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Original Article

Simultaneous analysis of 21 elements in foodstuffs by ICP-MS after closed-vessel microwave digestion: Method validation

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ABSTRACT

This paper describes a validation process for the simultaneous analysis of 21 elements: lithium (Li), aluminium (Al), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), arsenic (As), strontium (Sr), molybdenum (Mo), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), tellurium (Te), barium (Ba), mercury (Hg) and lead (Pb) in food samples by inductively coupled plasma-mass spectrometry (ICP-MS) after closed-vessel microwave digestion. This validation was realized in parallel with the analysis of the 1322 food samples of the second French Total Diet Study (TDS) by the National Reference Laboratory (NRL) of the French Food Safety Agency (AFSSA). Several criteria such as linearity, limits of quantification (LOQ), specificity, precision under repeatability conditions and intermediate precision reproducibility were evaluated. Furthermore, the method was supervised by several internal and external quality controls (IQC and EQC). Results indicate that this method could be used in the laboratory for the routine determination of these 21 essential and non-essential elements in foodstuffs with acceptable analytical performance.

1. Introduction

In 2006, the French Food Safety Agency (AFSSA) started the second French Total Diet Study (TDS) to estimate dietary exposure to essential and non-essential elements in 1322 different food samples. The goal of the TDS is an indirect assessment of foods found in a typical market basket and prepared for normal consumption. Often used, it is the most reliable way to estimate the dietary intake and the exposure to toxic chemicals by large population groups (WHO GEMS/Food, 2006; Zukowska and Biziuk, 2008). First, the TDS assesses the impact of common household cooking methods on the decomposition of the least stable chemical compounds and the formation of new chemical compounds (WHO GEMS/Food, 2006; Zukowska and Biziuk, 2008). Then data on the concentration of contaminants, minerals and nutrients, combined with dietary consumption data, make it possible to evaluate the levels of dietary exposure in population groups. Thus, the estimated intakes are compared with nutritional and toxicological reference values, such as the Recommended Daily Allowances (RDA) or the Recommended Daily Intake (RDI) for nutrients and the Provisional Tolerable Weekly Intake (PTWI) for toxic elements (WHO, 1995, 2010).

In the context of this second French TDS, the National Reference Laboratory (NRL) for heavy metals put in place the validation of a multi-elemental method by inductively coupled plasma-mass spectrometry (ICP-MS) to confirm that the analytical procedure employed was suitable for its intended use (multi-elemental routine analysis for studies of exposure through dietary intake and monitoring plans) (Fig. 1).

First, it was necessary to define the analytical requirements of the method (which element in which type of food, concentration range to be covered, acceptable uncertainty in the result, etc.) in accordance with the second French TDS monitoring exigencies (Millour et al., 2010). The method used for the analysis relied on the accredited method by the French Committee of Accreditation (COFRAC) for Cd, Pb, As and Hg in foodstuff of animal origin (Noël et al., 2005). This validation was based on the determination of generally well-defined and relevant performance characteristics

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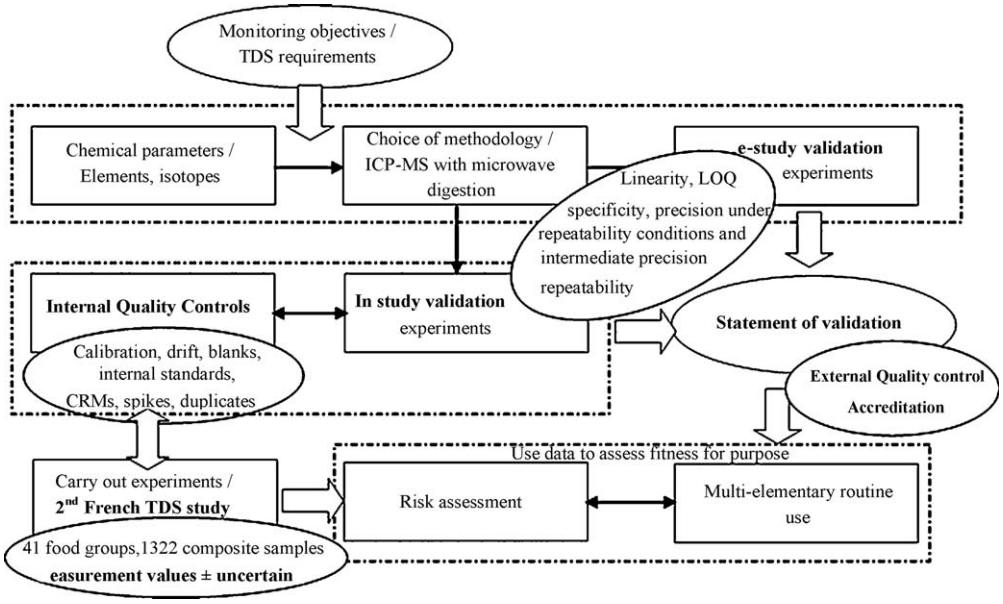

Fig. 1. Validation process of the ICP-MS methodology.

(linearity, limit of quantification (LOQ), specificity, precision under repeatability conditions and intermediate precision repeatability) NF EN 13804 (AFNOR, 2002a); NF V03-110 (AFNOR, 1998). Before ICP-MS methodology was routinely used for the TDS on unknown samples, a set of experiments was required to evaluate whether the method would be able to meet the criteria described above. This preliminary validation study generated enough information to guarantee that the analytical method will provide, in routine use, accurate measurements without being affected by other elements present in the sample, assuming that the methodology and related handling procedures remained unchanged. From this preliminary validation study, the decision to accept the analytical procedure set-up as valid for routine use was also based on the quality of future results, which were produced using the analytical procedure during the TDS, through an in-study validation and the implementation of internal quality controls (IQC) (Fig. 1). These IQC were essential to oversee the study and to ensure the reliable results in each analytical sequence, such as the calibration curve to monitor the linearity, blanks and the checking of LOQ, internal standards to obtain information about sensitivity drift in different mass region and to follow matrix effects, a standard every eight samples and at the end of the sequence to control the instrumental drift, spiked standard solutions on unknown samples to control the specificity, certified reference material (CRM) to monitor the trueness and duplicates to control the repeatability (Millour et al., 2010). Several computer-based aids were also used to make data processing easier and to follow the evaluation of individual and overall IQC with their specific acceptance criteria and finally, calculation of all percentage to conclude whether the results are acceptable or not.

The aim of the present work was to demonstrate that the method developed by the NRL about the analysis of 21 essential and non-essential trace elements (lithium (Li), aluminium (Al), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), arsenic (As), strontium (Sr), molybdenum (Mo), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), tellurium (Te), barium (Ba), mercury (Hg) and lead (Pb)) by ICP-MS after closed-vessel microwave digestion could apply to numerous types of matrices representative of French diet, while keeping adequate analytical performances. The results obtained with IQC used in the study and external quality controls (EQC) have also been presented.

2. Material and methods

2.1. Reagents and gas

All solutions were prepared with analytical reagent grade chemicals and ultrapure water (18 MΩ cm) obtained by purifying distilled water with the Milli-QTM PLUS system associated with an Elix 5 pre-system (Millipore S.A., St Quentin-en-Yvelines, France).

(a) Nitric acid: Suprapur HNO_3 (67% v/v) was purchased from VWR (Fontenay-sous-Bois, France).
(b) Standard solutions: (1) Standard stock solutions containing 1000 mg L^{-1} of each element and gold (Au) were purchased from Analytika (Prague, Czech Republic) and were used to prepare calibration standards. To avoid the mercury memory effect, gold chloride was added to maintain Hg as Hg^{2+} in solution (Lo and Wai, 1975; Varian, 1996). Working standards were prepared daily in 6% of HNO_3 and were used without further purification.
(c) Tuning solution: a 10 mg L^{-1} multi-element solution (Merck, Damstad, Germany) was used to prepare a tuning solution containing several elements such as indium (In), uranium (U), Ba, Li, that allowed to sweep a wide range of mass.
(d) Internal standard solutions: 1000 mg L^{-1} standard stock solutions of scandium (Sc), yttrium (Y), In, rhenium (Re), bismuth (Bi) were purchased from Analytika (Prague, Czech Republic). The five internal standards were added to all samples, calibration standards and blanks at the same concentration, to obtain information on changes in sensitivity in different mass regions. The software handles multiple internal standard in "interpolated" way: the target analyte is converted by a factor proportional to its mass difference between two internal standards in a profile of internal standard across the mass range.
(e) Certified reference materials: BCR 278R (mussel tissue) from the Community Bureau of Reference, IAEA 407 (fish tissue) from the International Atomic Energy Agency, INCT MPH 2 (mixed herbs of Polish origin) from the Institute of Nuclear Chemistry and Technology, were all purchased from LGC Standards (Molsheim, France).
(f) Ultrapure grade carrier (argon (Ar), 99.9995% pure) was supplied by Linde (Montereau, France).