Behaviour of the System: Lead–Sodium–Chloride Ions–Palladium During Atomization in Graphite Furnace Atomic Absorption Spectrometry

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It was found that the interference effect of chlorides at the lead determination by GF AAS depends on the properties of the chlorides and on the medium in which the sample is dissolved. In nitric acid solution one observes mainly the effects of cations contained in the chlorides. In hydrochloric acid or in a mixed nitric–hydrochloric acid medium the observed effects are due to the type of chlorides. The chlorides, which have a decomposition temperature higher than the used pyrolysis (charring) temperature, inhibit the reduction of lead chloride to the metal form and enable its losses by evaporation. Other chlorides, which decompose below the pyrolysis temperature, evolve free chlorine atoms and those form very volatile lead–chlorine compound evaporating already at about 200°C.

Palladium acts properly as modifier only in nitric acid solution. In the presence of a large excess of chloride ions, particularly in the hydrochloric acid medium, it is transformed, at least partially, into the form of thermally unstable chloride which causes the losses of lead during pyrolysis and, consequently, causes a strong suppression of the measured signal.

The explanation of the mechanism of all processes occurring in the graphite tube for the analytical system to be discussed has been proposed.
redukci chlorku ołowiu do ołowiu metalicznego i w ten sposób umożliwiają jego straty przez odparowanie. Chlorki rozkładające się poniżej temperatury pirolizy wydzielają wolny chlор, który tworzy z ołowiem połączenia bardzo lotne już w temperaturach powyżej 200°C.
Pallad pracuje poprawnie jako modyfikator tylko w środowisku kwasu azotowego. W obecności dużego nadmiaru jonów chlorkowych oraz w środowisku kwasu solnego przechodzi on, przynajmniej częściowo, w termicznie nietrwale chlorki powodujące straty ołowiu na etapie pirolizy, co w konsekwencji powoduje duże zmniejszenie mierzonego sygnału.
Dla rozważanego układu analitycznego podano wyjaśnienie mechanizmów procesów zachodzących w kuwecie grafitowej.

Graphite furnace atomic absorption spectrometry (GF AAS) is the principal method used for lead determination in environmental samples. Many authors reported, however, that the obtained results may be affected by interferents and the chlorides are mentioned as belonging to the most dangerous of them [1-4]. To remove these effects various matrix modifiers were proposed but, a great deal of interest has been generated in the use of palladium and magnesium mixture as the most effective and versatile one [5-7]. Some authors have presented also the investigations which should explain the mechanism of chloride activity and ways of its elimination by palladium [7-10]. These investigations throw some light on the processes occurring during the lead atomization in the presence of chlorides and palladium, however, the presented results are not always consistent and do not explain all observed effects.

The suppression of lead signal by chloride ions (e.g. in the form of sodium chloride) is explained by the formation of volatile lead chloride [8]. On the other hand the simple experiment shows that lead chloride (PbCl₂) in hydrochloric acid medium produces the same analytical signal as lead nitrate in nitric acid. A question arises why sodium chloride, which is very stable up to high temperatures even in liquid phase, is able to produce volatile lead chlorides whereas they are not formed at all from lead chloride. Another question is why palladium, that may be used as modifier also in the chloride form [7], added to the lead chloride solution in hydrochloric acid suppresses the lead signal and acts as a strong interferent?
The above facts indicate that the mechanism of considered processes is rather complex and its explanation requires further investigations. Therefore, the aim of the presented work was to examine systematically the behaviour of the system: lead-sodium-chloride ions-palladium under the conditions occurring during the total atomization process in the graphite tube.

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) has been used.

Uncoated graphite tubes were used for all measurements.
Reagents

All reagents used for 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 all solutions were purified by sub-boiling distillation. All 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.

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 (D\(_2\)) lamp was made for all measurements. All results were based on the peak height measurements.

RESULTS AND DISCUSSION

Processes during pyrolysis

The investigations of the system: lead–sodium–chloride ions–palladium were concentrated at first on the estimation of effects caused individually by lead, chloride ions, and palladium, respectively, on the absorbance value of lead. All test solutions were prepared in 1 mol l\(^{-1}\) nitric acid since the analytical samples are usually diluted in this medium. The absorbance of 20 ng ml\(^{-1}\) of lead is presented in Fig. 1 as a function of the sodium ion concentration added in the form of sodium chloride (curve A) and sodium nitrate (curve B). Although the curve for sodium chloride shows slightly stronger suppression of the measured signal the difference between both curves is surprisingly small and suggests that the observed effects are due to the sodium concentration. After addition of 300 µg ml\(^{-1}\) of palladium the suppression of the signal is eliminated completely (curves C and D). The presence of chlorides added in the form of sodium chloride seems to be without significance. This phenomenon may be easily explained.
The samples are in the nitric acid medium i.e. the nitrate ions are present in a very large excess. The added sodium chloride is mostly transformed into sodium nitrate and free hydrochloric acid. The equilibrium between sodium chloride and nitrate concentrations depends on the concentrations of both acids. Since hydrochloric acid is somewhat more volatile than nitric acid it evaporates faster from the graphite tube during the drying period and the equilibrium is shifted gradually in the direction of sodium nitrate. So, at the end phase of the drying period, almost the total sodium is present in the form of nitrate which then decomposes during the pyrolysis phase (charring phase) to sodium oxide and, under the conditions in the graphite tube, most probably farther to sodium metal. Therefore, both curves A and B (Fig. 1) represent the same effect of free sodium. Somewhat stronger suppression of the signal observed for the curve A is caused, probably, by the residual amount of sodium chloride that may be still present in the tube.

The elimination of sodium effect by various concentration of palladium (in the form of nitrate) is shown in Fig. 2 (curve A for sodium chloride and curve B for sodium nitrate). The shape of both curves indicates that the optimum concentrations of the added palladium are in the range of 200 to 500 μg ml⁻¹. Palladium added in the same way to the pure lead solution does not affect the lead signal at all up to the concentration of 500 μg ml⁻¹ and for larger concentrations gives a small suppression similar to that represented by curves A and B. The situation changes completely when palladium is added to the lead solution containing significant amount of free chloride ions (3000 μg ml⁻¹) in the form of hydrochloric acid (Fig. 2, curve C).
The system: Pb-Na-Cl-Pd in GF AAS

Figure 2. Effect of palladium concentration on lead absorbance. Test sample (sample): 20 ng ml$^{-1}$ of Pb in 1 mol l$^{-1}$ HNO$_3$ or HCl. Pd solution: variable concentration of Pd in 1 mol l$^{-1}$ HNO$_3$ or HCl. A - sample + 2 mg ml$^{-1}$ of Na$^+$ as NaCl in HNO$_3$ + Pd in HNO$_3$; B - sample + 2 mg ml$^{-1}$ of Na$^+$ as NaNO$_3$ in HNO$_3$ + Pd in HNO$_3$; C - sample + 3 mg ml$^{-1}$ of Cl$^-$ as HCl in HNO$_3$ + Pd in HNO$_3$; D - sample + 1 mg ml$^{-1}$ of Na$^+$ as NaCl in 1 mol l$^{-1}$ HCl + Pd in HCl.

A similar but stronger effect (curve D) is observed when palladium is added to a mixture of lead and sodium chlorides (all solutions in 1 mol l$^{-1}$ hydrochloric acid). In both cases palladium does not work as matrix modifier but it behaves as a strong interferent. For samples dissolved in hydrochloric acid or in a mixture of hydrochloric and nitric acids all components of the system are after the drying period in the form of solid chlorides or a mixture of chlorides and nitrates, respectively. Curves C and D suggest that palladium present in the form of solid chloride acts in the next stages of the process as a strong suppressor.

The examination of the pyrolysis (charring) phase provides more information on the mechanism of the processes occurring in the graphite tube. The dependence of lead nitrate (in a nitric acid medium) signal on the pyrolysis temperature is represented by curve A in Fig. 3. The signal is stable up to about 900$^\circ$C, and at higher temperatures drops down. Lead nitrate is decomposed to lead oxide already at 470$^\circ$C and then it is probably reduced to lead metal. The observed decreasing of the signal above 900$^\circ$C is due to the losses of the metal by evaporation since its vapour pressure achieves in this temperature range a significant level equal to 133 Pa (about 1 mm Hg) at 970$^\circ$C. Addition of palladium nitrate to the solution extends the range of stable signal to about 1100$^\circ$C (curve B). This observation confirms the statement that lead forms with palladium more stable intermetallic compounds [8].
The dependence of the signal of lead chloride in hydrochloric acid medium (curve C) is very similar to that in nitric acid (curve A). The lead chloride is much more volatile than metal and its boiling point is 950°C. The stability of the measured signal up to 900°C and its relatively small decrease at 1000°C indicates that lead chloride is reduced to metal by the hot graphite tube and, therefore, curves A and C are very close. Both of them illustrate the behaviour of metallic lead.

Completely different situation occurs when palladium chloride is added to the lead chloride in hydrochloric acid (Fig. 3, curve D). The significant losses of lead are observed already at the pyrolysis temperature of 300°C and they increase quickly with the increasing temperature. It confirms again that palladium in the chloride form does not work as a modifier and it becomes itself a strong suppressor of the measured signal. A strong dependence on the pyrolysis temperature suggests that the processes responsible for the observed effects occur in this stage.

When the system contains sodium nitrate or sodium chloride the dependence of lead signal on the pyrolysis temperature is represented by curves A and B in Fig. 4. In the range from 200°C to 600°C the signal is independent of the increasing temperature, however, it is lower than the signal of the pure lead shown by curve A in Fig. 3. The stability of the signal in this range suggests that the observed suppression is due to the processes occurring in the phase of atomization, that will be discussed below. Sodium nitrate decomposes completely at the temperature of 380°C and then probably is reduced to the metal. Vapour pressure of sodium is equal to 133 Pa at 440°C and to 1333 Pa (about 10 mm Hg) at 546°C.
The system: Pb-Na-Cr-Pd in GF AAS

Figure 4. Effect of pyrolysis temperature on lead absorbance. Test sample (sample): 20 ng ml\(^{-1}\) of Pb in 1 mol l\(^{-1}\) HNO\(_3\) or HCl. Pd solution (Pd soln.): 0.3 mg ml\(^{-1}\) of Pd as Pd(NO\(_3\))\(_2\) or PdCl\(_2\) in 1 mol l\(^{-1}\) HNO\(_3\) or HCl, respectively. NaN\(_3\) or NaCl added to the test sample in amounts corresponding to 2 mg ml\(^{-1}\) of Na. A - sample + NaN\(_3\) in HNO\(_3\); B - sample + NaCl in HNO\(_3\); C - Pd soln. in HNO\(_3\)+ sample with NaN\(_3\) in HNO\(_3\); D - Pd soln. in HNO\(_3\)+ sample with NaCl in HNO\(_3\); E - sample with NaCl in HCl; F - Pd soln.in HCl + sample with NaCl in HCl

It means that some losses of sodium can occur in these temperatures but its main bulk passes to the atomization phase. At the temperatures above 600°C the suppression of lead signal grows quickly with the increase of temperature and indicates the large losses of lead that under these conditions should be also in metallic form, as it was discussed above. The comparison of both curves discussed above with curves A and B in Fig. 3 proves that the observed losses of lead cannot be caused by the simple lead evaporation since that occur only at temperatures above 900°C. It has been reported [11] that lead forms with sodium, similarly as with palladium, few intermetallic compounds. Although no data on their volatility are available, it may be assumed that at least one of them is sufficiently stable to be able to distil together with sodium which vaporizes intensively above 600°C (boiling point 883°C). The addition of palladium nitrate to both systems causes that dependence of the lead signal on the pyrolysis temperature (curves C and D in Fig. 4) is identical with curve B in Fig. 1 obtained for pure lead nitrate in the presence of palladium. It means that palladium protects lead against the losses by vaporization to a temperature above 1000°C even when a large excess of sodium nitrate or sodium chloride is present in the sample.

The situation becomes more severe when lead is accompanied by sodium chloride in hydrochloric acid medium (Fig. 4, curve E). In the temperature range up to 600°C the lead signal is also stable but more suppressed than in nitric acid. Similarly as
before it may be assumed that this suppression is due to the activity of sodium chloride during the atomization phase. After exceeding of about 650°C the curve goes down steeply and indicates on large losses of lead. These losses cannot be explained by lead evaporation with sodium metal since sodium chloride does not decompose under the conditions in the graphite tube, what will be shown below. It seems to be evident that lead chloride, which in the pure form (PbCl₂) is decomposed in the hot graphite tube to lead metal (Fig. 3, curve C), whereas mixed with an excess of sodium chloride it is protected by this chloride against the decomposition. In this situation the observed lead losses are due to the simple evaporation of lead chloride. Its vapour pressures are very close to the vapour pressures of sodium metal and, therefore, it evaporates in the same temperature range as lead–sodium intermetallic compound (curves A and B in Fig. 4).

When the palladium chloride is added to the mixture of lead and sodium chlorides in hydrochloric acid (Fig. 4, curve F), it eliminates the suppression caused by sodium chloride only for pyrolysis temperatures up to 200°C, i.e. when only free acid is removed and all components of the sample pass into the atomization stage in the form of chlorides. The measured lead signal in this case is very close to those resulting from curves C and D in Fig. 4 and curves A and C in Fig. 3. It means that palladium chloride present in the tube during atomization phase works properly as a matrix modifier. When the pyrolysis temperature of the mixture of lead, sodium and palladium chlorides increases above 200°C the lead signal (curve F, Fig. 4) drops down very steeply. The mechanism of this phenomenon must be different from other mechanisms discussed above and corresponds to that represented by curve D in Fig. 3 and, to some extent, by curves C and D in Fig. 2. Palladium chloride decomposes easily at relatively low temperatures. The temperature of its total decomposition is equal to 500°C. The evolved free chlorine atoms affect lead chloride by transforming it to a volatile compound. However, the identity of that compound is not clear. The volatile lead tetrachloride decomposes immediately in the temperatures above 105°C. Wendl and Müller-Vogt [8] reported the existence of the volatile PbCl in the graphite tube during the atomization process but this concerns rather considerably higher temperatures. It seems that in the presence of the atomic chlorine unstable lead–chlorine compounds, volatile in the temperature range between 300°C and 500°C, might be formed. The hypothesis that palladium chloride suppresses the lead signal acting as a source of free chlorine atoms may be confirmed by replacing palladium chloride with ferric chloride. The latter decomposes completely at 315°C to ferrous chloride and free chlorine and its suppression effect on the lead signal is identical with that produced by palladium chloride.

Macro-scale investigations

The proposed explanation of the processes occurring in the graphite tube during the pyrolysis phase may be confirmed by the experiments performed in a macro-scale under conditions simulating the situation in the tube.

Some amount of the solid lead chloride or lead nitrate (about 0.2 g) mixed with a large excess of spectroscopic graphite powder and with other components, adequate
for a given experiment, were placed in a large silica test tube. The tube was closed by a stopper with a pipe carrying away the evolved gases. The gases were adsorbed in a silver nitrate solution used as chlorine detector. The lower part of the tube was heated to the specified temperature up to 900°C and the upper part was left cool as the place of condensation of the salts or elements evaporated from the sample.

From the mixture of lead chloride and graphite powder heated to the temperature of 600–900°C a significant amount of lead chloride was evaporated and condensed on the walls of the cool part of the test tube. Some amount of free chlorine was also detected. This fact indicates that, under the conditions of the experiment, lead chloride may be decomposed to lead metal. It also justifies the assumption, suggested by curve C in Fig. 3, that in the graphite tube, where only trace amount of PbCl₂ (e.g. 0.2 ng) forms a very thin layer on the graphite wall, the total amount of lead chloride is transformed into metal.

The mixture of the lead and sodium metal with graphite was melted quickly and, at temperatures of above 600°C, evolved the vapours which formed a gray metallic layer on the cool walls of the tube. After opening the tube this layer was oxidized and lead and sodium were detected in it.

The mixture of lead nitrate and sodium chloride, heated to a temperature below 500°C, evolved a large amount of nitrogen oxides and chlorine. Also some amount of lead chloride was evaporated and condensed on the tube walls. At the heating above 600°C lead and sodium metal evaporated.

The mixture of lead and ferric chlorides, heated to a temperature of about 300°C, evolved free chlorine and formed a large deposit of lead chloride. This indicates clearly that in the presence of free chlorine atoms easily volatile undefined lead–chlorine compounds are formed and transformed into PbCl₂ during condensation on the walls.

The heating of sodium chloride mixed with an excess of graphite powder did not give any effect up to 1000°C. Even after melting of the chloride, above 800°C, no traces of chlorine were detected. This indicates that sodium chloride is not able to affect the lead in a chemical way during the pyrolysis.

The results of the qualitative experiments in the macro-scale are consistent with the results obtained for pyrolysis in the graphite tube and confirm the suggested mechanism of the processes occurring during the pyrolysis phase.

Processes during atomization

It was mentioned above that sodium passes to the atomization phase either in metal form, when the sample is dissolved in nitric acid, or as sodium chloride when the sample is in hydrochloric acid. In both cases sodium affects the measured signals. The profiles of the lead evaporation peaks obtained for both media are shown in Figs. 5 and 6. The height of the peaks cannot be directly compared since in all cases the pyrolysis temperature was equal to 800°C and, therefore, lead is partially, but in different proportion, lost in the presence of sodium nitrate (Fig. 5, curve 2), sodium chloride (Fig. 6, curve 2) and palladium chloride (Fig. 6, curves 3 and 4).
Figure 5. Effect of sodium and palladium in 1 mol l\(^{-1}\) nitric acid medium on the position of lead absorbance peak. Test sample (sample): 20 ng ml\(^{-1}\) of Pb in 1 mol l\(^{-1}\) HNO\(_3\). Pd solution (Pd soln.): 0.3 mg ml\(^{-1}\) of Pd in 1 mol l\(^{-1}\) HNO\(_3\). 1 – sample; 2 – sample + 3 mg ml\(^{-1}\) of Na as NaNO\(_3\); 3 – Pd soln. + sample + 3 mg ml\(^{-1}\) of Na as NaNO\(_3\); 4: Pd soln. + sample

Figure 6. Effect of sodium and palladium in 1 mol l\(^{-1}\) hydrochloric acid medium on the position of lead absorbance peak. Test sample (sample): 20 ng ml\(^{-1}\) of Pb in 1 ml l\(^{-1}\) HCl. Pd solution (Pd soln.): 0.3 mg ml\(^{-1}\) of Pd in 1 mol l\(^{-1}\) HCl. 1 – sample; 2 – sample + 3 mg ml\(^{-1}\) of Na as NaCl; 3 – Pd soln. + sample + 3 mg ml\(^{-1}\) of Na as NaCl; 4 – Pd soln. + sample
The important information is provided by the position of the peak maxima on the time scale. The peaks of pure lead nitrate or chloride are identical and their maxima occur at about 0.9 s (peaks 1 in Figs. 5 and 6). In the presence of sodium nitrate or chloride (peaks 2 in Figs. 5 and 6) the maxima are shifted in the direction of a shorter time (to about 0.7 s). In these cases lead evaporates and it is atomized together with the main bulk of sodium or of sodium and chlorine atoms. At that moment the total atom pressure is relatively high and the free atoms leave quickly the hot area of the tube what results in decreasing of the measured signal. This phenomenon is responsible for the suppression of signal observed for curves A and E in Fig.4 in the range of pyrolysis temperature between 200°C and 600°C.

Palladium, when added to a sample, forms with lead less volatile intermetallic compounds and delays its evaporation. The positions of the peak maxima are shifted up to 1.1 s (peaks 3 and 4 in Fig. 5 and peak 3 in Fig. 6) or to 1.2 s (peak 4 in Fig. 6). In this case lead evaporates when the main bulk of sodium and chlorine atoms left already the tube and its signal is identical with that of a test sample containing only lead (compare curves C and D, Fig. 4).

Conclusions

The effect of chlorides on the lead signal at the graphite furnace atomization depends on their properties and on the parameters of the process:

For the samples in a nitric acid medium chlorides are transformed into nitrates during the drying phase and then, at the early steps of pyrolysis (charing) phase, they are gradually decomposed to oxides and to metals. The observed interference effects are due only to the properties of the cations contained in the chlorides. During the pyrolysis phase these cations may affect the behaviour of lead forming the intermetallic compounds, e.g. sodium increases the lead volatility causing its losses whereas palladium decreases it. The cations pass also, at least partially, to the atomization phase and then affect the signal, as it is observed for sodium and palladium.

For samples dissolved in hydrochloric acid or in a mixed hydrochloric–nitric acid medium the situation is more differentiated. The chlorides, that decompose below the pyrolysis temperature, e.g. palladium or iron chlorides, evolve the free chlorine atoms. The excess of chlorine forms with lead very volatile compounds that cause serious losses of lead already at relatively low temperatures above 200°C. The chlorides, that are stable to a temperature higher than the pyrolysis temperature, e.g. sodium chloride, are not able to affect lead chloride in a chemical way. However, their excess present in the sample may inhibit the reduction of the lead chloride by the hot graphite tube to the metal and cause thereby its losses in the form of chloride at a temperature above 600°C.

Palladium, used as the matrix modifier for a lead determination, can work properly only in a nitric acid solution. It may be added even as a palladium chloride since in the presence of a large excess of nitrate ions palladium chloride is transformed completely during drying stage into palladium nitrate.
When a sample is dissolved in hydrochloric acid or contains a large excess of chlorides the palladium nitrate is transformed, at least partially, into palladium chloride. During the pyrolysis it evolves free chlorine atoms causing significant losses of lead. This fact explains why some authors recommended to use the mixture of palladium with magnesium nitrate as a matrix modifier [5]. Magnesium nitrate is decomposed during the pyrolysis to the oxide or to the metal which binds the evolved free chlorine atoms by forming the very stable magnesium chloride and, thereby, improves the palladium action in the presence of chlorides.

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