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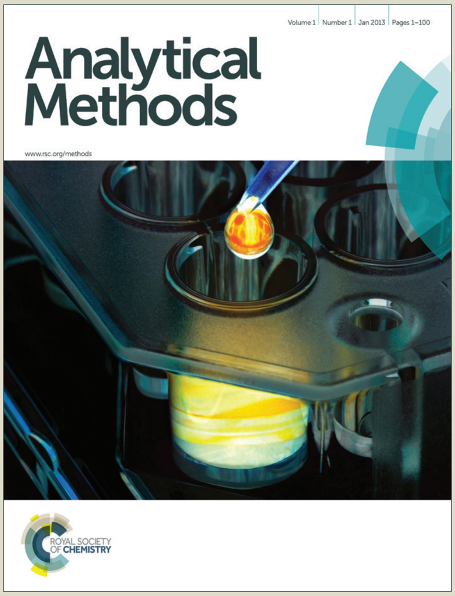

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Determination of As in particulate matter using Se as an internal standard by multi-element electrothermal atomic absorption spectrometry.

I.N. Pasias[1], K.G. Koukoulakis[1], G. Bartzis[2], A.I. Mologousi[1], E.B. Bakeas[1*]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens
Panepistimiopolis Zografou, 15771 Athens, Greece

[2]Department of Statistics and Insurance Science, University of Piraeus, Karaoli &
Dimitriou Str, 18534 Piraeus, Greece

[*]Corresponding author:

Evangelos B. Bakeas, Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens Panepistimiopolis Zografou, 15771 Athens, Greece.

Tel: +30 210 7274154,

Fax: +30 210 7274750

E-mail address: bakeas@chem.uoa.gr *(E.B Bakeas)*

ABSTRACT

In this study Se has been evaluated as a potential internal standard for the determination of As in particulate matter using Multi-element Electrothermal Atomic Absorption Spectrometry. The use of Se reduced matrix interferences improving the recoveries and method precision, especially at concentration levels near to the limit of quantification. Moreover, better linearity was achieved. The detection limits with and without the use of Se were 1.88 μg L^{-1} or 1.13 ng m^{-3} and 2.88 μg L^{-1} or 1.73 ng m^{-3}, respectively. The calculated recoveries were ranged from 98.9% to 110% rather than 41.5% to 114% without Se. In both cases, with and without the use of Se, the method uncertainty was calculated based on Monte Carlo analysis. The results showed that the uncertainty was reduced at the lower concentration levels, near to the limit of quantification, while was increased at the higher ones. The method was applied to determine As in PM10 samples from an industrial area near Athens. The mean annual concentration of As was found to be 5.69 ng m^{-3}, lower than the air quality limit set by the European Council.

Keywords: Arsenic; Multi-element Electrothermal Atomic Absorption Spectrometry; Internal Standardization; Atmospheric particulate matter; Monte Carlo Uncertainty.

Introduction

The occurrence of As in the atmospheric air is due to either anthropogenic or biogenic sources. It has been estimated that almost one third of the atmospheric air flux of As is of natural origin, mainly caused by volcanic action, from which only a small amount comes from vegetation or wind-driven dust. Mining, smelting of non ferrous metals, combustion of fossil fuels and the use of pesticides, are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water, and soil[1]. In the atmospheric air, arsenic mainly exists absorbed on particulate matter as a mixture of arsenite (AsIII) and arsenate (AsV)[2] in contents ranged from 1.5 to 10 ng m^{-3} [3-7]. The International Agency for Research on Cancer (IARC) has listed arsenic and its compounds as Group 1 human carcinogens[8].

The European Commission (EC) has decided the monitoring of As, among others in atmospheric particulates as well due to their detrimental effect on the human health. Monitoring of As was adopted by Member States and, according to European Commission legislation, it must be determined in atmospheric particulate matter[9-10]. Recently, the Joint Research Centre (JRC) of the EC had proposed the electrothermal atomic absorption spectrometry (ETAAS) as a method for the determination of As in PM_{10} during the first EC exercise for the measurement of heavy metals in PM_{10}[11]. However, this technique suffers from several drawbacks caused by high background levels, the interaction of arsenic and selenium with the heated carbon inside the atomizer and the volatilization losses of arsenic during the pyrolysis step. Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are also proposed for the determination of As providing many benefits such as, high sensitivity and low detection limits. However, they are expensive techniques for single-element determination and suffer from spectroscopic and non – spectroscopic interferences. On the contrary, the multi-element electrothermal atomic absorption spectrometry combines the benefits of both ETAAS and ICP techniques since it is a low cost technique and allows the use of the internal standard as a quantification method in order to compensate the random and systematic errors[12].

In the current work, the performance of an internal standard for the determination of As was tested by comparing parameters such as correlation coefficient, intercept and slope of matrix-matched standards calibration in order to investigate if the analytes and the chosen internal standard present comparable behavior. Se was used as an internal standard, since it provides similar physicochemical properties with As and similar atomization and pyrolysis temperatures. To the best of our knowledge, Se is used for the first time as an internal standard for the determination of As to atmospheric particulate matter by Simultaneous ETAAS. Zr-Ir was used as permanent modifier and the method has been applied to atmospheric particulate matter (PM_{10}) (86 samples) from an industrial area outside Athens, Greece, influenced by agricultural activities as well. The uncertainty of the method was also calculated based on the Monte Carlo Method (MCM). It is the first time, that MCM is used to compare the uncertainty of the results with and without the use of the internal standard method as quantification technique.

Experimental

Instrumentation

A Perkin Elmer SIMAA 6000 spectrometer equipped with a transversely heated graphite atomizer (THGA) graphite furnace with longitudinal Zeeman-effect background correction and an AS-72 autosampler was used. For the determination of As using Se as an internal standard, the spectrometer was performed in 2-element simultaneous mode, using electrodeless discharge lamps (EDL 2 System) As (193.7

nm and slit 0.7 nm) and Se (196.0 nm and slit 0.7 nm). The THGA graphite furnace was pretreated with 200 μg of Zr and 20 μg of Ir according to the procedure demonstrated by E.C.Lima et al. (1998)[13] and modified by Kalantzis et al (2012)[14]. A 20-μL volume of the standard or sample solutions was dispensed in the graphite tubes with the AS-72 autosampler. The digestion procedure of particulate matter was performed in a microwave oven, Perkin Elmer/Anton Paar Multiwave.

Reagents

All reagents used in this study were of analytical-reagent grade. All glass and polypropylene ware were kept in 10% v/v HNO_3 for at least one night and then rinsed with 1% v/v HNO_3 and subsequently with distilled water before use. The acids used for the digestion procedure were of SuprapuR grade (Merck, Darmstadt, Germany). The arsenic and selenium standards were prepared by diluting 1000 mg L^{-1} stock solution of each analyte (CertiPUR, Merck) with ultra pure water (MilliQ water, Millipore, Bedford, MA, USA) and acidified to a final HNO_3 concentration of 1% v/v. As permanent modifiers stock solutions 1000 mg L^{-1} iridium (High Purity Standards, Charleston, SC) and zirconium (High-Purity Standards) were used, all in 2% hydrochloric acid.

Determination of As in atmospheric particulates

Atmospheric particulate matter samples were collected according to EN 12341. This European Standard describes a method for the determination of PM_{10} or $PM_{2.5}$ mass concentrations in ambient air by sampling the particulate matter on filters and weighing them by means of a balance. A medium volume sampler (MVS) was used. The flow rate was set at 2.3 m^3 h^{-1} and the sampling time at 24 h. Glass fiber filters (47 mm) were used for the PM_{10} sampling. Procedural filter blanks were always run and contamination was never observed. Field filter blanks were always run and contamination was never observed. Measurement results are expressed in ng m^{-3}. Samples were collected for one year in order to compare the results with the air quality limits set by the relative EC Directives[9-10].

The filters after sampling were put in filter cassettes tightly closed in order to avoid contamination. The samples were transferred back to the Lab using a mobile refrigerator. The filter was subjected to a 5 mL HNO_3:HCl 1:3 extraction mixture in the microwave oven using the following programme (first stage at 100 W, Hold Time = 3 min, Ramp time = 1 min, second stage at 400 W, Hold Time = 5 min, Ramp time = 5 min, third stage at 800 W, Hold Time = 5 min). The resulting solution was filtered and diluted to 30.0 mL with ultrapure water (MilliQ water, Millipore). A 20 µL volume of the sample was injected into the graphite tube. The temperature programme followed is given in Table 1. Quantification was performed with the internal standard matrix-matched calibration curves.

[Insert Table 1]

Optimization of the analytical procedure

The method is based on the addition of a constant amount of Se to all blanks, standard solutions and matrix samples prior to the analysis and exploits the possibility if the analyte and the internal standard are similarly affected by the experimental and analytical procedure, by comparing the estimated accuracy and the precision of the method.

The choice of the internal standard was based on the following criteria: (a) similar physicochemical properties between the analyte and the internal standard and (b) similar pyrolysis and atomization temperatures. Another crucial parameter that must be taken into account is the appropriate concentration of the internal standard. Hence, the appropriate concentration of Se was found as follow: initially the calibration curves of both As and Se were constructed by at least 5 standard solutions in the linear range of both As and Se; afterwards the correct concentration of the internal standard is that one which provides integrated absorbance of the Se (Int. Abs. Se) equal to the integrated absorbance of the As (Int. Abs. As) in the middle of the linear range for As.

The pyrolysis and atomization curves (Figure 1) were constructed by spiking 20 μL of a digested sample fortified with 50 μg L^{-1} As and 100 Se μg L^{-1}. The optimal pyrolysis and atomization temperatures were achieved from the pyrolysis-atomization curves constructed from the ratio of the Int. Abs. As to the Int. Abs. Se.

[Insert Figure 1]

Method validation and Uncertainty Estimation

Calibration curves of the Int. Abs. As to the Int. Abs. Se in matrix solution were constructed and typical linear correlations of $r^2 \geq 0.99$ were obtained. The limit of detection, LOD (μg L^{-1}), was calculated from the equation LOD $=3.3\times S_{BL}/b$, where S_{BL} was the standard deviation of ten blank determinations. The LOQ (μg L^{-1}) was calculated from the equation LOQ $=3.3\times S_{BL}/b$ and was also verified experimentally. The inter and intra-day precision and the accuracy of the method were estimated with and without the use of Se as an internal standard. The particulate matter samples were fortified at four different concentration levels (three times each) of As. The optimal concentration of Se, the (%) recoveries and the (%) relative standard deviation (%RSD) values under repeatability (intra-day precision) and reproducibility (inter-day precision) conditions were calculated.

The estimation of the uncertainty with and without the use of Se as an internal standard was also undertaken at four different concentration levels using MCM and the Mathematica 9, Wolfram statistical software. The MCM performs random sampling from probability distributions of the input quantities; hence, there is no need to compute first-order derivatives. In addition, it gives the probability density function of the output quantity as the end result, from which the coverage interval can be determined[15-16]. More specifically, the MCM performs a characterization of the quantities measured based on the random sampling of the probability distribution functions. This numerical simulation tends to require around 10^6 trials (model evaluations)[17]. The MCM was preferred in the current study since it can overcome some of the major limitations of the traditional "Guide to the Expression of Uncertainty in Measurement" uncertainty framework (GUM)[18-20], such as that there is no need of linear dependence between the measurand and the factors of the measurement process, which means that the uncertainty can be also estimated for concentration levels close to the limit of detection and for concentrations over the linear range.

Results and discussion

Optimization of the instrumental parameters

Using the procedure described above the 100 μg L^{-1} was chosen as the optimal concentration for internal standard. Furthermore, by the pyrolysis-atomization curves it was found that the most appropriate temperatures were those where the ratio of the integrated absorbances of the analyte to the internal standard is stable and the ratio of the integrated background absorbance of As (Int. BG Abs. for As) is close to 1 (this means that both the analyte and the internal standard have the same matrix interference). Concerning the ratio Int.Abs.As/Int.Abs.Se, this was stable from 900^{o} C to 1100^{o} C and from 1900^{o} C to 2000^{o} C for the pyrolysis and atomization stages respectively. On the other hand, the ratio of the Int.BG Abs for As to the Int. BG Abs for Se was closer to 1 for the temperatures of 1000 and 1900 ^{o} C, and this is why these temperatures were chosen as optimal (Figure 1). The graphite furnace programme is summarised in Table 1.

Method Validation

Calibration curve in the 5 – 100 µg L^{-1} As concentration range was constructed by spiking 20 µL of five different concentration levels of As in a digested sample fortified with 100 µg L^{-1} Se (Table 2). This procedure was done automatically by the autosampler AS-72. Curve was established using the ratio Int.Abs.As/Int.Abs.Se, and typical linear correlation of r^2=0.999 was obtained. In order to evaluate the performance of the internal standard, calibration curve was also established by plotting the Int.Abs.As *versus* the As concentrations and correlation coefficient was equal to r^2=0.997. By comparing the obtained correlation coefficients it can be seen that the internal standard corrected the random errors provided by the construction of the calibration curve automatically using the autosampler.

The instrumental LOD (µg L^{-1}) was calculated from the equation LOD_{instr} (µg L^{-1}) =$3.3\times S_{BL}/b$, where S_{BL} was the standard deviation of ten blank determinations and b the slope of the internal standard calibration curve. The method LOD (ng m^{-3}) was calculated by multiplying the instrumental LOD with the final dilution volume of the samples (30 mL) and dividing by the final sampling volume (flow rate x sampling time). For the As determination the LODs without and with the use of Se as an internal standard were 2.88 µg L^{-1} or 1.73 ng m^{-3} and 1.88 µg L^{-1} or 1.13 ng m^{-3}, respectively. The results showed that the use of Se as an internal standard improved significantly the calculated LODs. The respective method limits of quantification without and with the use of Se as an internal standard were 8.64 µg L^{-1} or 5.19 ng m^{-3} and 5.64 µg L^{-1} or 3.39 ng m^{-3}, respectively (Table 2).

The (%) relative standard deviations (RSD) under repeatability (intra-day precision) conditions for four different matrix solutions containing 10-30-50-100 μg L^{-1} As and 100 μg L^{-1} Se measured three times each were 4.4%, 5.2%, 2.0% and 1.3% without the use of Se as an internal standard and 4.2%, 4.8%, 1.5% and 0.83% with the use of Se as an internal standard (Table 2). Furthermore, the (%) RSD values under reproducibility (inter-day precision) conditions at the same concentration levels measured in the next day by another analyst were 42%, 12%, 13% and 10% without the use of Se as an internal standard and 16%, 15%, 11% and 7.7% with the use of Se as an internal standard (Table 2). All values achieved with the use of Se as an internal standard were lower than the critical values, as described by the Horwitz equation[21], whereas this did not happen when As was determined without the use of Se (for the 10 μg L^{-1} concentration level). The results showed that the use of Se corrected significantly the random errors appeared during the digestion and analysis procedure, especially for concentration levels near the limit of quantification (10 μg L^{-1}). For the accuracy estimation the (%) recoveries were also calculated by spiking 10-30-50-100 μg L^{-1} As and 100 μg L^{-1} Se measured three times each and following the whole pre-treatment procedure. The (%) calculated recoveries were 41.5%, 99.8%, 110% and 114% without the use of Se as an internal standard and 98.9%, 106%, 104% and 110% with the use of Se as an internal standard. The results showed that the use of Se improved the accuracy of the method, especially at low concentration level, near the limit of quantification, where the (%) recovery was doubled (Table 2). The certified reference material NIST 1648a, urban particulate matter (National Institute of Standards and Technology) was also analyzed and the determined value (117.0±5.1 mg/kg, n=6) was in good agreement with the certified one (115.5 ± 3.9). However, this certified reference material cannot be used when Se is used as an internal standard, since it contains Se.

[Insert Table 2]

Monte Carlo uncertainty estimation

The MCM was used to estimate the uncertainty of the arsenic concentration in airborne particulate matter with and without the addition of selenium as an internal standard for three different fortification levels, the first close to the limit of quantification, the second at the middle of the linear range, and the third at the upper limit of the linear range. The estimation of the uncertainty was based on several independent parameters as (a) the flow rate uncertainty; (b) the stock standard solutions; (c) the volume uncertainty; (d) the calibration uncertainty; (e) the bias uncertainty, as calculated by the standard additions recoveries; and (f) the random errors uncertainty, as calculated by the (%) RSD values under reproducibility conditions. The mathematical model equations and the term definitions are presented in the Supplementary File. The results for a sample of $N=10^6$, and a 95% confidence level are presented in Table 2. According to Table 2, it is obvious that for concentration levels close to the limit of quantification (5.66 ng m^{-3}) the use of Se as an internal standard achieved to minimize the measurement uncertainty (from ±0.67 ng m^{-3} to ±0.11 ng m^{-3}), whereas for concentration levels from the middle to the upper limit of the linear range the use internal standardization as a quantification technique increased the measurement uncertainty. This is a very interesting observation concerning the use of the internal standard in chemical analysis and can be used in many analytical methods. In the current study, since all samples concentrations were close to the limit of quantification, the use of Se as an internal standard improved the accurate estimation of the As content in the airborne particulate matter with the minimum uncertainty.

Determination of As in atmospheric particulate matter

The method was applied for the determination of As in 86 PM_{10} samples from an industrial area, consisted mainly of steel industries and petrol refineries, near the urban area of Athens for one year. The meteorological conditions reported from the sampling area and the mean elemental contents (n=86) found for all sampling campaigns are presented in Table 3. Samples were collected and treated according to the procedure described in section 2.3. All samples were spiked with 100 μg L^{-1} Se, in order to use the internal standard matrix-matched quantification technique. The annual mean content of As was equal to 5.69 ng m^{-3} (ranged from <1.13 to 6.50 ng m^{-3}). This value is lower than the "target value" set by the European Council[9]. The "target value" is the mean concentration, over a given period, in the ambient air fixed with the aim of avoiding, preventing or reducing harmful effects on human health and the environment as a whole. The "target value", set by the European legislation, in the PM_{10} fraction averaged over a calendar year is equal to 6 ng m^{-3} for As[9]. More specifically, the distribution of all samples number (n=86) in different range of contents for As are presented in Figure 2 for all different sampling campaigns. As Figure 2 shows, the majority of the samples, had content lower than the limit of detection (n=53). Eighteen samples were ranged from <1.13 to 2.00 ng m^{-3}, and only 15 samples had content higher than 2 ng m^{-3}. In October 2012 the mean content of As was below the limit of detection, probably due to the shorter sampling period (only a month) compared to the other sampling periods (two months). These results are in good agreement with the results presented in a previous study from Pasias et al. (2013) who determined the content of As and other metals from an industrial area with the same characteristics near the city of Athens[7] and it has to be mentioned that the content of As in airborne particulate matter is significantly lower than the respective found in other industrial areas[3-6] by a factor of three to five times.

[Insert Table 3]

[Insert Figure 2]

Conclusions

In the current study a method for the determination of As using Se as an internal standard in airborne particulate matter was developed and validated. The use of Se as an internal standard improved the accuracy and the precision of the method, especially at low concentration levels, where the recovery was doubled, and the estimated measurement uncertainty was minimized. The method was applied successfully for the determination of As in 86 PM_{10} samples from an industrial area near Athens where the annual mean concentration was 5.69 ng m^{-3}, lower than the “target value” set by the European Council.

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Table 1: Temperature program for the determination of As using Se as an internal standard, in atmospheric particulate matter using THGA treated with Zr-Ir permanent modifier.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min^{-1})	Read
Drying 1	110	5	10	250	
Drying 2	130	15	15	250	
Pyrolysis	900	10	20	250	
Atomization	2100	0	5	0	ON
Cleaning	2450	1	3	250	

Table 2: Method's performance criteria for the determination of As using Se as an internal standard in particulate matter.

Performance Criteria	**Se was not used as an internal standard**	**Se was used as an internal standard**
Equation of matrix-matched calibration curves	$y = (23 \pm 0.70) \times 10^{-4}$ x - 0.017 (±0.0021)	$y = (34 \pm 0.67) \times 10^{-3}$ x -0.0057 (±0.019)
LOD (ng m^{-3})	1.73	1.13
LOQ (ng m^{-3})	5.19	3.39
Range of (%)RSD values under repeatability conditions (intra-day precision)	1.3-4.4	0.83-4.2
Range of (%)RSD values under reproducibility conditions (inter-day precision)	10-42	7.7-16
Mean (%)Recovery±Standard deviation (n=12)	92±34	104.7±4.6
Standard Uncertainty (ng m^{-3}) calculated for 5.66-17.0-28.3-56.6 ng m^{-3} content levels	0.62-0.58-0.94-3.29	0.11-0.67-1.28-6.50

Table 3: Meteorological data and mean arsenic content for the different sampling campaigns.

Sampling campaign (2012)	Temperature (^{o} C)	Amount of rain (mm)	Wind speed (km/h)	Wind direction	As content ±SD (ng m^{-3})	Range (ng/m^3)
01/01-28/02	9.5	38.2	4.6	N	1.17±0.88, (n=14)	<1.13-2.83, (n=14)
01/03-31/05	13.1	37.0	4.7	N	1.3±1.1, (n=15)	<1.13-3.53, (n=15)
01/06-31/07	28.1	0.0	6.0	N	1.4±1.3, (n=12)	<1.13-6.5, (n=12)
01/08-30/09	30.2	9.0	4.2	NNE	1.14±0.92, (n=15)	<1.13-3.72, (n=15)
01/10-31/10	22.4	11.6	3.3	N	<1.13, (n=15)	<1.13-2.06, (n=15)
01/11-31/12	11.7	101	3.2	N	1.25±0.91, (n=15)	<1.13-3.59, (n=15)

Figure Captions

Figure 1: The pyrolysis and atomization curves, constructed either from the Integrated Absorbance (Int. Abs.) or either from the ratio of the Integrated Absorbance (Int. Abs. As to the Int. Abs. Se) of a digested sample fortified with 50 μg L^{-1} As and 100 Se μg L^{-1}.

Figure 2: Distribution of the samples number in different range of As content for all sampling campaigns (n=86).

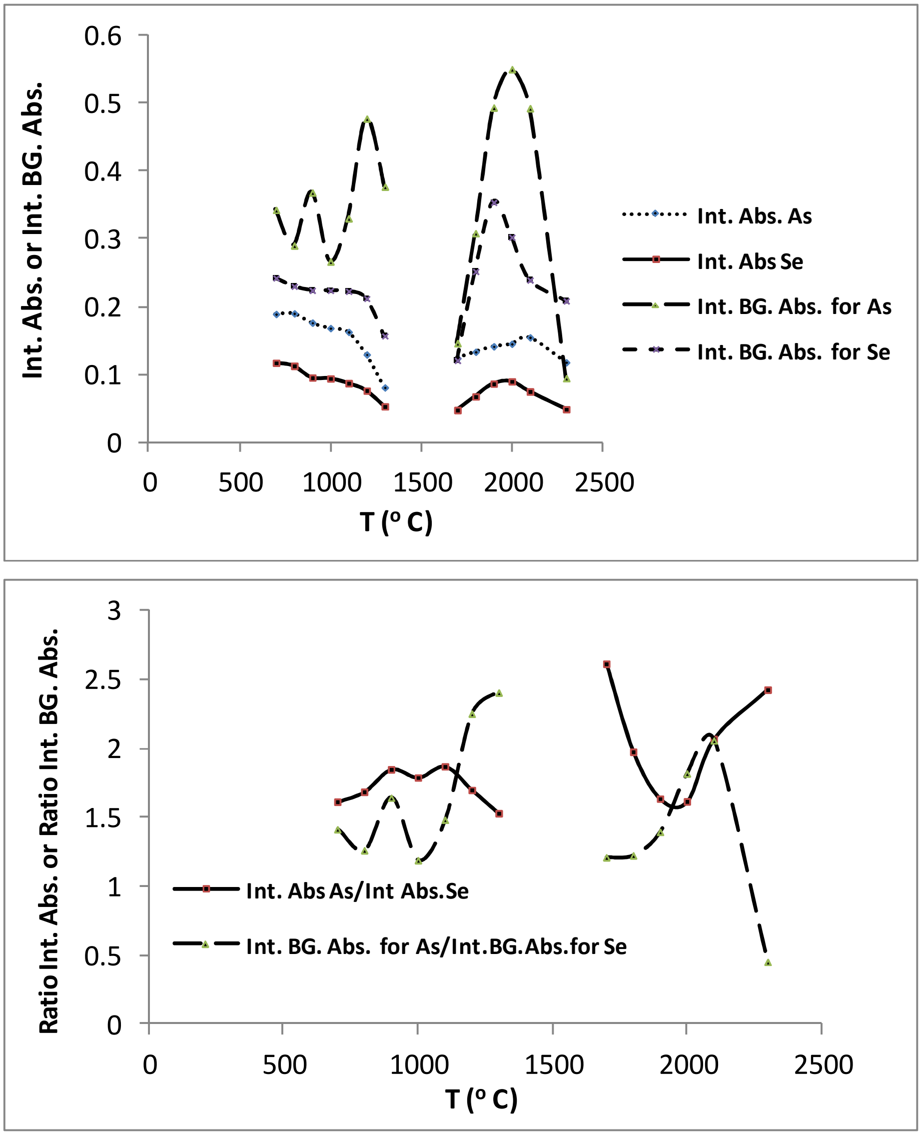
Int. Abs. or Int. BG. Abs.
0
0.1
0.2
0.3
0.4
0.5
0.6
0
500
1000
1500
2000
2500
T (º C)
Int. Abs. As
Int. Abs Se
Int. BG. Abs. for As
Int. BG. Abs. for Se
Ratio Int. Abs. or Ratio Int. BG. Abs.
0
0.5
1
1.5
2
2.5
3
0
500
1000
1500
2000
2500
T (º C)
Int. Abs As/Int Abs.Se
Int. BG. Abs. for As/Int.BG.Abs.for Se

Figure 1

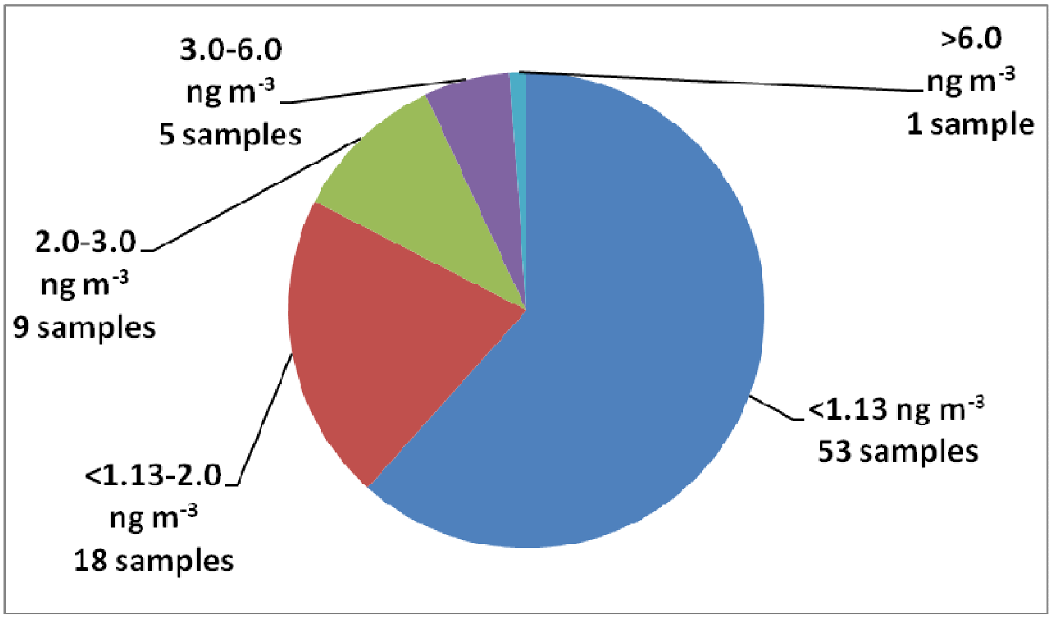
3.0-6.0
ng m^{-3}
5 samples
>6.0
ng m^{-3}
1 sample
2.0-3.0
ng m^{-3}
9 samples
<1.13 ng m^{-3}
53 samples
<1.13-2.0
ng m^{-3}
18 samples

Figure 2