

# Determination of stable cesium and strontium in rice samples by inductively coupled plasma mass spectrometry

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**Abstract.** For long-term radiation dose assessment models, food ingestion is one of the major exposure pathways to human. In general, the stable isotopes can serve as analogues of radioisotopes. In this study, rice samples were collected from 30 paddy fields in Si Sa Ket, Yasothon and Roi Et in the northeast of Thailand in November 2014. The concentrations of stable cesium (Cs-133) and strontium (Sr-88) in polished rice were determined by inductively coupled plasma mass spectrometry (ICP-MS). The standard reference material of rice flour (NIST 1568a) with spiked Cs and Sr was used to validate the analytical method. The concentration of Cs in polished rice from Si Sa Ket, Yasothon and Roi Et was  $0.158 \pm 0.167$  mg kg<sup>-1</sup>,  $0.090 \pm 0.117$  mg kg<sup>-1</sup> and  $0.054 \pm 0.031$  mg kg<sup>-1</sup>, respectively. The concentration of Sr in polished rice from Si Sa Ket, Yasothon and Roi Et was  $0.351 \pm 0.108$  mg kg<sup>-1</sup>,  $0.364 \pm 0.215$  mg kg<sup>-1</sup> and  $0.287 \pm 0.102$  mg kg<sup>-1</sup>, respectively. Comparison of the results with Japanese data before the Fukushima Di-ichi nuclear power plant accident showed that the concentrations of both Cs and Sr for Thai rice were higher than those for Japanese rice.

## 1. Introduction

Radioactive cesium (Cs-134;  $T_{1/2} = 2.06$  years, Cs-135;  $T_{1/2} = 2.3 \times 10^6$  years and Cs-137;  $T_{1/2} = 30.17$  years) and radioactive strontium (Sr-90;  $T_{1/2} = 28.1$  years) [1] have long half-lives and they play an important role to human because of their potential to harm the human body. Signs and symptoms of acute toxicity from external and internal exposure to high levels of radioactive cesium and radioactive strontium are similar to those observed in cases of high exposure to ionizing radiation. Depending on the radiation dose, symptoms may include those typical of acute radiation syndrome (vomiting, nausea, and diarrhea), skin and ocular lesions, neurological signs, chromosomal abnormalities, compromised immune function, and death. Limited human and animal data indicate that exposure to radioactive cesium can result in adverse effects such as reduced fertility, abnormal neurological development, genotoxicity, and possibly cancer [2]. Since radioactive strontium will accumulate in bone, bone itself and the soft tissues nearby may be damaged by radiation emitted over time. Radioactive strontium may cause cancer as a result of damage to the DNA in cells. An increase in leukemia was reported in one foreign population who swallowed relatively large amounts of Sr-90 (and other radioactive materials) in river water contaminated by a nuclear weapons plant. In the case of a breathing exposure, leukemia and cancers of the bone, nose, and lung were reported in animal studies. In addition, skin and bone cancer were reported in animals that received radiation at high doses to the skin [3]. In general, isotopes of the same element behave similarly in terms of their physical properties and chemical reactivity. Therefore soil to plant transfer factor of stable isotopes



can serve as analogues of radioisotopes, e.g., stable Cs for Cs-137 and stable Sr for Sr-90 [4]. Because of very low concentration of radioactive materials in the environment of most countries in the world, the concentration of stable element related to long-lived radionuclides was studied. For long-term radiation dose assessment models, food ingestion is one of the major exposure pathways to human [5]. Rice (*Oryza sativa*) is a diet staple for almost half of the world's population including Thailand. Rice is the most important economic crop of Thailand. Thailand is one of the world's biggest rice producers and exporter. Consequently, safety assessment for Thai is required to consider rice as the critical food. However the data of stable cesium and strontium in Thai rice are limited. Therefore, the levels of these elements in rice should be investigated.

Several methods have been widely used for the determination of elemental concentrations in rice samples including graphite furnace atomic absorption spectrometry (GFAAS) [6], x-ray fluorescence (XRF) [7], instrumental neutron activation analysis (INAA) [8-9], inductively coupled plasma optical emission spectrometry (ICP-OES) [8, 10] and inductively coupled plasma mass spectrometry (ICP-MS) [5, 11]. The Cs and Sr contents in rice samples analyzed by various techniques have been reported. González *et al* [12] studied the concentration of Sr in rice samples from Spain including Valencia, Tarragona, Murcia and Extremadura, Japan, Brazil and India by ICP-OES. Nadimi-Goki *et al* [13] investigated the Sr content in rice samples from Italy by ICP-OES. The concentrations of Cs and Sr in rice samples from Jamaican market were analyzed by INAA reported by Antoine *et al* [14]. The Cs and Sr compositions in rice samples collected from Japan were determined by ICP-MS studied by Uchida *et al* [5] and Tsukada *et al* [11]. Cheajesadagul *et al* [15] reported the Cs and Sr levels in Thai rice and foreign (France, India, Italy, Japan and Pakistan) rice samples analyzed by high resolution ICP-MS. Among the techniques widely used, ICP-MS is the most powerful technique for elemental analysis with the advantage of simultaneous determination of multi-element, wide linear range, low detection limit and rapid analysis.

In this study, rice samples were collected from 30 paddy fields in Si Sa Ket, Yasothon and Roi Et in the northeast of Thailand in November 2014. The concentrations of Cs and Sr in the polished rice (or white rice) samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). The obtained results of Cs and Sr concentrations of Thai rice were compared with available literature data.

## 2. Materials and methods

### 2.1 Reagents and standards

All the chemical reagents used were supra-pure analytical grade. Water (>18 MΩ cm) treated with a Milli-Q water system (Millipore Corporation; Billerica, MA, USA) was used throughout the research. The standard solutions were purchased from Agilent Technologies, (New Haven, CT, USA). Standard reference material used to validate the method was rice flour (NIST 1568a) from National Institute of Standards and Technology (NIST; MD, USA).

### 2.2 Sample collection and preparation

Rice samples were collected from 30 paddy fields in Si Sa Ket, Yasothon and Roi Et in the northeast of Thailand in November 2014. Rice grains (2-3 kg) were harvested from the paddy field. After dehulling and polishing, the polished rice or white rice samples were obtained. All polished rice samples were dried in an electric oven at 50-60°C and ground to a fine powder by the high speed blender (1093 Cyclotec Sample Mill, Hoganas, Sweden). The rice powders were dried again in an oven at 50-60°C till constant weight, kept in polyethylene containers and stored in a desiccator until chemical analysis.

All dry rice samples (0.5 g) were digested in PTFE vessels on a hot plate with 65% HNO<sub>3</sub> and 48% HF. After digestion, the samples were evaporated to dryness and the residues were dissolved in 65% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub>. After dryness again, the residues were dissolved with 2% HNO<sub>3</sub> as described by Ogiyama *et al* [10] with slight modifications. Sample digestions were done in triplicate.

### 2.3 Determination of Cs and Sr by ICP-MS

After diluting the digested samples to a suitable concentration, stable Cs and Sr in rice samples were determined by ICP-MS (Agilent 7900, Agilent Technologies, USA). The instrumental operating conditions for the determination of the elements are summarized in Table 1. Indium (In) was used for internal standard to compensate for change in analytical signal during the operation. Standard solutions were prepared from Agilent multi-element solution and used to get calibration curves. The quantification was based on at least 5 point external calibrations. Rice flour (NIST 1568a) with spiked Cs and Sr from Agilent multi-element solution was used to validate the analytical procedure.

**Table 1.** ICP-MS operating conditions.

Parameter	Condition
Nebulizer	Mira Mist
Spray chamber	Scott type
Sampling cone	Nickel
Skimmer cone	Nickel
RF power	1550W
Carrier gas flow	0.75 L min <sup>-1</sup>
Dilution gas flow	0.25 L min <sup>-1</sup>
Spray chamber temperature	2 °C
Nebulizer pump	0.1 rps

## 3. Results and discussion

### 3.1 Method validation

Measurement of calibration standard solutions provided linear response with correlation coefficients of 1.000 as shown in Table 2. The limit of detection (LOD) of Cs and Sr determined by ICP-MS was evaluated from three times the standard deviation of ten replicate blank measurements. The limit of detection (in mg kg<sup>-1</sup>) was obtained from LOD (in (µg L<sup>-1</sup>)) multiplied by the overall dilution factor given in Table 2 which is adequate for the determination of Cs and Sr concentrations in rice sample. The limit of quantification (LOQ) of Cs and Sr calculated from ten times the standard deviation of ten replicate blank determinations was also presented in Table 2.

**Table 2.** Equation of calibration curve, LOD and LOQ in ICP-MS measurement.

Element	Cs	Sr
Analytical mass	133	88
Regression equation	$y = 0.4826x + 0.0081$	$y = 0.4199x + 0.0143$
Regression, R <sup>2</sup>	1.000	1.000
LOD (µg L <sup>-1</sup> )	0.015	0.212
LOQ (µg L <sup>-1</sup> )	0.051	0.709
LOD (mg kg <sup>-1</sup> )	0.0015	0.021

Since there is no data of Cs and Sr in the standard reference material of rice flour (NIST 1568a), the standard reference material of rice flour spiked with Cs and Sr was included in the digestion and analytical procedure for quality control. The recoveries of Cs and Sr were summarized in Table 3. The result showed good agreement between techniques. The recoveries for reference materials spiked with Cs and Sr were within acceptable limits of ±15%. Precision, expressed as the relative standard deviation (RSD) of the three independent measurements was within 5%.

**Table 3.** Analytical results of rice flour (NIST 1568a) spiked with Cs and Sr obtained by ICP-MS (mean  $\pm$  standard deviation for  $n = 3$ ).

Spiked concentration (mg kg <sup>-1</sup> )	Recovery (%)
<i>Cs</i>	
0.025	88.2 $\pm$ 1.7
0.05	96.6 $\pm$ 0.1
0.25	96.6 $\pm$ 2.8
0.5	97.4 $\pm$ 1.1
0.75	97.1 $\pm$ 2.2
1.0	97.3 $\pm$ 1.2
<i>Sr</i>	
0.05	90.1 $\pm$ 0.9
0.1	93.4 $\pm$ 0.7
0.5	93.7 $\pm$ 0.4
1.0	94.2 $\pm$ 1.2
1.5	95.8 $\pm$ 0.9
2.0	95.9 $\pm$ 2.1

### 3.2 Stable Cs and Sr in rice samples

Summary Statistics of Cs and Sr concentrations in rice samples determined by ICP-MS were presented in Table 4. All rice samples had the Sr content higher than the Cs content. Both Cs and Sr showed the arithmetic mean concentration higher than the geometric mean concentration for all rice location. The arithmetic mean concentration of Cs was highest in rice sample from Si Sa Ket and lowest in rice sample from Roi Et. The concentration of Cs in polished rice from Si Sa Ket, Yasothon and Roi Et was  $0.158 \pm 0.167$  mg/kg,  $0.090 \pm 0.117$  mg/kg and  $0.054 \pm 0.031$  mg/kg, respectively. The arithmetic mean concentration of Sr was highest in rice sample from Yasothon and lowest in rice sample from Roi Et. The concentration of Sr in polished rice from Si Sa Ket, Yasothon and Roi Et was  $0.351 \pm 0.108$  mg/kg,  $0.364 \pm 0.215$  mg/kg and  $0.287 \pm 0.102$  mg/kg, respectively. The maximum/minimum concentration ratio of Sr was less than 10 showing the narrow distribution range for all location. Whereas, the wide distribution range of Cs was found with the maximum/minimum concentration ratio of 57, 25 and 20 for rice samples from Si Sa Ket, Yasothon and Roi Et, respectively. The concentrations of both Cs and Sr observed from this work were higher than the previous work reported by Cheajesadagul *et al* [15] possibly due to the different year of rice cultivation [16] and the polishing rate or milling ratio for rice preparation [17]. Tsukada *et al* [18] reported that 7% and 10% of the total stable Cs were found in polished rice and bran, respectively. 0.6% and more than 99% of the total Sr were observed in polished rice and in the non-edible parts [19].

The data of Cs and Sr from this study were also compared with the previous data as shown in Table 5. Both Cs and Sr data of Thai rice were higher than those of Japanese rice. Although the Cs concentration of Thai rice was higher than that of Jamaican rice, the Sr concentration of Jamaican rice was higher than that of Thai rice about 10 times. The Sr content of Thai rice was also lower than Spanish rice and Chinese rice. The levels of Cs and Sr in rice samples depend on the topography, soil properties and soil conditions [4, 20].

The estimated daily intake (EDI) of elements resulting from rice consumption was calculated from the elemental content multiplied by the average per capita daily consumption of rice. The daily average rice consumption in Thailand was about 233 g which is equivalent to yearly amount of about 85 kg per person [22]. The EDI of Cs and Sr for Thai rice consumption was 0.024 and 0.078 mg day<sup>-1</sup>, respectively. The EDI for male and female (in Table 6) was evaluated from the body weight of 69 and 57 kg, respectively. The EDI of Sr for male and female from this study was lower than the minimal risk level (MRL) of stable Sr for intermediate-duration oral exposure (2.0 mg kg<sup>-1</sup> day<sup>-1</sup>) [3]. The MRL

**Table 4.** Summary Statistics of Cs and Sr concentrations in rice samples determined by ICP-MS.

Location	Cs (mg kg <sup>-1</sup> )	Sr (mg kg <sup>-1</sup> )
<b>Roi Et</b>		
Number of sample	10	10
Minimum	0.005	0.182
Maximum	0.107	0.521
Max./Min.	20	3
Median	0.053	0.260
Arithmetic mean	0.054	0.287
Geometric mean	0.042	0.274
<b>Si Sa ket</b>		
Number of sample	10	10
Minimum	0.010	0.231
Maximum	0.557	0.501
Max./Min.	57	2
Median	0.133	0.312
Arithmetic mean	0.158	0.351
Geometric mean	0.086	0.337
<b>Yasothon</b>		
Number of sample	10	10
Minimum	0.015	0.107
Maximum	0.381	0.825
Max./Min.	25	8
Median	0.038	0.313
Arithmetic mean	0.090	0.364
Geometric mean	0.051	0.312

**Table 5.** Cs and Sr concentrations in rice samples from different countries.

Sample	Cs (mg kg <sup>-1</sup> )		Sr (mg kg <sup>-1</sup> )	
	Mean ± SD <sup>a</sup>	Range	Mean ± SD <sup>a</sup>	Range
Thai rice (this study) ( <i>n</i> =30)	0.101 ± 0.123	0.005 - 0.557	0.334 ± 0.149	0.107 - 0.825
Japanese rice ( <i>n</i> =37) [5]	0.003 <sup>b</sup>	0.0004 - 0.017	0.072 <sup>b</sup>	0.014 - 0.14
Japanese rice ( <i>n</i> =20) [11]	0.0017 ± 0.0017	0.00045 - 0.0065	0.070 ± 0.017	0.044 - 0.12
Jamaican rice ( <i>n</i> =1) [14]	<0.004	No data	3.16	No data
Spanish rice-Valencia ( <i>n</i> =52) [12]	No data	No data	0.9 <sup>b</sup>	<0.2 - 3.7
Spanish rice-Murcia ( <i>n</i> =11) [12]	No data	No data	1.5 <sup>b</sup>	1.1 - 3.0
Chinese rice ( <i>n</i> =18) [21]	No data	No data	1.582 ± 0.434	0.932 - 2.253

<sup>a</sup>Mean ± standard deviation<sup>b</sup>Mean**Table 6.** Estimated daily intake (EDI) of Cs and Sr for Thai rice consumption.

Element	EDI (mg day <sup>-1</sup> )	EDI (mg kg <sup>-1</sup> day <sup>-1</sup> )	
		Male	Female
Cs	0.024	0.0003	0.0004
Sr	0.078	0.0011	0.0014

represents an estimate of daily human exposure that is likely to be without an appreciable risk of adverse health effects. Thus the consumption of Thai rice would be safe for Sr. There is no data of oral or inhalation MRLs for stable Cs due to lack of available data, therefore it was not possible to compare the results.

#### 4. Conclusion

Stable Cs and Sr in rice samples collected from the paddy field in the northeast of Thailand were determined by ICP-MS. The ICP-MS technique proved to be accurate and reliable to analyze the Cs and Sr in rice samples. The obtained results would be valuable to be the database of Thai rice and further fundamental knowledge on the intake of Cs and Sr through food ingestion. For long-term radiation dose assessment models, these data would be useful to evaluate the transfers of Cs and Sr from soil to rice which they would be served as analogues of radioisotope information. Therefore the determination of stable Cs and Sr in the paddy soil samples with the same region of rice cultivation will be studied.

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