



Evaluation of pyrolysis curves for volatile elements in aqueous standards and carbon-containing matrices in electrothermal vaporization inductively coupled plasma mass spectrometry

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ABSTRACT

Pyrolysis curves in electrothermal atomic absorption spectrometry (ET AAS) and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) have been compared for As, Se and Pb in lobster hepatopancreas certified reference material using Pd/Mg as the modifier. The ET AAS pyrolysis curves confirm that the analytes are not lost from the graphite furnace up to a pyrolysis temperature of 800 °C. Nevertheless, a downward slope of the pyrolysis curve was observed for these elements in the biological material using ETV-ICP-MS. This could be related to a gain of sensitivity at low pyrolysis temperatures due to the matrix, which can act as carrier and/or promote changes in the plasma ionization equilibrium. Experiments with the addition of ascorbic acid to the aqueous standards confirmed that the higher intensities obtained in ETV-ICP-MS are related to the presence of organic compounds in the slurry. Pyrolysis curves for As, Se and Pb in coal and coal fly ash were also investigated using the same Pd/Mg modifier. Carbon intensities were measured in all samples using different pyrolysis temperatures. It was observed that pyrolysis curves for the three analytes in all slurry samples were similar to the corresponding graphs that show the carbon intensity for the same slurries for pyrolysis temperatures from 200 °C up to 1000 °C.

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1. Introduction

Electrothermal vaporization (ETV) is employed as a sample introduction technique for inductively coupled plasma mass spectrometry (ICP-MS), facilitating multi-elemental analysis in digested and solid samples with complex matrix. Partial removal of matrix compounds in the pyrolysis stage of the heating program of the furnace might avoid or reduce interference problems [1,2]. Measurement of pyrolysis and atomization curves is a common practice in electrothermal atomic absorption spectrometry (ET AAS) in order to optimize the temperature program for the determination of the analyte in a given sample type [3]. Chemical modifiers are routinely used in ET AAS in order to avoid analyte losses during pyrolysis and/or to promote matrix removal [3]. Similar procedures have been adopted in ETV-ICP-MS where pyrolysis and vaporization curves are established during method development [4,5] and chemical modifiers are added for the same purpose as in ET AAS [6]. However, there are some important differences between the two techniques:

1. In ETV-ICP-MS, *vaporization* processes take place in the graphite furnace, whereas *atomization* and *ionization* take place in the

plasma. In ET AAS, in contrast, *vaporization and atomization* have to proceed in the electrothermal atomizer.

2. In ET AAS the atomic absorption signal is measured in the graphite furnace whereas in ETV-ICP-MS the analyte has to be transported into the plasma by a flow of argon.
3. All vaporized analyte species that reach the plasma can be measured in ETV-ICP-MS while only analyte atoms are detected in ET AAS.
4. In ET AAS the modifiers only have to stabilize the analyte in order to facilitate removal of matrix components; the additives used in ETV-ICP-MS may also influence the analyte transport to the plasma.

The shape of pyrolysis curves obtained in ETV-ICP-MS is often different from the corresponding curves measured in ET AAS. In the latter technique pyrolysis curves usually show a plateau up to a certain maximum pyrolysis temperature; if this pyrolysis temperature is exceeded, part of the analyte will be lost. The strategy in ET AAS is to select a pyrolysis temperature that is low enough to keep the analyte in the atomizer and high enough to remove most of the matrix, so that the background correction system can handle the remaining background absorption in the atomization stage, and to avoid gas-phase interferences. Pyrolysis curves in ETV-ICP-MS, in contrast, often show a continuously decreasing sensitivity with increasing pyrolysis temperature. There is no clearly defined point that indicates where loss of

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analyte starts, and therefore it is difficult to decide which pyrolysis temperature should be used in this technique. At low pyrolysis temperatures, where the sensitivity is high, the matrix cannot be separated efficiently and may cause interferences in the determination; high pyrolysis temperatures, in contrast, allow efficient separation of matrix components, but the sensitivity is low.

Pyrolysis curves for a number of elements have been reported for ETV-ICP-MS analysis of coal [7–9], biological materials [10–15], sediments [16] and soil samples [17]. The selected pyrolysis temperatures were not always conclusive, but are usually a compromise between matrix removal and sensitivity. Chemical modifiers have also been used successfully in the analysis of coal and sediment samples, making possible calibration against aqueous standards [7–9,16], whereas analyte addition calibration or isotopic dilution methods were required for the analysis of biological samples [10–15].

According to Kantor [18] the sample is transported into the plasma in small particles formed by auto nucleation of sample matrix vapor. The clusters, which are produced by collisions in the gaseous phase, act as the initial condensation nuclei and increase in size up to the point where they condense. In general, analyte condensation on the nuclei improves the transport efficiency, resulting in a carrier effect. Ediger and Beres [6] proposed that the vaporized modifier, which is present in high concentration, condenses faster than the analyte. The vaporized analyte then preferentially condenses on the particles of the modifier and not on the cold parts of the vaporizer or transfer line, resulting in a more efficient analyte transport to the plasma and hence a higher sensitivity.

A mixture of palladium and magnesium nitrates (Pd/Mg) is a frequently used modifier in ET AAS and it has also been studied in ETV-ICP-MS [17,19,20]. Grégoire et al. [19] reported a five-fold improvement in peak area sensitivity for Ag, Sn and Pb when Pd/Mg was added. Kantor and de Loos-Vollebregt [20] observed non-linearity of the ETV-ICP-MS analytical curves for Cr, Cu, Mn, Fe and Pb in the 10–800 pg mass range when they used single-element and multi-element standards. This non-linearity could be eliminated by addition of the Pd/Mg modifier. The authors concluded that the effect of the modifier is more important at lower analyte mass when the self-nucleation process is limited.

The goal of this work was the evaluation of pyrolysis curves in ETV-ICP-MS for volatile elements in biological samples, coal and coal fly ash samples, and to compare the results with the corresponding pyrolysis curves obtained with ET AAS. Carbon signals were measured to see if there is a correlation between the vaporization behavior of carbon and the downward slope in the pyrolysis curves of ETV-ICP-MS.

2. Experimental

2.1. Instrumentation

An ELAN 5000 ICP-MS (Perkin-Elmer Sciex, Concord, Ontario, Canada) equipped with an HGA 600 MS graphite furnace and AS-60 auto sampler has been used for the ETV-ICP-MS measurements. Instrumental conditions for ICP-MS were optimized according to the

Table 2
Instrumental parameters for ICP-MS

RF power, W	1000
Carrier gas flow (Ar), L min ⁻¹	1.4
Plasma gas flow (Ar), L min ⁻¹	15
Auxiliary gas flow (Ar), L min ⁻¹	0.4
<i>Data acquisition parameters</i>	
Sampler and skimmer cones	Ni
Scanning mode	Peak hop transient
Signal measurement	Signal profile integrated
Dwell time/ms	20
Readings per replicate	70
Points per spectral peak	1
Sweeps per reading	1
ETV closure delay, s	–3
ETV read delay, s	2

manufacturer's instructions using a conventional pneumatic nebulizer; optimum signals were obtained for ¹⁰³Rh, with CeO⁺/Ce and Ba²⁺/Ba⁺ ratios below 3%. A test solution containing 10 µg L⁻¹ of Fe, Cr, Pb, Mn and Cu was measured daily in order to check the sensitivity of the ETV-ICP-MS instrument and to inspect the shape of the signals for ⁵⁶Fe, ⁵³Cr, ²⁰⁸Pb, ⁵⁵Mn and ⁶³Cu. The isotopes ⁷⁵As, ²⁰⁸Pb, and ⁸²Se were measured in aqueous standards, biological samples, coal and coal fly ash.

A Perkin-Elmer Zeeman 5100 (Perkin-Elmer, Norwalk CT, USA) atomic absorption spectrometer with Zeeman-effect background correction, equipped with an HGA 600 graphite furnace and AS-60 auto sampler was used for the ET AAS measurements. Integrated absorbance (peak area) was used for signal evaluation. The graphite furnace temperature program used with the Pd/Mg modifier is shown in Table 1.

Pyrolytically coated graphite tubes (Perkin-Elmer B009-1504) with platform have been used for ET AAS and ETV-ICP-MS measurements. Instrumental parameters and the temperature program for ETV-ICP-MS are shown in Tables 2 and 3, respectively. The same sample and modifier volumes were used for both techniques: 20 µL for aqueous standards and samples and 10 µL for the Pd/Mg modifier solution. The Pd/Mg solution was injected first and steps 1 and 2 of the temperature program in Table 3 were executed for drying before the standards and samples were injected.

A CEM MDS-2000 (Matthews, North Carolina, USA) laboratory microwave oven was used to digest the biological materials.

2.2. Reagents and samples

All reagents were of analytical grade. As, Se and Pb aqueous standards have been prepared from 1000 mg L⁻¹ stock solutions (Merck, Darmstadt, Germany) in 1% nitric acid obtained by diluting 65% m/v nitric acid (J.T. Baker, Deventer, Holland).

The Pd/Mg modifier solution was prepared by appropriate dilution from modifier stock solutions containing 10 ± 0.2 g L⁻¹ Pd and 10 ± 0.2 g L⁻¹ Mg, respectively, as the nitrates (Merck, Darmstadt, Germany), both in 15% m/v nitric acid medium. The mixed modifier was prepared

Table 1
Temperature program used in ET AAS

Step	Temperature °C	Ramp time s	Hold time s	Internal gas flow mL min ⁻¹
1	90	10	10	300
2	120	10	40	300
3	800	10	20	300
4 ^a	Ta	0	8	0
5	2600	1	4	300
6	20	1	20	300

Ta: atomization temperature 2100 °C for As and Se; 1700 °C for Pb.

^a Reading in this step.

Table 3
ETV temperature program used in ETV-ICP-MS

Step	Temperature °C	Ramp time s	Hold time s	Internal gas flow mL min ⁻¹
1	90	10	10	300
2	120	10	40	300
3	200 ^a	10	20	300
4 ^b	2400	0.1	8	200
5	2600	1	4	300
6	20	1	20	300

^a Pyrolysis temperature (unless reported differently).

^b Reading in this step.

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