Food Control 61 (2016) 227–234

Contents lists available at ScienceDirect

Food Control

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

Determination of Cd in food using an electrothermal vaporization capacitively coupled plasma microtorch optical emission microspectrometer: Compliance with European legislation and comparison with graphite furnace atomic absorption spectrometry

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
28 September 2015
Accepted 29 September 2015
Available online 1 October 2015

Keywords:
Cadmium in food
Capacitively coupled plasma microtorch
Optical emission spectrometry
Graphite furnace atomic absorption spectrometry
European legislation

Chemical compound:
Cadmium ion (PubChem CID:31193)

ABSTRACT

A precise, accurate and sensitive method based on electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometry for Cd determination in various dietary products was developed. The instrumentation is inexpensive as it includes a low power (15 W) and low argon consumption (150 ml min^{-1}) microplasma connected to a small-sized Rh electrothermal vaporization device and a low resolution microspectrometer. The sample was subjected to microwave assisted digestion in $HNO_3 - H_2O_2$ mixture and Cd was determined in 10 μl sample without preconcentration. The standard addition method was used to compensate for the non-spectral matrix effects. The new method was in-house validated by analyzing certified reference materials and test dietary samples for which the Cd maximum level was established in Commission Regulation 488/2014/EU. The figures of merit of the proposed method and the experimental results were compared to those obtained in graphite furnace atomic absorption spectrometry as standardized method and discussed in relation with the requirements in the Commission Decision 2002/657/EC and Commission Regulations 2011/836/EU and 2007/333/EC. The limit of detection in fresh sample (0.001–0.009 mg kg^{-1}), limit of quantification (0.002–0.018 mg kg^{-1}), recovery (103 ± 15%), trueness (−3.0)–(+7.3)% and precision (0.8–14.0%) were similar to those found in the reference method and comply with the minimal criteria imposed to a method to be used in official laboratories for Cd determination in food. Precision for Cd determination close to maximum admitted levels or higher was of 0.8–6.0%, while for lower concentration in the range 4.0–14.0%. The Bland and Altman statistical test allowed successful evaluation of the new method as an alternative to the well established graphite-furnace atomic absorption spectrometry. The proposed method has analytical potential and is easy to run, while the full miniaturized instrumentation could be considered as a useful tool for the future as an alternative to the traditional instrumentation.

1. Introduction

Among more than 30 metals considered harmful, Hg, Cd and Pb are categorized as priority hazardous even when present at trace levels in water and food. For this reason, highly sensitive analytical techniques are necessary to estimate dietary intake (Zukowska & Biziuk, 2008). Cadmium in environment is derived from both natural and anthropogenic sources, the latter associated to industrial and agricultural activities. Cadmium may enter the human body by ingestion of contaminated food and beverages, is partially retained in liver and kidney and very slowly eliminated. It results in a very

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http://dx.doi.org/10.1016/j.foodcont.2015.09.040
0956-7135/

long biological half-life ranging from 10 to 30 years and thereby renal dysfunctions may develop.

The International Agency Research on Cancer has classified Cd as a human carcinogen (Group I) with increased risk for lung, endometrium, bladder and breast cancer (IARC, 1993). World Health Organization (WHO) established Provisional Tolerable Weekly Intake (PTWI) of Cd of 7 μg kg^{-1} body weight for humans (FAO/WHO, 2010). Based on data covering the period from 2003 to 2007 on Cd occurrence in various food commodities received from 20 member states, the Scientific Panel on Contaminants in the Food Chain (CONTAM Panel) of the European Food Safety Authority (EFSA) concluded that the exposure level of the non-smoke population to Cd should be reduced at 2.5 μg kg^{-1} body weight (EFSA, 2009).

Advances in the analysis of clinical and biological materials, foods and beverages were recently reviewed (Taylor et al., 2015). The determination of Cd traces in food and beverages has been routinely achieved by flame atomic absorption spectrometry (FAAS) (Akinyele &. Shokunbi, 2015; Dasbasi, Sacmaci, Ulgen &. Kartal, 2015; Lemos & Oliveira, 2015; Mirabi, Dalirandeh, & Rad, 2015; Soylak & Yilmaz, 2015), graphite-furnace atomic absorption spectrometry (GFAAS) (Lopez-Garcia, Vicente-Martinez, & Hernandez-Cordoba, 2015), inductively coupled plasma optical emission spectrometry (ICP-OES) (Fernandez et al., 2015) and inductively coupled plasma mass spectrometry (ICP-MS) (Cordeiro et al., 2015; Fragni, Trifiro &. Nucci, 2015; Sorbo, Turco, Di Gregorio, & Ciaralli, 2014). When using FAAS, the low level of Cd in water and most foodstuffs requests a preconcentration step achievable by extraction/microextraction on solid phase (SPE/SPME) on a strong cation exchange resin (Dovex Marathon C) (Dasbasi et al., 2015), modified or non-modified magnetic Fe_3O_4 nanoparticles (Mirabi et al., 2015; Soylak & Yilmaz, 2015) and ultrasound-assisted temperature-controlled ionic liquid microextraction (Lemos & Oliveira, 2015). Cadmium can be determined without preconcentration in water and food only by GFAAS and ICP-MS.

The development and validation of new, sensitive and fast methods intended for the control of contaminants in food that meet requirements for methods used in official laboratories for food control set out in Commission Decision (2002/657/EC) and Commission Regulations (2011/836/EU; 2007/333/EC) represents one of the most important challenges. One option in this direction is the use of technology associated to microplasmas of low power and low Ar/He requirements, recently transferred in atomic spectrometry by interfacing with commercially available low resolution microspectrometers (Greda, Jamroz, & Pohl, 2014; Jiang, Chen, Zheng, & Hou, 2014; Kitano et al., 2011; Luo & Duan, 2012; Moss, Reinsberg, & Broekaert, 2014; Nguon, Huang, Gauthier, & Karanassios, 2014; Yuan, Tang, & Duan, 2011). It was recently demonstrated that the capacitively coupled plasma microtorch interfaced with a low resolution microspectrometer can be successfully used for Hg determination after cold vapor generation in water, food, plastics, packaging for water and food (Frentiu et al., 2015a, Frentiu, Butaciu, Darvasi, et al., 2015, 2015c, Frentiu et al., 2013; Frentiu, Mihaltan, Darvasi, Ponta, Roman & Frentiu, 2012; Frentiu et al., 2011), As and Sb after hydride generation in non- and biodegradable materials and packaging (Frentiu et al., 2014a; Mihaltan et al., 2013) and Li in bottled drinking water (Zsigmond, Frentiu, Ponta, Frentiu, & Petreus, 2013). The instrument proved to be also useful for the determination of several toxic elements in environmental microsamples introduced into plasma by electrothermal vaporization (Frentiu, Darvasi, Butaciu, Ponta, Petreus, Etz, et al., 2015, Frentiu, Darvasi, Butaciu, Ponta, Petreus, Mihaltan, et al., 2014).

This paper provides for the first time an analytical characterization of a sensitive and inexpensive method for Cd determination in food without preconcentration based on small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometry (SSETV-μCCP-OES). The proposed method was compared to GFAAS, the standardized and easily accessible method for Cd control in food (EN 14084:2003). The figures of merit of the new SSETV-μCCP-OES method are discussed in relation with requirements set in the European legislation for Cd control in food.

2. Material and methods

2.1. Reagents, CRMs and test samples

Monoelemental standard solution of 1000 μg ml^{-1} Cd, 60% (w/w) HNO_3 ultrapure and 30% (w/w) H_2O_2 pro-analysis used in the study were purchased form Merck (Darmstadt, Germany). Ultrapure water (18.2 MΩ cm resistivity) obtained in laboratory with the Millipore equipment (Bedford, USA) was used to prepare solutions. The CRMs (IC-CS-CR-2 Carrot root powder, BCR-185R Bovine liver, IRMM-804 Rice flour, IAEA-359 Cabbage, DOLT-4 Dogfish liver, TORT-2 Lobster Hepatopancreas, NIM-GBW10011 Wheat flour and BCR 191 Lyophilized brown bread) used to check the accuracy of measurements by SSETV-μCCP-OES and GFAAS were procured from LGC Promochem (Wesel, Germany), while the food test samples were purchased from food stores or collected (vegetables) from areas contaminated by cadmium from non-ferrous ore processing centers.

2.2. Sample preparation

All samples were lyophilized to constant mass, then ground in a mortar and sieved to a grain size less than 100 μm. The advantage of lyophilization is to provide a homogenous sample for analysis and then a rapid and easy dissolution. The Cd concentrations were calculated on the base of fresh weight.

Digestion was performed by the acidic microwave assisted procedure, widely used for food samples. Amounts of 0.5000–1.0000 g sample were mixed with 10 ml 60% HNO_3 and 2 ml 30% H_2O_2 in the PTFE vials of the digester and left for preliminary oxidation for 3–4 h at room temperature. Then the PTFE vials were sealed and samples were subjected to digestion according to the temperature program previously used for Hg determination in food (Frentiu et al., 2015a). The Berghof MW3S + microwave oven enables a rigorous control of temperature in each vial, while the high pressure up to 100 atm provides an efficient oxidation of organic matter (Frentiu et al., 2015a; Frentiu, Ponta, Darvasi, Frentiu & Cordos, 2012). After cooling, the digest was diluted to 25 ml with water. Determination of Cd by SSETV-μCCP-OES was carried out using the standard addition method to compensate for the non-spectral interference of the multimineral matrix as previously established in the analysis of soil samples (Frentiu, Darvasi, Butaciu, Ponta, Petreus, Etz, et al., 2015, Frentiu, Darvasi, Butaciu, Ponta, Petreus, Mihaltan, et al., 2014). Five aliquots of 1–4 ml digest were spiked with 0–8 ng ml^{-1} Cd and diluted to 5 ml with ultrapure water. A blank containing the same volume of reagents was run with each batch.

Cadmium determination by GFAAS was carried out using external calibration on the range 0–5 ng ml^{-1}.

2.3. SSETV-μCCP-OES instrumentation and working conditions

The SSETV-μCCP-OES system consists of a small-sized electrothermal vaporization device with Rh filament–Home-made, Babes-Bolyai University (Cluj-Napoca, Romania), a soft-controlled power supply for the electrothermal vaporizer–Home-made, Technical