrate and chloride) were prepared in concentrations of 10 mg ml⁻¹. Working solutions were prepared before use, by dilution of stock solutions with nitric acid, hydrochloric acid, or water, respectively.

Analytical conditions

All measurements were performed using: spectral band pass – 0.5 nm; lamp current – 7 mA; wavelength – 217.0 nm.

The graphite furnace time–temperature program used for all experiments is shown in Table 1.
Modifiers for the determination of Pb by GF AAS

Table 1. Graphite furnace time–temperature program

<table>
<thead>
<tr>
<th>Phase No.</th>
<th>Phase name</th>
<th>Temperature °C</th>
<th>Time, s</th>
<th>Temp. rise (ramping) °C s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>drying</td>
<td>120</td>
<td>30</td>
<td>10 (7)</td>
</tr>
<tr>
<td>2</td>
<td>pyrolysis (charring)</td>
<td>800</td>
<td>10</td>
<td>100 (4)</td>
</tr>
<tr>
<td>3</td>
<td>atomization</td>
<td>2000</td>
<td>3</td>
<td>&gt; 2000 (0)</td>
</tr>
<tr>
<td>4</td>
<td>cleaning</td>
<td>2600</td>
<td>3</td>
<td>&gt; 2000 (0)</td>
</tr>
</tbody>
</table>

Sample and matrix modifier aliquots were 10 µl in all cases.
Palladium matrix modifier was added into the tube before injection of the sample.
Eppendorf volumetric dispensing pipes were used for handling and transferring solutions into the graphite tubes.
Background correction using deuterium (D₂) lamp was made for all measurements.
All results were based on the peak height measurements.

RESULTS AND DISCUSSION

The effect of palladium on the lead absorbance as a function of atomization temperature is presented in Fig. 1. The horizontal lines A and B represent the lead absorbance without and with sodium chloride, both without palladium. The suppression of signal observed for line B is due to the losses of lead during pyrolysis (800°) and to the negative effects of sodium excess in the atomization phase [1]. In both cases, however, the signal is constant in the total temperature range. It indicates, that lead is transformed completely in the atomic vapours already at 1400°C.

![Absorbance of lead vs. atomization temperature](image)

**Figure 1.** Effect of the atomization temperature on the absorbance of lead. Test sample (sample): 20 ng ml⁻¹ of Pb in 1 mol l⁻¹ HNO₃. A – sample; B – sample + 2 mg ml⁻¹ of Na as NaCl; C – Sample + 0.3 mg ml⁻¹ of Pd as Pd(NO₃)₂; D – sample + 0.3 mg ml⁻¹ of Pd as Pd(NO₃)₂ + 2 mg ml⁻¹ of Na as NaNO₃; E – sample + 0.3 mg ml⁻¹ of Pd as Pd(NO₃)₂ + 2 mg ml⁻¹ of Na as NaCl
When palladium modifier is added (curves C, D and E) the suppression effects of sodium are removed but the full atomization of lead is not achieved until the temperature of 2000°C. This confirms again the formation of the refractory lead–palladium intermetallic compounds and indicates that, in the presence of palladium, the recommended atomization temperature should be higher than 2000°C, e.g. 2200°C.

It was found earlier [1] that palladium chloride, similarly as other thermally unstable chlorides, causes significant losses of lead at an early stages of pyrolysis. Therefore, palladium should not be used as a modifier when the lead is determined in hydrochloric acid medium. However, it is known that palladium compounds are active as modifiers after its decomposition to the metal form and this form is resistant against hydrochloric acid and does not form chlorides. Therefore, it may be assumed that any palladium compound, reduced preliminary in the tube to the metal form, before addition of the sample containing hydrochloric acid, should not cause the losses of lead. The results of such experiment are shown in Fig. 2. Palladium solution

![Figure 2](image.png)

**Figure 2.** Effect of the pretreatment temperature of palladium on the absorbance of lead. Test sample (sample): 20 ng ml⁻¹ of Pb in 1 mol ⁻¹ HCl. Pd solutions: 0.3 mg ml⁻¹ of Pd as Pd(NO₃)₂ or PdCl₂ in 1 mol ⁻¹ HNO₃ or HCl, respectively. A – Pd as Pd(NO₃)₂; B – Pd as PdCl₂; C – Pd as PdCl₂ added to the sample (without pretreatment).

was added to the tube, dried and pyrolysed in a required temperature (pretreatment temperature). Then the tube was cooled, the sample in hydrochloric acid was added and the normal time–temperature program was performed. The results obtained for palladium nitrate are presented by curve A. The fact that it is a horizontal straight line indicates that palladium nitrate is decomposed completely, already after pretreatment at the temperature of 200°C. Otherwise, the measured signal of lead in hydrochloric acid should be strongly suppressed. When the palladium chloride is used (curve B) its total decomposition occurs at a pretreatment temperature not lower than 800°C. Only above this temperature no losses of lead are observed. This curve is very close to that obtained by Rettberg and Beach [4] in a similar experiment. Curve C is given for comparison. It represents the lead signal, obtained in hydrochloric acid
solution with palladium chloride mixed directly with the sample (without pretreatment) as a function of pyrolysis temperature. The values of the applied pyrolysis temperature were equal to the values of the pretreatment temperature marked in the figure on the abscissa. The presented results indicate unambiguously that palladium modifier, reduced initially to the metal form, does not generate the losses of lead in hydrochloric acid medium.

The pretreated palladium protects the results of lead signals measured in hydrochloric acid against the interferences caused by an excess of sodium or sodium chloride (Fig. 3, curve A). It is not able, however, to protect lead against the losses arising in the presence of thermally unstable chlorides which may be present in a sample, e.g. ferric chloride (Fig. 3, curve B). In this case the observed losses of lead in the temperature range above 400°C are very similar to those caused by palladium when used in hydrochloric acid without pretreatment (Fig. 3, curve C). The difference between curves B and C grows in the direction of lower temperatures and it is due to the lower decomposition temperature of ferric chloride in comparison with palladium chloride. The fact, that the observed losses occur mainly in the temperature range below 400°C, suggests that the volatile lead–chlorine compounds are formed in these temperatures most effectively. At the higher temperatures they either cannot be formed or their formation is disturbed by the formation of the stable intermetallic lead–palladium compounds. The formation temperature of these compounds is not known, however, it was found [1] that at the temperatures above 600°C palladium protects lead against evaporation with sodium what suggests that in these temperatures the total amount of lead is already bound with palladium.

Figure 3. Effect of the pyrolysis temperature on the absorbance of lead in the presence of the thermally pretreated palladium. Test sample (sample): 20 ng ml⁻¹ of Pb in 1 mol l⁻¹ HNO₃ or HCl. Pd solution used for pretreatment: 0.3 mg ml⁻¹ of Pd in 1mol l⁻¹ HNO₃. A – sample + 2 mg ml⁻¹ of Na as NaN₂ in 1:1 mixed 1 mol l⁻¹ HNO₃ and HCl; B – sample + 0.5 mg ml⁻¹ of Fe as FeCl₃ in HCl; C – sample + 0.3 mg ml⁻¹ of Pd as PdCl₂ in HCl (without pretreatment)
The above results indicate that palladium, independently of its form, cannot remove the interference of thermally unstable chlorides. This effect may be removed only by the addition of compounds that are able to bind the evolved chlorine atoms by forming stable molecules with them [1]. Nitrates of alkali or alkaline earth elements seem to be the most promising group of such compounds.

Figure 4. Effect of magnesium and sodium nitrates on the absorbance of lead in the presence of chloride ions. Test sample (sample): 20 ng ml\(^{-1}\) of Pb + 0.3 mg ml\(^{-1}\) of Pd + 3 mg ml\(^{-1}\) of Cl\(^-\) as HCl in 1 mol l\(^{-1}\) HNO\(_3\). A - sample + variable conc. of Mg as Mg(NO\(_3\))\(_2\); B - sample + variable conc. of Na as NaNO\(_3\).  

Among these nitrates the lowest decomposition temperature has magnesium nitrate (330°C), that is mentioned by many authors [2, 3] as a very useful addition to palladium modifier. Sodium (380°C) and potassium (400°C) nitrates are the next in the row. Figure 4 demonstrates the elimination of the negative effect of palladium in the presence of hydrochloric acid by increasing concentrations of magnesium nitrate (curve A) and sodium nitrate (curve B). It results from the comparison of the both curves that magnesium nitrate is more effective than sodium nitrate, particularly, in the low range of concentrations. It is due to the lower decomposition temperature of magnesium nitrate. It should be kept in mind that the tabulated decomposition temperatures are not defined as very sharp points. The decomposition occurs usually in a large interval of temperatures and starts at the temperatures much lower than that mentioned in tables. This fact finds its confirmation in Fig. 4. The significant losses of lead, caused by free chlorine evolved by palladium chloride, occur already in the temperature range 200°C to 300°C (Fig. 3, curve C). At this temperature magnesium nitrate is decomposed to the oxide in a sufficient degree that in the concentration of about 300 μg ml\(^{-1}\) it is able to bind all free chlorine atoms and to save lead (Fig. 4, curve A). The decomposition degree of sodium nitrate is smaller in this temperature and, therefore, its required concentration is about 1000 μg ml\(^{-1}\) (Fig. 4, curve B).
The small but distinct difference observed between curves A and B at the concentra-
tion of 2000 μg ml⁻¹ suggests that sodium nitrate, even in large concentration, is not
able to neutralize the chlorine atoms in the very early phase of heating and, therefore,
some small but noticeable losses of lead occur.

Conclusions

The investigations described previously [1] and those presented now enable to
formulate precisely the role of palladium and magnesium nitrate, as modifiers for
determination of lead.

Palladium modifier, after its thermal decomposition, forms with lead stable
intermetallic compounds. In this way it protects lead against its losses by evaporation
in the form of lead chloride, lead–sodium intermetallic compounds or lead metal and
it enables to expand the range of pyrolysis temperature even up to 1100°C. Palla-
dium–lead compounds play also an important role during atomization phase. They
delay the formation of the cloud of lead atomic vapour to the time when the main
bulk of the volatile components of the sample is already removed from the tube and
the measured lead signal is not suppressed by it. For the same reason the lowest
acceptable temperature for lead atomization in the presence of palladium is 2000°C.
Palladium modifier, however, is not able to protect lead against the losses caused by
thermally unstable chlorides, e.g. ferric chloride, which evolve the free chlorine
atoms in the temperatures when the palladium–lead compounds cannot yet be formed.
Moreover, when a sample contains sufficiently high concentration of chloride ions,
palladium may be partially transformed into the chloride form and to become itself
a very strong interferent of similar type.

The above mentioned negative effects may be removed by addition to the sample
some amount of magnesium nitrate. This compound decomposes easily to the oxide
which binds the evolved chlorine atoms and plays the role of the additional modifier
saving lead against losses in the early stage of the pyrolysis phase when the sample
contains some thermally unstable chlorides. The similar role can play sodium nitrate
and, probably, other nitrates of alkali or alkaline earth elements, however, magnesium
nitrate is the most effective since its very low decomposition temperature.

It seems, however, that the most rational way to remove the effect of thermally
unstable chlorides is to dissolve the analytical sample in nitric acid (if it is possible)
or to acidify the sample solution with sufficiently high concentration of nitric acid.
All chlorides are transformed then almost completely into the nitrates and the formed
amounts of hydrochloric acid and the excess of nitric acid are removed by evaporation
during the drying phase. In this way one avoids the introducing into the sample a
large excess of magnesium or sodium which can additionally deteriorate the condi-
tions during atomization.

Palladium as a modifier should be used in the form of nitrate. The use of
palladium chloride may be without any negative consequences, when the sample
contains sufficient excess of nitrate ions, however, it always increases the risk of
some losses of lead, particularly, when the sample itself contains a large amount of
chlorides.
REFERENCES


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