RESEARCH ARTICLE

Production and Certification of In-house Rice Flour Reference Material

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ABSTRACT An in-house reference material for trace metals in rice flour was produced. Certification of concentrations of fifteen elements based on at least two independent methods was carried out. The analytical techniques included ICP-AES, ICP-MS, ETAAS, FAAS and voltammetry. Out of the 15 elements, 13 elements, namely Na, K, Mg, Ca, Ba, Cu, Zn, Fe Mn, Co, Ni, Pb and Cd, could be certified whereas only reference values were given to Cr and V because the concentrations of these two elements were so low that only one analysis method could successfully detect them.

Statistical tests for the study of homogeneity at 95 % confidence level did not reveal significant differences between the within-bottle and between-bottle variation. The rice flour material is considered to be homogeneous at 250-650 mg sample sizes. No significant change was observed in a long-term stability study of the material over a period of 5 months and a short-term stability study at an elevated temperature of 50 °C for a period of 5 weeks. A comparison of results obtained from independent methods was made before certified values were calculated using both means and weighted means. The reference materials have been distributed for use in laboratory quality assurance.

KEYWORDS: In-house, reference material, rice flour, metal concentration.

INTRODUCTION

Reference materials (RMs) and certified reference materials (CRMs) make possible the transfer of the values of measured or assigned quantities (physical, chemical, biological or technical) between one place to another. They are widely used for calibration of measuring apparatus, for the evaluation of methods of analysis or test and for long-term quality assurance of measurements. All kinds of RMs and CRMs are playing an increasingly important role in national and international standardizing activities, in proficiency testing and in accreditation of laboratories.[1] A laboratory may attempt to develop its own in-house RMs inplace of expensive or absent CRMs. Various approaches for the certification of reference materials are given in ISO Guide 35[2], and many references can be used.[3-8] In this work, an in-house rice flour RM was produced and certified in order to serve as an inexpensive CRM for local laboratories.

Rice is a major dietary source for most Asians. Thailand is one of the world's major producers of rice products. To consistently produce quality and contaminant-free rice, close monitoring of mineral and toxic elements in rice products is important. Use of certified reference materials is necessary to validate analytical procedures and performance. At present, several international organizations have issued a variety of rice flour CRMs.[9-11] However, not many laboratories in the Thailand can afford using commercial CRMs on a regular basis, owing to their rather high prices. Therefore, the aim of this work was to produce an in-house reference material of rice flour to be distributed nationally and to serve as a study of the potential for producing similar types of other reference materials locally. Fifteen trace metals (Na, K, Mg, Ca, Ba, Cu, Zn, Fe, Mn, Co, V, Cd, Pb and Cr) were the target elements for certification, using two or more independent analytical techniques. The certification procedure includes a within-bottle and between-bottle homogeneity study, short-term and long-term stability study and the statistical treatment of analytical results.

MATERIALS AND METHODS

Preparation and bottling of rice flour material

Rice flour material was prepared from 1.5 kg of polished rice. The polished rice was washed 4 times with pure water. The sample was then dried in a clean oven. The dry polished rice was pulverized with a rotor speed mill (Tecator, Cyclotec 1093) and then mixed in a prewashed plastic bag. The homogenized rice flour was then manually bottled in amber glass bottles. Each bottle was closed with an insert and a screw cap. The mixing and bottling were performed in a clean laminar-flow surface. The sealed bottles were irradiated with g- radiation and stored at ambient temperature in a desiccator. Thirty-five bottles, each containing 40 g rice flour, were produced. Moisture content in rice flour was determined by taking three separate portions of known amount of samples (approximately 1 g) in preweighed containers and then drying in the oven at $105 \pm 5\,^{\circ}C$ for 12 hours. The samples were then weighed and the average moisture content was calculated. Correction was made for this moisture content for the determination of the final concentration of each element on a dry weight basis.

Instrumentation

Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were performed with a Perkin Elmer OPTIMA 3000, Radial view model with an autosampler (Perkin Elmer Corp, Norwalk, CT, USA). Background corrections were performed on each element at wavelengths chosen after examination of the spectral profiles.

All inductively coupled plasma mass spectrometry (ICP-MS) measurements were made on a Perkin Elmer ELAN 6000 (Perkin Elmer SCIEX, Thornhill, Ontario, Canada) and a class 100 clean air hood was suspended above the sample introduction system of the ICP-MS.

All electrothermal atomic absorption spectrometry (ETAAS) measurements were conducted with a Perkin Elmer atomic absorption spectrometer AANALYST 100 (Norwalk, CT, USA) equipped with a deuterium-arc background corrector and HGA 800 heated graphite atomizer together with AS-72 autosampler. The flame atomic absorption spectrometry (FAAS) measurements were obtained with a Perkin Elmer atomic absorption spectrometer model 3100 (Norwalk, CT, USA) with deuterium-lamp background correction system.

Dissolution of rice flour material was achieved using three different commercial microwave ovens model MDS-81 CEM (Mathews, NC, USA), MDS 2100 Microwave digestion system CEM (Indian trail, N C, USA) and MLS-1200 MEGA Milestone (Bergamo, Italy).

Voltammetric measurements were performed using a voltammetric analyzer model 693 VA Processor equipped with 694 VA Stand (Metrohm, Herisau, Switzerland). The three electrode system included a hanging mercury drop electrode, a silver-silver chloride electrode and a platinum rod.

Chemicals and reagents

Nitric acid used in this work was purified from an analytical grade acid by a sub-boiling distillation units from Seaster Chemicals (Seattle, WA, USA) or from Berghof. Both systems were operated in laminar flow hoods. High-purity deionized water was obtained from a Nanopure (Barnstead) water purification system. Enriched spike isotopes, [57]Fe, [62]Ni, [65]Cu, [67]Zn, [111]Cd, [207]Pb, were obtained from Oak Ridge National Laboratory (Oak Ridge, TN, USA) and [137]Ba from US Services (Summit, NJ, USA).

Procedure for sample dissolution and metal determination using spectrometric methods

Preparation of standard solutions

All standard solutions were prepared in 10% sub-boiling distilled nitric acid using high purity deionized water. All standard preparations were carried out in the cleanest environment available (in a clean room Class 100 working environment at NRCC or on clean benches or in a laminar flow atmosphere at Mahidol University) in order to minimize contamination. All glasswares, polyethylene bottles, pipette tips and other materials were carefully cleaned by washing with detergent to remove dust, particulate remnants, then washing with deionized water and filling with 30% analytical reagent nitric acid for at least 3 days. The bottles or containers were kept filled until use and rinsed with pure water and sample solution 3 times before use.

The mixed working standard solutions for ICP-AES (Na, K, Ca, K, Ba, Cu, Fe, Mn, Co, V, Cd, Pb, Cr and Ni) and FAAS (Na, K, Mg, Ca and Zn) were prepared in a matrix of rice flour digest solutions in order to perform the addition calibration by spiking each stock standard solution in the digest solution. Calibration curves were performed from at least 3 point standards. The standard additions were carried out for ICP-MS measurement of Co, V, Mn and Cr.

For the isotope dilution analyses, the enriched spike isotopes ([57]Fe, [62]Ni, [65]Cu, [67]Zn, [137]Ba, [111]Cd and [207]Pb) were added to samples prior to the digestion. Aliquots of the enriched spike isotope solutions were added to obtain a ratio near 1 for each of the isotope pairs in the sample. The reference /spike isotopes were as follows: [56]Fe / [57]Fe, [54]Fe / [57]Fe, [60]Ni / [62]Ni, [63]Cu / [65]Cu, [66]Zn / [67]Zn, [138]Ba / [137]Ba, [114]Cd / [111]Cd, and [208]Pb /[207]Pb. For the isotope ratio measurement, checks for mass bias were made with 100 μgL^{-1} natural abundance solutions of each element, except for lead, which there was no correction for mass bias because standard solution with certified isotope composition could not be obtained.

The mixed standard solutions of Cu, Fe and Mn 100 mg L^{-1} were diluted to 20-100 mg L^{-1} in 10% nitric acid.

Procedure for dissolution of rice flour

The dissolution of rice flour material for ICP-AES, ETAAS and FAAS measurements was carried out by microwave digestion systems. In the certification, at least three separate portions of each bottle of approximately 250 mg were weighed accurately into the Teflon high-pressure digestion vessels. For Na and Ca determination by FAAS, approximately 500 - 650 mg of rice flour were required. Sub-boiling distilled nitric acid (3 mL) were then added and the vessels were then sealed. The contents were digested with the digestion program as recommended by the manufacturer. Two blanks were carried with each set of four samples. The dissolved solutions were diluted to 25.0 mL with purified water.

For standard addition ICP-MS determination of Co, V, Mn and Cr, the dissolution procedures were the same as described above except that after digestion, the contents were evaporated to dryness at 60 °C on a hot plate and under an infrared lamp in a laminar fume hood. Sub-boiling distilled nitric acid (0.5 mL) was then added to the residue. The final contents were diluted to 25.0 mL with deionized water and stored in clean polyethylene bottles. These solutions contained 2% nitric acid, which were suitable for ICP-MS measurement.

For isotope dilution-ICP-MS, the dissolution and evaporation of samples were the same as for standard addition ICP-MS, but the appropriate amounts of enriched spike isotopes were added together with the nitric acid. A separate set of isotope dilution analyses was also performed to determine blanks for the dissolution procedure. Two blanks were carried with each set of ten samples.

ID-ICP-MS measurement

Isotope ratio measurements of reference/spike isotope of each pair were carried out by isotope ratio measurement mode in the ELAN software. Corrections of known isobaric interferences were also made automatically by software where necessary. Analyte concentrations in rice flour were calculated by means of Equation 1.[12]

$$C = \frac{M_s K (A_s - B_s R)}{W (BR - A)} \qquad (1)$$

where *C* is the analyte concentration in micrograms per gram, M_s is the mass of the stable isotope spike in micrograms, *A* is the natural abundance of the reference isotope, *B* is the natural abundance of the spike isotope, A_s is the abundance of the reference isotope in the spike, B_s is the abundance of the spike isotope in the spike, *K* is the ratio of the natural and spike atomic mass, *W* is the sample weight, *R* is the measured isotope ratio with mass bias correction. The correction factors (CF) were obtained from the comparison of the values of isotope ratio as measured from a pure solution of the element with natural ratio.[13]

Procedure of sample dissolution and voltammetric measurement

Complete digestion of sample organic matter is very important for successful subsequent voltammetric measurements. Therefore, rice flour samples were digested with a mixed acid of HNO_3 and $HClO_4$ as suggested by Stryjewska.[14] Microwave digestion was carried out using 2 mL HNO_3 and 2 mL $HClO_4$ for 0.5 g rice flour sample. After complete digestion to clear solution, the solution was allowed to cool and transferred to evaporate to dryness on a hotplate. The residue was then dissolved in 0.1M HCl and made up to 25 mL in a volumetric flask.

Sequential determination of Cd, Pb, Cu, Zn, Mn, Ni and Co was performed as shown in Figure 1. The experimental details were explained in a separate report (to be published). An aliquot of 7 mL of the acid digest was pipetted into a small plastic vessel placing inside the voltammetric glass vessel. The pH was adjusted to approximately 2.0 using a 4M ammoniacal buffer solution for simultaneous determination of Cd and Pb by Differential Pulse Anodic Stripping Voltammetry (DPASV). The solution was purged with oxygen free nitrogen for 3 min to remove any dissolved oxygen. The deposition step was then initiated in stirred solution at a fixed

potential for 300 s. A stripping step was then carried out and voltammograms were recorded.

After completion of Cd and Pb measurement, the solution pH was raised to 8.4 using the same buffer solution for Cu DPASV measurement.

Measurement of Zn and Mn was then performed by a Cathodic Differential Pulse Voltammetry (CDPV) method. Stripping was not necessary for these two elements because of their adequately high concentrations. Finally, the pH was increased to 8.6 and DMG (to obtain approx 0.3mM) or DMG (0.3mM) + EDTA (0.1mM) was added for subsequent reverse and normal differential pulse adsorption stripping voltammetry (DPAdSV) measurements, respectively.

Procedure for homogeneity study

The within-bottle homogeneity test was carried out by analyzing ten sub-samples taken from one randomly picked bottle. The between-bottle homogeneity test was performed by analyzing one sub-sample from each of six different bottles randomly selected from 35 bottles with a minimum of three independent replicate determinations of each. Eight elements were determined, 5 elements (Na, K, Mg, Ca and Zn) using FAAS and 3 elements (Fe, Cu and Mn) using ETAAS.

The one-way analysis of variance (ANOVA) was applied to compare the variation of within-bottle homogeneity and between-bottle homogeneity, using the data analysis tool in the Microsoft-Excel program. The coefficient variation (CV) and uncertainty of CV (U_{cv}) were evaluated following the BCR's reports [15-21] using Equation 2

$$U_{cv} = CV2 / \sqrt{2n} \qquad (2)$$

where n is number of determination

Procedure for stability study

The long-term stability of trace element contents in rice flour was tested. One bottle stored at ambient temperature was sampled and analyzed 3 4 times during a period of 5 months. The changes of metal contents were examined to evaluate the long-term stability.

The relative variations observed were calculated following Equation 3[15-21].

$$R_t = X_t / X_o \qquad (3)$$

where R_t is the ratio of the mean value (X_t) of at last three measurements made after a period of t and

the mean X_o obtained from determination at the beginning of this study.

The uncertainty U_{Rt} of the ratio R_t was obtained from the coefficient of variation of each set of determination as shown in Equation 4.

$$U_{Rt} = (CV_t^2 + CV_o^2)^{1/2}(R_t/100) \qquad (4)$$

where CV_t and CV_o are the coefficient variations of X_t and X_o respectively.

The short-term stability study was carried out by sampling and analyzing a sample stored at 50 °C for 5 times during a period of 5 weeks. Determinations of metal content were performed on at least three replicates. Instability caused by temperature was examined by comparing the metal contents in sample stored at 50 °C with that stored at ambient temperature. The relative variation of short-term stability and its uncertainty U_{Rt} observed were calculated as shown previously in Equations 3 and 4.

RESULTS AND DISCUSSION

Selection of elements and methods for the certification of in-house rice flour reference material

The selection of chemical methods is usually based on accuracy, precision, analysis cost and
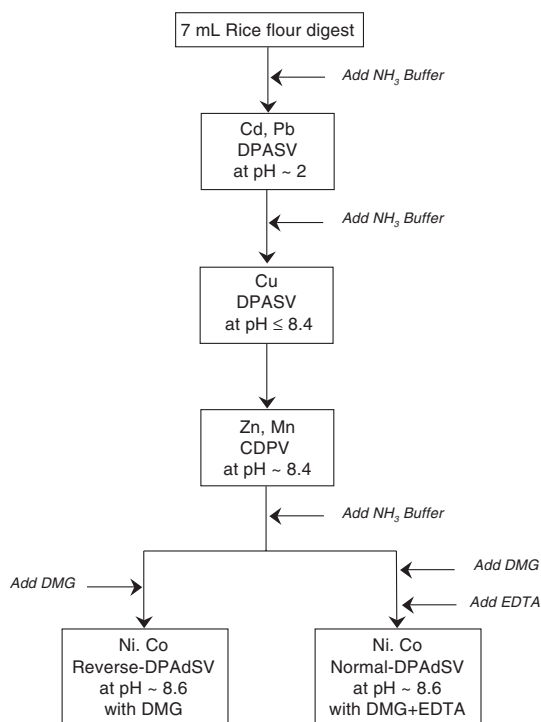

Fig 1. Schematic diagram of sequential determination of Cd Pb Cu Zn Mn Ni and Co by voltammetry.

availability of equipment.[22] Considering that the independent methods concept is most widely accepted by international standard organizations[3-9], the certification in this work was based on the results of determinations using at least two independent methods of analysis. Firstly, spectrometric methods were carried out in the homogeneity study, stability study and in the obtaining of analytical data for as many certifiable elements as possible. Then voltammetric methods were considered for uncertified elements in order to obtain more certified elements.

Homogeneity study

Homogeneity testing of RMs is one vital component of the certification process, as it indicates the validity of the certified values and their uncertainties in the analysis of individual units or portions thereof.[23] Regarding the state-of-art in reference materials certification, as appeared in ISO Guide 35 [2] and some BCR publications[15-21] concerning the homogeneity study, ANOVA and F-test are normally used to determine the discrepancy between the variances of within- and between- bottle homogeneity. In the present work, all parameters concerned will be estimated by one-way analysis of variance (ANOVA) using the data analysis tool in the Microsoft-Excel program at a significance level of $\alpha = 0.05$ or otherwise indicated. Coefficient variations of method, within- and between- bottles analyses are plotted in Figure 2. In most cases, no heterogeneity was detected, since the variability of the within-bottle and the between-bottle was comparable or better than the variability due to method. Therefore, the rice flour reference material is considered to be homogeneous.
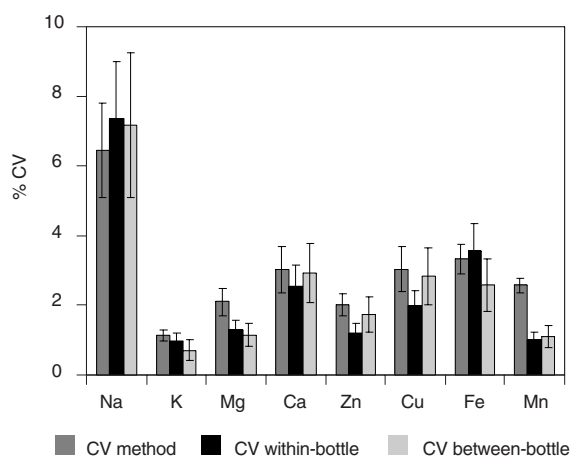
Stability study

The results of long-term stability study (5 months) were obtained. In all cases, the R_t values were found to be between 0.9-1.1. The results of short-term stability test at elevated temperature also gave R_t values for all elements in the range of 0.9-1.1. No trend of instability was observed for all elements studied. In addition, the variations of R_t in the vicinity of 1.0 were observed in both positive and negative bias from unity indicating analytical errors or uncertainties of measurement rather than indication of instability. It was concluded that no instability could be demonstrated in the period of 5 months and the material was considered suitable for certification.

Analytical results of in-house rice flour reference material

Results of spectrometric methods

Once the in-house rice flour material was proved to be homogeneous and stable, determination of targeted elements was carried out to obtain the certified values.

The results of determination of trace metals in rice flour by independent analytical methods and their uncertainties at 95 % confidence level are compared in graphical plots in Figure 3. The data from various independent methods were evaluated by ANOVA except for Ba, which was evaluated by t-test because variances of the two methods used differed significantly. The ANOVA test at a significance level of 0.05 did not reveal significant differences between methods for Na, K, Mg, Ca, Fe and Mn For Zn. The results from ICP-MS and FAAS did not indicate a significant difference between methods of analysis at 95% confidence level. For Cu, the results from ETAAS and ICPAES were not significantly different at 95 % confidence level. Ba, For there was indicated no significant difference between independent methods at the level of 98.4%. These nine elements could be certified by two independent spectrometric methods.

To confirm the accuracy of analytical methods used, evaluation of analytical method for some elements (Na, K, Mg, Ca, Cu, Zn, Fe and Mn) in rice flour analysis was also done by analyzing commercial rice flour certified reference material SRM 1568a. The analytical results were in good agreement with the certified values as shown in Table 1.

Fig 2. Results of the homogeneity study for Na, K, Mg, Ca, Zn, Cu, Fe and Mn in rice flour. The error bar represents 2 U_{cv}.

Results of voltammetric methods

Only 9 out of 15 elements were successfully determined by spectrometric methods and could be certified. For Cd, Pb and Co, results from ICP-MS only was obtained because of the very low concentration levels of these elements in rice flour.

Therefore, electrochemical methods were investigated for Cd, Pb, Cu, Co, Ni and Zn. The most sensitive voltammetric methods were chosen for study, namely, differential pulse anodic stripping voltammetry (DPASV), cathodic differential pulse voltammetry (CDPV), normal differential pulse
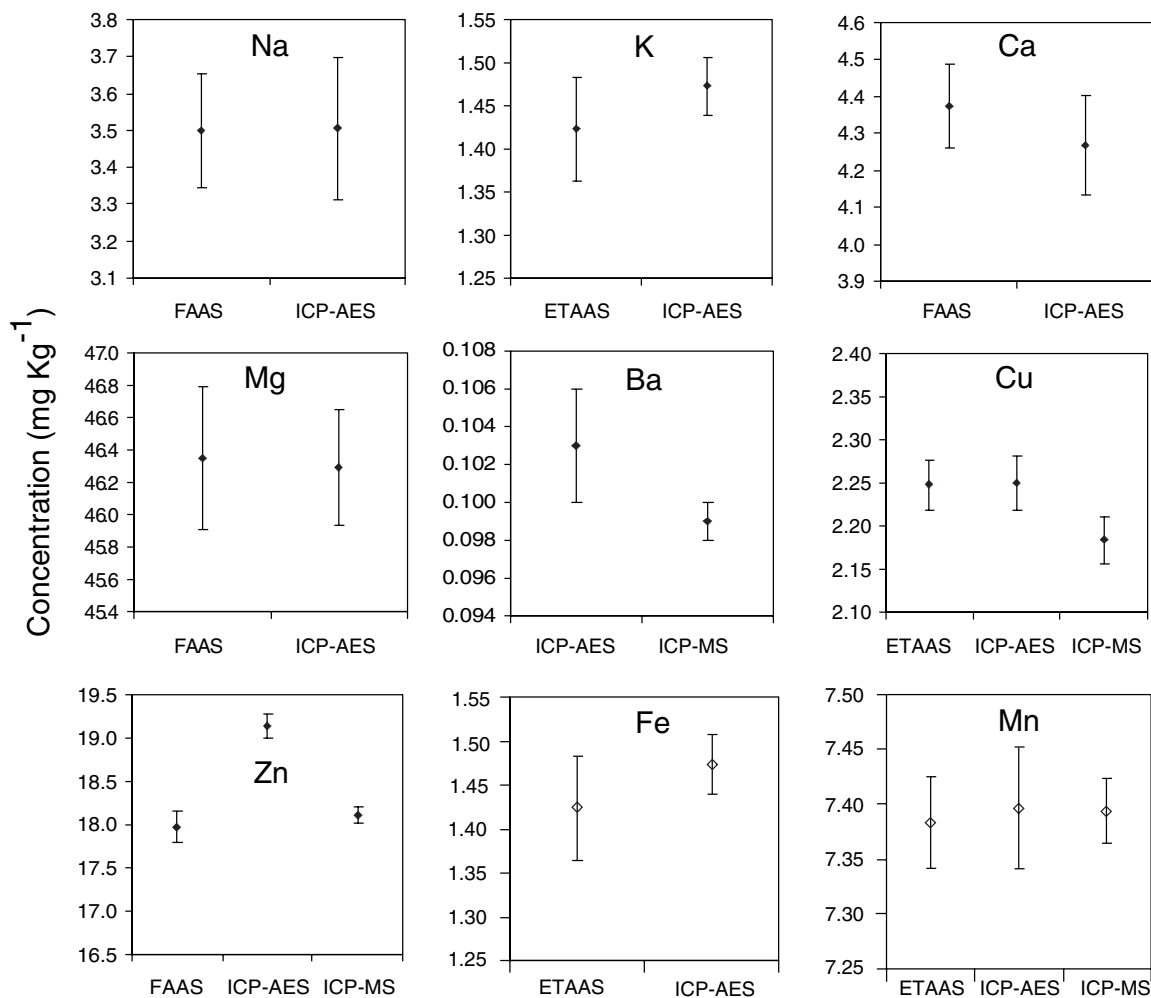

Fig 3. Concentrations and 95% confidence interval for elements in in-house rice flour reference material.

Table 1. Analytical results of NIST rice flour reference material SRM 1568a.

Element	Method	Found (mg Kg⁻¹)	Certified value (mg Kg⁻¹)
Na	FAAS	7.0 ± 0.3	6.6 ± 0.8
K	FAAS	1283 ± 2	1280 ± 8
Mg	FAAS	572.7 ± 4.8	560 ± 20
Ca	FAAS	120 ± 1	118 ± 6
Zn	FAAS	19.6 ± 0.3	19.4 ± 0.5
Cu	ETAAS	2.6 ± 0.2	2.4 ± 0.3
Fe	ETAAS	7.0 ± 0.2	7.4 ± 0.9
Mn	ETAAS	19.6 ± 0.8	20 ± 1.6

adsorption stripping voltammetry (N-DPAdSV) and reverse differential pulse adsorption stripping voltammetry (R-DPAdSV). Figure 1 shows schematically the procedure for sequential determination of 6 elements by voltammetry. The results of analysis are shown in comparison with the spectrometric methods in Table 2. For Cd and Pb, the results agree at 99.5 % confidence level between electrochemical and ICP-MS methods. The results of Co also agreed at 99.5 % confidence level for two electrochemical methods but disagreed with the ICP-MS method. The results of Ni also agreed at the same confidence level for two electrochemical methods, but it was undetectable by ICP-MS. Therefore, Co and Ni were certified by two electro-chemical methods.

The certified values for Na, K, Mg, Ca, Ba, Cu, Zn, Fe, Mn, Cd, Pb, Co and Ni in rice flour based on 95 % confidence limit of the mean and the computation of the weighted mean and its uncertainty as proposed from NIST[23, 25, 26] are presented in Table 3. Vanadium and chromium were detected by only ICP-MS method, so only reference values were given in Table 4.

Table 2. Analytical results of voltammetric determination of 6 elements in rice flour in comparison with those of spectrometric methods.

Metal	Concentration found (mg Kg⁻¹)			
	EC	AAS	ICP-MS	ICP-AES
Cd	0.0032 ± 0.0004^a	ND	0.0038 ± 0.0002	ND
Pb	0.0048 ± 0.0015^a	ND	0.0049 ± 0.0004	ND
Cu	2.07 ± 0.08^a	2.248 ± 0.028	2.184 ± 0.026	2.25 ± 0.03
Co	0.018 ± 0.001^b, 0.022 ± 0.001^c	ND	0.0103 ± 0.0017	ND
Ni	0.078 ± 0.005^b, 0.088 ± 0.002^c	ND	ND	ND
Zn	18.13 ± 0.17	17.97 ± 0.17	18.11 ± 0.09	19.14 ± 0.13

a: DPASV; b: R-DPAdSV; c: N-DPAdSV; d:CDPV
ND for not detectable

Table 3. Certified values of elements in in-house rice flour reference material.

Element	Concentration (mg Kg⁻¹)		Method
	Mean ± Uncertainty (95 % confidence level)	Weighted mean ± Uncertainty (95 % confidence level)	
Na	3.50 ± 0.10	3.50 ± 0.64	ICP-AES, FAAS
K	334.7 ± 1.5	334.7 ± 6.6	ICP-AES, FAAS
Mg	46.32 ± 0.23	46.31 ± 1.41	ICP-AES, FAAS
Ca	4.321 ± 0.080	4.328 ± 0.409	ICP-AES, FAAS
Ba	0.101 ± 0.003	0.101 ± 0.006	ICP-AES, ID-ICP-MS
Cu	2.227 ± 0.037	2.226 ± 0.202	ICP-AES, ID-ICP-MS
Zn	18.04 ± 0.10	18.41 ± 1.51	ICP-AES, ID-ICP-MS
Fe	1.448 ± 0.032	1.456 ± 0.136	ICP-AES, ETAAS
Mn	7.390 ± 0.020	7.390 ± 0.218	ICP-AES, ETAAS
Cd	0.0036 ± 0.0002	0.0032 ± 0.0010	ID-ICP-MS, DPASV
Pb	0.0049 ± 0.0014	0.0049 ± 0.0015	DPASV, ICP-MS
Co	0.0020 ± 0.0012	0.0021 ± 0.0006	DPAdSV ,R-APAdSV
Ni	0.080 ± 0.013	0.081 ± 0.031	DPAdSV, R-APAdSV

Table 4. Reference values of elements in in-house rice flour reference material.

Uncertified element	Mean ± uncertainty (µg Kg⁻¹) (95% confidence level)
V	0.0014 ± 0.0005
Cr	0.0013 ± 0.0008

Conclusion

The certified values could be assigned to 13 elements (Na, K, Mg, Ca, Ba, Cu, Zn, Fe, Mn, Cd, Pb, Ni and Co) for an in-house rice flour reference material, whereas reference values could be given for Cr and V, because only one analytical method was successfully performed. Certified values based on two calculation methods were presented. One was based on mean and the other on weighted mean. The evaluation of analytical methods was conducted by analyzing a commercial certified rice flour reference material SRM 1568a. In-house rice flour reference material is homogeneous at 250 mg sample size. For a long-term stability study of material in a period of 5 months and a short-term study at an elevated temperature of 50 °C for a period of 5 weeks, no significant change was observed indicating the stability of the material. The material was considered suitable for the certification. The uncertainties of analytical results were generally low for the first nine elements, which were of mg Kg^{-1} levels. For elements of μg Kg^{-1} levels (Cd, Pb, Co, Ni, V and Cr), the uncertainties were higher because the concentrations of these elements in rice flour were close to the detection limits of the methods used.

Acknowledgements

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