Trends in Analytical Chemistry 76 (2016) 216–226

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Assessment of technical problems in the analysis of inorganic elements in squid through proficiency testing

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ARTICLE INFO

Keywords:
Inorganic elemental analysis
Squid
ISO/IEC 17043
International harmonized protocol
Proficiency testing (PT)
E_n-number
z-score

ABSTRACT

Results of proficiency testing (PT) undertaken to assess the analytical skills in Japanese laboratories are presented. The PT was coordinated jointly by the National Metrology Institute of Japan (NMIJ) and the National Food Research Institute (NFRI), in which the determination of As, Cd, Fe, Mn and Zn in a dried powdered squid powder was carried out in compliance with the international standard ISO/IEC 17043:2010. A prescribed protocol for the determination of the moisture content of the sample was given to the participants beforehand. Any sample preparation/extraction methods were not prescribed, and a variety of methods was thus applied by the 118 participants. Reported results were assessed using the E_n-number and *z*-score approaches in accordance with ISO/IEC 17043 and the international harmonized protocol for PT. Results of this PT are reviewed in detail, and technical problems leading to some unsatisfactory results are discussed.

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http://dx.doi.org/10.1016/j.trac.2015.11.015
0165-9936/

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1. Introduction

Proficiency testing (PT) uses interlaboratory comparisons and pre-established criteria to evaluate participant performances in chemical analysis laboratories, and is an effective process for quality assurance and capability monitoring [1–3]. Some organizations provide PT for laboratory analysts and researchers to assess their technical qualities and assist in finding aspects for improvement [4].

To promote technical improvement in the analysis of inorganic constituents in environmental and food samples in Japan, the National Metrology Institute of Japan (NMIJ) has conducted PT exercises since 2009. PT for tea leaf powder analysis was carried out in 2009, for river water in 2010, and for lead-free solder alloy in 2010. In addition, NMIJ and the National Food Research Institute (NFRI) of the National Agriculture and Food Research Organization (NARO) of Japan have conducted PT for brown rice powder in 2011-2013 [5,6]. These were package programs comprising PT and a follow-up technical lecture. The performance of the participants was quantitatively evaluated by calculating the E_n-numbers and z-scores for their reported values in accordance with the document standard of the International Standards Organization (ISO) and the International Electrotechnical Commission (IEC) 17043:2010 [1], and the international harmonized protocol for PT [3]. And, one advantage of our PT exercises is that a follow-up lecture focuses in detail on how to solve the analytical problems found from the participants' reports.

In 2014, we provided a new training program for the determination of As, Cd, Fe, Mn and Zn in squid powder. Marine organisms are very important components of the Japanese / Asian diet, and squid is a particularly popular food item. The Codex Alimentarius Commission, administered jointly by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO), the organization that regulates the concentrations of toxic elements and their compounds in food, approved a maximum level of 2.0 mg kg^{-1} for Cd in cephalopods (squid, octopus, cuttlefish) [7]. However, there are no CRMs available to validate an analytical procedure for the cephalopod matrix, and PT for such matrix components have not been carried out. Thus, to date, analytical quality control for such matrices has not been necessarily enough. In this article, the PT results and analytical procedures employed by the participants are reviewed in detail, and possible technical reasons for questionable or unsatisfactory results are discussed.

2. Test material

2.1. Preparation of the test material

Fresh squid (120 kg) was rinsed to remove seawater, freeze-dried, sieved (<100 μm), and homogenized. The resulting powder was placed into amber glass bottles (*ca.* 30 g each) and sterilized with ^{60}Co gamma radiation (20 kGy). The bottles were individually sealed in aluminum bag packages, and 416 bottles were prepared.

2.2. Homogeneity and stability

The uncertainties arising from sample inhomogeneity (u_{hom}) were assessed within NMIJ, in accordance with ISO Guide 35:2006 [8], by using the same manner described in our previous papers [6,9]. In the assessment, between-bottle homogeneity (s_{bb}) and in-bottle homogeneity ($u_{in\text{-}b}$) were studied by determining the concentrations of the elements in three sub-samples taken from ten bottles selected at random from the total 416 bottles. Each element was determined by inductively coupled plasma mass spectrometry (ICP-MS) calibrated with the Japan calibration service system (JCSS) single element standard solutions after microwave assisted digestion with HNO_3-H_2O_2-HF. The results are shown in Table 1. The values of u_{hom} for the elements were not large when compared with the uncertainties resulting from the analytical techniques. Hence, it was considered that the sample was sufficiently homogeneous for its intended purpose. A short-term stability monitoring for each element in the test material at room temperature (25°C) was conducted in accordance with the international harmonized protocol for PT [3]. The concentrations of all the elements remained constant for 3 months.

Table 1
Results of homogeneity (among group and within group, relative value) study

Element	Bottle number	n	Between-bottle		Within-bottle		
			s_{bb}	u_{bb}	MS_{within}	S	$u_{in\text{-}b}$
As	10	3.0	––	0.32%	1.00%	0.70%	––
Cd	10	3.0	––	0.31%	0.95%	0.39%	––
Fe	10	3.0	––	0.72%	2.21%	0.77%	––
Mn	10	3.0	0.52%	0.21%	0.63%	0.89%	––
Zn	10	3.0	––	0.60%	1.83%	0.62%	––

––: The variances calculated using ANOVA were negative.

2.3. Distribution of the test material to participating laboratories

A hundred twenty-five participants registered to this PT program. On 24th September 2014, the test material (*ca.* 30 g in an amber glass bottle) was distributed to each participant together with an instruction and a report form in excel format.

The participants were asked to perform pretreatment on at least three sub-samples and make at least 3 measurements of each sub-sample. The details of sample pretreatment method / procedure, the sources of calibration standard solutions and the measurement concentration ranges were also asked to report. Any combination of elements selected from As, Cd, Fe, Mn and Zn was allowed. The participants were asked to determine the concentrations of the selected elements on both an undried (as received) basis and a dry mass one, in which the moisture content of a sample was defined as the ratio of the mass of water to the total mass of the undried sample. Drying conditions were specified as oven drying at 105°C for 5 h [10]. Samples for determination of moisture content and for pretreatment were taken consecutively from a bottle of the test material. After completion of the testing, each participant was asked to return the report to NMIJ by 21st November, 2014. A hundred eighteen reports from 116 participants (9 participants cancelled) were returned to NMIJ.

2.4. Assigned values

Two assigned values were obtained for evaluating the reported values: one was the assigned value 1 for calculating E_n-score, the other was the assigned value 2 for calculating z-score.

The assigned value 1 with expanded uncertainties of the analytes were characterized by NMIJ using more than one independent analytical methods in accordance with ISO guide 35:2006 based on