

# Thermogravimetric investigations on the mechanism of decomposition of Pb compounds on a tungsten surface

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## Abstract

Tungsten coils are used as electrothermal atomizers in atomic absorption spectrometry (ETA-W), but despite successful applications the atomization mechanism is still obscure. The use of the thermogravimetry (TG) can bring some information on decomposition pathways for atom formation, simulating the drying and pyrolysis steps employed in typical heating program cycles. Thermogravimetric curves of Pb salts with and without chemical modifiers, such as ascorbic, oxalic, tartaric acids, and glucose, or interferences (e.g.  $\text{NaNO}_3$ ) were obtained using a lab-made tungsten sample holder in an 90% Ar plus 10%  $\text{H}_2$  atmosphere usually employed in ETA-W. Intermediaries and residues of the pyrolysis step were characterized by X-ray diffraction. These data allows a better establishment of parameters for ETA-W and can help to find proper conditions to decrease interferences. It was showed that the general decomposition route is the formation of  $\text{PbO}$  by heating, oxide reduction by  $\text{H}_2$  in the purge gas followed by volatilization of Pb. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermogravimetry; Lead; Atomization pathways; Tungsten surface

## 1. Introduction

Atomic absorption spectrometry with electrothermal atomizers is one of the best techniques for determination of trace levels of metals in complex samples, such as body fluids and tissues. The most conventional atomizer is the graphite tube, that after a critical stage in the 1970s attained maturity in the 1980s with the proposal of the stabilized temperature platform furnace concept [1]. In addition to its superb sensitivity, this closed atomizer is virtually interference free

owing to its design that allows reaching isothermal furnace conditions. Open atomizers, such as metallic coils and strips, also attained excellent sensitivities for most metals [2,3] however due to its non-isothermal ambient the occurrence of interferences is a critical issue that limits their applicability [4].

The tungsten coil electrothermal atomizer (ETA-W) was proposed by Lund and Larsen [5,6] and after a long period without large use it was reinvestigated by Berndt and Schaldach [7] using 150 W tungsten coil of projector lamps. Subsequently, the ETA-W was mainly used in studies dealing with the determination of trace metals, e.g. Cd in biological materials [8], Cr in hair and urine [9], Pb in hair and paints [10], and Pb in blood [11,12]. In all these studies the quantification

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was performed by matrix matching or standard additions method. The use of reference solutions prepared in acid medium was unsuitable owing to the severe occurrence of matrix interference processes. A separation procedure was also proposed for removing interferences before determination of Pb in residual waters [13]. More recently an on-line electrodeposition procedure was implemented to remove interferences before Pb determination in waters [14].

Despite all the practical analytical difficulties for obtaining accurate results, the ETA-W is evolving and it may have a market as a dedicated analytical instrument. The research developed by Jones and coworkers [15,16] is an important route towards the development of a practical instrument arrangement.

To complement the development of the instrumentation, it is need to investigate the mechanism of atomization to try to understand the interference processes. The studies about mechanisms occurring on metallic atomizers are scarce, and the few researches described dealt with tungsten tube atomizers [17–21]. Nevertheless, despite the use of the same metal, this closed atomizer is completely different of the ETA-W. The tungsten tube atomizer is an isothermal system as demonstrated by Chakrabarti et al. [22]. However, both tungsten atomizers are critically dependent on the presence of hydrogen in the purge gas to promote reduction of oxides involving the analyte and to protect the metallic surface from fast oxidation and destruction.

The mechanism of action of chemical modifiers in the ETA-W is also practically unknown, despite some advantages coming from its use, such as extended coil lifetime and better repeatability [23,24]. In the work related to the atomization of Pb, Bruhn et al. [23] demonstrated that interferences caused by Na are condensed phase processes. This is in opposition to the expected since the non-isothermal ambient should aggravate gas phase recombination and condensation processes. Thus, considering that condensed phase processes are operative for Pb, the use of thermal analysis could bring a better understanding of them. Alvarado used thermogravimetry to investigate mechanisms of atomization of Fe, Co, and Ni in a graphite tube atomizer [25].

The present work evaluated the thermal decomposition of  $\text{Pb}^{2+}$  salts alone or in media containing chemical modifiers. The thermogravimetric curves

up to 900°C in a Ar/H<sub>2</sub> dynamic atmosphere and the characterization of the solid residues by powder X-ray diffraction generated useful data to a better comprehension of the processes occurring during dry and pyrolysis steps in the ETA-W.

## 2. Experimental

### 2.1. Reagents

Analytical grade  $\text{Pb}(\text{NO}_3)_2$  was used after recrystallization. The salts  $\text{PbCl}_2$  and  $\text{PbSO}_4$  were prepared by reacting  $\text{Pb}(\text{NO}_3)_2$  with HCl and  $\text{H}_2\text{SO}_4$ , respectively. All the salts were dried for 4 h at 80°C in a vacuum oven.

Mixtures of  $\text{Pb}(\text{NO}_3)_2$  and organic compounds (tartaric, oxalic and ascorbic acids, and glucose) were also prepared by dissolving them in 1:2 mol ratio (inorganic:organic) in water. To obtain a solid mixture containing both compounds the solvent was eliminated by heating. The solid formed was dried in an oven at 120°C, except the glucose mixture which was dried at 60°C under reduced pressure. A mixture containing  $\text{NaNO}_3$  plus  $\text{Pb}(\text{NO}_3)_2$  was similarly prepared.

### 2.2. Instrumentation

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded on a TG-2050 thermogravimetric module coupled to a 2100 thermal analyser, both from TA Instruments under a gas flow of 90 ml min<sup>-1</sup> (90% Ar+10% H<sub>2</sub> mixture v/v) in a lab-made tungsten crucible at 10°C min<sup>-1</sup> heating rate and using samples of about 5 mg of each compound. The sample holder was prepared by folding a piece of 10×15 mm of a tungsten foil (tungsten foil 99.9% of purity, 0.05 mm thick, Aldrich). The folded foil was then perforated at each extremity and a Ni–Cr wire was used as a hanging loop. The final masses of such sample holders was around 300 mg. The final temperature was 900°C for all the TG experiments.

X-ray diffractograms (XRD) were obtained in the D5000 Siemens diffractometer. The XRD powder diffractograms were recorded using the  $\text{CuK}_\alpha$  (radiation at 2θ angle range from 25 to 75).

### 3. Results and discussions

The electrothermal heating conditions were simulated in the thermogravimetric experiment employing the lab-made tungsten sample holder under an Ar+H<sub>2</sub> atmosphere. This gaseous mixture is usually employed as purge gas in ETA-W for extending the coil lifetime and for increasing efficiency of the atom formation.

The choice of the Pb salts was made considering the acids commonly used for sample preparation, i.e. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl. The presence of organic compounds as concomitants or chemical modifiers is also usual [26,27].

The application of heating rates varying from 5 to 40°C min<sup>-1</sup> led to similar decomposition profiles for PbC<sub>2</sub>O<sub>4</sub>, with minor variations of the initial and final decomposition temperatures. The heating rate of 10°C min<sup>-1</sup> was selected for all TG experiments trying to reach the best resolution for overlapping thermal events.

The effect of sample mass was investigated in the 1–20 mg range. A distortion was observed in the TG curves with 1 mg sample due to the compensation system of the thermobalance. Sample masses of 3–5 mg showed suitable behavior and the last one was used in all TG runs, in order to obtain enough sensitivity in low mass changes.

Both heating rate and sample mass parameters require careful analysis when comparing TG and

ETA-W experiments. On the one hand, the typical heating rates of TG is significantly lower than those employed in ETA-W even during dry and pyrolysis steps. On the other hand, the sample mass is appreciably lower in this latter technique, for example a sample volume of 10 µl for a lower than 10 µg l<sup>-1</sup> solution, i.e. an analyte mass of 0.1 ng. Therefore, the results must be carefully interpreted to avoid erroneous inferences.

#### 3.1. Decomposition of Pb(NO<sub>3</sub>)<sub>2</sub>, PbSO<sub>4</sub>, and PbCl<sub>2</sub>

The thermal behavior of these inorganic compounds in the tungsten surface and under N<sub>2</sub> atmosphere was studied for comparison purposes.

Table 1 summarizes the mass losses, temperature ranges, and thermal events observed in each step of TG curves. The TG curves for Pb compounds are presented in the Fig. 1 under Ar/H<sub>2</sub>. The products formed in each step are proposed on basis of their X-ray diffraction patterns characterization.

The thermal decomposition of Pb(NO<sub>3</sub>)<sub>2</sub> was similar under both N<sub>2</sub> or Ar/H<sub>2</sub> atmospheres. A crepitation process was observed in both cases between 180 and 380°C, previously to the decomposition. Data obtained by XRD for the solid residues formed at 532°C, confirmed the formation of PbO and W<sub>5</sub>O<sub>14</sub> in the sample holder surface. The final residue obtained at 633°C was characterized by XRD as Pb<sup>0</sup>.

Table 1  
Mass losses and temperature range corresponding to the decomposition of the Pb compounds

Process	TG data temperature interval (°C)	Mass loss or residue (%)	
		TG	Calculated
<i>90% Ar+10% H<sub>2</sub> mixture</i>			
PbCl <sub>2</sub> (s)→PbCl <sub>2</sub> (g)+H <sub>2</sub> (g)→Pb(g)+2HCl(g)	442–558	52.2 <sup>a</sup>	– <sup>c</sup>
Pb(g)→Pb(l) <sup>d</sup>	Starting at 710	28.3 <sup>a</sup>	–
Pb(NO <sub>3</sub> ) <sub>2</sub> →PbO <sup>d</sup>	191–512	66.4 <sup>b</sup>	67.4
PbO+H <sub>2</sub> (g)→Pb <sup>0</sup> (l)+H <sub>2</sub> O	512–671	63.3 <sup>b</sup>	62.6
Pb <sup>0</sup> (l)→Pb <sup>0</sup> (g) <sup>c</sup>	Starting at 700		–
PbSO <sub>4</sub> →PbO <sup>d</sup>	594–753	27.7 <sup>a</sup>	–
PbO+H <sub>2</sub> (g)→Pb <sup>0</sup> (l)→Pb <sup>0</sup> (g) <sup>c</sup>	Starting at 753	23.4 <sup>a</sup>	–

<sup>a</sup> Relative to mass loss.

<sup>b</sup> Relative to residue.

<sup>c</sup> Vapor pressure.

<sup>d</sup> Characterized by XRD.

<sup>e</sup> Not calculated, mixture.

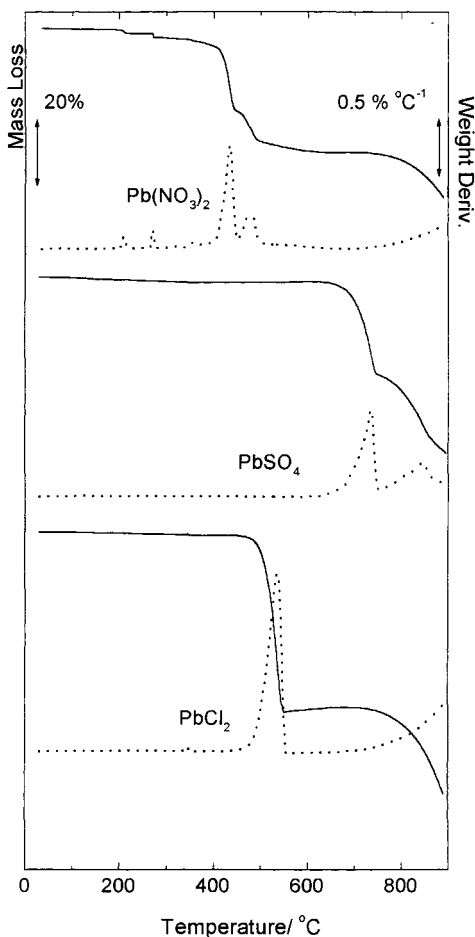
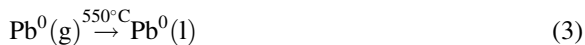
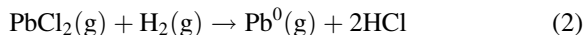


Fig. 1. TG (solid)/DTG (dot) curves obtained for some Pb salts on the W crucible, under a dynamic Ar/H<sub>2</sub> atmosphere (gas flow of 90 ml min<sup>-1</sup>, sample mass around 5 mg, 10°C min<sup>-1</sup> heating rate).

Lead chloride was completely removed by volatilization in a N<sub>2</sub> atmosphere. However, under Ar/H<sub>2</sub> the decomposition occurred in two steps. According to XRD data, at the end of the second step (558°C) the sample holder was totally recovered by Pb<sup>0</sup>. In addition the amount of experimental residue was smaller than that calculated at 558°C for metallic lead. It is known that in a graphite tube the PbCl<sub>2</sub> can react with H<sub>2</sub> in the gas phase generating Pb<sup>0</sup> and HCl [28]. We proposed that in ETA-W the PbCl<sub>2</sub> is partially removed by the purge gas, while some amount is reduced to Pb<sup>0</sup> (g) which condenses on the tungsten sample holder surface since Pb<sup>0</sup> is liquid at 327.4°C

[29]. Finally, the Pb<sup>0</sup> volatilizes above 750°C. The process is summarized by the following equations



The decomposition of PbSO<sub>4</sub> under N<sub>2</sub> showed that the salt decomposes only above 800°C. On the other hand, under Ar/H<sub>2</sub>, two steps were observed. The first one was attributed to the formation of PbO (594–753°C) and the second one is related to the oxide reduction and formation of Pb<sup>0</sup>.

The anticipation of PbSO<sub>4</sub> decomposition and the reduction of the PbCl<sub>2</sub> evidenced the influence of the reductive character of the atmosphere and its effects on ETA-W atomization processes. These processes are important to understand the atom formation in ETA-W. As previously mentioned, this is a non-isothermal atomizer and consequently the formation of atoms is dependent on thermochemical processes involving compounds generated during dry and pyrolysis steps. Contrary to the graphite tube atomizer, processes promoted by thermal dissociation in the gas phase are less operative due to the low temperature. Therefore, the atom formation processes seem to be caused by H<sub>2</sub> related reactions. In this sense the purge gas could be named as the atomization gas in addition to H<sub>2</sub> action to increase tungsten coil lifetime.

### 3.2. Decomposition of Pb(NO<sub>3</sub>)<sub>2</sub> in the presence of the organic modifiers

Recently, it was studied the determination of Pb in urine. Alkaline and alkaline-earth elements caused a negative interference on Pb atomization. The authors also investigated the effect of ascorbic, oxalic, and tartaric acids as organic modifiers. All these compounds can be a source of C and reductive gases as CO formed during their decomposition. Such conditions may contribute to the oxides reduction and formation of Pb<sup>0</sup> in the condensed or gaseous phase [30].

The TG curves for Pb mixtures are presented in the Fig. 2 under Ar/H<sub>2</sub>. The mass losses, temperature ranges and final decomposition products, observed in

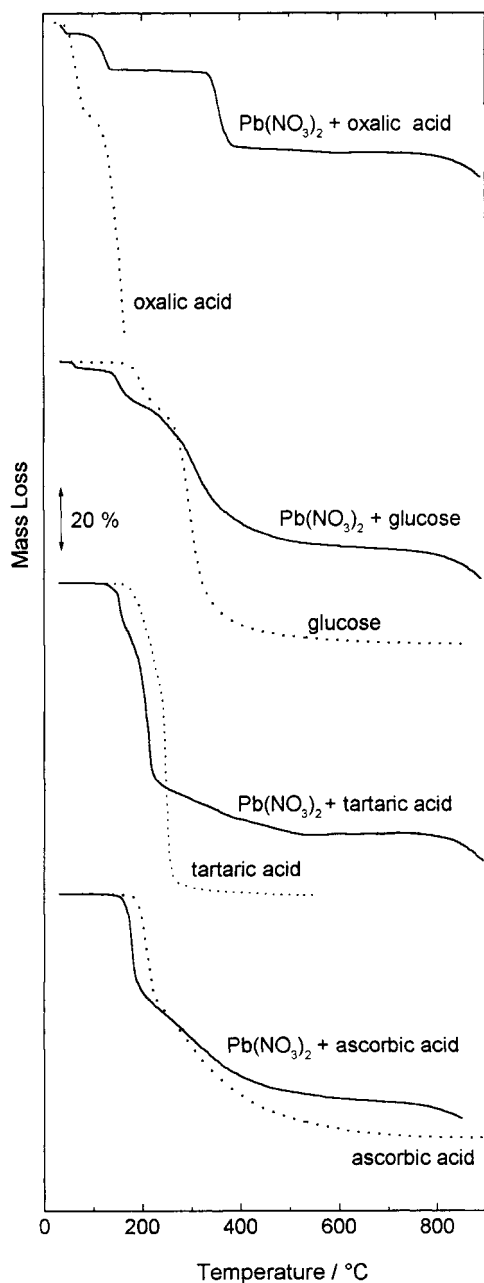


Fig. 2. TG curves for mixtures of  $\text{Pb}(\text{NO}_3)_2$  and organic modifiers (solid) and for the pure modifiers (dot), on the W crucible, under a dynamic  $\text{Ar}/\text{H}_2$  atmosphere (gas flow of  $90 \text{ ml min}^{-1}$ , sample mass around  $5 \text{ mg}$ ,  $10^\circ\text{C min}^{-1}$  heating rate).

each step of TG curves, are presented in Table 2. The products formed in each step are proposed on basis of their XRD patterns characterization.

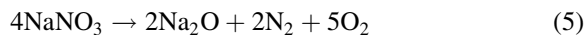
Lead nitrate and each organic modifier were mixed in solution and the dry step was simulated out of the thermobalance, in order to prevent mass losses by crepitation. As expected, the presence of the organic compounds induced the reduction of  $\text{PbO}$  to  $\text{Pb}^0$  at lower temperatures than observed for  $\text{Pb}(\text{NO}_3)_2$  alone. The temperatures in which  $\text{Pb}^0$  is formed in the tungsten crucible surface in presence of each modifier are presented in Table 3. These attributions reflect a combination of data obtained by TG and XRD. The results are in agreement with ETA-W data showing the increment of sensitivity in media containing organic modifiers evidencing the importance of the presence of such compounds in the condensed phase, to promote the formation of the atomic cloud. Once again, these processes confirmed that thermochemical processes must be understood to improve the efficiency of atomization in the ETA-W. However, the presence of a high content of C cannot be fully exploited analytically to increment sensitivity owing to the reduction of the tungsten coil lifetime caused by the formation of brittle and less refractories tungsten carbides.

The TG curve profile for the thermal decomposition of  $\text{PbC}_2\text{O}_4$  is similar to the TG decomposition curve of the mixture  $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{C}_2\text{O}_4$ . The formation of  $\text{PbC}_2\text{O}_4$  could be proposed on the basis of its  $K_s$  of  $8.3 \times 10^{-12}$  [29] and the mixture preparation procedure. After decomposition of the excess of organic acid ( $25\text{--}160^\circ\text{C}$ ), the mixture showed only one mass loss ( $320\text{--}410^\circ\text{C}$ ), resulting in  $\text{PbO}/\text{Pb}$  at  $435^\circ\text{C}$  according to the XRD data.

### 3.3. Decomposition of $\text{Pb}(\text{NO}_3)_2$ in the presence of $\text{NaNO}_3$

Sodium is a severe interference in the Pb determination using ETA-W [23]. In the Fig. 3, TG and DTG curves are presented for  $\text{NaNO}_3$  and its mixture.

In a Pt sample holder the decomposition of  $\text{NaNO}_3$  was expected to occur via a thermal decomposition process ( $800^\circ\text{C}$ ) such as [31]:



However, on a W sample holder the TG residue at  $428^\circ\text{C}$  is 65.4% while the calculated for the  $\text{Na}_2\text{O}$  is 36.5%.

The XRD results for the sample holder surface showed the presence of  $\text{Na}_2\text{O}$  and  $\text{W}_2\text{O}_3$  and  $\text{W}_2\text{O}_5$

Table 2  
Mass losses and temperature range corresponding to the decomposition of the Pb mixtures

Process	TG data temperature interval (°C)	Mass loss or residue (%)	
		TG	Calculated
<i>90% Ar+10% H<sub>2</sub> mixture</i>			
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O→H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +2H <sub>2</sub> O	27.0–92.4	29.4 <sup>a</sup>	28.6 <sup>a</sup>
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> →total decomposition	92.4–168	No residue	– <sup>f</sup>
<i>Pb(NO<sub>3</sub>)<sub>2</sub>+oxalic acid mixture</i>			
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O→H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +2H <sub>2</sub> O	32.4–60.7	3.33 <sup>a</sup>	–
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> decomposition	81.5–146	11.2 <sup>a</sup>	–
PbC <sub>2</sub> O <sub>4</sub> →PbO <sup>d</sup> +CO+CO <sub>2</sub>	322–410	23.8 <sup>a</sup>	–
PbO*+H <sub>2</sub> →Pb <sup>0</sup> (l) <sup>d</sup> +H <sub>2</sub> O→Pb(g) <sup>c</sup>	Starting at 700	50.2 <sup>b</sup>	–
Ascorbic acid→3H <sub>2</sub> O	170–221	29.7 <sup>a</sup>	30.7
Ascorbic acid decomposition	221–800	46.2 <sup>a</sup>	–
<i>Pb(NO<sub>3</sub>)<sub>2</sub>+ascorbic acid mixture</i>			
Ascorbic acid→3H <sub>2</sub> O	120–222	34.9 <sup>a</sup>	–
Pb(NO <sub>3</sub> ) <sub>2</sub> +ascorbic acid→PbO <sup>d</sup> +Pb(l) <sup>d</sup>	222–604	29.8 <sup>a</sup>	–
Pb <sup>0</sup> (l)→Pb(g) <sup>c</sup>	Starting at 604	29.4 <sup>b</sup>	–
Tartaric acid→CO <sub>2</sub> +CO+H <sub>2</sub> O <sup>c</sup>	151–552	1.2 <sup>b</sup>	–
Pb(NO <sub>3</sub> ) <sub>2</sub> +tartaric acid→Pb <sup>0</sup> (l) <sup>d</sup>	112–530	79.5 <sup>a</sup>	–
Pb <sup>0</sup> (l)→Pb(g) <sup>c</sup>	Starting at 715	12.0 <sup>b</sup>	–
Glucose→2H <sub>2</sub> O	146–233	14.5 <sup>a</sup>	16.7
Glucose decomposition	233–730	10.6 <sup>b</sup>	–
Pb(NO <sub>3</sub> ) <sub>2</sub> +glucose→PbO <sup>d</sup> +Pb <sup>0</sup>	121–416	49.6 <sup>a</sup>	–
PbO→Pb <sup>0</sup> (l) <sup>d</sup>	416–601	5.91 <sup>a</sup>	–
Pb <sup>0</sup> (l)→Pb(g) <sup>c</sup>	Starting at 700	30.1 <sup>b</sup>	–
NaNO <sub>3</sub> →Na <sub>2</sub> O+tungstates	298–397	31.0 <sup>a</sup>	–
Pb(NO <sub>3</sub> ) <sub>2</sub> +NaNO <sub>3</sub> →Na <sub>2</sub> WO <sub>4</sub> <sup>d</sup> +Na <sub>2</sub> W <sub>2</sub> O <sub>7</sub> <sup>d</sup> +PbWO <sub>4</sub> <sup>d</sup>	327–471	29.6 <sup>a</sup>	–
Na <sub>2</sub> WO <sub>4</sub> +Na <sub>2</sub> W <sub>2</sub> O <sub>7</sub> +PbWO <sub>4</sub> →Na <sub>2</sub> WO <sub>4</sub> <sup>d</sup> +NaWO <sub>3</sub> <sup>d</sup>	545–900	52.3 <sup>b</sup>	–

<sup>a</sup> Relative to mass loss.

<sup>b</sup> Relative to residue.

<sup>c</sup> Vapor pressure.

<sup>d</sup> Characterized by XRD.

<sup>e</sup> Ref. [33].

<sup>f</sup> Not calculated, mixture.

even in the reductive atmosphere (500°C). The presence of the tungsten oxides explains the difference.

In the presence of NaNO<sub>3</sub> the temperature on which decomposition of Pb(NO<sub>3</sub>)<sub>2</sub> begins shifted to a higher

value (327°C), in comparison with the salt alone (190°C). X-ray diffraction data showed the presence of Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub>, Na<sub>2</sub>WO<sub>4</sub> and the PbWO<sub>4</sub>, on the tungsten sample holder surface. These compounds exerted a significant influence on the Pb(NO<sub>3</sub>)<sub>2</sub> decomposition since these W oxides are reduced only above 900°C.

According to Mellor [32]:

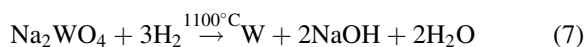
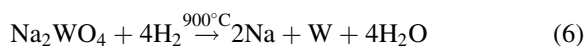


Table 3  
Effects of organic compounds on the temperature of Pb<sup>0</sup> formation

Modifier	T (°C)
Tartaric acid	527
Ascorbic acid	600
Glucose	650
Oxalic acid	700

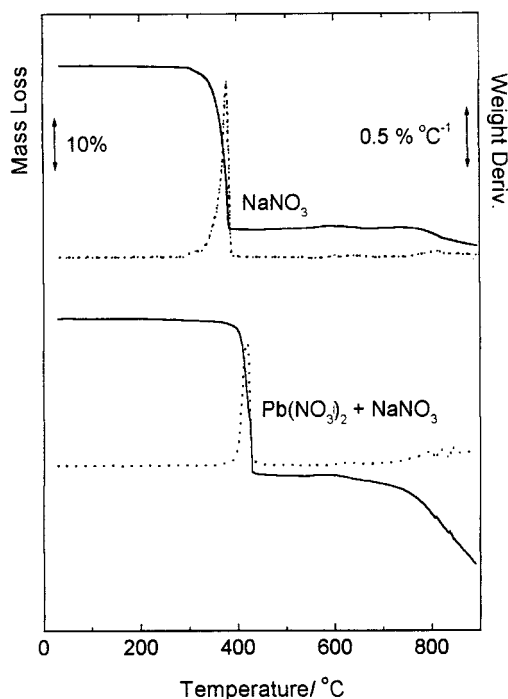


Fig. 3. TG (solid)/DTG (dot) curves obtained for mixture of  $\text{Pb}(\text{NO}_3)_2 + \text{NaNO}_3$  and for  $\text{NaNO}_3$ , on the W crucible, under a dynamic  $\text{Ar}/\text{H}_2$  atmosphere (gas flow of  $90 \text{ ml min}^{-1}$ , sample mass around 5 mg,  $10^\circ\text{C min}^{-1}$  heating rate).

These oxides are refractories and additionally the W oxides compete with Pb for  $\text{H}_2$  in the atmosphere and reductor compounds in the condensed phase, retarding the Pb atomization.

#### 4. Conclusion

The experimental data obtained combining TG and XRD were the first evidences of the processes involved in the atoms formation of Pb in the ETA-W. The effects of the purge gas as an atomization gas was clearly proved and the beneficial effects caused by reductor compounds generated in the condensed phase on the sensitivity were explained. The severe interference caused by Na on Pb atomization was also understood and the formation of refractories tungstates that trapped the Pb compounds seems to be the operative process. The data can be used to drive both the heating program and the chemical conditions towards better efficiency of atomization, but the route

to overcome interferences still need further experiments. It should be mentioned that contrary on the paradigms of the electrothermal atomization based on STPF conditions, the interference processes studied are mainly related to condensed phase reactions that generate compounds that cannot be easily thermally decomposed by the low gas phase temperature. Probably the open W coil atomizer should be modified to create a hotter gas medium with enough thermal energy to promote thermal decomposition of complex compounds originated during dry and pyrolysis steps.

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