Determination of Heavy Metal Elements in Different Vegetable Edible Oils in China

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The content of nine heavy metals in vegetable edible oils has been determined using inductively coupled plasma-optical emission spectrometer (ICP-OES) after microwave digestion. The method has been validated by recovery experiments in different oil samples, obtaining satisfactory results in the range of 90 to 107 %. The relative standard deviations ranged from 2 to 7 % in samples spiked with 1 µg/g of each metal, respectively. The proposed method was applied to determination of copper, lead, zinc, chromium, cadmium, nickel, ferrum, aluminium and manganese in vegetable edible oils. In addition, a comparison relevance between the heavy metal level distributed and different production process types were observed in vegetable edible oils.

Keywords: Vegetable edible oils, Heavy metals, Microwave digestion, ICP-OES, Production process.

INTRODUCTION

China is one of the largest producers and consumers of vegetable edible oils in the word. Vegetable edible oils are widely used in cooking and it's safety concern has more and more significant in recent years. There are two main processes: traditional squeeze technique and extraction process. However, to our best of knowledge, there is no report until on the determination of heavy metal elements in different used for vegetable edible oils produced in China.

The potentially of toxic elements in vegetable edible oils are important because of assessment of oils quality with regard to freshness, storability and their influence on human health by the determination of several heavy metals. The content of heavy metals may be naturally present in vegetable edible oils that were absorbed by the vegetable mainly from the soil where it was grown and may be introduced during into oil from outer sources the production process, such as bleaching, hardening, refining and deodorization or by contamination from the metal processing equipment [1,2]. The heavy metals are very harmful even at low concentration when ingested over a long time period [3]. The essential metals may produce harm effects when the metal intake are excessively elevated [4]. It is necessary to appraise the concentration of heavy metals in vegetable edible oils and to report possible pollution that would represent a health hazard. A few researches [5-9] have made some progress on the determination of heavy metals in vegetable edible oils.

In addition, sample preparation [10-12] has been acquired more attention, because pretreatment process may represent a high potential source of errors in the analytical sequence. Microwave digestion is the most common sample preparation method under the diluted nitric acid and oxygen atmosphere, because of its availability, high efficiency and reduce risks of losses and contamination in comparison with traditional digestion way in laboratories.

In this work, the inductively coupled plasma-optical emission spectrometer (ICP-OES) method was applied to quantitative analysis of nine heavy metals (Pb, Cd, Cr, Cu, Zn, Ni, Fe, Mn, Al) after microwave digestion and estimate the content of trace metal elements in different technologies applied to produce vegetable edible oils.

EXPERIMENTAL

The instrument of ICP-OES (from Agilent Technologies, CA, USA) was employed, which was operated in standard mode throughout the work. The operating conditions for determination are listed in Table-1. The analytical emission lines (nm) chosen were as follows: Pb (220.3), Cd (214.4), Cr (267.7), Cu (327.4), Zn (206.2), Ni (231.6), Fe (238.2), Mn (257.6) and Al (396.2).

Marx5 digestion microwave system (from CEM Matthews, NC, USA) equipped with a rotor for 40 high-pressure PTFE vessels (capacity of 50 mL, maximum pressure and operation

TABLE-1
OPERATING CONDITIONS OF ICP-OES

Parameters	
RF power (W)	1000
Gas flow rate (L/min)	
Auxiliary gas	1.5
Plasma gas	15
Integration time (min)	5.0
Pump speed (rpm)	15
Observed altitude (mm)	10
Number of replication	3
Background subtraction	Displacement spike and fitting

TABLE-2
OPERATING PROGRAM FOR THE
SAMPLE MICROWAVE DIGESTION

Step	Power (W)	Initial temp. (°C)	Final temp. (°C)	Hold time (min)
1	600	25	80	10
2	1000	80	150	15
3	1000	150	200	10

were used as blank and the analyte addition technique. The analysis results acquired were evaluated based on the intensity of the corrected blank.

temperature of 1500 psi and 250 °C, respectively) was used for the samples.

Reagents and standards: A multi-element stock solution (CRM/RM Information center of China, Beijing, China) containing 100 mg/L of each element was used to prepare the calibration solution by sequential dilution with ultrapure water. The ultrapure water (18.2 MΩ cm) generated by a purification system (Milli-Q™ Plus, Millipore Corp., USA). Guarantee reagent grade nitric acid (65 %; Chongqing, China) and hydrogen peroxide (30 %; Chongqing, China) were used for the microwave digestion of the oil samples.

Sample collection and market survey: Along with people living standard enhancement and with the increase in food security awareness, purchase traditional squeeze technique edible oils also in enhancement. Rapeseed oil, soybean oil, peanut oil and sunflower oil are major vegetable edible oils in China.

The most frequently consumed 15 brands, such as arawana, red dragonflies, fulinmen and carp, of vegetable edible oils were selected and 36 samples including 15 rapeseed oil, 5 soybean oil, 8 corn oil, 4 sunflower oil, 2 peanut oil, 1 rice oil and 1 canola oil were purchased in Walmart supermarkets. In terms of market share, traditional squeeze technique about have a 70 % and extraction process 30 % market share. Extraction process technology has been mainly adopted for soybean oil and rapeseed oil and traditional squeeze technique adopted for high-grade edible oil (such as sunflower oil, peanut oil *etc.*). The mostly widely accepted and most frequently consumed 3 brands such as red dragonflies, arawana and carp were selected. The vegetable edible oil samples were selected from different technologies with homology material and stored in polyethylene bags until analysis.

Microwave digestion: Accurately weighing 0.5 g samples, the samples were digested with 6 mL of nitric acid (65 %) and 1.5 mL of hydrogen peroxide (30 %) in microwave digestion system for 35 min and the operating program for the sample microwave digestion system is shown in Table-2. After cooling at room temperature and filter film filtering, all the digestion liquors were quantitatively transferred into plastic volumetric flask and diluted to 10 mL with 2 % nitric acid solution. The reagents blank digest was carried out in the same way.

Calibration procedure: The calibration curves were carried out using five different concentrations ranging from 0.010 to 10 μg/g. Standard solutions were prepared in 2 % nitric acid solution by diluting a multi-element standard solution containing all the elements. Non-spiked vegetable edi ble oil

RESULTS AND DISCUSSION

Validation of the method: In order to check the applicability of the method to the analysis of vegetable edible oil samples and there are no certified reference materials for the different kinds of vegetable edible oil. So we used the recovery experiments to validate the proposed method. The recovery studies for all the elements were performed in soybean oil and rapeseed oil at 1.0 μg/g concentration level. The recoveries, depicted in Table-3, were in the range 90-103 % with relatived standard deviations (n = 5) lower than 7 %, in all cases. The obtained recoveries confirmed that no significant metal losses occurred during the microwave digestion process.

TABLE-3
RECOVERIES (%) FOR SPIKED OILS

Element	Spike recoveries (%) ± RSD (%)	
	Soybean oil	Rapeseed oil
Pb	99.8 ± 5.2	98.2 ± 4.6
Cd	100.2 ± 3.2	102.4 ± 1.7
Cr	97.6 ± 3.8	101.1 ± 1.5
Cu	94.8 ± 4.4	93.1 ± 2.2
Zn	100.7 ± 4.3	97.0 ± 1.3
Ni	98.9 ± 7.0	103.3 ± 1.4
Fe	98.7 ± 1.2	96.5 ± 2.1
Mn	97.6 ± 6.7	99.1 ± 4.7
Al	90.3 ± 1.7	93.3 ± 7.0

Analytical parameters: The analytical results were carried out using the full quantitative mode analysis. The linear correlation coefficients curves were above 0.9918 and showing a good linear relationships between 0.01 to 10 μg/g for all the metals. The limits of detection and quantification were based on the usual definition as the concentration of the analyte yielding a signal equivalent to three times the standard deviation of the blank signal, using 10 measurements of the blank for this calculation in agreement with IUPAC recommendations. The reagents blank solution was prepared in the same way as way as the sample. Analytical parameters for all the metals were shown in Table-4.

The proposed method has been applied to the determination of 9 heavy metals present in vegetable edible oil and the another goal of this study was to compare the levels in traditional squeeze technique and extraction process. In the proposed study, both production process types have been included in the same raw material (material come from the same origin) because of both the favourite among consumers and extremely high market share and the measuring data the

TABLE-4
ANALYTICAL PARAMETERS FOR DETERMINATION OF
HEAVY METALS IN VEGETABLE EDIBLE OILS SAMPLES

Element	Calibration equation $(A = aC + b)$*	Correlation coefficients (R)	LOD (ng/g)	LOQ (ng/g)
Pb	$A = 10.748C + 0.04$	0.9918	0.60	2.0
Cd	$A = 101.2C + 3.7$	0.9999	0.06	0.2
Cr	$A = 4.5C + 7.0$	0.9987	0.34	1.1
Cu	$A = 4791.2C + 8.1$	0.9999	0.12	0.4
Zn	$A = 13.1C + 3.9$	0.9995	0.33	1.1
Ni	$A = 61.4C + 5.5$	0.9999	0.18	0.6
Fe	$A = 430.1C + 101.0$	0.9992	0.90	3.0
Mn	$A = 5023.4C + 42.7$	0.9998	0.15	0.5
Al	$A = 1208.0C + 409.4$	0.9988	0.30	1.0

*A = Absorbance; a = Slope; C = Concentration (µg/g); b = intercept

two kind production process were comparable with the same analytical method. Each sample was independently digested and analyzed by triplicate. The average concentrations for each of all heavy metals in the different production technology types and categories of sample were shown in Table-5.

TABLE-5
RESULTS OBTAINED IN THE DETERMINATION OF
HEAVY METALS AND COMPARATIVE PRODUCTION
PROCESS IN VEGETABLE EDIBLE OILS SAMPLES

Element	Soybean oil (µg/g) ± RSD (%)		Rapeseed oil (µg/g) ± RSD (%)	
	Squeeze	Extraction	Squeeze	Extraction
Pb	0.0205±4.5	0.0124±5.5	0.0315±3.5	0.0421±4.1
Cd	0.0241±3.5	0.0214±3.2	0.0185±2.6	0.0135±0.7
Cr	3.7220±2.7	2.5788±3.8	3.8591±3.7	5.7647±1.5
Cu	0.0146±4.1	0.0054±4.4	0.0112±4.0	0.0216±2.2
Zn	0.1009±2.6	0.0415±4.3	0.1589±0.4	0.0971±1.3
Ni	0.0458±3.7	0.0524±6.9	0.0371±3.4	0.0496±1.4
Fe	0.8410±1.3	0.9884±1.2	0.6814±2.6	0.6878±2.1
Mn	0.0035±7.0	0.0060±6.7	0.0232±5.4	0.0034±4.7
Al	0.5998±1.2	0.4480±0.7	0.3079±4.8	0.5887±7.0

The comparison experiments demonstrate that the heavy metals distribution is little effect of different production process types of vegetable edible oil products. The high concentration heavy metals in the squeeze technics vegetable edible oil is not "high level" as is popularly believed, because our current squeeze technics can't reach the national standard, so vegetable seed oil needs refining and removing part of heavy metals. In addition, test samples with heavy metals level are distributed irregularly and they are random. This presence can be due to the following factors such as different materials, different growing areas, treatment processes or packaging procedures.

Conclusion

In this paper, the developed procedure provides a sensitive and simple approach for the determination of heavy metals was carried out using microwave digestion with nitric acid followed by ICP-OES analysis. Different samples were analyzed and results obtained were used to make a comparison different production process types of vegetable edible oils. To the best of our knowledge, this is the first time that this comparison was studied in China. In addition, the results observed in the analysis of the spiked samples clearly showed that the method could be used very reliably in the heavy metals analysis of vegetable edible oil by ICP-OES.

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