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Original Article

Instrumental neutron activation analysis to determine inorganic elements in paddy soil and rice and evaluate bioconcentration factors in rice

Prapamon Seeprasert,[a, c, 1] Patana Anurakpongsatorn,[a, *, 1] Sirinart Laoharojanaphand,[b]
Arporn Busamongkol[b]

[a] Department of Environmental Technology and Management, Faculty of Environment, Kasetsart University, Bangkok, 10900, Thailand
[b] Thailand Institute of Nuclear Technology (TINT), Ladyao, Chatuchak, Bangkok, 10900, Thailand
[c] Occupational Health and Safety Program, School of Health Science, Mae Fah Luang University, Chiang Rai, 57100, Thailand

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ABSTRACT

Increased anthropogenic activity, especially in thriving industries and mining activity, has led to the accumulation of inorganic elements in the soil. This study applied neutron activation analysis for the determination of inorganic element concentrations in paddy soils and quantified the nutrient value of paddy rice cultivated on various agricultural sites throughout Thailand. The determination accuracy of the elements—U, As, Sb, W, Mn, K, La, Cr, Hf, Cs, Sc, Fe, Co, Cd and Zn was assessed using National Institute of Standards and Technology standard reference materials; the results were satisfactory, showing low relative error. High analytical precision was also observed. Cadmium was selected to check the linearity of the calibration curve against a Cd standard. For a calibration curve in the range 1–9 μg, a correlation coefficient of 0.997 was found. Trace amounts of U, As, Sb, W, Mn, K, La, Cr, Hf, Cs, Sc, Fe, Co, Zn and Cd were also found in the soil samples. However, the Co, Cd, and Zn concentrations were especially high in agricultural sites in Tak province. The elemental concentrations in rice followed the order K > Zn > Mn. The data obtained are of potential benefit for the development of trace element supplementation in food.

Introduction

Increased anthropogenic activity, especially in thriving industries and mining activity, has led to the accumulation of inorganic elements in soil (Alloway, 1995). Some inorganic elements are non-biodegradable, have no metabolic role in living organisms, are intoxicants to humans and have no constructive purpose in the human body (Smolders, 2001). Although some are micronutrients for plants, at high soil solution concentrations, they can become toxic to plants and microorganisms (Martin et al., 2007). The activation of elements with neutrons has been used as an analytical procedure. The approach has been compared with techniques such as atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) to analyze some selected elements in rice samples collected from the market in Portugal and Spain (Tsukada et al., 2005; Parengam et al., 2010; Pinto et al., 2016). They found the mean contents of essential elements were: P (1189 μg/g), K (746 μg/g) Mg 294 μg/g, Ca 84.7 μg/g, Zn (13.3 μg/g), Na (8.8 mg/kg), Mn (8.3 μg/g), Fe (7.5 μg/g), Cu (1.9 μg/g), Mo (0.55 μg/g), Se (0.18 mg/kg) and Co (0.12 mg/kg). However, methods such as AAS and ICP-MS have several disadvantages, such as only allowing single-element analysis and the sample are destroyed during the analysis. Neutron activation analysis (NAA) is suitable for multi-element analysis (Tsukada et al., 2007) and is non-destructive. The reasons for the selection of NAA as the main analytical method in the current study were its high sensitivity and the ease with which data can be computer processed.

Rice is a staple cereal crop in a large part of the world and in Thailand, the production and exportation of rice represents a significant component of the economy (Office of Agricultural Economics, 2016). The elemental composition of rice is of great importance in relation to its nutritional value (Jiang et al., 2008).

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[*] Corresponding author.
E-mail address: fscipna@ku.ac.th (P. Anurakpongsatorn).
[1] Prapamon Seeprasert and Patana Anurakpongsatorn contributed equally to this work.

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However, the critical paths of nutrients in rice differ across harvest sites due to agricultural field conditions, such as the type of rice and the element concentrations in the soil and in general, the element contents of rice follow the order Mn > Zn > Al (Isao et al., 2005; Liu et al., 2007; Laoharojanaphand et al., 2009). However, the trace metals Mo, Cu and Co have also been found in red rice from Japan (Isao et al., 2005). Thai jasmine rice was found to contain two minor (K and Mg) and six trace (Al, As, Br, Cl, Mn and Zn) nutrient elements (Laoharojanaphand et al., 2009). Kongsri et al. (2016) reported on selected elements in Thai jasmine rice cultivated in different regions: K (0.08–0.17%) > Mn (8.22–25.17 μg/g) > Br (0.1–0.75 μg/g) > As (0.04–0.4 μg/g).

The bioconcentration factor (BCF) is calculated by dividing the concentration of an element in an unpolished grain by its concentration in the soil rhizosphere. It is an important parameter that is widely used to estimate the uptake of elements from soils to plants; a value of BCF >1 indicates that the plant can translocate, absorb and accumulate the element in its tissue (Liu et al., 2007). There are scant data on the elemental concentrations in paired rice grain and soil samples collected from a variety of sites, especially in Thailand. The aims of the current study were to apply the NAA technique to determine element concentrations in paddy soil and rice and to assess the nutrient value of Thai paddy rice cultivated at various agricultural sites in Thailand.

Materials and methods

Sample collection and preparation

The soil and rice samples were collected from paddy fields in Tak, Angtong and Phattalung provinces, Thailand. A stainless steel core sampler was used to collect soil cores to a 20 cm depth in each field. Rice samples were of different species depending on the paddy field. As such, Thai jasmine rice (Khow Dawk Ma Li 105) was sampled in Tak province, Thai Pathumthani fragrant rice in Angtong province and red rice (Sung Yod) in Phattalung province. The soil samples were dried at 105 °C and the rice was threshed and dried at 70 °C. NAA samples were pulverized using an agate mill.

Neutron activation analysis procedure

The elemental concentrations of the soils and rice were determined based on methods from a previous study (Laoharojanaphand et al., 2009). In brief, approximately 50 mg of soil and 100 mg of rice were separately sealed in small polyethylene bags. Several bags were placed together into a polyethylene capsule or aluminum can. Samples were irradiated at 1200 kW in the open pool-type Thai research reactor (TRR-14/MI) at the Thailand Institute of Nuclear Technology, which uses low-enriched uranium as the fuel and light water as a moderator and coolant. Standard reference materials (SRMs), prepared using the same procedures, were also irradiated in this way. The concentration of each element was determined by comparison with the appropriate SRM. The irradiation conditions were as follows.

Intermediate irradiation for intermediate half-life radionuclides (U, As, Sb, W, Mn, K and La): Each sample was irradiated for 9–12 h at an epithermal out-core neutron flux of 1.8–2.7 × 10^9 n/cm/s, where n is the neutron density, followed by a decay time of 13 h. For Cd, the irradiation was carried out on a rotary specimen rack (a “Lazy Susan” type) at a neutron flux of 4.47 × 10^{11} n/cm/s for 12 h followed by a decay time of 3 d.

Long irradiation for long half-life radionuclide (Cr, Hf, Cs, Sc, Fe, Co and Zn): Each sample was irradiated for 48 h on a rotary specimen rack at a neutron flux of 4.5 × 10^{11} n/cm/s followed by a decay time of 14 d.

After the appropriate decay time, each sample was placed above a high-purity germanium detector in a fixed position. The gamma-ray activities of the radioisotopes in each sample were counted for 1200–1800 s. The gamma-ray spectra were processed using the HPGe detector with digital gamma-ray spectrometer (DSPEC jr 2.0 model, ORTEC; Oak Ridge, TN, USA) and GammaVision Gamma Spectroscopy software (Version 6.1; ORTEC; Oak Ridge, TN, USA) for peak area evaluation. Peak areas were compared with the SRMs. The SRMs used in this study were “2711 Montana Soil” and “2702 Inorganics in Marine Sediment” from The National Institute of Standards and Technology (NIST).

Calculation of element concentrations

The concentration of each element was determined using a comparison technique as shown in Equation (1):

$$W_{sample} = \frac{\left[A_{0\ Sample}\right]\ \left[M_{standard}\right]\ \left[W_{standard}\right]}{\left[A_{0\ standard}\right]\ \left[M_{sample}\right]} \tag{1}$$

where W is the concentration of the sample or SRM, A_0 is the peak area of gamma-ray activity at time = 0 for the sample or SRM and M is the weight of the sample or SRM.

The peak area of gamma-ray activity at time = t was calculated using Equation (2):

$$A_0 \ = \ A_t\, e^{\lambda t} \tag{2}$$

where A_0 is the peak area of gamma-ray activity at time = 0 for the sample or SRM, A_t is the peak area of gamma-ray activity at time = t for the sample or SRM, λ is the decay constant.

Determination of limit of detection

The limit of detection (LOD) was determined according to Gilmore and Hammimgway (1995) using the standard peak and background of the samples. A standard cadmium working solution and the SRMs were irradiated, decayed and counted using previously obtained optimum conditions and LOD was determined using Equation (3):

$$\mathrm{LOD} = \ 2.71 + 3.29\sqrt{\mathrm{B}\left(1 + \frac{\mathrm{n}}{2\mathrm{m}}\right)} \tag{3}$$

where n is the number of channels within the peak region, m is the number of channels within the background region, B_1 is the sum of activity counts at lower background region m channels, B_2 is the sum of activity counts at upper background region m channels and $B = [(B_1 + B_2)\ n]/2m$.

Determination of accuracy and precision

The SRMs “2711 Montana Soil” and “2702 Inorganics in Marine Sediment” were analyzed using the NAA technique under the previously obtained conditions and with other SRMs as comparators for quality assurance in terms of accuracy, relative error and percent relative standard deviation (%RSD). For Cd, standard solutions with concentrations in the range 1–9 μg were placed in clean polyethylene bags. Several bags were heat-sealed and then irradiated. The standard Cd working solutions and SRMs were irradiated, decayed and counted under the previously obtained conditions. The concentrations of Cd in the SRMs were compared to the standard Cd working solution.

Results and discussion

Fourteen elements—U, As, Sb, W, Mn, K, La, Cr, Hf, Cs, Sc, Fe, Co and Zn—were found in the SRMs, including the “2711 Montana Soil” and “2702 Inorganics in Marine Sediment” (Table 1). It is possible to analyze one SRM using the NAA technique and to use another as a comparator for quality assurance, that is for the determination of accuracy. Cd was only found in “2711 Montana Soil”. Then, the concentration of Cd in the SRMs was obtained by comparison with the standard Cd working solution. The relative error and precision are shown in Table 1.

The accuracy of NAA determination of all elements was satisfactory, with low relative errors in the range −3–2%, indicating that the measured and certified values did not differ significantly. The precision of the analysis was high, with less than 6% RSD. Overall, it was found that NAA had high precision (less than 10% RSD) and good accuracy (relative error of less than 10%). The linearity of the Cd calibration curve over the range 1–9 μg was confirmed with a correlation coefficient of 0.997. It can be concluded that NAA is a reliable method for the determination of various inorganic elements in soil.

Element concentrations

The concentrations of inorganic elements in the soil samples are shown in Table 2. The mean concentration ranges were: U (5.6–18.2 μg/g), As (6.1–23.6 μg/g), Sb (1.45–3.3 μg/g), W (2.7–8.2 μg/g), Mn (172–479.6 μg/g), K (0.7–1.5%), La (36.8–55.7 μg/g), Cr (44.8–73 μg/g), Hf (16.4–26.2 μg/g), Cs (8.6–16.7 μg/g), Sc (10.1–12.01 μg/g), Fe (1.8–3.5%) and Co (5.6–15.1 μg/g). Notably, Zn (82.6 μg/g) and Cd (59.9 μg/g) were only detected in soil collected from Tak province.

Most soil elements arise from natural weathering processes or anthropogenic activity, though an enhancement of U in the soil may derive from the use of chemical fertilizers (Tsukada et al., 2007). The presence of Zn and Cd in the soil samples from Tak province might have been due to non-ferrous mining adjacent to the sampling site (Pollution Control Department, Ministry of Natural Recourses and Environment, 2004; Simmons et al., 2005).

Table 2
Concentrations (mean ± standard deviation) of elements in soil samples (based on dry weight, n = 3).

Element	Province		
	Tak	Angthong	Phatthalung
U (μg/g)	11.35 ± 0.01	5.60 ± 0.32	18.23 ± 0.21
As (μg/g)	23.56 ± 4.29	6.13 ± 0.18	8.75 ± 0.01
Sb (μg/g)	3.34 ± 0.33	1.45 ± 0.27	1.61 + 0.06
W (μg/g)	2.66 ± 0.19	3.61 ± 0.50	8.20 ± 0.37
Mn (μg/g)	479.60 ± 3.17	254.35 ± 3.88	171.95 ± 2.50
K (%)	1.18 ± 0.33	1.52 ± 0.57	0.67 ± 0.03
La (μg/g)	36.76 ± 5.06	45.16 ± 0.51	55.69 ± 3.30
Cr (μg/g)	70.11 ± 0.02	72.95 ± 2.01	44.75 ± 0.20
Hf (μg/g)	16.66 ± 0.18	16.38 ± 0.19	26.15 ± 0.11
Cs (μg/g)	15.59 ± 0.09	8.57 ± 0.20	16.67 ± 0.13
Sc (μg/g)	12.01 ± 0.14	10.58 ± 0.16	10.08 ± 0.05
Fe (%)	3.51 ± 0.10	1.98 ± 0.03	1.75 ± 0.08
Co (μg/g)	15.12 ± 0.09	6.58 ± 0.49	5.63 ± 0.11
Zn (μg/g)	82.56 ± 13.50	LD*	LD*
Cd (μg/g)	59.87 ± 11.78	LD*	LD*

*LD = lower detection limit.

Table 3
Concentrations (mean ± standard deviation) of elements in rice samples (in dry weight, n = 3).

Element	Province		
	Tak*	Angthong†	Phatthalung‡
Mn (μg/g)	14.81 ± 0.33	23.58 ± 1.6	25.38 ± 0.14
K (%)	0.36 ± 0.02	0.36 ± 0.01	0.31 ± 0.01
Co (μg/g)	0.15 ± 0.01	LD§	LD§
Zn (μg/g)	28.68 ± 0.49	25.44 ± 1.08	29.83 ± 2.09

*Khow Dawk Ma Li 105, † Thai Pathumthani Fragrant Rice, ‡ red rice (Sung Yod), §LD = lower detection limit.

Table 1
Validation (n = 6) of neutron activation analysis for investigation of standard reference materials (SRMs).

Element	SRMs*	Mass fraction		Relative standard deviation (%)	Relative error (%)
		Current work	Certified value		
U (μg/g)	SRM 2702	10.51	10.4	2.28	1.06
As (μg/g)	SRM 2711	101.79	105	3.22	−3.06
Sb (μg/g)	SRM 2711	19.33	19.4	5.33	−0.36
W (μg/g)	SRM 2702	6.12	6.2	3.91	−1.29
Mn (μg/g)	SRM 2702	1760.75	1757	4.59	0.21
K (%)	SRM 2711	2.43	2.45	5.76	−0.82
La (μg/g)	SRM 2702	72.87	73.5	5.93	−0.86
Cr (μg/g)	SRM 2702	355.53	352	3.01	1.00
Hf (μg/g)	SRM 2702	12.73	12.6	1.41	1.03
Cs (μg/g)	SRM 2702	7.06	7.1	3.26	−0.56
Sc (μg/g)	SRM 2702	26.06	25.9	3.18	0.62
Fe (%)	SRM 2702	8.00	7.91	3.25	1.14
Co (μg/g)	SRM 2702	27.68	27.8	1.48	−0.43
Zn (μg/g)	SRM 2702	495.64	485.3	2.53	2.13
Cd (μg/g)	SRM 2711	42.05	41.7	1.47	1.01

*SRMs; 2702 = Inorganics in Marine Sediment and 2711 = Montana Soil.

The concentrations of elements in the rice samples are shown in Table 3. The concentration ranges of essential elements in the different species of rice were: Mn (31.2–14.8 μg/g), K (0.43–0.29%) and Zn (32.58–22.6 μg/g). The mean concentrations of essential elements were highest in red rice (Sung Yod) from Phattalung province. The concentration of Co in Khow Dawk Ma Li 105 rice from Tak province was 0.15 μg/g. Other elements besides these studies were reported by Laoharojanaphand et al. (2009). They determined three kinds of major elements (Ca, K, and Mg) and eight trace elements (Al, As, Br, Cl, Fe, Hg, Mn, and Zn) in four varieties of Thai rice; brown jasmine rice, white jasmine rice, white glutinous rice and black glutinous rice. Al, Br, Cl, Hg, K, Mg, Mn, and Zn were found in all samples. The dominant mineral found in all studied samples was K (ranging from 61.8 mg/100 g in white jasmine rice). Samples of the rice group had highest concentrations of Mg, Zn, Mn, and Al, in the ranges of 4.05–79.16 mg/100 g, 2.18–2.73 mg/100 g, 0.73–2.46 mg/100 g and 1.02–1.99 mg/100 g, respectively. Cl and Br concentrations were lower in the rice group (ranges of 0.26–0.34 mg/100 g and 0.04–0.09 mg/100 g, respectively). Differences in the element contents of unpolished rice may affect their antioxidant properties (Isao et al., 2005). It is expected that this will be the focus of future food research.

BCF is calculated by dividing the concentration of an element in rice by its concentration in rhizosphere soil. The BCF values for Mn were 0.03, 0.09 and 0.16 and for K were 0.45, 0.21 and 0.42 for rice from Tak province, Angtong province and Phattalung province, respectively. The BCF for Co was 0.01 for rice from Tak province, indicating that red rice (Sung Yod) from Phattalung province is an excellent source of elements such as Mn, K and Zn. Khow Dawk Ma Li 105 rice from Tak province and Thai Pathumthani fragrant rice from Angtong province are also higher sources of elements such as Mn, K and Zn compared with the rice in other countries such as Tanzania, Portugal and Spain where the respective elements have ranges of 8.3–19 μg/g, 0.74–0.12% and 13.3–30 μg/g (Mohammed and Spyrou, 2009; Pinto et al., 2016). Mn is associated with rice quality and plays a role in aroma formation in fragrant rice (Li et al., 2016).

LOD

The LOD for Cd in soil samples was 15.21 ± 3.21 μg/g and for Zn was 15.94 ± 0.94 μg/g. NAA was a suitable method for determining Cd and Zn in the soil samples when the concentrations were higher than the LOD. The LOD for Co in the rice samples was 0.06 ± 0.01 μg/g. The LOD was affected by the sample matrix. The nuclear reaction was affected by the sample matrix and the neutron flux that affected the background region (Yeh et al., 1976).

Conclusion

NAA is suitable for the determination of elements in environmental samples. The relative error for this method was lower than 2% and the precision was also high, with less than 6% RSD. The linearity of the Cd calibration curve over the range 1–9 μg was confirmed with a correlation coefficient of 0.997. Using NAA methods, it was found that the analysis of various elements (U, As, Sb, W, Mn, K, La, Cr, Hf, Cs, Sc, Fe, Co, Zn and Cd) showed good accuracy and precision. The detection limit was 15 μg/g for Cd and 16 μg/g for Zn. Because NAA is a non-destructive method, the loss of elements due to destruction processes is mitigated.

These studies on the nutrient value of Thai rice using the BCF indicated that red rice (Sung Yod) from Phattalung province is an excellent source of elements such as Mn, K and Zn. The Khow Dawk Ma Li 105 rice from Tak province and the Thai Pathumthani fragrant rice from Angtong province were also significant sources of elements such as Mn, K and Zn.

Conflict of interest

The authors have no conflict of interest to declare.

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