Food Control 59 (2016) 447–453

Contents lists available at ScienceDirect

Food Control

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

A fast alkaline treatment for cadmium determination in meat samples

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ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form
5 June 2015
Accepted 6 June 2015
Available online 17 June 2015

Keywords:
Alkaline extraction
Meat samples
Factorial design
GF AAS

ABSTRACT

This study proposes a simple and fast sample treatment to determine cadmium levels in meat samples (edible offal) of several animal species by graphite furnace atomic absorption spectrometry, GF AAS, as an alternative to the calcination method, currently employed by Official Food Control department of the Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA). In the proposed method minimum meat sample amount (0.5000 g) was previously hydrated and treated using 0.50 mL of tetramethylammonium hydroxide (TMAH), which provides stable and homogeneous slurry at room temperature in less than 10 min. For the optimization of the sample treatment parameters, fractional and factorial designs were employed. The accuracy of the method was evaluated using reference material, with recovery of 100 ± 7% (n = 7), and limit of quantification of 3.0 μg kg^{-1}, for Cd determination. Applying the proposed method, the meat samples amount used to determine the cadmium concentration was reduced by 20-fold compared to the sample amount required for the calcination conventional method. In fact, the sample preparation time was also reduced by 500-fold in the proposed method compared to the calcination method, which was very favorable for a routine laboratory analysis.

1. Introduction

Meat can be part of a balanced diet, contributing with valuable nutrients that are beneficial to one's health. Meat and meat products contain important levels of protein, vitamins, minerals, and micronutrients, which are essentials for the growth and development of humans. Meat is composed of water, amino acids, fats, fatty acids, and small quantities of carbohydrates (Food and Agriculture Organization). In addition, meat contains many inorganic compounds that comprise approximately 1% of its total composition (Zenebon, Pascuet, & Tiglea, 2008).

Among the toxic elements that may occur in tissues and products of animal origin, resulting of exposure to these elements from soil, industrial pollution, waste disposal, and/or agricultural inputs (Brazil, Normative Instruction n° 42, 1999), cadmium is among the substances controlled by Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA), through the National Plan for Control of Residues and Contaminants (PNCRC), in the muscle and edible offal of animals, such as: bovines, swine, poultry, horses, ovines, and caprines (Maurício, Lins, & Alvarenga, 2009).

The cadmium monitoring in foodstuffs, the main source of exposure for the non-smoking population, is important for commercial reasons associated to national and international laws, such as public health issues, since cadmium presents a number of toxic effects on animals and humans, affecting kidneys, hematopoietic system, bones and liver (European Food Safety Authority EFSA 2009a, 2009b; Groten & van Bladeren, 1994).

Due to low concentrations of some inorganic constituents in this kind of sample, highly sensitive techniques are required to determine these concentrations. There are several suitable analytical methods for determining inorganic contaminants in foods, such as inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GF AAS), and hydride generation atomic absorption spectrometry (HG-AAS) (European Food Safety Authority EFSA 2009a, 2009b). Although the GF AAS technique is less sensitive than ICP-MS, it is less expensive and may provide high detectability for low sample volumes; in addition, GF AAS is relatively easy to operate and maintain (European Food Safety Authority EFSA 2009a, 2009b; Welz & Sperling, 1999). Besides, for the inorganic elements quantification GF AAS does not require a drastic sample treatment, which makes the method significantly faster. It is well known that the sample preparation is a critical step in any analytical procedure, especially when it involves

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http://dx.doi.org/10.1016/j.foodcont.2015.06.015
0956-7135/

a complex matrix. Almost all sample preparation procedures (Cabrera et al., 1994; Demirel, Tuzen, Saracoglu, & Soylak, 2008; Dionísio, Gonzales, & Nóbrega, 2011; Matos et al., 2009; Muñiz-Naveiro et al., 2005; Saracoglu, Tuzen, & Soylak, 2009; Shah et al., 2009; Tuzen, Silici, Mendil, & Soylak, 2007) are based on the use of concentrated acids for promoting an aggressive attack, particularly under high temperature and pressure when using closed and pressurized reaction vessels (Nóbrega et al., 2006). However, in Brazil, specifically in Agricultural National Laboratories, called LANAGRO, the calcination method is used for sample treatment for cadmium monitoring in edible offal of several animal species. This accredited official method is generally time consuming, aggressive, and occasionally limited by the availability and capacity of a muffle furnace that must be employed for the sample treatment step. Then, an alternative sample treatment method that can overcome these limitations related to calcination method, reducing the time of sample treatment and allowing the increase of operational capacity in routine analytical laboratory is required.

The use of an alkaline media is a simple alternative for sample preparation that can involve a large group of analytes in different types of samples (Nóbrega et al., 2006). Biological samples, primarily animal tissues, can be significantly solubilized with tetramethylammonium hydroxide (TMAH), a strong organic base that is soluble in water and alcohols and can complex and stabilize volatile elements (Ghisi, Ribeiro, Vieira, & Curtius, 2007), at room temperature, without application of energy for heating and providing homogeneous slurry (Ghisi et al., 2007; Martins, Pozebon, Dressler, & Kemieciki, 2002). Solubilization with TMAH generally requires small amounts of sample and reagents, prevents problems associated with digestion procedures and reduces the sample preparation time (Ghisi et al., 2007; Damin, Zmozinski, Borges, Vale, & Silva, 2011; Nunes et al., 2013; Oreste et al., 2013), allowing an increase in the number of samples treated simultaneously and improving the capacity of a routine analytical laboratory. In this context, the aim of this work was the development and validation of a simple sample treatment in alkaline media with TMAH as an alternative method for cadmium quantification in meat samples by GF AAS, taking into account the requirements of the National Plan of Residues and Contaminants Control of Brazilian government, and the MERCOSUL and European legislations (Brazil MAPA, 2011; MERCOSUL/GMC/RES n° 12, 2011; European Commission (EC) n° 1881, 2006; (EC) n° 96/23, 2002; (EC) n°333, 2007). Multivariate optimization strategies were employed during the method development.

2. Material and methods

2.1. Reagents and materials

All solutions were prepared with analytical-grade chemical reagents and deionized water (resistivity higher than 18.2 MΩ cm) obtained from Milli-Q water purification system (Millipore, Bedford, MA, USA).

The acid solutions were prepared using 65% v/v of nitric acid (VETEC, Duque de Caxias, Brazil), which was previously distilled in a quartz sub-boiling system (Milestone, Sorisole, Italy). The standard cadmium solutions were prepared by appropriate dilutions of 1000 mg L^{-1} stock solution (Fluka Analytical, Buchs, Switzerland). A mixture solution containing 10000 mg L^{-1} $Pd(NO_3)_2$ and 10000 mg L^{-1} $Mg(NO_3)_2$ (both from Perkin Elmer, Norwalk, CT, USA) was used as chemical modifier for the determination of cadmium by GF AAS. A TMAH solution (25% w/v) in methanol (Sigma–Aldrich, St. Louis, MO, USA) was used to solubilize the samples.

The poultry kidney samples used in this study were obtained from poultry farms from different locations in the Mato Grosso do Sul and Santa Catarina Brazilian States. A freeze-dried bovine liver reference material (Programme of the Community Reference Laboratory for Chemical Elements in Food of Animal Origin at the Istituto Superiore di Sanità – CRL-ISS, Rome, Italy) was used to evaluate the accuracy of the proposed method. This reference sample (bovine liver) was used because it has similar characteristics to the samples used in this work (ovine, caprine, ostrich, kidney and liver samples), allowing to evaluate the accuracy of the proposed method.

2.2. Apparatus

All samples were weighed using an analytical balance (Model AY 220, Shimadzu, São Paulo, Brazil) with 0.0001 g of precision. A lyophilizer, model Terroni LS3000 (São Carlos, Brazil), was used to freeze-dry the samples.

The cadmium integrated absorbance and correspondent concentration was determined using GF AAS (Model AA600, Perkin Elmer, Norwalk, CT, USA) equipped with a background corrector based on the longitudinal Zeeman effect and transversal heating. The spectrometer was operated with an electrodeless discharge lamp source at 228.8 nm wavelength, a spectral band pass of 0.2 nm, and a lamp current of 230 mA.

2.3. Optimization strategies: alkaline meat samples treatment and instrumental conditions of GF AAS

Considering the meat moisture level, approximately 500 mg of fresh contaminated samples or 110 mg of dried samples were directly treated in 15.0 mL falcon tubes. The following variables: ratio between the TMAH volume and sample weight (2 or 5 mL g^{-1}), sample moisture (lyophilized or fresh), hydration time (30 or 60 min), and extraction time (20 or 45 min), were studied employing a 2^{4-1} fractional factorial design for their screening (Martins et al., 2002) in order to find which ones of these previously selected variables can significantly affect the sample treatment, taking into account also possible interactions.

The extraction procedures were performed at room temperature, and the samples were diluted to 10.0 mL with deionized water. The recovery values of cadmium obtained by factorial design experiments were used in these studies as an evaluation parameter of the different experimental conditions analyzed. These experiments were performed randomly, and the statistical procedures were carried out employing the Statistica 7.0 software (StarSoft, Tulsa, USA). Then, the 2^3 factorial design was carried out to refine the experimental conditions. The GF AAS quantification was performed under the conditions recommended by the manufacturer, as reported in Table 1.

The pyrolysis and atomization temperatures for cadmium determination were optimized using a Central Composite Design (CCD), and these temperatures were varied from 360 to 640 °C and from 1360 to 1640 °C, respectively. For each instrumental condition analyzed by DCC design, meat samples previously spiked with 5 μg L^{-1} of cadmium standard solution were evaluated and the recovery values obtained were compared with the values obtained by cadmium standard solutions in the same concentration. These experiments were also performed randomly, and the statistical procedures were done using Statistica 7.0 software (StarSoft, Tulsa, USA).

2.4. Determination of cadmium in meat samples

About 500 mg of meat sample was weighed in polypropylene tubes and hydrated with 8.0 mL of deionized water during 4 min, followed by addition of 500 μL of 25% (w/v) TMAH solution. After 4 min, the slurry obtained was diluted to 10.0 mL with deionized