Application Note: 43034

The Analysis of Cadmium in Chocolate by Graphite Furnace Atomic Absorption Spectrometry

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Key Words

- Atomic Absorption
- Graphite Furnace
- Zeeman
- Cadmium
- Chocolate

Key Benefits

- The Thermo Scientific iCE 3500 Atomic Absorption Spectrometer provides a simple and uncomplicated solution for the analysis of trace elements
- The wizard-driven Thermo Scientific SOLAAR Software allows quick and easy optimization and method development.
- Analysis by graphite furnace is easy with Graphite Furnace TeleVision (GFTV), which allows viewing of the sample inside the cuvette.

Summary

The Thermo Scientific iCE 3500 Atomic Absorption Spectrometer is the ideal tool for the simple and easy analysis of cadmium in chocolate. A straight forward sample preparation procedure combined with a fully optimized analysis method resulted in accurate detection well below current recommended limits for the concentration of cadmium in foodstuffs.

Introduction

Cadmium is a heavy metal used in a variety of applications, such as steel plating, as a pigment in plastics and glasses, and in the production of batteries. These industrial activities are the main route through which cadmium is released into the environment where it accumulates in water and soil, and subsequently plants, animals and fish through uptake and ingestion. One of the main routes of human exposure to cadmium is therefore through the ingestion of foodstuffs.

The provisional tolerable weekly intake (PTWI) of cadmium is currently 7 µg/kg body weight, however the recommendation is to limit cadmium intake as it offers no nutritional benefit. Typical maximum levels of cadmium in foodstuffs are currently between 0.05 – 0.2 mg/kg wet weight.[1-3] Excessive cadmium consumption can cause nausea, gastrointestinal pain, softening of bones and kidney damage. Cadmium accumulates within the kidneys and can eventually cause renal failure.

Chocolate and chocolate-based sweets and candies are common treats, snacks, or gifts for children and adults alike. The main ingredients in chocolate consist of cocoa, milk and fats, each of which is a potential source of cadmium. The determination of cadmium levels in chocolate is therefore an important issue for chocolate consumers and manufacturers around the globe.

Method

Reagents

- Nitric acid, 69 %, trace metal grade
- Hydrogen peroxide, > 30 % w/v, trace metal grade
- 1000 mg/l Cadmium master standard used to prepare sub-standards
- Ammonium nitrate

All standards and reagents purchased from Fisher Scientific.

Sample Preparation

Approximately 0.3 g pieces of chocolate (popular global brands of milk and dark variety) were accurately weighed and transferred to microwave digestion vessels. 7 ml of nitric acid and 1 ml of hydrogen peroxide were added and left to stand for 5 minutes, before the vessels were sealed and samples digested in a high pressure microwave digestion system by ramping to 200 °C over 10 minutes. Samples were maintained at 200 °C for twenty minutes before being allowed to cool. The contents of the vessels were then quantitatively transferred to 100 ml volumetric flasks with deionised water and made up to a final volume of 100 ml.

(It is recommended to leave the samples in the sealed vessels for several hours to cool before transfer of the contents to ensure the minimal loss of volatile elements, and to carry out multiple rinses of the vessels to ensure all digested material is transferred to the volumetric flask).

Standard and Reagent Preparation

A 1 mg/l cadmium sub-standard was prepared in deionised water for spiking of samples prior to digestion. The 1 mg/l sub-standard was then used to prepare a 10 µg/l sub-standard for calibration. The 10 µg/l sub-standard was made up in 7 % nitric acid and 1 % hydrogen peroxide to matrix match to the digested samples. Blank and diluent were also prepared at 7 % nitric acid and 1 % hydrogen peroxide. A matrix modifier was prepared at 2 g/l to allow deposition of 20 µg of ammonium nitrate in a 10 µl aliquot.

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Furnace Method

Furnace temperature parameters are shown in Table 1:

Phase	Temperature / °C	Time / s	Ramp / °C/s
Dry	110	30	10
Ash	400	20	150
Atomize	1300	3	0
Clean	2500	3	0

Table 1: Furnace parameters for the analysis of cadmium in chocolate.

The *optimize furnace parameters* wizard in the SOLAAR software was used to determine the most suitable temperatures for drying and ashing of the digested chocolate samples. Graphite Furnace TeleVision (GFTV) was used to optimize the position of the injection capillary and to observe the deposition of the sample into the cuvette. The 10 µg/l cadmium solution was used as the master standard for the method. The autosampler was programmed to automatically generate calibration standards at 2, 4, 6, 8 and 10 µg/l. All samples, blanks and standards were injected at a constant fixed volume of 10 µl, alongside an additional aliquot of 10 µl of matrix modifier into an electrographite cuvette. Cadmium was analyzed at 228.8 nm and Zeeman background correction was used throughout. Peak areas were measured for the production of the calibration and subsequent determination of the sample concentrations.

Results and Discussion

A segmented fit curve was used for generation of the calibration for the analysis of cadmium in chocolate. The calibration curve for cadmium is shown in Figure 1.

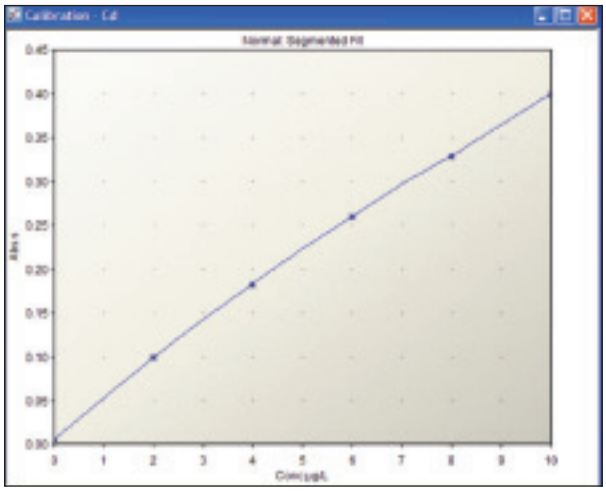

Figure 1: Calibration curve for the analysis of cadmium in chocolate.

Spiked samples were prepared to evaluate the recovery of cadmium. This was done by adding 0.5 ml aliquots of the 1 mg/l cadmium standard to samples of chocolate and then preparing and analyzing using the proposed method. (0.5 ml of 1 mg/l cadmium results in addition of 5 µg/l to the final sample).

Results for the analyzed samples are shown in Table 2

SAMPLE	MEASURED CONCENTRATION / µg/l	CONCENTRATION IN ORIGINAL SAMPLE / mg/kg	CALCULATED SPIKED RECOVERY / %
USA Origin, Milk	0.030	0.010	
USA Origin, Milk, Spiked	5.095		101
UK Origin, Milk	0.038	0.012	
UK Origin, Milk, Spiked	5.182		103
USA Origin, Dark	0.124	0.042	
USA Origin, Dark, Spiked	4.761		93

Table 2: Results for the analysis of cadmium in chocolate following analysis by graphite furnace atomic absorption spectrometry.

Cadmium was detected in small amounts in all three chocolate samples, with the maximum calculated at 0.04 mg/kg. However, all samples fell below typical current legislation for the recommended maximum levels of cadmium in foodstuffs.

(Fact: For an average adult of weight 70 kg, approximately 12 kg per week of the dark chocolate analyzed in this experiment would need to be consumed to exceed the PTWI. However – this would not be advisable for a balanced and healthy diet!)

Spiked recoveries were performed on the three analyzed samples and were all found to be good. In addition, the method detection limit and characteristic concentration were calculated using the *check instrument performance* wizard in the SOLAAR software. The method detection limit was found to be 0.029 µg/l and the characteristic concentration 0.060 µg/l.

Conclusion

Cadmium in chocolate was analyzed following a simple digestion procedure, and matrix matched standards were used to accurately determine cadmium concentration. Cadmium was found in all three samples but was below the recommended limits for cadmium in foodstuffs. The method was verified against spiked recoveries and the method detection limit was found to be 0.029 µg/l. Wizards in the SOLAAR software were used for uncomplicated method development. The iCE 3500 Atomic Absorption Spectrometer provides a simple, easy and accurate tool for the analysis of cadmium in foodstuffs.

References

1. Codex General Standard for Contaminants and Toxins in Foods, Codex Stan 193-1995, Rev.3-2007
2. Peoples Republic of China, FAIRS Product Specific Maximum Levels of Contaminants in Foods 2006
3. Commission Regulation (EC) No 1881/2006 of 19 December 2006: Setting Maximum Levels for Certain Contaminants in Foodstuffs

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