Talanta 134 (2015) 224–231

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Direct solid sample analysis with graphite furnace atomic absorption spectrometry—A fast and reliable screening procedure for the determination of inorganic arsenic in fish and seafood

Ariane V. Zmozinski [a,*], Toni Llorente-Mirandes [b], Isabel C.F. Damin [c], José F. López-Sánchez [b], Maria Goreti R. Vale [a,d], Bernhard Welz [d,e], Márcia M. Silva [a,d]

[a] Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil
[b] Department of Analytical Chemistry, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain
[c] Faculdade Dom Bosco de Porto Alegre, Porto Alegre, RS, Brazil
[d] Instituto Nacional de Ciência e Tecnologia do CNPq, INCT de Energia e Ambiente, Universidade Federal da Bahia, 40170-115 Salvador, BA, Brazil
[e] Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

ARTICLE INFO

Article history:
Received 25 September 2014
Received in revised form
4 November 2014
Accepted 5 November 2014
Available online 15 November 2014

Keywords:
Inorganic arsenic
Arsenobetaine
Seafood
Direct solid sample analysis
Graphite furnace AAS

ABSTRACT

Direct solid sample analysis with graphite furnace atomic absorption spectrometry (SS-GF AAS) was investigated initially with the intention of developing a method for the determination of total As in fish and other seafood. A mixture of 0.1% Pd+0.06% Mg+0.06% Triton X-100 was used as the chemical modifier, added in solution over the solid samples, making possible the use of pyrolysis and atomization temperatures of 1200 °C and 2400 °C, respectively. The sample mass had to be limited to 0.25 mg, as the integrated absorbance did not increase further with increasing sample mass. Nevertheless, the recovery of As from several certified reference materials was of the order of 50% lower than the certified value. Strong molecular absorption due to the phosphorus monoxide molecule (PO) was observed with high-resolution continuum source AAS (HR CS AAS), which, however, did not cause any spectral interference. A microwave-assisted digestion with HNO_3/H_2O_2 was also investigated to solve the problem; however, the results obtained for several certified reference materials were statistically not different from those found with direct SS-GF AAS. Accurate values were obtained using inductively coupled plasma mass spectrometry (ICP-MS) to analyze the digested samples, which suggested that organic As compounds are responsible for the low recoveries. HPLC–ICP-MS was used to determine the arsenobetaine (AB) concentration. Accurate results that were not different from the certified values were obtained when the AB concentration was added to the As concentration found by SS-GF AAS for most certified reference materials (CRM) and samples, suggesting that SS-GF AAS could be used as a fast screening procedure for inorganic As determination in fish and seafood.

1. Introduction

The consumption of fish has many benefits for the human health [1]. Fish provides a significant amount of polyunsaturated and highly unsaturated fatty acids and animal proteins [2]; however, fish can also absorb metals with bioaccumulative properties, such as arsenic, through the membrane surfaces, tissues and by ingestion of food and suspended material in water [3].

The toxicity of As compounds depends on their oxidation state, chemical form and solubility in the biological system. As(III) is more toxic than As(V) and the inorganic species are more toxic than the organic ones. As(III) is 10 times more toxic than As(V) and 70 times more toxic than monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [4]. Arsenic can cause deleterious effects in the human body even at low concentration; increased risk of cardiovascular diseases and cancers in internal organs, skin and lung have been linked to arsenic contamination [5,6]. The organic species dominant in most seafood is arsenobetaine (AB) [7], which, in spite of the limited evidence, is considered non-toxic [8].

In Brazil, the Ministry of Agriculture, Livestock and Food Supply (MAPA) is responsible for the control of contaminants and residues in all kinds of food supplies. The National Agricultural Laboratories (LANAGRO) are part of MAPA and are recognized reference centers, acting in the development of analytical methods, as well as in research and monitoring programs of food contaminants [9]. Due to its high potential toxicity [10] arsenic is included in the list of the substances controlled by MAPA. The maximum level of As established by the Brazilian National Program for Residue and

* Corresponding author. Tel.: +55 51 33086307.
E-mail address: arianezmozinski@gmail.com (A.V. Zmozinski).

http://dx.doi.org/10.1016/j.talanta.2014.11.009
0039-9140/

Contaminant Control (NPRCC) in fish is 1 mg kg^{-1} [11]. Thus, the monitoring of this element by highly sensitive, fast and reliable analytical methods is necessary for an efficient control of contamination and to increase the sample throughput.

Recent reviews indicate that the main techniques used for the determination of arsenic in biological samples are graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS) and hydride generation atomic absorption spectrometry (HG AAS) [12,13]. Appropriate selection of the sample preparation procedure in trace analysis is essential due to the integrity of chemical information that strongly depends on the initial steps. The most frequently used methods in the preparation of food samples are dry ashing and microwave-assisted acid digestion [14].

An additional problem in the determination of total arsenic in fish and marine species by GF AAS is the presence of arsenobetaine. The AB, considered as non-toxic to humans, is a stable metabolic species and its chemical decomposition is very difficult [15,16]. The conversion of all organic arsenic species into inorganic As is usually required for the determination of total arsenic by atomic spectrometry. Consequently, the high stability of AB becomes unfavorable for the determination of the total As content [7]. Wet digestions using strong oxidizing agents combined with strong acids and high temperatures, are required for complete degradation of AB [17]. In some cases, even with the use of these reagents at higher temperatures, AB is not degraded completely and the result for the total concentration of arsenic is lower than the actual value [18,19].

Unfortunately, the reports in the literature about this issue are not conclusive. Narukawa et al. [18] reported that complete decomposition of AB was achieved only in the presence of $HClO_4$ and temperatures of 320 °C. Slejkovec et al. [20] developed a digestion method using the mixture of $HNO_3+H_2SO_4+H_2O_2$ and a temperature of 300 °C. Shah et al. [21] used a microwave-assisted digestion with concentrated $HClO_4$ and $Fe_2(SO_4)_3$ prior to the determination of inorganic As in fish tissue, and Duarte et al. [22] used a microwave-induced combustion prior to total As determination in seafood samples. In contrast to this, Shah et al. [23] used a comparably mild microwave-assisted digestion with HNO_3/H_2O_2 prior to the determination of total As by HG AAS, and Carioni et al. [24] used slurry sampling GF AAS and slurry sampling HG AAS, i.e., no digestion at all, for the determination of total As in a tuna fish candidate reference material.

In spite of all these discrepancies about the best procedure for the determination of total As, this value is not of great importance because of the tremendous differences in toxicity of the different As species; however, the content of total As in various food and feed samples is the only one currently required by legal authorities. Nevertheless, research should continue to search for simple and reliable methods at least to distinguish toxic, i.e., inorganic As (iAs) and essentially non-toxic organic As compounds, mostly AB. Shah et al. [21] developed an extraction method with chloroform, followed by microwave-assisted digestion for the determination of iAs in fish tissue and Rasmussen et al. [25] used a solid-phase extraction followed by HG AAS for the same purpose. Anawar [26] published a review article about As speciation analysis in environmental samples by GF AAS and HG AAS.

Unfortunately, most of the procedures proposed for As speciation analysis, including the determination of iAs only, are still too complicated for routine analysis. We therefore decided to explore the potential of SS-GF AAS for the determination of total As or iAs as a fast routine procedure. The advantages of direct SS-GF AAS are well known and described in several reference articles [27,28], and this technique, to the best of our knowledge, has not been described up to now for the determination of As in fish and seafood.

2. Experimental

2.1. Instrumentation

Two different atomic absorption spectrometers were used in this work: a Model AAS Zeenit 650P line source graphite furnace atomic absorption spectrometer with Zeeman-effect background correction and a Model contrAA 700 high-resolution continuum source atomic absorption spectrometer (both from Analytik Jena, Jena, Germany). Both instruments were equipped with a similar transversely heated graphite tube atomizer.

An As hollow cathode lamp was used as the radiation source for the Zeenit with a lamp current of 6.0 mA. The analytical line at 193.7 nm was used with a spectral bandpass of 0.8 nm. The experiments were carried out using solid sampling (SS) platforms (Analytik Jena Part no. 407-152.023) and SS tubes without a dosing hole (Analytik Jena Part no. 407-152.316).

The contrAA 700 is equipped with a xenon short-arc lamp with a nominal power of 300 W operating in a hot-spot mode. The high-resolution double monochromator with a prism pre-monochromator, a high-resolution echelle monochromator and a linear charge coupled device (CCD) array detector with 588 pixels has a spectral resolution of 1.2 pm per pixel at the 193.696 nm As resonance line. Atomic absorption was measured using the center pixel (CP) and the two adjacent pixels (CP $\pm$ 1), corresponding to a spectral interval of 3.6 pm; however, the entire spectral range $\pm$ 0.12 nm around the analytical line was displayed by the 200 pixels that are used for analytical purposes. The iterative background correction (IBC) mode was used throughout. The experiments were carried out using the same SS platforms (Analytik Jena Part no. 407-152.023) and SS tubes without a dosing orifice (Analytik Jena Part no. 407-A81.303).

An M2P microbalance (Sartorius, Göttingen, Germany) with an accuracy of 0.001 mg has been used for weighing the samples directly onto the SS platforms, which were introduced into the graphite tube using a pair of pre-adjusted tweezers, which is part of the SSA 6 manual SS accessory (Analytik Jena). The sample mass was transmitted to the instrument's computer to calculate the 'normalized integrated absorbance' (integrated absorbance calculated for 0.1 mg of sample) after each measurement. The aqueous standards and modifier solution were injected manually onto the platform using a micropipette. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas. The flow rate was 2.0 L min^{-1} during all stages, except during atomization, when the argon flow was interrupted. The parameters for the graphite furnace temperature program optimized for the determination of As are shown in Table 1.

A Model 7500ce inductively coupled plasma mass spectrometer (ICP-MS, Agilent, Germany) with a BURGENER Ari Mist HP type nebulizer was used to measure the total arsenic content. A Model 1200 LC quaternary high-performance liquid chromatography (HPLC)

Table 1
Graphite furnace temperature program for the determination of As in fish samples by SS-GF AAS and HR-CS SS-GF AAS.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)
Drying 1	110	15	20
Drying 2	150	20	45
Ash[a]	600	200	30
Pyrolysis	600	0	10
Pyrolysis	1200	300	35
Atomization	2400	FP[b]	8
Cleaning	2400	1000	8

[a] Air used as an alternate gas.
[b] FP: full power.