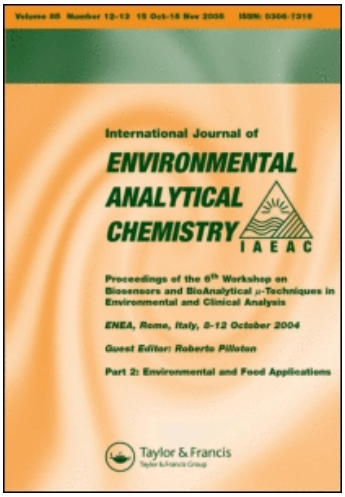

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Micro Dry Ashing for Trace Selenium Determination in Organic Matrices†

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A specific sample treatment method was established for determination of ng levels of Selenium in microquantities of organic compounds. Our task was determination of Selenium traces, in a new pharmaceutical product, as a result of a laboratory scale synthesis, in an amount of several tens of mg. GFAAS was chosen as an analysis method, due to its sensitivity and rapidity. Among the wet and dry methods for organic material digestion tried, the low temperature dry ashing using ashing aid, was the only one which gave satisfactory recoveries of Selenium. Micro dry ashing was performed, using an Ethanol solution of Magnesium Nitrate on samples spiked with Selenium Nitrate in the range of concentration of 1–6 ng mg^{-1} at a temperature of 450°C for two hours. The presence of Magnesium Nitrate and the heating suppress the atomization with approximately 15–25%. Recoveries of Selenium varies as a function of the organic matrix: for polyaromate compounds as Chrysene and Fluoranthene they lie between 90–103% and for oxygenated compounds as Dimethoxybenzoic acid or Phthalates 23–50% respectively.

Another aspect of chemical interference by organic matrices and the way how to overcome it, has been clarified.

KEY WORDS: Micro dry ashing, selenium trace, organic matrices.

INTRODUCTION

Selenium is now recognised as an essential trace element which is present almost everywhere. The physiological significance of selenium

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depends very much on its concentration: it is an essential nutrient at trace levels[1] and toxic when ingested in excess[2].

Apart from the overall beneficial biological role of selenium, it is established that this element plays a protective role in poisoning with heavy metals.

Therefore marketing of commercial pharmaceutical preparations or as a single selenium compound or by adding it to vitamine E or C, is widely used.

The small amounts of selenium present in biological material and in pharmaceutical preparations and its known volatility complicates its determination.

Among the methods used for determination of traces of selenium in biological matrices flameless A.A.S. found a broad application[3,4]. In using this method two main problems have to be solved: one, to eliminate as much as possible, the chemical interferences due to the organic matrix and the second, to avoid the volatilization of selenium, during the sample preparation.

For elimination of the matrix effect, destruction of the organic compounds is necessary. Digestion with HNO_3—H_2SO_4, H_2O_2—H_2SO_4[5], H_3PO_4—HNO_3—H_2O_2[6], HNO_3—$HClO_4$—H_2SO_4[7], HNO_3—$HClO_4$[8] or oxygen flask combustion followed by cation exchange extraction of the interfering cations[9], is widely used elsewhere. The results for combined acid digestion shows poor recovery of 70–125%[10].

Dry ashing is another approach for organic matrix destruction. Determination of volatile trace metals as Cd, Hg[11] were performed by dry ashing using magnesium nitrate dissolved in ethanol as ashing aid. The use of a saturated aqueous magnesium nitrate solution is described[6] for low temperature dry ashing of samples on macro scale (0,5–1,0g sample). A suspension of magnesium oxide and magnesium nitrate was used for decomposition of 1–10g samples[12].

To overcome the volatility of selenium at the charring temperature, addition of salts as nickel[4], molybdenum[13], copper[8] is used elsewhere. It is likely that formation of a metal-selenide compound which is stable up to 1400°C prevents the selenium volatilisation. We were faced with a special problem which made our task much more difficult: to measure ng levels of selenium in a pharmaceutical product as a result of a laboratory scale batch

synthesis—the quantity of the sample to be analysed was just the order of several tens of mg. Having the opportunity of performing trace analysis on a microamount of sample, we tried to work out a procedure which can be used on different groups of chemical substances.

At the first stage, we tried to establish the optimal conditions to overcome the chemical matrix interference effect, using Vitamine D_2 as matrix (a compound similar to the sample to be analysed 1α-hydroxy-vitamine D_3). The matrix was spiked with known amounts of selenium to cover the concentration range of 10–90 ppm referring to 10 mg matrix. Different digestion methods were tried, to find the one which has the best selenium recovery. The low temperature dry ashing using an ethanol solution of magnesium nitrate as ashing aid, was found to be the only one which gave good results.

Recovery studies of selenium in presence of other matrices such as poly-nuclear hydrocarbons, oxygenated organic compounds was also performed. All the selenium determinations were performed by using electrothermal A.A.S., as it is described in the experimental section.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 305A atomic absorption spectrophotometer, equipped with a deuterium background corrector and a HGA-500 graphite furnace with pyrocoated graphite tubes connected to an HGA-500 programmer, a selenium hollow cathode lamp and a Yokogawa chart drive recorder, were used for all atomic absorbtion measurements.

A hot plate (Zivan) and a muffle furnace (Bifa-Eurotherm) were used for drying and ashing.

The instrument setting parameters can be seen summarised in table I.

Reagents

All solutions were made using reagent grade quality chemicals and deionized water.

TABLE I
Instrument settings for A.A.S.

Instrumental parameters	Settings
Wavelength	196,0 nm
Spectral bandwith	0,7 nm
Hollow cathode lamp power	16 mA
Background corrector	on
Damping	1
Signal mode	peak height
Sample volume	20 μL
Recorder range	5 mV
Recorder speed	2 cm/h

Standard Selenium (IV) solution 1000 ppm was prepared from metallic selenium (J. T. Baker 4–3395) dissolved in a stochiometric amount of nitric acid, dried up expelling NO_2 and diluted with deionized water. Working solutions of 1μg/mL were obtained by successive dilution in 1M HNO_3. They were prepared fresh daily.

Nickel solution 1% prepared from nickel nitrate A.R.
Magnesium nitrate solution 10% w/v in 95% ethanol (Frutarom)
Fluoranthene Fluka 46530 (purum)
Chrysene Fluka 27220 (purum)
Bis-(3, 3, 5-trimethylcyclohexyl) phthalate Fluka 80060 (puriss) α-3, 5 resorcyclic acid Sygma Chem. Corp.
3, 4-Dimethoxybenzoic acid Aldrich D 13180-6
Calciferol
Argon-commercial grade (used as purge gas, for GFAAS)

Procedure

To 10 mg of matrix weighted in a 4, 5 mL screw cap septum vials amounts of 10–90 mg Se and quantities of 20 μL $Mg(NO_3)_2$ 10% solution, 50 μL $Ni(NO_3)_2$ 1% solution and 50 μL HNO_3 1OM were added, using a Finpipette delivery system. Mixtures were dried on a thermoregulated hot plate at a temperature of 120°C and ashed in a muffle furnace at 450°C for 2 hours. If the digestion was not complete and the sample remained dark colored or even black, 500 μL of HNO_3 1M and a drop of 30% H_2O_2 is added to the

mixture, then warmed again until dryness. After cooling, another 500 μL of HNO_3 1M is added the septum vial is closed and the sample is ready for selenium determination. For each set of determinations a dublicate is run. Blanks were prepared for each matrix, containing all the reagents added- as described above.

Samples to be analysed, are undergoing the same treatment procedure and analysis, as is described above.

Parameters used for selenium determination by flameless electrothermal atomic absorbtion spectrophotometrie are described in table II.

TABLE II

Parameters for selenium determination by G.F.A.A.S.

Step	Temp. °C	Ramp time s.	Hold time s.	Argon flow mL/min
Drying	130	5	25	300
Charring	1000	5	25	300
Atomization	2550	1	5	0

RESULTS AND DISCUSSION

The atomization process in the graphite tube atomizer is a rather slow process, which lasts several tenths of a second. Furthermore the gas movements in the tube destroy the gradually growing cloud of atoms. For this reason, we never measure the whole cloud of atoms but only the maximum density occuring during the atomization process. This explains why the reproducibility of measurements depends on the ability to reproduce the whole atomization process— it is obvious that the matrix has a major influence in this regard.

Therefore a calibration graph of selenium in the range of 10–50 ng selenium in 500 μL HNO_3 1M and 10% $Ni(NO_3)_2$ was performed, using direct measurements of absorbtion as is described in the experimental section. The same measurements were performed after adding 4 g/L magnesium nitrate to each 500 μL sample and heating at the ashing temperature. The peak heights obtained are plotted in Fig. 1. It can be seen that the presence of magnesium nitrate and the heating supress the atomization by approximatively 15–25%.

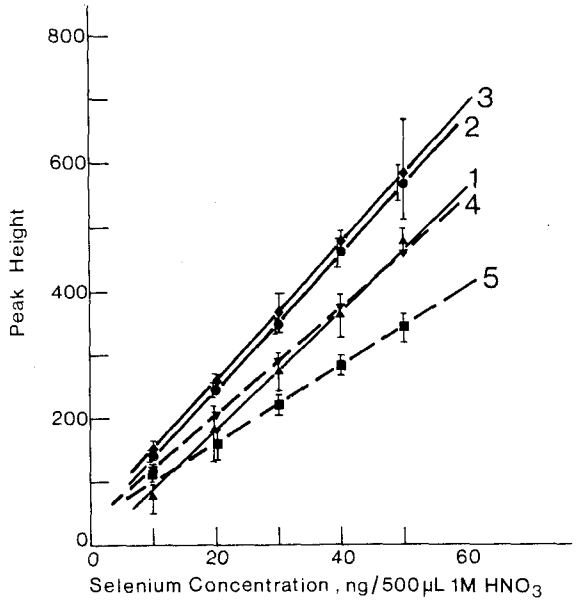

FIGURE 1 Selenium Calibration Graphs.

1, 2, 3: Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ without ashing.
4, 5: Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + ashing.
Each result is a mean of 10 measurements of 2 samples.

Absorbtion measurements of selenium from different organic matrices spiked with 10–90 ng selenium nitrate, using the same pretreatment procedure, are shown in Fig. 2. It is obvious that the presence of the organic matrix has influence on the peak height obtained. On the other hand, attempts of selenium determination without our pretreatment (low temperature dry ashing) or using any other wet digestion method[3–8] leads to almost complete loss of selenium. At the same time, the low slope of the curves of selenium absorbtion in the presence of resorcylic acid and bis-(3, 3, 5-trimethylcyclohexyl) phthalate gives indication of different kind of interferences. It has to be mentioned however, that we did not have the possibility to make a comparison in behaviour of selenium using an organic selenium compound versus our spiked ones. We think there is reason to try such an experiment.

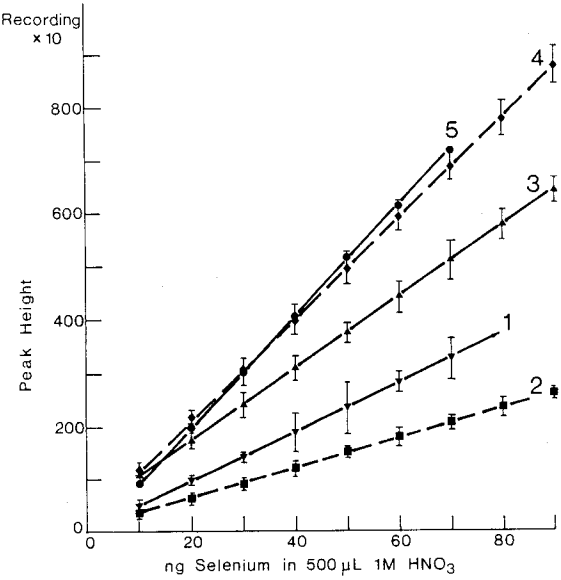

FIGURE 2 Influence of Organic Matrix on Selenium Determination After Treatment.

1. Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + − resorcylic acid with ashing.
2. Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + bis-(3, 3, 5 trimethylcyclohexyl) phtalate with ashing.
3. Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + fluoranthene with ashing.
4. Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + chrysene with ashing.
5. Selenium in HNO_3 1 M matrix of 10% $Ni(NO_3)_2$ + 4 g/L $Mg(NO_3)_2$ + 3, 4 dimethoxybenzoic acid with ashing.

Each result is a mean of 12 measurements of 2 samples.

Each result is a mean of 5 measurements of 1 sample.

The signals obtained for selenium absorbtion by atomization in GFAAS are tabulated in table III. For inputs of selenium in the range of 10–50 ng in 500 L HNO_3 1M, we obtained results which varied in relation to the absolute value of input, up to 75%. However selenium outputs in matrices of chrysene and fluoranthene show good recoveries. The results presented indicate that one must

TABLE III

Selenium recovery using low temperature dry ashing pretreatment.

	10		20		30		40		50	
Selenium input ng Se/500μL 1 M HNO_3 Matrix Composition	Se found ng	SD	Se found ng	SD	Se found ng	SD	Se found ng	SD	Se found ng	SD
+10% $Ni(NO_3)_2$	10.00[a]	0.39	18.33[a]	2.45	28.53[a]	0.29	39.10[a]	1.65	49.53[a]	2.45
+10% $Ni(NO_3)_2$ + 4 g/L^{-1} $Mg(NO_3)_2$ (matrix A)	9.00[b]	1.41	19.50[b]	4.24	23.55[b]	8.41	33.40[b]	8.20	46.55[b]	8.41
A + Bis(3, 3, 5) trimethyl-cyclohexyl) phthalate	2.35[d]	0.18	4.75[d]	1.06	6.50[d]	0.35	7.95[d]	2.01	13.96[d]	0.65
A + 3, 4, Dimethoxybenzoic acid	8.00[b]	1.41	10.24[b]	0.07	16.05[b]	3.18	18.65[b]	0.49	21.40[b]	1.27
A + Chrysene	10.41	2.95	17.79	2.18	30.37	1.59	41.21	1.36	51.37	7.71
A + Fluoranthene	10.52[c]	1.80	15.96[c]	5.36	27.05[c]	1.48	32.20[c]	1.84	40.75[c]	11.66
A + Resorcylic acid	4.91[c]	0.70	6.74[c]	0.59	15.91[c]	3.77	22.17[c]	4.59	21.70[c]	6.08

[a]Mean of 12 measurements from 3 samples.
[b]Mean of 6 measurements from 2 samples.
[c]Mean of 12 measurements from 2 samples.
[d]Mean of 10 measurements from 2 samples.

be very cautious in interpreting the outcome of trace analytical measurements, but they demonstrate that the flameless A.A.S., in combination with proper methods for sample pretreatment, can indeed yield useful and reliable results.

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