TRACE ANALYSIS OF ULTRAPURE ARSENIC AND SELENIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Jirina KORECKOVA[a] and Josef MUSIL[b]

[a] *Institute of Analytical Chemistry, Academy of Sciences, 142 00 Prague 4, The Czech Republic*
[b] *Ministry of Environment, 100 10 Prague 10, The Czech Republic*

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A method for the determination of trace and ultratrace impurities like Co, Cu, Cr, Fe and Ni in pure arsenic and selenium by graphite furnace atomic absorption spectrometry has been developed. The sample preparation and the measurement was performed in a clean laboratory with HEPA filtrated air providing a class 100 working environment. For correction on the blank the expected values estimated from a set of blanks were used respecting the distribution (normal or lognormal) tested by Shapiro–Wilk test. Detection limits for the whole procedure estimated according to the IUPAC 3 σ definition are somewhat higher for the Se matrix, but still allow the analysis of As and Se samples of 5N5 purity as required.

Arsenic and selenium are used to prepare chalcogenide glasses, which have been developed for infrared window optical applications [1 – 3]. The introduction of other elements like Ge and Te into those type of glasses results in a shifting of infrared absorption edge toward longer wavelengths. However, chalcogenide glasses might be also interesting as core materials for optical fibres for transmission mainly in the 6 – 12 μm range, especially when short lengths and flexibility are required. Coupling the fibre with a CO_2 or CO laser opens up large possibilities in the laser surgery including the cancer treatment[4]. Also As_2Se_3 and its alloys are commonly used as photoconductor materials in electrographic applications[3].

An important factor influencing low optical losses of fibres and some chemical and physico-chemical properties of glass is the purity of basic substances which has to be tested. Chalcogenide glasses must be prepared from substances of at least 99.999% (5 – 6 N) purity[2], i.e. the sum of relevant impurities should be lower then 1 ppm. At such low contents, a non-Gaussian distribution of results is more likely[5] than normal distribution. An analytical method enabling the determination of main metallic impurities of interest like Fe, Co, Cr, Cu and Ni has been proposed. It serves for a quality control of distillation procedure used for purification of arsenic and selenium in the

laboratory. An adequate approach to evaluation test and suitable estimation of correction on blanks are also presented in this work.

EXPERIMENTAL

Instrumentation

All analyses were performed on a Perkin–Elmer 4000 atomic absorption spectrometer equipped with a graphite furnace HGA 500 and an autosampler AS 40. Data System 3700 was used to visualize the analytical signals for studies of possible interferences. Hollow cathode lamps and pyrolytic graphite coated tubes were used for all analytes in this study. All instrumental parameters are given in Table I. Owing to a similar behaviour of the analytes an universal temperature programme of the graphite furnace was used. There was not any difference in the sensitivity for individual analytes using the programme according to Table I in comparison with the sensitivity under experimental conditions recommended by the manufacturer.

Reagents

Ultrapure water produced by Nanopure system (Barnstead) was used throughout. High-purity subboiling distilled HNO_3, HCl and HBr were prepared in the trace laboratory using a quartz still (Acidest, Heraeus, Germany). The quality of the distilled acids was comparable with Suprapure acids produced by Merck. Measurable contents of Fe has been found in distilled as well as in the Merck Suprapure HCl. Contribution of the other impurities are negligible in comparison with the other sources of contamination.

The inert gas used to purge the HGA 500 graphite furnace was 99.999% argon.

TABLE I
Furnace programme and instrumental parameters. Pyro-coated tube, HGA 500, 20 µl aliquots by AS 40

Parameter	Step			
	1	2	3	4
Temperature, °C	160	900	2 400	2 700
Time – ramp, s	20	20	0	1
Time – hold, s	10	20	3	3
Argon flow, ml min^{-1}	300	300	0	300
AA Spectrometer Perkin–Elmer 4000				
	Co	Cu	Cr	Fe	Ni
Wavelength, nm	240.7	324.7	357.9	248.3	232.0
Slit, nm	0.2	0.7	0.7	0.2	0.2
BG correction (lamp)	D_2	W	W	D_2	D_2
Signal mode	peak height mode				

Stock standard solutions of analytes, 1 000 μg ml^{-1}, (Merck, Germany) were used for the preparation of mixed calibration solutions.

Plastic vessels and quartz dishes for sample dissolution were cleaned in an ultrasonic cleaner. Solutions were pipetted by adjustable-volume Finnpipettes with disposable tips.

The sample preparation and the measurement was performed in a clean laboratory overpressured with HEPA-filtrated air providing a class 100 working environment.

Procedure for Sample Preparation

An arsenic sample (0.1 g) was dissolved in a quartz dish with 1 ml of a mixture of concentrated HNO_3 and HCl (3 : 2) by gently heating on the hot plate at 100 °C. The solution was evaporated to dryness and 1 ml of HBr was added to remove arsenic as a volatile bromide. The excess of bromine was removed by 0.5 ml of concentrated HNO_3 and the solution was evaporated to dryness. The residue was digested by 3 vol.% HNO_3 and the final volume adjusted to 10 ml.

A selenium sample (0.1 g) was dissolved in a quartz dish under a quartz lid with 1 ml of concentrated HNO_3 on the hot plate at 120 °C. After dissolution the lid was removed and the solution was evaporated to dryness. Solution was removed by gently evaporating to dryness with 1 ml of HBr, which step has been repeated to volatile selenium quantitatively. The residue was digested by 3 vol.% HNO_3 and the final volume adjusted to 10 ml.

Simultaneously with samples a set of blanks were prepared by the same procedure described above for arsenic and selenium, respectively. At least 7 blanks have been prepared with every set of samples analyzed.

RESULTS AND DISCUSSION

Interferences and Calibration

To avoid serious interferences from sample matrices the decomposition procedure has been chosen enabling to remove arsenic and selenium by evaporation. A simple calibration using the acidified pure solutions is another advantage of the sample preparation.

Signals of individual analytes from samples and calibration solutions were compared due to investigate any possible interferences. No differences in peak shapes as well as in the position on time/temperature scale has been found. Compared absorption signals of checked analytes were identical which proves that no interferences occur and that the suggested calibration is suitable for analyses of samples under study. Evaluation from peak heights was prefered to peak areas since better absorbance reading occurred for some analytes (Mn, Co).

Evaluation of Results

The measured analytical signal (absorbance) is transformed into the concentration according to an analytical function established by the calibration procedure. In a trace analysis the rough result c' obtained in an individual determination should be treated as

a sum of the actual analyte content in the sample c and a contribution of contaminations c_0:

$$c' = c + c_0 \quad . \tag{1}$$

The term c_0 presents a total contamination which occurs during the sample preparation and measurement as a sum of contributions from reagents (acids and water), dishes, pipettes, cups as well as from air aerosol particles etc.

Performing a statistical set of n parallel determinations on the same sample the best estimation of the c' is an expected value $E(c')$ in the n term set $\{c'\}$, i.e.

$$E(c') = E(c + c_{0,\mathrm{i}}) \quad . \tag{2}$$

The sample content c and the actual contamination $c_{0,i}$ in a parallel determination are independent values, thus

$$E(c + c_{0,\mathrm{i}}) = E(c) + E(c_{0,\mathrm{i}}) \quad . \tag{3}$$

Assuming a homogeneous sample, the c is a constant in the set of parallel determinations (i.e. the actual analyte content) and the last term $E(c_{0,\mathrm{i}})$, representing a mean contamination, is not measurable directly. Thus, an estimation based on a set of blanks should be performed. This indispensable step in the trace analysis is based on a presumption of the statistical regularity of the whole analytical procedure. The Eqs (*2*), (*3*) can be used if the statistical set of results exists, i.e. if more than let's say 5 (better if more than 10) determinations have been parallely performed.

Distribution of Results

The estimation of expected values from the experimental data sets should be performed with respect to the distribution of results. In a common laboratory, an asymmetrical distribution of trace results frequently occurs, especially in the blank result sets, what is reasonable with regard to the air aerosol particle contamination mechanism and the lognormal distribution of the particle diameter[6].

Being positively skewed (to the right) in most cases, the experimental distribution is often satisfactory approximated by the lognormal distribution. Since the large particles are eliminated by filtration the normal distribution is usually an appropriate model in case of ultratrace laboratory. If, however, the particles containing the analyte are generated inside the laboratory room the lognormal model is valid again. Decision between the normal and lognormal model was based on the Shapiro–Wilk test, which superiority

over the other distribution tests consists particularly in a higher test power for the small data sets[7,8].

In some cases, both tested models are unsuitable probably because of few dates in the set, resulting a "polymodal" histogram. No histogram showed a negative skewness. Thus, as far as the probability of the lognormal distribution according to the Shapiro–Wilk test was greater then the probability of the normal distribution and simultaneously was not negligible, the estimation of correction has been calculated according to the formula valid for the expected value $E(x)$ of lognormal distribution $LN(\mu, \sigma)$:

$$E(x) = \exp [\mu + \sigma^2/2] \ , \qquad (4)$$

where μ is arithmetic mean, σ is standard deviation.

In all other cases (inclusive of the case when both distribution probabilities are small) the arithmetic mean was used corresponding to the normal distribution as well as to a general (non-specified) distribution with a lower efficiency of estimation. Statistics and results of the Shapiro–Wilk test for data sets obtained by measurement are given in Table II. The distribution of analytes in blanks depends on the up-to-date state of the purity of the clean room atmosphere which in turn depends on the type of the analytical work taken place there.

For samples the same reasoning is valid with respect to the contribution of contaminations. However, the distribution of results is often controlled by random analytical errors which predominate especially for the higher contents of analyte. Thus, according to the general experience in the trace analysis the lognormal model is indispensable for the estimation of correction from results of blanks. Using arithmetic mean, an overcorrection often occurs and the corrected results are negative. Our results show that the lognormal model was indispensable in the evaluation of correction for Fe, in case of Cr, Cu, and Ni it was required less often. A markedly right skewned distribution of sample results was rarely found thus differences between arithmetic mean and the $E(x)$ value based on the lognormal model are very small.

Detection Limit

The lower limit of applicability of an analytical method is given by the requirement of discerning the signal of sample containing analyte from the signal of the blank. In sense of the IUPAC definition[9,10], the set for establishing the detection limit of an analyte comprehends all results of 10 complete determinations, performed with a real sample in which the analyte concentration was at the level of the final detection limit. Since it was not always possible to find an appropriate sample for an analyte (i.e. contents were too high), the set of blanks has been used for evaluation[11].

The described procedure involves the contribution of contaminations to the variability of results. In order to obtain a correct detection limits the contribution of calibration uncertainty (a contribution of the calibration procedure to the total uncertainty of results) should be also respected. The omission of it results in a too optimistic (erro-

TABLE II
Statistics[a] and Shapiro–Wilk test results

Description	General statistics, ppb			$E(x)$, ppb	S.–W. test probability	
	$\bar{x}$	s	$\tilde{x}$		norm.	lognorm.
As blanks						
Co	7	3	8	7	0.470	0.163
Cr	5	6	3	8	0.018	0.252
Cu	57	34	42	59	0.135	0.549
Fe	883	189	820	906[b]	0.103	0.478[b]
Ni	73	46	69	76	0.282	0.781
As samples						
Co	11	4	12	11	0.177	0.115
Cr	1 425	1 120	1 417	1 426	0.249	0.244
Cu	254	49	262	255	0.803	0.650
Fe	4 818	311	4 911	4 819	0.128	0.095
Ni	1 069	85	1 053	1 070	0.639	0.711
Se blanks						
Co	3	1	4	3	0.001	0.001
Cr	14	5	13	14	0.336	0.687
Cu	37	28	32	129	0.427	0.001
Fe	791	272	650	836[b]	0.080	0.502[b]
Ni	7	7	5	13	0.063	0.172
Se samples						
Co	5	5	7	[c]	0.335	0.068
Cr	71	24	69	72	0.024	0.466
Cu	92	14	93	92	0.939	0.902
Fe	1 519	436	1 385	1 608[b]	0.061	0.322[b]
Ni	90	22	92	91	0.964	0.559

[a] $n = 10$, $\bar{x}$ arithmetic mean, s standard deviation, $\tilde{x}$ median, $E(x)$ estimated values from lognormal model; [b] evaluated as shifted lognormal distribution; [c] lognormal model quite unsuitable.

neously low) detection limit. Thus, the recalibration step should be regularly implemented into the measurement layout during the detection limit estimation procedure in the same intervals as in the routine analysis of samples. Estimated detection limits of analytes are given in Table III.

The sum of the detection limits of the analytes of interest is 0.82 and 1.05 ppm for As samples and Se samples, respectively. Thus, the 5N5 purity can be reliably certified[5] using the proposed method, considering only the metallic impurities which influence optical losses of fibres.

TABLE III
Detection limits of analytes in ppm

Analysis of	Co	Cr	Cu	Fe	Ni
Pure As					
Estimated from sample	0.012	[a]	0.12	[a]	[a]
Estimated from blanks	0.009	0.018	0.08	0.57	0.14
Pure Se					
Estimated from sample	0.015	0.070	[a]	[a]	0.066
Estimated from blanks	0.003	0.015	0.084	0.82	0.021

[a] Not estimated.

TABLE IV
Recovery test (spikes of 10 μg l^{-1})

Matrix	x^a/s, μg l^{-1}				
	Co	Cr	Cu	Fe	Ni
As blank	10.52	10.76	10.14	10.50	10.52
	0.67	0.67	0.59	2.63	0.50
As sample	10.16	10.82	10.29	13.13	10.30
	0.87	2.26	0.94	5.34	1.35
Se blank	9.90	9.31	10.50	10.48	10.67
	0.11	0.36	1.23	2.05	0.49
Se sample	10.18	9.68	9.54	10.12	9.31
	0.82	0.75	0.99	0.35	0.51

[a] $n = 5$.

Accuracy of Results

There were neither certified reference samples of pure arsenic or selenium nor an appropriate comparison method available. Thus the recovery test was used to verify accuracy of results. In order to distinguish between acids and matrix interferences an appropriate amount of the standard solution of analytes has been added to the blanks and to the sample prior to the decomposition step. No *t*-test significant difference was found between the given and found amounts of analytes, see Table IV.

An example of results obtained from purified samples by the proposed method is given in Table V.

TABLE V
An example of impurities content found in purified As and Se samples

Analyte	x^a/s, ppm				
	Co	Cr	Cu	Fe	Ni
As sample	<0.012	1.42	0.20	3.90	1.00
	–	0.11	0.05	0.31	0.08
Se sample	<0.015	<0.07	<0.08	<0.82	0.08
	–	–	–	–	0.02

[a] $n = 5$.

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