Investigation of the mechanism of the electrothermal atomization of platinum in a graphite furnace from aqueous solutions and serum samples

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The mechanism of platinum atomization in electrothermal graphite atomizers was investigated in aqueous solutions and in serum samples. The methods of Rojas-Olivares and Yan et al., representing a chemical approach to the investigation of atomization mechanisms, as well as the physical approach developed by L’vov, were used. The activation energies for 1–8 ng of Pt in aqueous solution, calculated with use of the first two methods, increased with the increase of Pt mass, ranging from $E_a = 245 \pm 13$ kJ mol$^{-1}$ to $E_a = 387 \pm 11$ kJ mol$^{-1}$. The change of ratio $T_{app}/E$ from 6 to 4 with increasing Pt masses suggests that the atomization mechanism of Pt is progressively changing from an adsorption to an evaporation process. In serum samples, for all the Pt masses examined, one mechanism is observed. The calculated activation energy had a mean value of $E_a = 203 \pm 8$ kJ mol$^{-1}$ and is ascribed to an atomization mechanism via thermal desorption of Pt atoms from the carbon residue produced by the pyrolysis of the organic matrix. Confirmation of the above conclusions is provided by the physical method of L’vov, as the ratio $T_{app}/E$ was approximately 8 in the presence of serum matrix. All the methods used gave consistent conclusions rendering them more reliable.

Introduction

The determination of platinum in various types of samples has been widely studied, with the main problem being the low sensitivity. Interest is mainly focused on biological samples, like whole blood, blood serum and urine, because of the toxicological action of platinum-containing drugs against different types of cancer. The levels of Pt in these biological samples must be controlled. In routine laboratories, electrothermal atomic absorption spectrometry (ETAAS) is the method of choice for such determinations. However, ETAAS Pt determination suffers from low sensitivity and interferences: the sensitivity is surface dependent and appropriate chemical modifiers must be used. Moreover, understanding the mechanism of the formation of atomic vapor in ETAAS is of importance because this information could explain the experimental results, such as the low sensitivity of the determination and/or the beneficial use of a possible chemical modifier that could be used for the improvement of the determination. The most common methods for the calculation of the kinetic parameters have been those developed by Rojas and Olivares and Yan et al. These methods make use of Arrhenius-type diagrams as with the previously developed methods, but they were derived with the minimum number of assumptions. However, the atomization mechanism of platinum in the graphite furnace has only been investigated in aqueous standard solution and in the absence of modifiers. Schlemmer and Welz suggested that for Pt, but also for other elements of the platinum group, such as Pd, Ir and Ag, little or no interaction can be expected with the graphite or with oxygen in the gas phase because the metals are expected to be reduced to their elemental state in the condensed phase prior to the atomization step. Therefore, the appearance temperature is unaffected by the tube material. However, on going from pyrolytically coated graphite to uncoated or to glassy carbon, the absorption pulses clearly became lower with an increased tailing. Moreover, the characteristic mass of the above noble metals, which is a measure of the atomization efficiency, was lower in a pyrolytically coated graphite tube compared with other tube materials. The interaction of all noble metals with the carbon was attributed to physical adsorption rather than a chemical reaction. This dependency of Pt atomization efficiency on the tube material has also been mentioned by Van Warmerdam et al. and Tibben et al. They found that the AA signal of Pt was significantly depressed with a small change of graphite surface during the repeated atomization cycles, while the imperfections and the porosity of the surface increased, making indispensable the frequent replacement of the graphite tube. Rowston and Ottaway observed that, during the atomization of 20 μg of Pt (a very high mass for ETAAS) in aqueous solutions, the appearance temperature ($T_{app}$) is higher than the melting point of the metal (m.p. Pt = 2042 K) and the calculated atomization energy ($E_a$) coincides with the enthalpy of its evaporation ($\Delta H_{ev} = 565$ kJ mol$^{-1}$). The suggested mechanism was atomization via evaporation of the free metal, after its reduction to the elemental state at temperatures much lower than the $T_{app}$. The same mechanism was proposed by L’vov et al. for about 0.5 μg of Pt, and by Susuki and Ohta for 1 μg of Pt atomized in a tungsten microprobe atomizer. On the contrary, Akman et al. suggested an atomization mechanism via thermal dissociation of Pt dimers in the gas phase, using a much lesser mass of Pt (4 ng), compared with the previous studies. In that case, the heating rate was too high (> 2000 K s$^{-1}$), so Pt was vaporized into a very narrow temperature range and the atomization mechanism was not able to be depicted on an Arrhenius plot. Akman et al. proposed that, due to the fast atomization process, the concentration of atoms of Pt in the gas phase increased steeply, forming dimers by collision. The dimers dissociated at a high temperature of about 1800 K. Byrne et al. studied the atomization of the noble metals, including Pt, by ETV-ICP-MS. The atomization of 0.2 ng Pt gave single atomic absorption signals without shoulders,
suggesting the release of a single species in the furnace during the atomization step. It was shown from the pyrolysis and the atomization curves that the atoms, which are lost at the pyrolysis step, were the same as those released at the atomization step. The sublimation of the pure metal was suggested as the possible atomization mechanism, as the decomposition of the oxide takes place at a temperature much lower than $T_{\text{app}}$.35

The initial aim of this study was the development of a method for the determination of Pt in serum. Sixteen metals were tested as potential modifiers and none has improved the sensitivity of determination significantly. However, changes in the electrothermal behaviour of Pt were observed in the presence of serum matrix. For that reason, the main aim of the study is the investigation of the atomization mechanism of Pt aqueous and serum solutions. Two approaches were used for that purpose: the chemical and the physical. The former makes use of Arrhenius-type diagrams derived from the models of Rojas and Olivares 199 and Yan et al.20 The latter was developed by L’vov, 36-38 In this study it was shown that the complementary use of both approaches provides higher reliability of results. It is especially useful when the kinetic parameters fail to provide a possible atomization mechanism or a representative surface distribution of the analyte. This is the case for atomization processes with an order of release greater than unity (as observed in this work for Pt) or for multiple release mechanisms.

**Experimental**

**Instrumentation**

A PerkinElmer Model 5000 atomic absorption spectrometer equipped with HGA-400 graphite furnace was used for the atomic absorption measurements. Pyrolytically coated graphite tubes were used throughout the study. A Raytek ThermaIert TX, high temperature, close focus, optical pyrometer was used for temperature measurements in the range 500-2500 °C. The absorbance and the temperature signals were recorded with an IBM compatible PC interfaced with the spectrometer and data were acquired at 20 ms intervals. A 20 µl volume of each sample solution was injected in the graphite tube with an AS-1 autosampler and a 5 µl volume of the modifier solution was injected with a Finnpipette with disposable polypropylene tips. The instrumental settings and the graphite furnace programs are presented in Table 1.

**Reagents**

All of the chemicals used in this study were of analytical grade. All glass and polypropylene ware was kept in 10% v/v HNO$_3$ for at least one night and then rinsed with 1% v/v HNO$_3$ and subsequently with distilled water before use. The nitric acid was of Suprapur grade (Merck, Germany). Platinum standards were prepared by diluting a 1000 mg l$^{-1}$ Pt (as PtCl$_6^{2-}$) stock solution (Titrisol, Merck, Germany) with deionized distilled water and acidifying with HNO$_3$ to a final concentration of 0.1% v/v. Serum samples were prepared by dilution 1 : 1 with 0.4% v/v Triton-X 100 (Serva) and spiked with a Pt standard solution of appropriate concentration.

**Procedures**

During the development of the method for the determination of Pt in serum, the pyrolysis and atomization curves for Pt in aqueous solutions and in serum samples, in the absence and in the presence of several modifiers, were constructed. Validation of the method followed the optimization of the experimental parameters. The analytical characteristics of the matrix matched calibration curve were calculated. Peak area measurements were used for quantification. The characteristic mass, $m_c$, is calculated as $m_c = 0.0044 \times 20/b$ (for 20 µl of injected sample) and the limit of detection is calculated as LOD = $3 \times s_{BL}/b$, where b is the slope of the calibration curve and $s_{BL}$ is the standard deviation of 10 blank measurements.

For the investigation of Pt atomization mechanism in aqueous solutions and in serum samples the absorbance signals of 1, 2, 4 and 8 ng of Pt were recorded in triplicate. At the same time, the temperature profiles were also recorded by the use of the optical pyrometer. In all experiments, 20 µl of a Pt standard solution or serum sample spiked with a concentration of 50, 100, 200 and 400 µg l$^{-1}$ was injected into the graphite tube. The instrumentation parameters and the temperature programs used are shown in Table 1.

**Determination of the atomization energy, $E_a$, and the order of the reaction, $x$**

For the determination of the atomization energy, $E_a$, and of the order of the reaction, $x$, the method of Rojas and Olivares 19 (RO-method) and the method of Yan et al.20 (Yan-method) were applied. In the first method, an Arrhenius-type plot of ln $W_x$ as a function of $(1/RT)$ gives a linear curve for the appropriate order of $x$, from the slope of which $E_a$ can be calculated. The parameter $W_x$ was calculated by the equation$^{19}$:

$$W_x = \frac{k_2 A + dA/dt}{\int k_2 Adt - A}$$  \hspace{1cm} (1)

where $k_2$ is the rate constant of atom dissipation. In the second method, the Arrhenius-type plot was constructed using the equation$^{20}$:

$$\Delta(A) = x - E_a \frac{\Delta(1/RT)}{\Delta(B)}$$  \hspace{1cm} (2)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Instrumental operating conditions and temperature programme for the determination of kinetic parameters for the atomization of platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>265.9 nm</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>Lamp current</td>
<td>15 mA</td>
</tr>
<tr>
<td>Sample volume</td>
<td>20 µl</td>
</tr>
<tr>
<td>Temperature programme for aqueous solutions</td>
<td></td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>90</td>
</tr>
<tr>
<td>Temperature programme for serum samples</td>
<td></td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>80</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>120</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>120</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>2500</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>2700</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>1</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>1</td>
</tr>
</tbody>
</table>

Published on 12 January 2005. Downloaded by Universidade Federal de Juiz de Fora on 10/07/2013 16:37:46.
where \( A = \ln \left[ k_2 A + (d A/d t) \right] \) and \( B = \ln \left( \sum_{i} k_2 A + d A/d t \right) \). \( E_a \) and \( x \) were determined from the slope and the intercept, respectively.

The dissipation rate constant of the atomic vapor, \( k_2 \), was calculated from the slope of the plot \( \ln A = f(t) \). Determination of \( k_2(T) \) taking into account diffusion and expansion was not used, as the comparison of the kinetic parameters resulted from the plot \( \ln A = f(t) \) and from the calculation of the rate constants for the dissipation of the analyte atoms by diffusion and thermal expansion proved that the results were in good agreement and the temperature dependence of \( k_2 \) had no significant effect on the values of \( E_a \) and \( x \). All calculated values are the results of three measurements and are given with their standard deviations (\( \pm s, n = 3 \)).

The physical approach developed by L'vov and others was also applied. This approach suggests two possible atomization mechanisms: a condensation/evaporation or a desorption/adsorption process. In the first case the original samples, just as the possible products of the condensation, are assumed to be distributed in microcrystallites or microdroplets possessing thermochemical characteristics for bulk amount of these substances. In the second case, the analyte at the instant of entering the gas phase is assumed to be distributed in a monolayer over the graphite surface or in the form of individual atoms or molecules bound to the surface by physical or chemisorption forces. From the measured \( T_{\text{app}} \) and the determined \( E_a \) from the RO-method, the ratio \( T_{\text{app}}/E_a \) is calculated in order to decide which of the two proposed mechanisms takes place during Pt atomization.

### Results and discussion

#### Determination of Pt in serum by ETAAS

To improve the sensitivity of Pt determination in serum samples from patients receiving platinum-containing drugs, several metals were tested as chemical modifiers on the basis of their isomorphism with Pt, \(^{43}\) such as Ag, Au, Ir, La, Pd, Zr, Y, Ta, Sr, Rh (perfect isomorphism), Cr, Mn, Ni, Ti, Ru and Re (medium isomorphism). From all the investigated metals only La slightly improved the sensitivity of Pt in aqueous solutions. The effect of La mass on the signal of the Pt was studied and 0.2 \( \mu g \) were selected as the optimum mass, because they caused an increase of the peak height of 1 ng Pt at about 30\%, while the peak area was not affected significantly. Under these conditions, a characteristic mass, \( m \), of 114 pg, a pyrolysis temperature (\( T_{\text{pyr}} \)) of 1200 \( ^\circ \)C and an atomization temperature (\( T_{\text{atom}} \)) of 2700 \( ^\circ \)C were obtained, using peak area measurements. The \( T_{\text{pyr}} \) and \( T_{\text{atom}} \) temperatures in serum, in the absence and presence of modifiers, were 1400 \( ^\circ \)C and 2500 \( ^\circ \)C. Therefore no modifier was used for the determination of Pt in serum samples. The sensitivity in the presence of serum matrix was slightly decreased (approximately 10\%), giving a characteristic mass of 126 pg from peak measurements. Therefore, a matrix matched calibration curve was used for quantification and a linear range from 50 \( \mu g \) \( \text{L}^{-1} \) to 400 \( \mu g \) \( \text{L}^{-1} \) Pt was obtained. The limit of detection (LOD) was 39 \( \mu g \) \( \text{L}^{-1} \). Recovery was studied for 50, 100, 150 and 200 \( \mu g \) \( \text{L}^{-1} \) Pt and it was calculated from 95 (for 100 \( \mu g \) \( \text{L}^{-1} \)) to 103 (for 50 \( \mu g \) \( \text{L}^{-1} \)). The repeatability was 1.79% as RSD (for 100 \( \mu g \) \( \text{L}^{-1} \) Pt).

The above results (change in \( T_{\text{pyr}} \) and \( T_{\text{atom}} \) and the slight decrease in sensitivity) indicated a possible change in the atomization process of Pt in the presence of serum matrix and prompted us to investigate and compare the atomization mechanism of Pt in standard solutions and in the serum matrix.

#### Determination of the kinetic parameters of Pt atomization

The absorbance profiles of several masses of Pt in aqueous solutions and in serum samples as a function of the temperature are presented in Fig. 1. All AA signals are characterized from a slow increase at the onset of atomization that indicates an interaction between Pt and the atomization surface. The interaction is not very strong and must be of a physical nature, because stronger interactions are correlated with a steep gradient in the AA signal. \(^{44}\) This interaction is more intense in serum samples, where the increase in AA signals is much slower and the peaks more broadened compared with the respective AA signals in aqueous solutions.

From the values of \( T_{\text{app}} \) and \( T_{\text{peak}} \) given in Tables 2 and 3, the order \( x \) of the atomization mechanism in each case can be estimated, according to the method of peak alignment proposed by Holcombe and co-workers. \(^{55,15,46}\) A change in these parameters is observed when moving from the aqueous solutions to the serum samples. In aqueous solutions, \( T_{\text{peak}} \) decreases slightly but progressively for increasing Pt masses, indicating an order of release, \( x \), greater than unity. \(^{46}\) In serum samples, \( T_{\text{peak}} \) increases progressively with the increase of Pt mass, indicating a fractional order of release. \(^{46}\)

The absorbance, \( A \), its time derivative, \( dA/dt \), and the integral \( I = \int k_2 A dt \) were calculated, as shown in Fig. 2, for 1 ng of Pt in serum samples. The AA signal consisted of a single peak with no shoulders, as is clearly revealed from its derivative. This suggests that a single species is released from the furnace during the atomization step.

The calculated values of the dissipation rate constant of the atomic vapor, \( k_2 \), are given in Tables 2 and 3. The increase of \( k_2 \) with the increase of Pt mass from 1 ng to 4 ng, can be ascribed to a secondary generation process at the falling part of the AA signal in which strong interactions between Pt and carbon prevail. \(^{44}\) Consequently this process is a surface dependent process, as was discussed earlier. \(^{12,17,10}\)

![Fig. 1](View Article Online)

**Fig. 1** AA profiles for 1, 2, 4 and 8 ng of Pt as a function of temperature, (a) in aqueous solutions and (b) in serum samples.
Table 2 Appearance temperature, $T_{\text{app}}$, temperature of maximum absorbance, $T_{\text{peak}}$, and dissipation rate constant, $k_2$, relevant to the atomization of various masses of Pt in aqueous solutions ($n = 3$)

<table>
<thead>
<tr>
<th>m Pt/ng</th>
<th>$T_{\text{app}}$/K</th>
<th>$T_{\text{peak}}$/K</th>
<th>$k_2$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1722 ± 8</td>
<td>2036 ± 5</td>
<td>1.03 ± 0.06</td>
</tr>
<tr>
<td>2</td>
<td>1711 ± 9</td>
<td>2051 ± 5</td>
<td>1.14 ± 0.01</td>
</tr>
<tr>
<td>4</td>
<td>1696 ± 4</td>
<td>2025 ± 2</td>
<td>1.34 ± 0.05</td>
</tr>
<tr>
<td>8</td>
<td>1656 ± 9</td>
<td>2019 ± 3</td>
<td>1.34 ± 0.02</td>
</tr>
</tbody>
</table>

Table 3 Appearance temperature, $T_{\text{app}}$, temperature of maximum absorbance, $T_{\text{peak}}$, and dissipation rate constant, $k_2$, relevant to the atomization of various masses of Pt in serum samples ($n = 3$)

<table>
<thead>
<tr>
<th>m Pt/ng</th>
<th>$T_{\text{app}}$/K</th>
<th>$T_{\text{peak}}$/K</th>
<th>$k_2$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1718 ± 5</td>
<td>2045 ± 3</td>
<td>1.22 ± 0.08</td>
</tr>
<tr>
<td>2</td>
<td>1685 ± 13</td>
<td>2060 ± 2</td>
<td>1.29 ± 0.11</td>
</tr>
<tr>
<td>4</td>
<td>1656 ± 9</td>
<td>2083 ± 2</td>
<td>1.42 ± 0.07</td>
</tr>
<tr>
<td>8</td>
<td>1617 ± 14</td>
<td>2090 ± 2</td>
<td>1.43 ± 0.17</td>
</tr>
</tbody>
</table>

Fig. 2 AA signal as a function of time (AA), its time derivative ($\frac{dA}{dt}$), the integral $I = \int k_1 A dt(I)$ and the temperature profile ($T$), for the atomization of 1 ng Pt from serum matrix.

In Fig. 3 and Fig. 4, the RO- and Yan-plots for the atomization for 1 ng of Pt in aqueous solutions and in serum samples are shown. In all cases one linear region is observed, suggesting that only one mechanism for Pt atomization is taking place. The best linearity in the RO-plots is observed for $x = 3/2$ in aqueous solution (Fig. 3(a)), and $x = 3/4$ in serum matrix (Fig. 3(b)).

I. Investigation of the atomization mechanism in aqueous solutions. The activation energy, $E_a$, and the order of release, $x$, determined by the RO-method and the Yan-method for the atomization of 1, 2, 4 and 8 ng of Pt, in aqueous solutions, are summarized in Table 4.

The values of the activation energy, $E_a$, given in Table 4, are characterized by an increase from 245 kJ mol$^{-1}$ to 387 kJ mol$^{-1}$ as the mass of Pt is increased from 1 to 8 ng. The dependence of $E_a$ on the analyte mass suggests that the interactions among the atoms of analyte and the size of its clusters increase.\textsuperscript{57,48} The atomization mechanism of Pt may progressively change from a desorption mechanism, which is predominant at low Pt masses, to an evaporation mechanism, which is predominant at high Pt masses. At the higher masses, the appearance of the atomic vapor begins at lower temperatures, where the atomization takes place via evaporation of Pt atoms from the surface of the aggregates. The $E_a$ value determined for all masses is much lower than the enthalpy of evaporation of Pt, $\Delta H_{\text{ev}} = 565$ kJ mol$^{-1}$,\textsuperscript{49} for the vaporization of Pt a mass greater than 0.5 $\mu$g is demanded as is confirmed by previous studies on the Pt atomization mechanism.\textsuperscript{31–33,35} Consequently, despite the assumption of aggregates, atom distribution is far from what is characteristic for bulk samples.\textsuperscript{47,48}

An atomization mechanism via the dimer Pt$\textsubscript{2}$ dissociation, as proposed by Akman et al.,\textsuperscript{34} was not confirmed in the present study, because the $E_a$ value determined cannot be attributed to the dimer dissociation energy of the Pt–Pt bond $D_{\text{Pt-Pt}}^\text{d} = 357.3$ KJ mol$^{-1}$, probably because different heating rates are applied in each case: 2070 K s$^{-1}$ by Akman and 340 K s$^{-1}$ in this study.

The orders of reaction, $x$, for Pt atomization, presented in Table 4, varied from 3/2 (for 1 ng and 2 ng of Pt) to 2 (for 4 ng and 8 ng of Pt). A possible explanation could be that the peaks arising from a secondary atomization mechanism are not satisfactorily described by the kinetic models used.\textsuperscript{50} An order $x$ greater than unity can be assumed to represent not the distribution of Pt on the graphite surface, but the number of gaseous atoms involved in a gas phase reaction, namely evaporation via collisions.\textsuperscript{56}

II. Investigation of the atomization mechanism in serum samples. The activation energy, $E_a$, and the order of release, $x$, determined by the RO-method and the Yan-method, with the region of temperature in which they were calculated, are summarized in Tables 4 and 5, for the atomization of serum samples spiked with 1, 2, 4 and 8 ng of Pt.

For the Pt atomization from serum samples, a single $E_a$ value of about 200 kJ mol$^{-1}$ is determined for all masses. This $E_a$ is characteristic of the required energy for the thermal desorption of atoms, which is a first order reaction.\textsuperscript{31,51} This energy is observed even for the 8 ng of Pt. It is known that the
size and the dispersion of the particles of a metal depend on the presence of organic compounds. The pyrolysis of serum proteins and Triton X-100 results in the formation of a carbon residue with carbon active sites. These active sites form a uniform coating on the graphite surface, on which Pt is uniformly dispersed as individual atoms. Analogous uniform dispersion on the pyrolysis residue of the organic material was observed for Pd in the presence of citric acid and Au in the presence of ascorbic acid. For this reason, the distribution of Pt on the atomization surface is very close to the monatomic, as the order suggests, this value being very close to unity.

The small deviation of the order of release from unity can be ascribed to the action of the enriched carbon substrate, which can limit the dispersion of Pt atoms. Nevertheless, the order \( x \) is 3/4 higher than \( x = 1/2 \), \( x = 1/3 \) or \( x = 2/3 \), characteristic for atomization from ‘islands’, ‘caps’ or spheres, respectively.

### Investigation of Pt atomization using the physical approach of L’vov

Using the measured \( T_{app} \) presented in Tables 2 and 3 and the \( E_a \) determined by the RO-method presented in Tables 4 and 5, the ratio \( T_{app}/E_a \) was calculated. The results are presented in Table 6 and can be used to investigate the atomization mechanism of Pt applied to the physical approach of L’vov.

According to the theory developed by L’vov, the primary stage of the Pt atomization mechanism should be its vaporization (vaporization of simple substances), with the gaseous Pt atoms being the primary products. At the same time, the inverse reaction, namely condensation, is taking place and equilibrium is established between the gaseous atoms and the condensed phase via collisions. The total reaction is described by the chemical equation:

\[
P_t^{(g)} \rightarrow P_t^{(cond)} \approx P_t^{(solid)}
\]

and the primary vaporization products are the same as those at equilibrium in the case of Pt. Equilibrium is established immediately and the atomization rate is determined by the reaction of the formation of atomic vapor Pt(g).

From the values of the experimental \( T_{app}/E \) ratio and by using the criteria that allow selection between the two possible processes, condensation/evaporation or adsorption/desorption, conclusions for the atoms’ distribution at the beginning of the atomization can be derived. As observed for the aqueous solutions, the atomization mechanism progressively changes from an adsorption/desorption mechanism to a condensation/evaporation mechanism with increasing Pt masses. The first mechanism is obviously predominant at low masses, with a \( T_{app}/E \) ratio close to the theoretical \( T_{app}/E = 5.9 \text{ K mol}^{-1} \text{kJ}^{-1} \), while the participation of the second mechanism, with a \( T_{app}/E \) ratio close to the theoretical \( T_{app}/E = 3.6 \text{ K mol}^{-1} \text{kJ}^{-1} \), is getting more and more intense as the mass of Pt increases. These values suggest that, for Pt masses close to 1 ng or lower, the Pt atoms in the solid phase, as well as the condensed atoms, are distributed on the graphite surface as a monolayer or as

### Table 4 Kinetic parameters \((E_a \text{ and } x)\) relevant to the atomization of various masses of Pt from aqueous solutions \((n = 3)\)

<table>
<thead>
<tr>
<th>m Pt/ng</th>
<th>RO - method</th>
<th>( E_a ) kJ mol(^{-1} )</th>
<th>( T ) K</th>
<th>Yan-method</th>
<th>( E_a ) kJ mol(^{-1} )</th>
<th>( T ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/2</td>
<td>242 ± 13</td>
<td>1800–1990</td>
<td>1.52 ± 0.06</td>
<td>242 ± 13</td>
<td>1830–1970</td>
</tr>
<tr>
<td>2</td>
<td>3/2</td>
<td>333 ± 6</td>
<td>1760–1960</td>
<td>1.37 ± 0.03</td>
<td>319 ± 20</td>
<td>1800–2020</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>380 ± 6</td>
<td>1730–1950</td>
<td>2.07 ± 0.06</td>
<td>382 ± 3</td>
<td>1780–1900</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>387 ± 11</td>
<td>1660–1990</td>
<td>1.95 ± 0.04</td>
<td>388 ± 17</td>
<td>1750–1890</td>
</tr>
</tbody>
</table>

### Table 5 Kinetic parameters \((E_a \text{ and } x)\) relevant to the atomization of various masses of Pt from serum samples \((n = 3)\)

<table>
<thead>
<tr>
<th>m Pt/ng</th>
<th>RO-method</th>
<th>( E_a ) kJ mol(^{-1} )</th>
<th>( T ) K</th>
<th>Yan-method</th>
<th>( E_a ) kJ mol(^{-1} )</th>
<th>( T ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/4</td>
<td>195 ± 9</td>
<td>1750–1990</td>
<td>0.75 ± 0.05</td>
<td>192 ± 8</td>
<td>1830–1930</td>
</tr>
<tr>
<td>2</td>
<td>3/4</td>
<td>204 ± 6</td>
<td>1700–1980</td>
<td>0.78 ± 0.03</td>
<td>199 ± 10</td>
<td>1830–1940</td>
</tr>
<tr>
<td>4</td>
<td>3/4</td>
<td>203 ± 3</td>
<td>1700–1990</td>
<td>0.75 ± 0.01</td>
<td>206 ± 2</td>
<td>1850–2030</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>209 ± 2</td>
<td>1760–2030</td>
<td>0.89 ± 0.05</td>
<td>216 ± 6</td>
<td>1920–2020</td>
</tr>
</tbody>
</table>
individual atoms bonded to the surface through physical adsorption forces. On the contrary, Pt masses close to 8 ng or higher result in a distribution in microcrystallites or microdroplets.

The results of the method of L’vov for aqueous solutions confirmed those by the RO- and Yan-methods, according to the observed increase of $E_a$ to the $AH_{app}$.

The physical method can give an explanation for the calculated order of $\alpha$ that is close to 2.0, whereas the RO- and Yan-methods cannot give an adequate speculation of Pt distribution on the atomization surface. The order $\alpha = 2$ for the highest Pt masses possible represents collisions between two gaseous atom, and the diffusion of which in gaseous phase is controlled by their interaction with the graphite, as revealed from the slow increase in AA signal on the onset of the atomization, and leads to the production of condensed Pt atoms.

As for the atomization with serum samples, the values of $T_{app}/E$ ratio are obviously representative of an adsorption/desorption mechanism, where the particles of Pt are distinctively distributed on the atomization surface. This conclusion is consistent with the conclusion of the RO- and Yan-methods, where the calculated order $\alpha$ is very close or equal to unity. The calculated $T_{app}/E$ values are larger enough than the mean experimental value calculated by L’vov for an adsorption/desorption mechanism. This observation does not diminish the reliability of the results, because such high values have been calculated by L’vov, based on the experimental results of other researchers, for two other elements of the platinum group (PMGs), Pd and Ru, in sub-nanograms amounts. High $T_{app}$ and low $E_a$ characterize these two metals, so that the $T_{app}/E$ ratio is greater than that for other elements. Moreover, the value of $E_a$ for Pt atomization in serum decreases even more due to the influence of the serum’s organic matrix.

Conclusions

The methods developed by Rojas-Olivares and Yan et al. were applied for the evaluation of the kinetic parameters of Pt atomization in aqueous solutions and in serum samples. The results of this study complete previous studies because this investigation extends to lower masses of Pt and to the atomization in the presence of a serum matrix. The atomization was also investigated by the theory of physical approach developed by L’vov.

In aqueous solutions, the calculated $E_a$ increased with the increase of Pt mass, indicating increase of analyte–analyte interaction and cluster size. The atomization mechanism of Pt is then suggested to change progressively from an adsorption mechanism to an evaporation mechanism, when the mass of Pt increases. For all masses of Pt in serum samples, an atomization mechanism via thermal desorption of Pt atoms from the carbon residue produced by the pyrolysis of serum proteins and Triton X-100 is proposed. In aqueous solutions, the physical approach supports the progressive change of the atomization mechanism from adsorption–desorption to condensation–evaporation with the increase of Pt mass. In serum samples, an adsorption–desorption mechanism takes place during the atomization of Pt for all studied masses, according to the physical approach.

The conclusion about the distribution of the atoms of Pt drawn from using the method of L’vov is similar to those produced by the methods of RO and Yan, providing a considerable confirmation of the assumptions of L’vov. These conclusions are not only the result of a theory based on the kinetics of homogeneous reactions, transferred to the theory of heterogeneous reactions without appropriate theoretical valuation, but also of a validated theory. Moreover, the physical approach gives an adequate prediction of the particles’ distribution when the other methods fail, as in the case where the order of the atomization reaction is greater than unity and cannot be representative of the particles size. The physical approach could also be useful for multiple release mechanisms, where the order is determined from the high temperature region of the RO- and Yan-plots. On the contrary, the physical approach investigates the mechanism at the beginning of atomization, close to $T_{app}$ without providing any information about possible reactions that follow the formation of primary products.

In conclusion, the chemical and the physical approach can give complementary information about the atomization mechanism of an analyte. The two approaches do not oppose but complement each other and their combination constitutes a valuable tool for the investigation of the reactions taking place in a graphite furnace during atomization by ETAAS.

References


Table 6 Experimental ratio $T_{app}/E$ for the atomization of Pt ($E$ obtained from the RO-method)

<table>
<thead>
<tr>
<th>$m_{Pt}/ng$</th>
<th>Aqueous solutions $T_{app}/E$ [K mol J$^{-1}$]</th>
<th>Serum samples $T_{app}/E$ [K mol J$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0 ± 0.1</td>
<td>8.8 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>5.1 ± 0.1</td>
<td>8.3 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>4.5 ± 0.1</td>
<td>8.2 ± 0.1</td>
</tr>
<tr>
<td>8</td>
<td>4.3 ± 0.1</td>
<td>7.7 ± 0.1</td>
</tr>
</tbody>
</table>