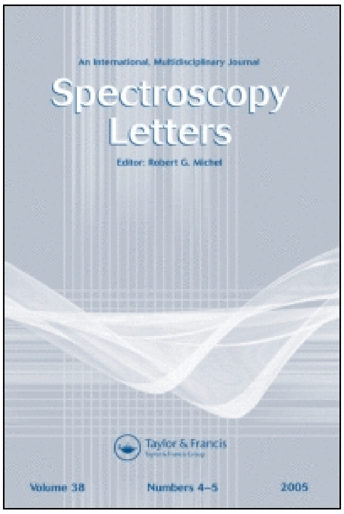

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Kinetic Approach to the Interpretation of Analyte Losses During the Preatomization Thermal Treatment in Electrothermal Atomization Atomic Absorption Spectrometry

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KINETIC APPROACH TO THE INTERPRETATION OF ANALYTE LOSSES DURING THE PREATOMIZATION THERMAL TREATMENT IN ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

KEY WORDS: Atomic Absorption Spectrometry, Electrothermal Atomization, Graphite Furnace, Model of Analyte Losses, Arrhenius Plots, Activation Energies, Chemical Modification, Tungsten Modifier.

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ABSTRACT

A method for evaluating E_a(loss), the apparent activation energy of the analyte loss process during the high-temperature thermal pretreatment stage in electrothermal atomization atomic absorption spectrometry (ETA-AAS) has been developed. The method is based on extracting information from the declining portion of thermal pretreatment curves (in this case presented as

absorbance *vs* pyrolysis time at various fixed temperatures). Five volatile analytes (As, Pb, Sb, Se, and Sn) have been studied in the presence of tungsten chemical modifier (20 μg of W in H_2O_2).

The data on E_a(loss) have been utilized together with those obtained from treating the atomization peaks E_a and with literature data on known values of bond energies and enthalpies of certain chemical reactions. Possible mechanisms of analyte losses and atomization are discussed.

INTRODUCTION

In the literature on ETA-AAS are known several approaches to the treatment of the formation and dessipation of the atom cloud [1-3]. On the basis of these approaches, are developed several models and methods, deriving information from the absorbance peaks[4-8].

The determination of volatile and moderately-volatile analytes (more then 30 elements) is often performed in the presence of chemical modifiers ("matrix modifiers" [9]), as reviewed recently [10].

A popular experimental approach to chemical modification studies in ETA-AAS consists in plotting the so called "thermal pretreatment curves" (pyrolysis curves, decomposition curves), i.e. absorbance *vs* the pretreatment temperature at fixed pyrolysis times and atomization temperature. The kinetics of analyte losses[11,12] has not attracted much attention in chemical modification studies. Recently, Rayson and Fresques[12] reported on "analyte loss kinetic studies" (ALKSs) of the effect of Pd and Mg as modifiers but no details were available in the conference abstract[12].

In an effort to extract more information from the declining portion of thermal pretreatment curves, we have proposed and evaluated a simplified kinetic approach to the elucidation of possible mechanisms of analyte stabilization and losses in the presence of modifier. The experimental part is based on our experience with the W modifier[13] which exibits efficient thermal stabilizing action on numerous volatile analytes.

THE MODEL

Let M(t) be the amount of analyte in the condensed phase on the atomizer surface. The mass balance of the analyte which is vaporized at a given time could be generally expressed as

$$-\frac{dM}{dt} = V_v(t) - V_c(t), \qquad (1)$$

where: $V_v(t)$ is the rate of evaporation from the surface,

$V_c(t)$ is the rate of re-condensation of the analyte on the surface of the electrothermal atomizer.

The purge-gas flow (e.g., 300 $ml.min^{-1}$) during the thermal pretreatment stage contributes to a substantial dilution and removal of analyte vapor, therefore under "gas-flow" conditions the rate of re-condensation should be negligible, i.e., $V_c(t) << V_v(t)$. Hence Eqn 1 could be simplified:

$$\frac{dM}{dt} = - V_v (t) \qquad (2)$$

For a process of analyte losses of an n-th order, the rate of volatilization is given by Eqn 3:

$$V_v (t) = k(t) . M^n \qquad (3)$$

The rate constant of the vaporization process, k(t), could be expressed by the Arrhenius equation:

$$k(t) = C . e^{-\frac{E_a(loss)}{RT(t)}} , \qquad (4)$$

where: C is the frequency factor,

E_a(loss) is the activation energy of the process of analyte losses, and

R is the gas constant.

Substitution of Eqn 3 and Eqn 4 into Eqn 2 yields:

$$\frac{dM}{dt} = - M^n . C .e^{-\frac{E_a(loss)}{RT(t)}} \qquad (5)$$

E_a(loss) could in principle be found from the numerical solution of Eqn 5 on the basis of experimental data for M(t) and T(t), at varying values of the fitting parameter, n.

Alternatively, Eqn 5 could be simplified, taking into account the following assumptions:

(i) A first-order reaction could be postulated, i.e., analogously to the Langmuir adsorption model, the analyte species should not interact with each other, moreover, in the presence of excess chemical modifier;

(ii) The process of analyte losses could be considered as taking place under isothermal conditions. (In fact, experimental "ramp times" are much shorter than the "hold times" of thermal pretreatment).

Thus, Eqn 3 is simplified to

$$\frac{dM}{dt} = -k . M , \qquad (6)$$

and after being integrated yields:

$$M = M_o . e^{-k.t} , \qquad (7)$$

where: M_o is the initial amount of the analyte.

Considering the proportionality between the integrated absorbance (A) and the amount of analyte (M) (Beer' law), Eqn 7 could be rewritten as

$$A = A_o \cdot e^{-k.t} , \qquad (8)$$

Taking the logarithm of Eqn 8 gives

$$\ln A = \ln A_o - k.t \qquad (9)$$

From this equation, the ln A *vs* t plot gives the rate constant (k) of the analyte loss at a given temperature. Then, from the well-known Arrhenius equation:

$$\ln k = \ln C - \frac{E_a(\text{loss})}{RT} \qquad (10)$$

The ln k *vs* 1/T plot could be exploited to derive the activation energy of the vaporization process, E_a(loss).

EXPERIMENTAL

Apparatus

The experiments were carried out using two atomic absorption spectrometers: (i) a Perkin-Elmer Model 2380 G equipped with a HGA-400 graphite furnace and deuterium background corrector, with pyrolytic-graphite coated tubes, was used in studies of analyte losses (E_a(loss) and maximum pretreatment temperature) in the presence of W chemical modifier; (ii) a Varian SpectrAA 300 equipped with a GTA 96 atomizer, deuterium background corrector, programable sample dispenser and pyro-coated graphite "portioned" tubes, IBM PS/2 computer, and Epson LX-800 printer, was used in studies of atomization peaks (E_a and appearance temperature, T_{app}) in the presence of W

TABLE 1

Temperature Program for the HGA-400

Parameter	Step					
	1	2	3	4	5	6
Temperature /^{o}C	120	300	900[a]	var[c]	2400[b]	2500
Ramp time /s	10	10	5	1	0	1
Hold time /s	5	5	0	var[c]	3	2
Read /s	-	-	-	-	*	-
Ar flow /ml.min^{-1}	300	300	300	300	0	300

TABLE 2

Temperature Program for the GTA 96

Parameter	Step				
	1	2	3	4	5
Temperature /^{o}C	120	300	1000[a]	2400[b]	2500
Ramp time /s	10	10	5	0	1
Hold time /s	5	5	1	3	2
Read /s	-	-	-	*	-
Ar flow /ml.min^{-1}	300	300	300	0	300

[a,b] Except for Pb *a*: 700^{o}C; *b*: 2000^{o}C.

[c] Varried; See Figures 1a through 5a.

modifier. Temperature programs used for the HGA-400 and GTA 96 are shown in Tables 1 and 2, respectively.

Reagents

All solutions were prepared from analytical-grade reagents in doubly-distilled water (from an all-quartz still).

0.1% m/V acidic solution of W (V) was prepared from W powder dissolved in H_2O_2 (1ml of 30% m/m H_2O_2 per 0.25 g of W).

RESULTS AND DISCUSSION

Interpretation of the Declining Portion of Thermal Pretreatment Curves

On the basis of the model of analyte losses during the thermal pretreatment stage were plotted the curves of absorbance *vs* pyrolysis time for five volatile analytes (As, Pb, Sb, Se, and Sn) in the presence of 20 μg of W (Figures 1 to 5). From the slopes of the ln A/t plot (Eqn 9 and Figures 1b to 5b) were evaluated the rate constants for the vaporization (loss) process. The ln A/t plots could be approximated by two straight lines with different slopes; hence two rate constants could be calculated for each experimental curve. The first one describes an initial, fast, and highly temperature-dependent process of analyte loss which

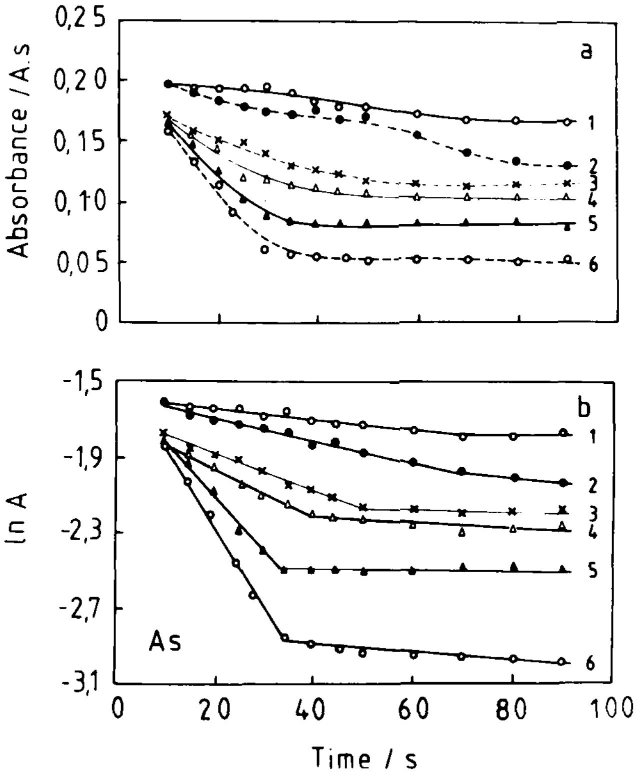

FIG. 1. Kinetics of arsenic losses: integrated absorbance *vs* preatomization treatment time. 1.2 ng As + 20 μg W. Pyrolysis temperatures in °C: 1-1450°; 2-1500°; 3-1550°; 4-1600°; 5-1650°; 6-1700°.

could be interpreted as a process of decomposition and/ or evaporation. The second one, rather slow process could be ascribed to the analyte diffusion through the bulk matrix of the modifier and/or through the graphite.

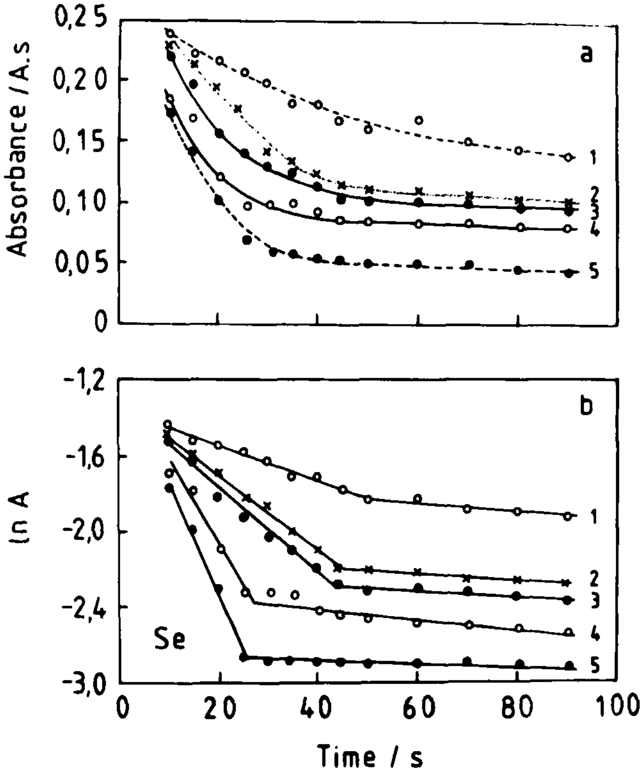

FIG. 2. Kinetics of selenium losses: integrated absorbance *vs* preatomization treatment time. 3 ng Se + 20 μg W. Pyrolysis temperatures in ^{o}C: 1-1600^{o}; 2-1650^{o}; 3-1700^{o}; 4-1750^{o}; 5-1800^{o}.

Very slight temperature dependence is observed for this second kind of losses.

From the slope of Arrhenius plots of ln k *vs* 1/T (Eqn 10 and Figures 6 and 7) could be derived the activation energies of the analyte loss process,

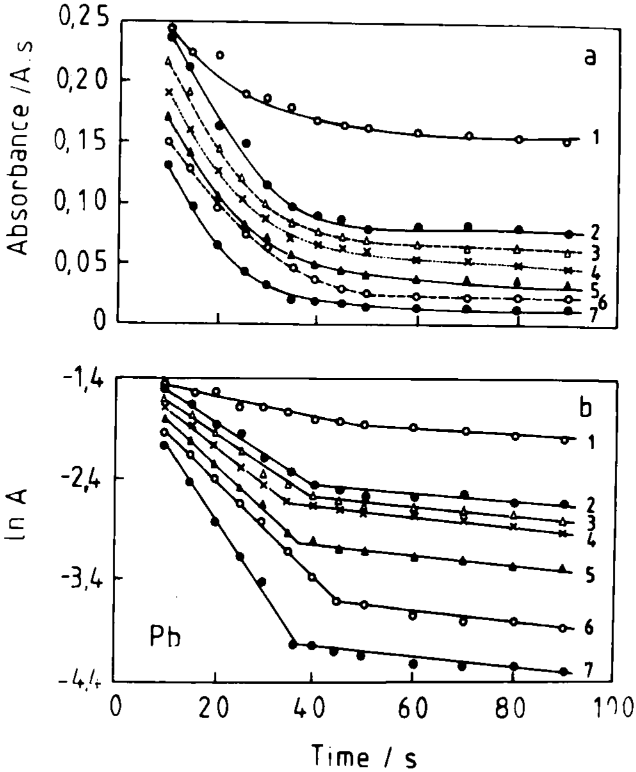

FIG. 3. Kinetics of lead losses: integrated absorbance *vs* preatomization treatment time.

4 ng Pb + 20 μg W. Pyrolysis temperatures in °C: 1-900°; 2-950°; 3-1000°; 4-1050°; 5-1100°; 6-1150°; 7-1200°.

E_a(loss). These values are tabulated together with the maximum pretreatment temperatures in Table 3 and will be discussed later.

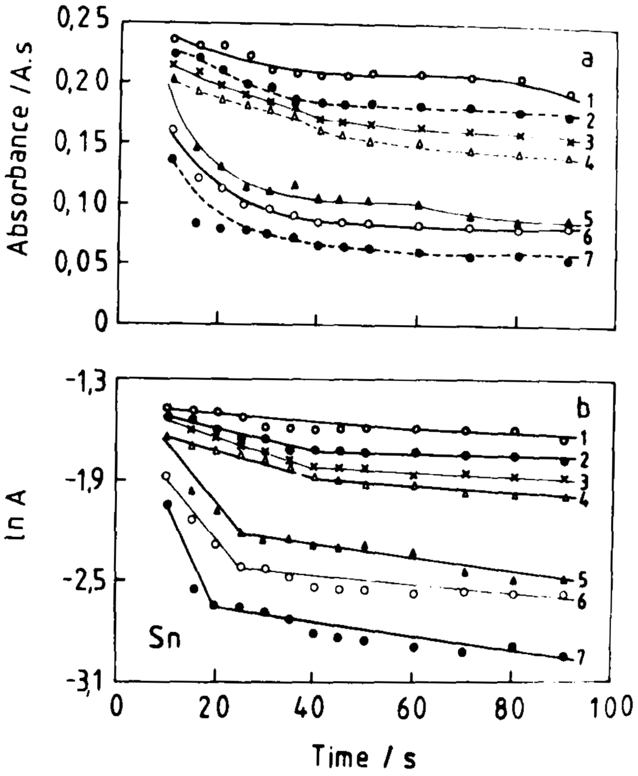

FIG. 4. Kinetics of tin losses: integrated absorbance *vs* preatomization treatment time.

4 ng Sn + 20 µg W. Pyrolysis temperatures in °C: 1-1400°; 2-1450°; 3-1500°; 4-1550°; 5-1600°; 6-1650°; 7-1700°.

Interpretation of the Leading Edge of Absorbance Peaks

Typical atomization peaks (A *vs* t) for As, Pb, Sb, Se, and Sn in the presence of W modifier are shown in Fig. 8. A specially-profiled graphite tube was used in

TABLE 3

Maximum Pretreatment Temperatures T_{max} and Activation Energies E_a(loss) in the Presence of 20 µg W. (mean of 3-5 measurements ± confidence interval)

Analyte	As	Pb	Sb	Se	Sn
T_{max} /K	1720	1170	1670	1820	1670
E_a(loss)/ $kJ.mol^{-1}$	324±42	62±6	238±20	246±12	244±6

order to insure more isothermal conditions of heating and a slight "platform effect". The activation energy for the atomization process (E_a) was evaluated according to Sturgeon et al.[5], utilizing the Arrhenius plots of ln A_T *vs* 1/T (Figures 9 and 10):

$$\ln A_T = -(E_a + \Delta H^o) / R.T + A_o , \qquad (11)$$

where: ΔH^o is the standard enthalpy change accompanying the phase transition,

E_a is the activation energy,

A_T is the absorbance at a given temperatute, T,

A_o is a constant.

The estimated values of E_a and T_{app} are compiled in Table 4, together with some relevant literature data.

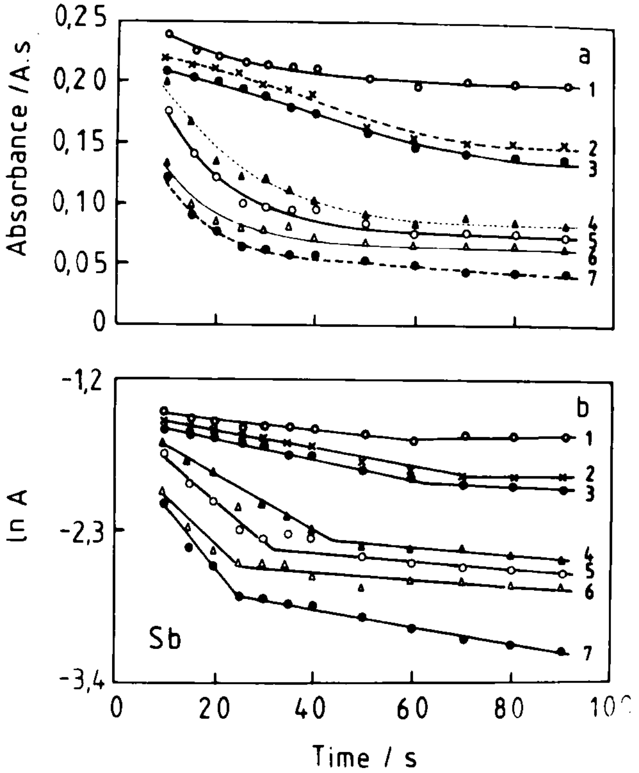

FIG. 5. Kinetics of antimony losses: integrated absorbance *vs* preatomization treatment time. 4 ng As + 20 μg W. Pyrolysis temperatures in °C: 1-1400°; 2-1450°; 3-1500°; 4-1550°; 5-1600°; 6-1650°; 7-1700°.

Possible Mechanisms and Schemes of Thermal Stabilization and Loss (Vaporization)

An attempt to combine the results for E_a(loss) and E_a with thermodynamic data for the enthalpies of

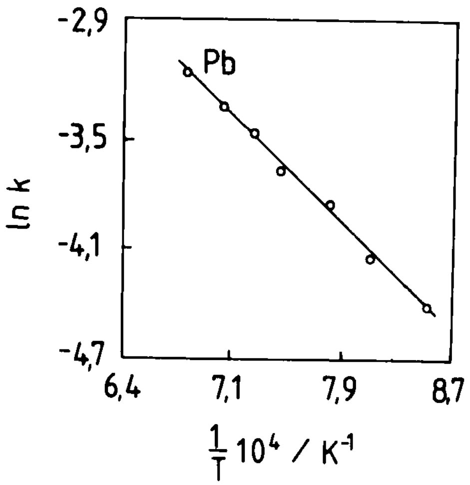

FIG. 6. ln k *vs* 1/T x 10^4 for Pb.

k: rate constant for the analyte loss reaction in the presence of modifier (20 μg W).

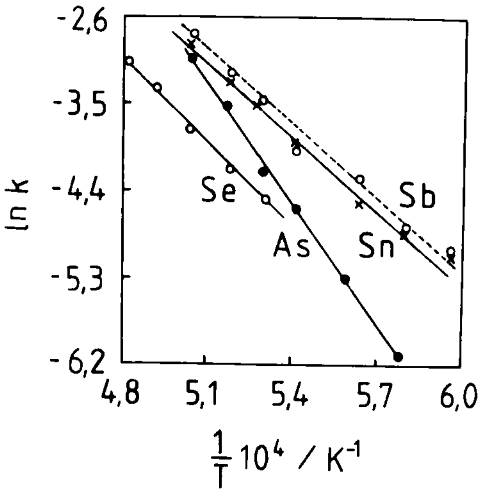

FIG. 7. ln k *vs* 1/T x 10^4 for As, Sb, Se, and Sn.

k: rate constant for the analyte loss reaction in the presence of modifier (20 μg W).

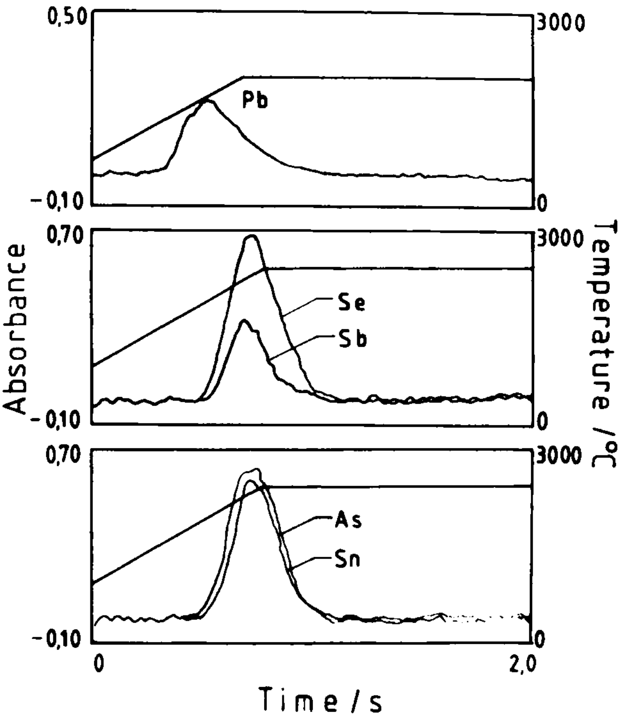

FIG. 8. Typical absorbance peaks (A *vs* time) for As (0.5 ng), Pb (0.5 ng), Se (1 ng), Sb (2 ng), and Sn (2 ng) in the presence of 20 μg W.

chemical reactions and phase transitions, bond energies, etc. - despite of its possible drawbacks and limitations (e.g.[17]) - could promote understanding of possible reaction mechanisms and schemes.

Lead

The E_a(loss) for lead (62 kJ.mol^{-1}) practically coincides with the ΔH of the reaction: $PbO.WO_{3(s)} \longrightarrow$

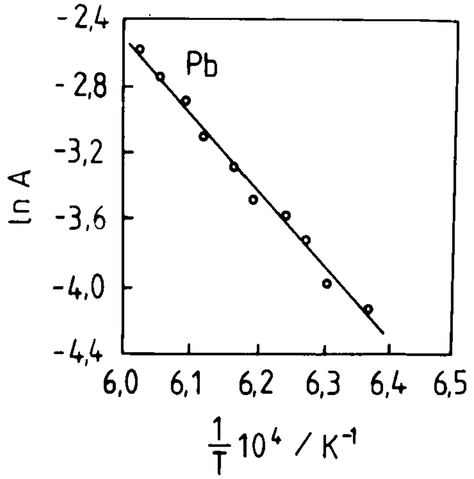

FIG. 9. Arrhenius plot for Pb (atomization process; Sturgeon et al.[5] method).

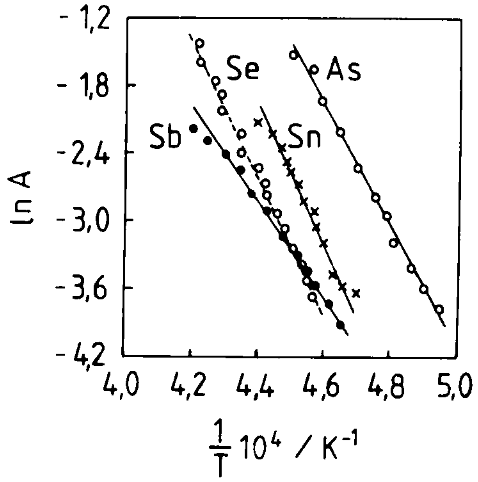

FIG. 10. Arrhenius plots for As, Sb, Se, and Sn (atomization process; Sturgeon et al.[5] method).

TABLE 4

Activation Energies of Leading Edge E_a and Appearance Temperatures T_{app} in the Presence of 20 µg W (mean of 3-5 measurements ± confidence interval)

Analyte	As	Pb	Sb	Se	Sn
T_{app} /K	2130	1590	2150	2200	2140
E_a /kJ.mol^{-1}	490±27	389±24	477±47	525±13	564±1
Bond Energy/ kJ.mol^{-1} [a]	481±8	377.8±4	372±84	429.3	548±21
Heat of transition/ kJ.mol^{-1} [b]	-	-	99.3	112.6	-

[a] Literature data for element-oxygen bond[16].

[b] Literature data for ΔH of sublimation of oxides[14,15].

$PbO_{(s)} + WO_{3(s)}$ at 1100 K (62 kJ.mol^{-1})[14]. The formation of mixed oxide of $PbO.WO_3$ could be responsible for the thermal stabilization of Pb by this modifier up to 1170 K. (Lead tungstate, $PbWO_4$, was considered by Ortner et al.[18]). The decomposition of the mixed oxide with the release of volatile PbO (m.p. 1158 K) could be supposed. The value of E_a = 389 kJ.mol^{-1} agrees with the bond energy of 377.8 kJ.mol^{-1} for the Pb-O bond[16]. Thus, the scheme of analyte loss and vaporization in the presence of W modifier could be expressed as follows:

$$\begin{tikzcd}
PbO.WO_{3(s)} \arrow[r, "62\ kJ.mol^{-1}"] & PbO_{(s)} \arrow[d] + WO_{3(s)} & \\
& PbO_{(g)} \arrow[r, "389\ kJ.mol^{-1}"] & Pb_{(g)} + O_{(g)}
\end{tikzcd}$$

Antimony, Arsenic, Selenium, and Tin

The E_a(loss) values are close for all these analytes (Table 3) and are of the same order as the ΔH of the reaction: $WO_{2(s)} + 3C \longrightarrow WC_{(s)} + 2CO$ at 1700 K (280 $kJ.mol^{-1}$)[14]. These analytes could be expected to persist on heating as oxygen-containing species within the crystal lattice of $WO_{2(s)}$. (Isomorphous substitution for WO_4^{2-} by AsO_4^{3-}, SbO_4^{3-}, SeO_3^{2-}, and SeO_4^{2-} has been supposed[13]). Thus the physico-chemical transformations of the modifier species (WO_3, WO_x, and WO_2) could be responsible for the evaporation of O-species of these analytes. The schemes shown below do not contradict to the experimental and literature data.

The matrix:

$$WO_{2(s)} + 3C \longrightarrow WC_{(s)} + 2CO_{(g)}$$

The analytes:

$$SeO_{2(s)} \xrightarrow{525\ kJ.mol^{-1}} Se_{(g)} + O_{(g)}$$

$$AsO_{(g)} \xrightarrow{490\ kJ.mol^{-1}} As_{(g)} + O_{(g)}$$

$$SnO_{(g)} \xrightarrow{564\ kJ.mol^{-1}} Sn_{(g)} + O_{(g)}$$

$$Sb_2O_{3(s)} \xrightarrow{477\ kJ.mol^{-1}} Sb_{(g)} + O_{(g)}$$

CONCLUSION

A kinetic model of analyte losses during the thermal pretreatment stage and the associated experimental method of deriving activation energies, E_a(loss), are proposed and evaluated. For the analytes (As, Pb, Sb, Se, and Sn) studied with the W/H_2O_2 chemical modifier are probable stabilization mechanisms as analyte-oxygen-tungsten species within the refractory matrix of modifier, while preatomization losses could be attributed to lower oxides of the analyte elements.

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