Sensitive and Direct Determination of Lead in Coffee Drinks by Graphite Furnace Atomic Absorption Spectrometry After In-Furnace Digestion

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INTRODUCTION

Coffee is the most popular beverage in many countries and is part of people's lifestyle and an everyday habit. Coffee is consumed for many reasons, including its stimulatory effects resulting from caffeine, rich phytochemicals, and primarily, the excellent taste and aroma. The health benefits [e.g., prevention of prostate cancer (1), liver diseases (2), diabetes (3), and stroke (4)] of coffee have been demonstrated in recent years. The improved overall survival has been demonstrated in a variety of disease states. Moreover, coffee consumption is associated with a decrease in "all-causes" mortality (3). However, daily consumption of coffee can also lead to a significant source of exposure to potential hazardous chemicals, such as pesticides and toxic elements (5). Consequently, the chemical composition of coffee drinks (i.e., essential, non-essential, and toxic elements) has to be determined and kept under control in terms of its safety, and thus assists in its quality, nutritional value, and certain sensorial properties. Since some elements are toxic at trace or even ultra-trace levels, the coffee producers and consumers are paying more and more attention to the safety issues.

Coffee drink as a liquid beverage has a complex matrix with a high content of organic compounds

ABSTRACT

A fast and efficient method was developed for the direct determination of lead in coffee drinks by graphite furnace atomic absorption spectrometry after in-furnace digestion. The coffee drink samples were diluted with nitric acid and Triton X-100 for direct analysis by GFAAS. The use of Pd (chemical modifier) permitted the direct determination of Pb in these samples. The experimental conditions, including the graphite furnace heating program, sample preparation conditions, and analytical figures of merit, were investigated and are discussed in detail. The limit of detection (LOD, 3σ) was 0.24 ng mL^{-1} , and the relative standard deviation (RSD) was 3.1% ($10 \text{ ng mL}^{-1} \text{ Pb}$). To validate the accuracy of the proposed method, spike recovery experiments and comparison experiments between in-furnace digestion and wet digestion were carried out with satisfactory agreement of the obtained values.

such as proteins and fats from the production process. The sample digestion procedures for the decomposition of biological samples are often complicated (6,7). Most analytical techniques for metals determination in coffee drinks generally require a sample decomposition method via solubilization by alkaline or concentrated acids with oxidizing properties (8). Sample decomposition involves a long preparation time and may lead to analyte loss or contamination. Recently, intriguing approaches to

the direct measurement of elements by graphite furnace atomic absorption spectrometry (GFAAS) without initial decomposition of the samples have been reported, relying on in-furnace digestion of biological solid or slurry samples (9-12). In comparison to the analysis of digested sample solutions, the in-furnace digestion methods certainly offer very high sensitivity for trace elements due to the absence of any sample dilution, as well as minimum risk of contamination (lower blanks) or loss of elements due to the reduced amount of reagents required for sample preparation (13-17).

In this work, the sensitive and direct determination of lead in coffee beverages after in-furnace digestion is presented using GFAAS analysis. Due to its cumulative properties in the body, the World Health Organization has proclaimed lead a potential chemical hazard above $10 \mu\text{g L}^{-1}$ in water (18-20). Lead is present in drinking water as a result of its dissolution from natural sources and household plumbing systems. Epidemiological evidence shows that excess levels of lead damage the nervous, alimentary, and hemopoietic systems (21). Thus, low lead levels in drinking water is a prerequisite for the production of healthy coffee and to protect the consumer. Lead levels in the final product and during the production of coffee are used as biological indicators for the estimation of its exposure (8). The experimental conditions, including the graphite furnace heating program, sample preparation conditions,

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analytical figures of merit, and method validation, were investigated and are discussed in detail.

EXPERIMENTAL

Instrumentation

An AAnalyst™ 800 atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used throughout this work, and the instrumental parameters are listed in Table I. The instrument is equipped with a graphite furnace atomizer and an AS 800 autosampler to facilitate sample introduction and free atom generation. A hollow cathode lamp (HCL, PerkinElmer Lumina™, Part No. N305-0157) of lead was used as the radiation source. The signal measurements were performed using the peak area (integrated absorbance) method.

Reagents and Standard Solutions

All reagents were of at least analytical reagent grade. Deionized water (DIW) was used throughout this study from a water purification system (ULUPURE, Chengdu, P.R. China). A standard stock solution of lead (1000 mg L^{-1}) was purchased from the National Center for Reference Material (Beijing, P.R. China). The lead working standard solutions of $50 \mu\text{g L}^{-1}$ were obtained by stepwise dilution from the stock solution with 0.2% (v/v) HNO_3 solution. A solution of $\text{Pd}(\text{NO}_3)_2$ (GR,

Merck, Darmstadt, Germany), 1000 mg L^{-1} in 0.2% (v/v) nitric acid and 0.1% (v/v) Triton® X-100 [4-(1,1,3,3-tetramethylbutyl)phenyl-hydroxypoly(oxyethylene)] was employed as the chemical modifier. High purity argon gas (99.99%) was used as the purge gas.

Procedure

The working standard solutions of Pb were prepared by serial dilution of the standard stock solution of Pb in 0.2% (v/v) nitric acid and 0.1% (v/v) Triton X-100. The coffee drink samples were diluted 10 times with 0.2% (v/v) nitric acid and 0.1% (v/v) Triton X-100 for direct analysis by GFAAS.

For analysis of the samples, $20\text{-}\mu\text{L}$ aliquots of working standard solutions or sample solutions and $5 \mu\text{L}$ of 1000 mg L^{-1} Pd chemical modifier were directly delivered to the atomizer platform. All measurements of integrated absorbance were made at least in triplicate. The thermal stabilization studies of Pb during the pyrolysis and atomization stages were investigated in a coffee drink sample containing 10 ng mL^{-1} Pb. The proposed procedure was applied to the Pb determination in coffee drinks without treatment and after wet digestion. The temperature program of the graphite furnace atomizer is listed in Table II.

For wet digestion, a volume of 2.5 mL of sample was transferred to polytetrafluoroethylene (PTFE)

beakers, followed by addition of 8 mL of concentrated nitric acid and 2 mL of concentrated perchloric acid. The solution was digested on an electric hot plate at 80°C for 15 minutes and at 200°C until nearly dry. The digests were transferred to 25-mL volumetric flasks, and the volume completed with de-ionized water. In addition, recovery tests were also performed in triplicate by adding a Pb standard solution to the coffee samples.

RESULTS AND DISCUSSION

Optimization of GF Heating Program

Pyrolysis

Considering the high content of organic matter in the samples and to obtain complete digestion, the conditions used in the pyrolysis step were optimized. Mineralization curves were obtained for Pb in coffee beverage samples containing 10 ng mL^{-1} Pb. Pyrolysis temperatures were optimized from 600°C to 1300°C . Figure 1a shows the obtained pyrolysis curves. It was found that a constant signal was obtained at the interval between $600\text{--}1000^\circ\text{C}$ in the presence of Pd chemical modifier. At higher temperatures, the analytical signal decreases. In order to obtain complete in-furnace digestion of the sample, the pyrolysis temperature was set to 900°C . As shown in Figure 1a, without a Pd chemical modifier, the signal decreased continuously with a pyrolysis tempera-

TABLE I
GFAAS Instrumental Parameters

Parameters	Values
Hollow cathode lamp	283.3 nm , 10 mA
Slit width	0.7 nm
Read mode	Peak area
Read time	5 s
Sample volume	$20 \mu\text{L}$
Background correction	Zeeman effect

TABLE II
Temperature Program of Graphite Furnace Atomizer

Steps	Temperature ($^\circ\text{C}$)	Ramp Time (s)	Hold Time (s)	Ar Gas Flow (mL min^{-1})
1. Drying	110	1	30	250
2. Drying	130	15	30	250
3. Cooling	20	1	10	250
4. Pyrolysis	900	10	20	250
5. Atomization	1500	0	5	0
6. Clean	2450	1	3	250

Fig. 1. (a) Pyrolysis curve and (b) atomization curve of 10 ng mL^{-1} lead.

ture higher than 700°C . The pyrolysis temperature of 900°C with the Pd chemical modifier was chosen for subsequent experiments.

Atomization

After the optimum conditions for the pyrolysis step were fixed, the atomization curves were investigated, as shown in Figure 1b. The atomization temperatures were set by taking into account the highest peak areas, the narrowness of the absorbance profiles, and the repeatability of the measurements. The highest signals were obtained between 1400 and 2000°C . Considering the absorbance profiles and signal repeatability, the atomization temperature was fixed at 1500°C .

Optimization for Sample Preparation

Effect of Triton X-100

Triton X-100 is a poly(ethylene glycol) terminating with a 4-(2,4,4-trimethylpentan-3-yl) phenyl group at one end. It is a non-ionic surfactant that has a hydrophilic polyethylene oxide chain (on average it has 9.5 ethylene oxide units) and an aromatic hydrocarbon lipophilic or hydrophobic group. The application of Triton X-100 in the sample preparation of coffee drink samples can provide perfect dispersion of the samples as aqueous emulsion, and then result in highly stable signal intensity. Triton X-100 in the values of 0%, 0.05%, 0.1%, 0.2%, and 0.5% (v/v) were used to dilute the coffee drink samples. A stable signal was obtained with Triton X-100 of higher than 0.1% (v/v). Since bubbles easily form with high

Fig. 2. Calibration curve of lead by the proposed method.

Triton X-100 concentrations, 0.1% (v/v) was used for subsequent experiments.

Effect of Nitric Acid

Nitric acid was added to coffee drink samples to prevent the hydrolysis of Pb compounds and assist the in-furnace digestion. A stable absorbance signal was obtained with nitric acid concentrations from 0.1% to 0.2%. A concentration up to 0.3% can sometimes cause precipitation, which results in low signal intensity of the samples and high signal variability. In addition, high acid concentrations can lower the lifetime of graphite tubes and thus, a concentration of 0.2% was used for subsequent experiments.

Analytical Performance

Under the optimized conditions, a series of Pb standard solutions were prepared and analyzed by GFAAS. The atomic absorbance of the analyte was found to be linearly proportional to the concentration of the analyte. The calibration curve shown in Figure 2 exhibits good linearity. The limit of detection (LOD, 3σ) was 0.24 ng mL^{-1} , thus suitable for the sensitive analysis of Pb in food samples. The

repeatability and intermediate precision were evaluated by analyzing a control sample nine times sequentially, without changing any operating conditions. The relative standard deviation (RSD) was calculated as 3.1% for 10 ng mL⁻¹ Pb.

Validation of the Method

In order to validate the applicability of the proposed method for trace lead determination in coffee drinks, a series of samples using different brands of coffee, bought at a local supermarket, were analyzed. As shown in Table III, the recoveries of the samples spiked with 2 ng mL⁻¹ and 4 ng mL⁻¹ of Pb ranged from 94% to 105%. In order to further verify the accuracy and precision of the method, all of these samples were analyzed with the wet digestion-based method, which revealed good agreement between the results of the two alternative approaches of in-furnace vs. wet digestion (Table IV).

CONCLUSION

The fast and sensitive determination of Pb concentrations in a series of coffee beverage samples was performed by GFAAS after in-furnace sample digestion. The limit of detection (LOD, 3σ) was 0.24 ng mL⁻¹, and the relative standard deviation (RSD) was 3.1% (10 ng mL⁻¹ Pb). This method does not require a sample pre-digestion step, and minimizes time, cost, and contamination of the samples. According to the results of this study, chemical modification was very important. The use of Pd (as a chemical modifier) permitted the direct determination of Pb in the samples. Employing optimized conditions, matrix effects were eliminated, and the aqueous calibration curve can be used. This analytical method can also be applied for GFAAS analysis of other organic substances similar to coffee beverages, e.g., milk, vinegar, alcoholic drinks, and other kinds of beverages.

TABLE III
Detection Results and Recoveries in Coffee Drink Samples

Sample	Added (μg L ⁻¹)	Detected (μg L ⁻¹)	Recovery (%)
Coffee 1	0	1.61	-
	2	3.72	105
	4	5.51	97
Coffee 2	0	1.95	-
	2	3.82	94
	4	5.77	95
Coffee 3	0	2.17	-
	2	4.30	107
	4	6.49	108
Coffee 4	0	N.D.	-
	2	2.11	105
	4	4.12	103

N.D. = not detected.

TABLE IV
Comparison of Analytical Results for In-Furnace vs. Wet Digestion Method

Sample	In-Furnace Digestion (μg L ⁻¹)	Wet Digestion (μg L ⁻¹)
Coffee 1	1.61	1.78
Coffee 2	1.95	2.06
Coffee 3	2.17	2.44
Coffee 4	N.D.	N.D.

N.D. = Not detected.

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