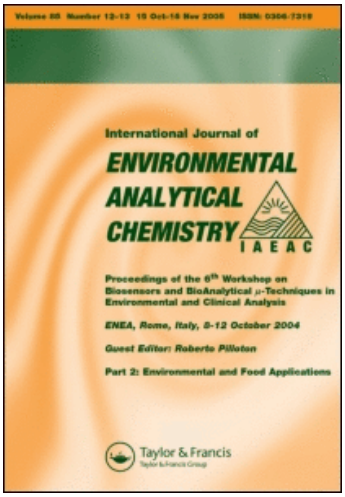

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Determination of Selenium and Arsenic in Animal Tissues with Platform Furnace Atomic Absorption Spectrometry and Deuterium Background Correction

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Determination of selenium and arsenic in animal tissues is disturbed mainly by spectral interferences, uncorrectable with the dueterium arc. These interferences are produced by the calcium and magnesium phosphates always present in these matrixes.

In animal tissue solution this disturbance may be avoided by addition of 20 μg of Ni (nitrate) for a 10 μl sample. A lower amount of nickel does not allow a correct development of analyte absorbance signals whereas an excess induces a loss of sensitivity for the two elements studied.

Measurement of peak-height proved to be most suitable, integrated absorbance being partially influenced by the matrix. The slope constants of working curves obtained with different animal matrixes are very close and direct calibration becomes possible. This was confirmed by analysis of several reference materials.

KEY WORDS: Selenium, arsenic, animal tissues, electrothermal atomic absorption spectrometry, structured background.

INTRODUCTION

Several researchers have shown that selenium and arsenic determination by atomic absorption spectrometry with electrothermal atomization (ETA-AAS) has to cope with various analytical problems and

this probably more so than for any other metal.

First, the volatility of these elements may lead to preatomization losses. Indeed, the possible formation of volatile compounds such as As_2 molecules is reported.[1] The problems may be avoided by the addition of various matrix modifiers, e.g. nickel.[2,5] Second, arsenic may give rise to gaseous molecules in the presence of sulphur of chlorine.[3] Therefore, the determination of these elements in environmental samples usually requires extraction of the analyte.

Moreover, arsenic or its compounds may interact with the graphite tube material in the presence of phosphorus. Arsenic and phosphorus, being chemically similar, may compete for graphite surface active sites needed for the formation of interlamellar compounds which favor an efficient atomization.[4]

Also, a structured background produced by phosphates in the sample may cause serious spectral interferences.[5] The deuterium arc, usually an adequate background corrector, becomes ineffective under these conditions since the background measurement does not occur at the analyte line what results is an over- or undercorrection of actual background absorbance.[6]

Other correction systems allow to avoid these shortcomings (Zeeman, Smith-Hieftje). However, since correction by deuterium arc is used in many laboratories it would be useful to define the conditions of arsenic and selenium determination in the above mentioned situations. This concerns, for example, the determination of these elements in animal tissues.

EXPERIMENTAL

Equipment

All analytical work was performed on a Varian AA-1275 spectrometer with GTA-95 graphite furnace including a programmable autosampler. Arsenic (Visimax II) and selenium (Visimax I) hollow cathode lamps were operated at 10 and 8 mA respectively. All experiments were performed at 193.7 nm for arsenic and 196.0 nm for selenium with a spectral width of 1.0 nm in each case. The atomizer parameters are summarized in Table I. The programme conditions reflect the handling of acid digested solutions of animal tissues. After dispensing of the sample on the preheated platform (130°C), sample

TABLE I

GTA parameters for arsenic and selenium platform determination. ($<30\,\mu l$ samples)

	Dispensing on platform	Dry	Char			Atomize	Cool
Tube wall temperature (°C)	130	600	1200 1400	(Se) (As)	1200 1400	2700	130
Ramp (s)	—	40	4		—	0.7	12
Hold (s)	—	—	15		2	3	—
Ar flow (l/min)	—	3	3		0	0	3

drying in the heating ramp to 600°C was followed by eye using a small mirror. Pyrolytically coated tubes (Varian part no. 63.100002.00) with solid pyrolytic graphite platforms (Varian part no. 63.100004.00) were used. Absorbance-time profiles were recorded using a Hewlett-Packard 82905A printer.

The main matrix elements of animal tissues have been determined by ICP spectrometry (Instrumentation Laboratory, IL PLASMA-200).

Materials

Nickel matrix modifier solution (1% Ni) was prepared by dissolving the nickel oxide (NiO, Specpure Johnson & Matthey) in HNO_3 (Suprapure Merck). The arsenic and selenium standards were diluted with deminearlized, distilled water and nitric acid from commercial standard solution (Titrisol Merck).

All synthetic matrix solutions were prepared from analytical-reagent grade compounds.

Mineralization procedure

0.1 g of lyophylized or 1 g of fresh tissue was placed into a high pressure teflon lined acid digestion bomb, Parr 4746. After the addition of 2 ml HNO_3 the bomb was heated in the oven at 150°C for 1 hour. After cooling, clear solutions were diluted with water to 10 ml.

RESULTS AND DISCUSSION

Matrixes studied

Errors in selenium and arsenic determination arise especially from spectral interferences. Manning[7] showed that with a deuterium arc the presence of high amounts of iron in the sample produced an over-correction on the principal selenium line at 196.0 nm. Calcium phosphates have been shown to produce the same effect.[5,8,9] A similar interference has been observed at 193.7 nm, the most sensitive line of arsenic.[5] The overcorrection manifests itself in all cases by negative signals due to the structured background produced by P_2 and PO molecules.

Animal matrix contains five essential elements: K, Na, Ca, Mg and P (Table II). When a deuterium arc device is used the mentioned interferences will certainly affect the results of arsenic and selenium determination in animal tissue since phosphorus is one of the main matrix elements. Iron was not considered in the present study, because its content in animal tissues is too low to produce the effect described by Manning.[7]

TABLE II

Main matrix elements in animal tissues

Matrix element	Range[a] ($\mu g \cdot ml^{-1}$)[b]	Synthetic test-solution ($\mu g \cdot ml^{-1}$)[c]
P	40–288	300
Ca	1–30	30
Mg	3–28	30
Na	62–260	300
K	100–380	400

[a]The ranges concern about 50 samples of sea-fishes and their organs. Also mammalian data[12,13] are included.

[b]For 1 g of the fresh sample in 10 ml.

[c]The synthetic solution represents the heaviest animal matrix (except for crustaceans not included in this study).

Interference effects

The determination of selenium and arsenic is affected in two ways by the matrix elements. The first way, concerning non-spectral interferences, is strong depression of analyte absorbance in the presence

of phosphorus (as orthophosphoric acid). No negative signals due to structured background were observed in this case. The second way is the synergic effect of other matrix elements with phosphorus on analytical response: the simultaneous presence in the sample of phosphorus, calcium, magnesium and less so for potassium gives rise to negative signals. This spectral interference is uncorrectable by the deuterium arc device (Figure 1).

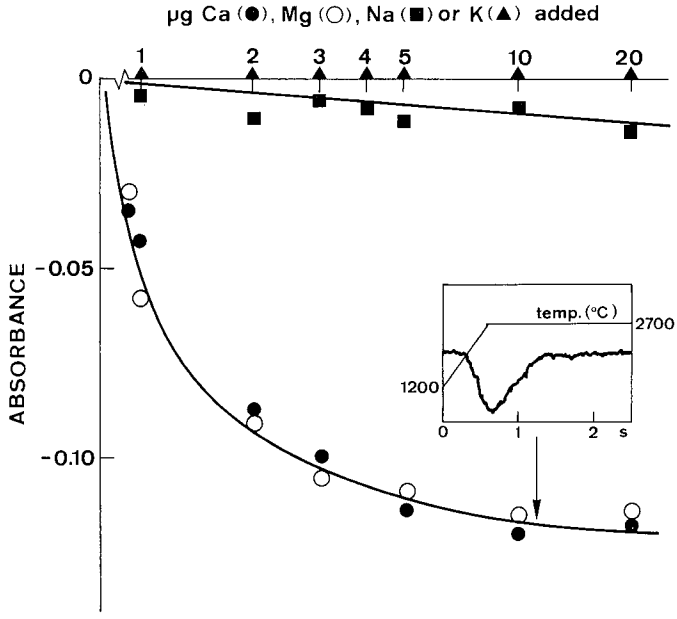

FIGURE 1 Negative signals (peak-height) generated at selenium 196.0 nm line in presence of phosphorus (4 μg) and other matrix elements.

The two effects are cumulative and make any arsenic or selenium determination impossible, because the working curves established in animal matrix solution pass below zero.

The role of nickel in arsenic and selenium determination is apparent from Figures 2 and 3. In a simple nitric acid medium it prevents only the analyte preatomization loss, the optimum nickel addition being 3 μg. Higher amounts produce a progressive suppression of the analyte absorbance signal. This stands in contrast to observations of Saeed and Thomassen using a HGA atomizer without platform.[5] In an animal matrix the nickel has a supplemen-

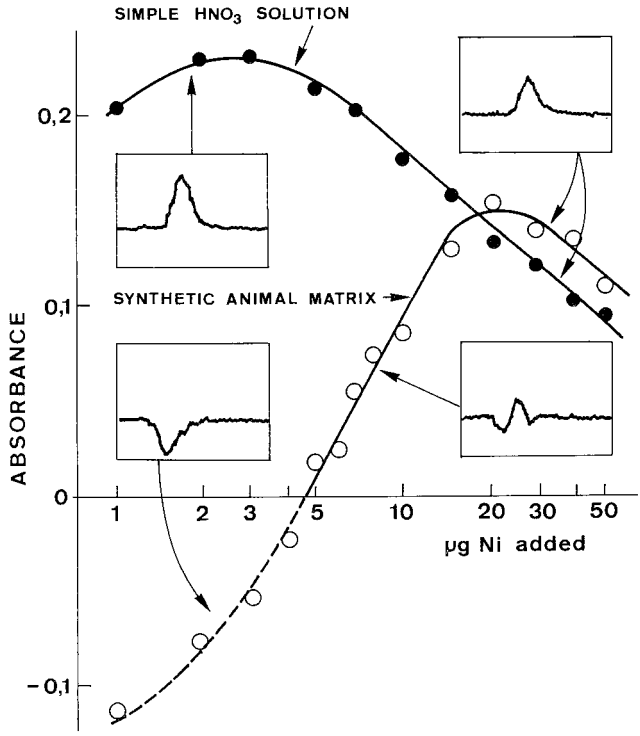

FIGURE 2 Effect of nickel (nitrate) on selenium (400 pg) absorbance signal (peak-height).

Absorbance-time profiles shown in the four insets illustrate the situation at different stages.

tary role: to prevent the formation of phosphorus molecular species causing a structured background. With increasing amounts of nickel the negative absorbance signal first changes into a positive signal and then increases to reach the optimum with 20 μg of nickel added. The signal depression observed with the higher amounts of nickel in a simple nitric acid solution is observed also in complex medium: thus only nickel controls the analyte atomization. However, it should be noted that nickel only acts as a modifier when in its nitrate form. When nickel chloride is used the analyte absorbance signals are reduced by more than 60%. This is probably due to the formation of non-dissociated gaseous molecules of arsenic and selenium with chlorine.

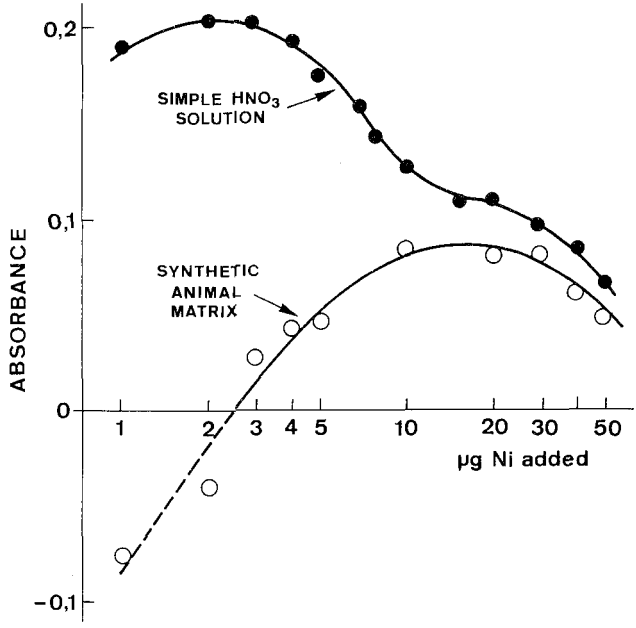

FIGURE 3 Effect of nickel (nitrate) on the arsenic (500 pg) absorbance signal (peak-height).

Signal processing

Several reports have shown the advantage of integrated absorbance measurements, mainly during atomization under isothermal conditions with the use of the L'vov platform.[10] When the atomization rate is controlled by the matrix, the peak-height will necessarily vary with the matrix, whereas the peak-area remains practically unchanged. Therefore, the peak-area should preferentially be employed. However, in some cases, especially with low absorbance signals near detection limits, measurement of peak-height is more reliable since peak-area is more affected by the possible baseline drifts.[11]

Arsenic and selenium are typical examples for the preferential choice of peak-height values if a deuterium background correction is used. We have shown that it is only nickel, when present in a certain concentration, that controls the process of atomization (Figures 2 and 3). The absorbance-time profiles represented in Figure 4 validate

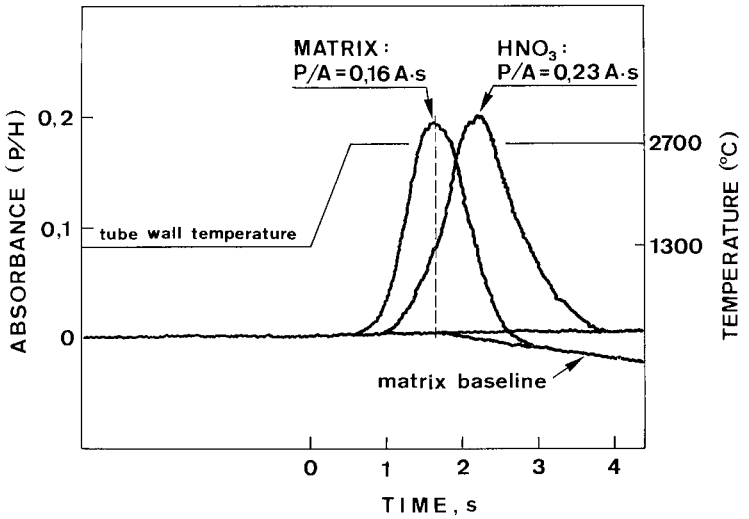

FIGURE 4 Significance of the peak-absorbance (P/H) and the integrated absorbance (P/A) of selenium in simple acid medium (profile 1) and synthetic animal matrix (profile 2).

Se: 300 pg, Ni: 20 μg.

clearly the usefulness of peak-height measurements; the peak-area being strongly altered by the baseline drift in the presence of animal matrix. Measurements of the peak-height are unaffected since the drift follows the peak-value. Use of peak-area is not valid in these cases: the working curves established in this mode pass below zero.

Performances

In the simple nitric acid medium, the addition of a small amount of nickel (3 μg) is sufficient to prevent volatilization losses of selenium and arsenic. The most favorable characteristic masses obtained are equal to 8 pg and 11 pg/0.0044 A, respectively. For an animal matrix, addition of 3 μg nickel is insufficient because the generation of phosphorus molecular species has to be inhibited as well. In this case 20 μg of nickel is the optimal amount for the two analytes and the characteristic masses of selenium and arsenic are 13 and 20 pg/0.0044 A, respectively.

The amounts of selenium and arsenic to be determined in 10 μl

animal sample range from 0.06 to 0.6 ng and 0.3 to 2.5 ng respectively. The sensitivities of our apparatus can therefore easily deal with these concentrations.

Recovery tests of the described procedure performed on lyophylized fish samples with known additions of selenium and arsenic before mineralization indicated that recoveries of both elements vary from 95 to 103%. Table III shows very good agreement of our results with the recommended values of five reference materials and indicates the reliability both of the mineralization procedure and the analytical approach used. The results were obtained independently by the standard addition method and by direct calibration method. The full analytical procedure, including the mineralization and the furnace determinations, results in relative standard deviations from 5 to 14% ($n=3$) depending on the magnitude of the measured concentrations. For the 20 species of seafishes checked, the variation of the slope of working curves does not exceed the analytical error. For the direct calibration, the standard solutions were prepared with the synthetic matrix (Table II) because the slope of the single element standard curve was slightly steeper in the case of arsenic and lower in the case of selenium. With the synthetic matrix, these small differences disappear and the working curves are parallel with those obtained with real fish samples.

TABLE III

Selenium and arsenic content (in $\mu g \cdot g^{-1}$ dry matter) in standard reference materials

	Selenium		Arsenic	
	Recommended value	Found value[c]	Recommended value	Found value[c]
Albacore tuna[a]	3.6±0.4	3.4±0.4	3.3±0.4	3.2±0.3[d]
Bovine liver[a]	1.1±0.1	1.1±0.1	—	[d]
Fish MAA-2[b]	1.7±0.3	1.4±0.2	2.6±0.1	2.6±0.2
Scallops[c]	0.62±0.30	0.72±0.10	7.1±2.1	7.8±0.4
Plaice[c]	2.35±0.55	2.0±0.2	4.6±1.6	3.6±0.2

[a]National Bureau of Standards (NBS), SRM 50 and 1577.

[b]International Atomic Energy Agency (IAEA).

[c]Preliminary results from 7th International Intercalibration Exercise 1983, International Council for the Exploration of the Sea (ICES).

[d]Below the determination limit (0.5 μg As/g^{-1} dry matter, 10 μl sample).

[e]Three complete determinations including the mineralization procedure.

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