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Detection of Heavy Metal Contents in Sesame Oil Samples Grown in Korea Using Microwave-Assisted Acid Digestion

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ABSTRACT - This study aimed to determine heavy metal contents in sesame oil samples produced in Korea through microwave-assisted acid digestion without using an emulsifier. Three heavy metal, cadmium (Cd), lead (Pb) and arsenic (As) in twelve sesame oil samples were determined by ICP-MS. The validation of analysis method was checked by standard addition method (10 and 100 μg/kg). As a result, linearity (R^2) was above 0.999 and RSDs were lower than 4%. The recovery of Cd, Pb and As ranged between 98.5-101.6%, 100.3-101.3%, and 102.1-111.2%, respectively. The detected ranges in sesame oil samples were as follows; N.D. to 0.109 μg/g for Cd, 0.014 to 0.200 μg/g for Pb and 0.014 to 0.125 μg/g for As, respectively. Therefore, sesame seeds and products grown in heavy metal-polluted regions which are used as food should be given priority attention and consideration.

Key words: *heavy metal, microwave-assisted acid digestion, sesame oil*

Introduction

Vegetable oils are widely used in cooking, food processing, cosmetics, pharmaceuticals, and chemical industries[1]. Among many vegetable oils, sesame oil is described to be of high nutritive and biological values as well as excellent quality taste. These qualities make sesame oil an irreplaceable and a regular condiment on Korean dining table[2,3]. About 60,000 tons of sesame seeds were used in sesame oil production in Korea whose total domestic sesame oil consumption is 90,000 tons[4].

An important deciding factor in the assessment of quality on edible oils is the heavy metals composition. It is known that heavy metals affect the oils rate of oxidation, nutritional value, preservation properties, and storability. As such, the determination of heavy metal in vegetable oils is very important[5].

Korea has set the legal limits for lead (Pb) and arsenic (As) at 0.1 μg/g in edible oil, and Codex Alimentarius Commission (Codex) has the statutory limit in vegetable oils as well[6]. The European Community also fixed the legal limits for Pb concentration in vegetable oils at 100 μg/kg[7]. However, there is no international legal limit on cadmium (Cd) in vegetable oils or edible oils. Some researches on vegetable oil samples showed that there is no accumulation of heavy metals, especially cadmium, in oil[8], while other researchers suggested opposite results[9]. There have been numerous reports on levels of heavy metals in various foods. However, there are limited reports in oil products[8-10].

These are due to some difficulty in determining the heavy metals in organic liquids, such as edible oils, which may have relatively high matrix effect for analyzing quantitatively low concentration level of heavy metals[11,12]. Various articles have been published on the determination of heavy metals in edible oils at parts-per-billion (ppb) levels using different spectroscopic techniques[13,14] or emulsifiers[5,15]. In most cases, these methods are long and tedious with the consequent risk of sample contamination without any loss of analyte.

This study used an alternative procedure of simple dilution of oil with inorganic solvent, such as nitric acid, to determine the heavy metals in sesame oil samples. The quantitative analysis of As, Cd and Pb in twelve newly breaded varieties of sesame oil using a microwave-assisted acid digestion method without an emulsifier was investigated.

Materials and Methods

Reagents

Analytical grade reagents of nitric acid (Dongwoo Fine-Chem, Kyounggi, Korea) and hydrogen peroxide (Sigma-Aldrich, St. Louis, MO, USA) were used in the acid digestions. Each standard solution of As, Cd and Pb was prepared by diluting with 2% (v/v) nitric acid. To avoid contamination from various ions, all sorts of laboratory glasswares and plastic

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wares used were immersed in approximately 20% nitric acid and rinsed with ultrapure water prepared from a Milli-Q SP Reagent Water System (18 MΩ, Millipore, Bedford, MA, USA).

Sample Preparation

Five samples of different varieties of sesame seeds were obtained from Rural Development Administration (Suwon, Korea), and another seven samples of those were collected from the sesame producing districts in Korea. These samples of sesame seeds were put in an electric roaster and roasted for 25 minutes at 135°C temperature. The samples of sesame oil were produced by mechanical pressing unit with a 600 kgf/cm from the roasted sesame seeds[2,16].

Digestion of samples

A modified version of digestion method by Tinggi [1998][17] was used to determine the content of heavy metals in twelve samples of sesame oil. Portions of around 0.2 g of each sesame oil sample was added with 7 ml mixture of acid and oxidant, nitric acid (65%) and hydrogen peroxide (30%) at 9:1 ratio in Teflon vessels, and then placed in a microwave oven (CEM Mars, CEM Corp., Matthews, NC, USA) for digestion. The digestion was carried out at four stages. Instrumental parameters for microwave digestion are shown in Table 1.

The digestion flasks were cooled to room temperature. The extracts were then evaporated to a semidried mass to remove excess acid and diluted with 50 μg/L indium (In) in 2% nitric acid to 10 ml volumetric flasks. To assure the accuracy of the data, a regent blank (without sample) was performed in triplicate through the same procedures. Blanks and standard solutions were prepared in a similar acid matrix. All experiments were conducted at room temperature.

Table 1. Experimental scheme for the digestion of sesame oil using microwave oven

Step	Temp (°C)	Time (min.)	Max. power(W)
1	0-120	5	1,000
2	120	5	
3	120-200	10	
4	200	30	

Table 2. Optimal ICP-MS conditions using analytical method of sesame oil

Descriptions	Conditions
RF power/W	1300
Nebulizer	Concentric type
Plasma gas flow rate/ L min^{-1}	10.00
Auxiliary gas flow rate/ L min^{-1}	0.50
Nebulizer gas flow rate/ L min^{-1}	0.95

Analytical conditions of the ICP-MS

The heavy metals in sesame oil samples were quantitatively measured by an Agilent 7500a ICP-MS (Agilent Technologies, Tokyo, Japan). The ICP-MS measurement condition was optimized for the determination of In. An internal standard of m/z 115, 20 μg/L was used in the quantitative analysis of this study. The optimal analysis conditions for ICP-MS are shown in Table 2.

Method validation

Little suitable Standard Reference Material (SRM) was commercially available for determining the heavy metal contents in edible oil or fat. In other studies conducted determination of heavy metals contents in oily food, the SRM have been replaced by the typically agricultural SRM or others as in water dropwort powder[18,19]. In this study, the accuracy of this method was validated by analyzing SRM of spinach leaves 1577c (NIST, USA), which have a certified value of Cd, Pb and As.

Some reported that the spiked concentration of heavy metals in edible oil were at very low level which is below 10 μg/kg and have resulted to noise and instrumental interference effects[20]. Also, in this study, the efficiency of the microwave-assisted digestion method was checked by the spiked levels of heavy metals in sesame oils samples at 10 and 100 μg/kg. The calibration was performed by using standard solutions in 2% nitric acid and the calibration curve levels of Pb, Cd and As were 0, 1, 5, 10, 25, 50, 100 μg/kg.

Results and Discussion

Validation and analysis method

This study used the microwave-assisted acid digestion method without emulsifier to analyze more easily and quickly the heavy metals contents in sesame oils. The data revealed an excellent coefficient of correlation range; linearity (R^2) of Cd, Pb and As were all above 0.999 and Relative Standard Deviations (RSDs) were lower than 4% (Table 3). The method detection limit (MDL) and method quantification limit (MQL) was calculated using the sigma method[21]; the MDLs

Table 3. Validation method of Cd, Pb and As in sesame oil using ICP-MS

	Cd	Pb	As
MDL (μg/L)	0.59	0.47	0.55
MQL (μg/L)	1.19	0.94	1.11
Linear equation	Y = 0.98X – 0.18	Y = 5.31X + 0.58	Y = 0.87X – 0.02
R^2	0.9998	0.9999	0.9998
Precision (%)	2.24	2.87	3.42
Recovery (%)	100.1	100.8	106.7

Table 4. Results of recovery test using standard addition method in sesame oil

Heavy metal	Spiked conc.			
	10 μg/kg		100 μg/kg	
	Detected conc. (μg/kg)	Recovery (%)	Detected conc. (μg/kg)	Recovery (%)
Cd	10.2 ± 2.2	101.6	98.5 ± 1.5	98.5
Pb	10.0 ± 2.2	100.3	101.3 ± 4.3	101.3
As	11.1 ± 2.5	111.2	102.1 ± 2.5	102.1

Table 5. The efficiency of heavy metal concentrations in standard reference materials (NIST SRM 1577c spinach leaves)

Heavy metal	Certified value (μg/g)	Detected value (μg/g)	Efficiency (%)
Cd	2.890	2.529 ± 0.090	87.5
Pb	0.200	0.226 ± 0.006	112.8
As	0.068	0.059 ± 0.006	86.9

were 0.59, 0.47 and 0.55 μg/L, and MQLs were 1.19, 0.94 and 1.11 μg/L for Cd, Pb and As, respectively.

In order to check the accuracy of the proposed methodology, the spike and recovery experiments were carried out for each element at 10 and 100 μg/kg. The results are shown in Table 4. The accuracy and precision of the results, estimated in a percent average of the standard addition recoveries, was higher than 98% at both spiked levels; Recoveries were found to be 98.5-101.6%, 100.3-101.3% and 102.1-111.2% for Cd, Pb and As, respectively.

The accuracy and precision of this method was further validated by analyzing the SRM1577c, spinach leaves which have a certified value of Cd, Pb and As. Table 5 showed good results with certified values achieved.

There have been many attempts of using emulsifiers to the analysis of heavy metals in edible oils and fats[5,15,22]. Emulsifiers such as Triton X-100, Tween 20 and Span 20 were used in the analysis of edible oils and fats. According to the results, the optimum amount of oil in the emulsion was in the range *ca.* 2-35% in most of the surfactants studies and the digestive method using emulsifiers may reduce the organic content of the sample by at least 95%. However, the problem when using emulsions may reside in maintaining the stability of samples for an acceptable period of time. Therefore, in analyzing method using emulsion was to obtain optimum formation and stabilization conditions of the emulsion, type and quantity of the emulsifier, stirring time and mode, *etc*. Study for quantitative determination of metals in olive oil using direct emulsion nebulization suggested that the most stable emulsion be obtained with Triton X-100 and the emulsion may be stable with 1.5 ml Triton X-100 for at least 4 hours with up to 4 g of oil[15].

In this study, microwave digestion employed nitric acid as digesting acid and hydrogen peroxide as alternative to break down the bonds in lipid molecules. The digestive method in this study takes less than 1 hour, saving more time to reach complete digestion. Chen et al. reported that sulfuric acid *per se* as digesting acid was unable to completed digest lipid, but mixtures of sulfuric acid and nitric acid presented comparable digestive efficiencies[13]. On the other hand, the digestive was vigorous during the heating processes, when the digestion was carried out in the mixture of sulfuric acid and nitric acid. Therefore, these results suggested that the microwave-assisted digestion with nitric acid may offer a safe and simple alternative for the analysis of a large number of oil samples at a given a minimum time.

Heavy metal contents in sesame oil samples

Twelve samples of sesame oil were analyzed for their heavy metals contents by ICP-MS with microwave-assisted acid digestion method as described above. The heavy metal contents in twelve samples of sesame oil grown in Korea are shown in Table 6. The detected ranges in sesame oil samples were as follows: N.D. to 0.109 μg/g for Cd, 0.014 to 0.200 μg/g for Pb and 0.014 to 0.125 μg/g for As, respectively.

According to Korea's maximum permitted concentration (MPC) for heavy metals in edible oils, about 17% and 7% samples of sesame oils grown in Korea were above the legal limit for Pb and As, respectively. However, an excess rate of legal limit for Cd could not be estimated in sesame oil samples grown in Korea, because no legislation for Cd limits in edible oils currently exists in Korea and in other countries as well. These results suggested to set up domestic legal limits of Cd to ensure the quality assurance of sesame oils.

Table 7 showed the contents of heavy metals in vegetable oil samples in other countries as cited in literatures[1,13,19,20,23-25]. Vegetable oil samples, including sesame oils, grown in China were reported to range from 3.34 to 5.44 μg/g for Cd contents while oil samples from Turkey, Italy and Pakistan has much higher Cd contents compared to other countries. The detected values for Cd in sesame oil samples grown in Korea were much lower than the reported values in most other countries as shown in Table 6.

According to the results by Zhu et al.(2011), the Pb and As levels of vegetable oils in China ranged from 0.006 to 0.014 μg/g and 0.007 to 0.018 μg/g, respectively[19], similarly

Table 6. The contents of heavy metals (μg/g) in sesame oil samples, N = 12

Heavy metals	Mean	Range	Limit level in Korea
Cd	0.018	ND~0.109	-
Pb	0.055	0.014~0.200	0.1 (edible oils)
As	0.038	0.014~0.125	0.1 (edible oils)

Table 7. Reported contents of heavy metals (μg/g) in vegetable oil samples

Country	Oil samples	Cd	Pb	As	Reference
China	Sesame oil	5.27~5.44	0.014~0.018	0.015~0.018	19
	Olive oil	2.39~2.64	0.009~0.013	0.008~0.012	
	Sunflower oil	3.34~3.51	0.006~0.010	0.007~0.011	
UK	Sesame oil	-	ND~0.051	-	23
Italy	Sunflower oil	0.51~4.15[a]	0.005~0.016	-	1
Turkey	Olive oil	0.15[a]	0.03	-	25
	Sunflower oil	0.004	0.01	-	
	Olive oil	0.002	0.010	-	20
	Sunflower oil	0.7~1.9[a]	0.011~0.023	-	
Pakistan	Sunflower oil	1.70~6.18	0.79~4.29	-	24
Taiwan	Sesame oil	-	-	0.006, 0.011	13
	Olive oil	-	-	0.006, 0.012	
	Sunflower oil	-	-	0.005, 0.006	
	Vegetable oil	-	-	0.011	

[a]μg/kg

with those in other countries, except in Pakistan[1,13,19,20,23-25]. The Pb and As contents in sesame oil samples showed also similar range with other vegetable oils in China, although limited data about the presence of the heavy metals in sesame oil samples[13,13,19,23].

In terms of the mean value detected for Pb and As, sesame oil samples were found to have a similar values with those in other literatures. However, the maximum values (0.200 μg/g and 0.125 μg/g for Pb and As, respectively) detected in sesame oils grown in Korea were much higher compared to the top values detected in sesame oils in other literatures.

The sesame oil, among other sesame products, has been the main commercial product from sesame seeds in domestic markets[4] and it's consumption may be the contributing factor of dietary exposure route of heavy metals in Korean. The heavy metals have been known as hazardous substances when taken and accumulated in the human body may harm human organs since they do not decomposed. It is proven that Cd highly accumulated in human kidney and liver and causes "leukemia"[19]. Therefore, sesame seeds and products grown in heavy metal-polluted regions being used as food should be given priority attention and consideration.

For future study, the transition rate of Cd ion through the extraction process from sesame seed to sesame oil should be further investigated. Likewise, there should be an in-depth study, in terms of the relationship of each heavy metal-contaminated level in seeds.

요 약

본 연구에서는 유화제를 사용하지 않고 초단파 산분해법을 이용해 우리나라에서생산된 참기름의 중금속을 측정하고자 하였다. ICP-MS를 통해 12개의 참기름 시료에 오염된 카드뮴, 납, 비소의 3종 중금속을 분석하였다. 분석법의 검증 결과 카드뮴, 납, 비소 모두 직선성((r^2))이 0.99 이상이며 RSD는 4% 이하였다. 또한, 분석법의 정확성 및 효율성 측정을 위해 중금속 10 μg/g 과 100 μg/g 을 첨가한 시료를 분석한 결과, 회수율이 카드뮴 98.5-101.6%, 납 100.3-101.3%, 비소 102.1-111.2%로 우수하게 나타났다. 본 분석법을 이용하여 분석한 참기름 시료의 중금속 함량은 카드뮴 불검출~0.109 μg/g, 납 0.014~0.200 μg/g, 비소 0.014~0.125 μg/g 이었다. 따라서, 중금속 오염지역에서 생산된 참깨 및 이를 이용한 가공품의 경우 섭취에 주의할 필요가 있다.

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