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NIM'S ROLE IN DEVELOPING NATIONAL SYSTEM OF METROLOGY IN CHEMISTRY FOR FOOD ANALYSIS

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Abstract – The growing attention is paid to food analysis area in recent years. National Metrology Institutes have been playing the important roles in obtaining reliable, comparable and traceable analytical data. In this paper, the tasks and performances of National Institute of Metrology (NIM) China in the National System of Metrology in Chemistry (NSMiC) for food analysis are reviewed in the following aspects including: establishing the national primary standards, developing CRMs, organizing national proficiency tests, participating in CCQM comparisons and claiming Calibration Measurement Capabilities (CMCs). Finally, future perspective for the metrological underpinning to the development of food analysis is overviewed.

Keywords: food analysis, metrology, National System of Metrology in Chemistry

1. INTRODUCTION

In recent years, food safety has been a global concerned issue. More and more attention have been paid to maintaining and improving the quality of data resulting from food analysis, because it not only relates to effective assurance of the quality and safety of food, underpinning of risk assessment studies, but also to sustainable development of national economy and stabilization of society.

The requests are multidimensional in terms of food analysis, such as a large number of chemical entities, a wide variety of matrices, and mass fractions ranging from $<10^{-12}$ to 1. In addition, with the innovations of scientific technology, various measurement methods are rapidly developed and applied to food analysis. How to obtain accurate measurement results from such complex system and how to guarantee the traceability and reliability analytical findings for such huge amount of the analytical data are the challenges for the analytical scientists.

Metrology, standardization and conformity assessment have gradually been recognized as three indispensable "pillars" to support the sustainable development worldwidely and to establish equal and fair trade relationship internationally in the future. As one of the main parts in metrology, chemical metrology aims to obtain the measurement results with the characteristics of accuracy, reliability and comparability, which are the basis for mutual acceptance for analytical results.

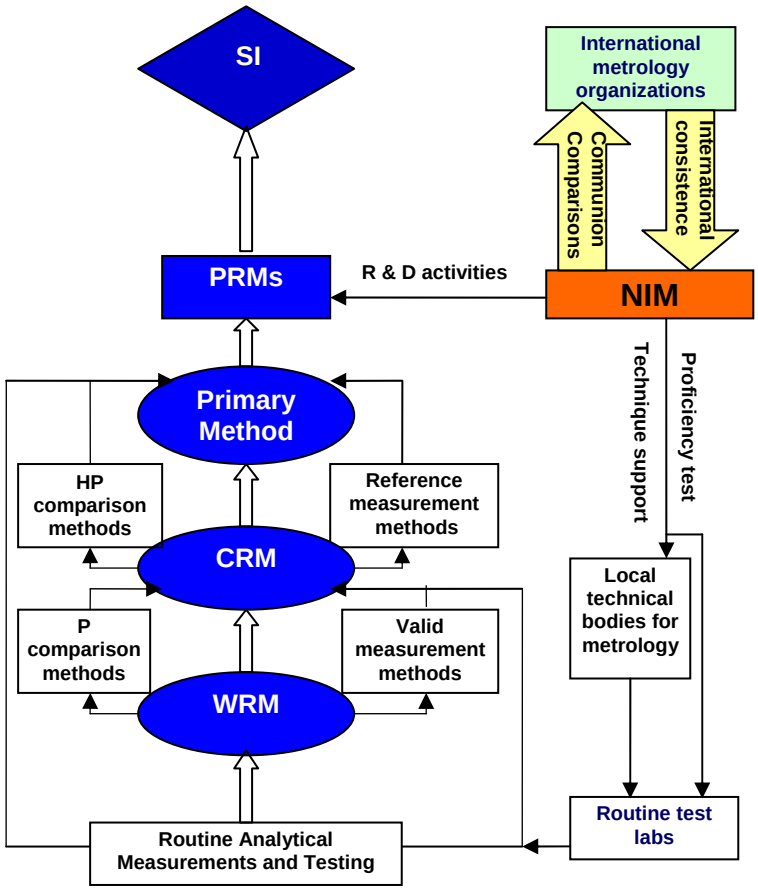

Fig.1 NIM's role in the NSMiC

Based on the analysis of the functions and features of metrology, the concept of National System of Metrology in Chemistry (NSMiC) is defined. As China's national metrology institute, National Institute of Metrology (NIM) has been playing a great role in the process of developing NSMiC (Fig.1). NIM carries on the scientific research activities and metrological services to the customers at the top level of NSMiC. NIM takes part in technical activities organized by international and regional metrology organizations, participates in comparisons to achieve the international consistency in terms of chemical metrology study, establishes and develops the good relationship with other NMIs.

The tasks and achievements of NIM in NSMiC for food analysis are reviewed in this paper in the following aspects.

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- Establishing and maintaining national measurement standards
- Studying methodology
- Developing food-matrix CRMs
- Participating in international comparisons studies in the food arena and claiming relevant CMCs
- Organizing proficiency test schemes

These activities have and will ensure the reliable, comparable and traceable measurement results for food analysis.

2. ESTABLISHING AND MAINTAINING NATIONAL MEASUREMENT STANDARDS

NIM is the origin, to which all quantity values nationwide are traceable. NIM is a national legal technical body implementing the Law on Metrology of China. Division of Chemical Metrology and Analytical Science is one of the nine professional divisions of NIM. The mission of Chemical Metrology division is responsible for developing, improving and maintaining national measurement standards and reference materials for metrology in chemistry, working to ensure the accuracy and international consistency of China's chemical measurements and analysis.

With regards to methodology study, we carry out the study of primary methods in chemistry to establish a traceability system for national chemical metrology, among which including isotope dilution mass spectrometry (IDMS) for trace chemical components in various matrix samples, Coulometry and Freezing point degression methods for high pure substance analysis, etc. These primary methods have been employed in developing certified reference materials and establishing national measurement capabilities. In order to produce reliable analytical data method validation is an essential component of the measures that we implement during the application of a primary method. We make use of a set of tests to demonstrate whether the method is fit for a particular analytical purpose in terms of applicability, selectivity, calibration, precision, recovery, operating range, limit of quantification, limit of detection, sensitivity, and ruggedness [1].

Up to now, we have established 6 national primary standards for pH, Electrolytic Conductivity, chemical purity determination, Combustion Heat, Viscosity and Humidity, respectively. 42 national standards for chemical measurements, such as AAS, ICP-OES, GC, LC, GC-MS etc. have been established. Thus, the quantity values nationwide of chemical measurements are able to be traceable these national primary standards.

3. DEVELOPING FOOD-MATRIX CRM'S

Certified Reference Material (CRM) is a reference material characterised by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability. CRMs play a key role in the proper implementation of analytical methods aiming at reliable results. CRMs are used to assess measurement method and procedure, to assign value to measurand, to provide quality assurance for measurement trueness control. The use of CRMs is not only test and evaluate capability of a laboratory, but offers also an added value for laboratories that want to improve their capability to provide analytical quality of high order. NIM established a set of quality assurance system for development of CRMs. The system is in accordance with ISO/REMCO guides 30,31,34 and 35 and fully implements ISO/IEC guide17025. Fig2 presents the technical route for development of CRMs in NIM.

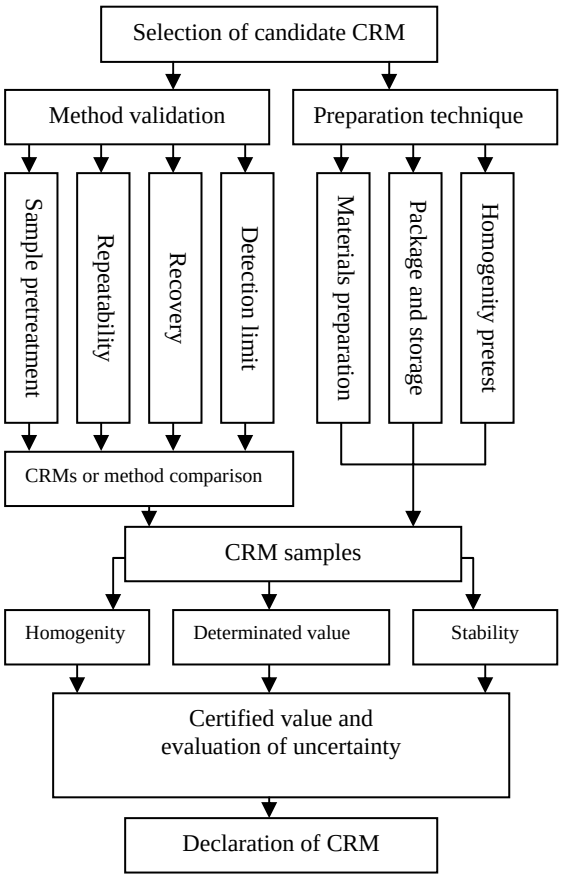

Fig2 Technical route for developing CRMs in NIM

For food analysis, we have developed more than 20 food-matrix CRMs, such as milk powder, agricultural products, Chinese herbal medicine, feed, seafood, package materials, etc. The properties of CRMs are focused on toxic/harmful elements and elemental speciations, food additives, pesticide residue, veterinary drugs, and nutritional components. More than 200 kinds of mono/multi-element solution CRMs and high purity compound CRMs are available for the purpose of calibrating analytical instruments and using as working standards. In addition, in order to better use IDMS method, we have developed enriched isotope spike CRMs as well as isotope CRMs. Some typical CRMs for food analysis are showed in table 1. Certified values of these CRMs are measured by primary methods or several independent reference methods. The possible sources of the uncertainty for CRM are evaluated including homogeneity and stability of the materials.

NIM also puts efforts to study the standard measurement methods and development of CRMs for emergency accidents in the food safety field. It enables NIM to provide powerful technical support to food safety issues that affect human health. For example, NIM was actively involved in Melamine analysis in tainted milk in 2008 and a LC-UV standard method and a Melamine reference material developed by NIM were available timely.

Nowadays there are the continued and increased needs for appropriate analytical methods and CRMs for food and feed analysis due to their importance in assuring the quality and metrological traceability of measurement results and determining their measurement uncertainty. Certified reference materials, validated measurement methods and procedures, and reference laboratories with demonstrated competence, are components of a reference measurement system providing food analysis laboratories with tools to achieve valid and traceable measurement results.

Table 1. CRMs for food analysis

Materials	Analytes	Methods for certified value
Corn powder	Pb, Cd	ID-ICP-MS,ICP-OES,AAS
Red wine	Pb, Mn, Cu, Fe	ID-ICP-MS, ICP-OES, AAS
Nonfat milk Powder	Se, Zn, Fe, As, Na, Mg, Ca, Cu, Mn, Pb, N, P, Cl	ID-TIMS, ICP-OES, AAS, IC
Laver	Pb, As, Cd	ID-ICP-MS, AFS ,ICP-OES , AAS, INAA
Tuna fish	MeHg, Hg	HPLC-ID-ICPMS, HPLC-ICPMS
Salmon	DDT,DDE, Hexachlorobenzene, Chlordane	ID-GC-MS
Salmon oil	7 PCBs	ID-GC-MS
Solution	MeHg, EtHg	HPLC-ID-ICPMS, ICP-OES, ICP-MS
	AsB, AsC	ICP-MS , HPLC-ICPMS, ICP-AES
Enriched isotope spike solution	^{207}Pb, ^{111}Cd, ^{202}Hg	ID-ICP-MS, MC-ICP-MS
Isotope solution	Zn, Nd, Sm, Li, Fe	TIMS, MC-ICP-MS
High purity materials	10 amino acids	Titration, HPLC, IR

3. PARTICIPATING IN INTERNATIONAL COMPARISONS IN THE FOOD ARENA AND CLAIMING CMCS

Participating in interlaboratory comparisons among national metrology institutes (NMIs) is an efficient path for realizing validation of methods and achieving mutual recognition for measurement results. Food safety has been a global concerned issue. Worldwide equivalence of food measurements is necessary for trade and regulatory enforcement. In recent year, CCQM OAWG & IAWG have organized a number of key comparisons and pilot studies as well which focuses on food analysis. NIM has been actively participating in those CCQM comparisons, and moreover, NIM has successfully conducted three food analysis comparisons as a coordination laboratory. Table 2 shows part of key comparisons on food analysis, where NIM's results are all within the degree of equivalence (http://kcdb.bipm.org/AppendixB). Fig 3,4 show the results of CCQM-K49[2] and CCQM-K21[3] respectively.

The mutual recognition arrangement (MRA) drawn up in 1999 by the CIPM. It is a response to the growing need for an open, transparent and comprehensive scheme to give users reliable quantitative information on the comparability of national metrology services and to provide the technical basis for wider agreements negotiated for international trade, commerce and regulatory affairs. This is normally achieved through international comparisons of measurements performed at NMIs and Designated Institutes to provide an independent assessment of performance.

A CMC is a calibration and measurement capability available to customers under normal conditions:*(a)* as published in the BIPM key comparison database(KCDB) of the CIPM MRA; or*(b)* as described in the laboratory's scope of accreditation granted by a signatory to the ILAC Arrangement[9]. On the basis of related comparisons, NIM has 18 CMCs in food analysis, 31 CMCs in purity chemicals and 56 CMCs in organic/inorganic solutions published in BIPM KCDB by the end of 2008.

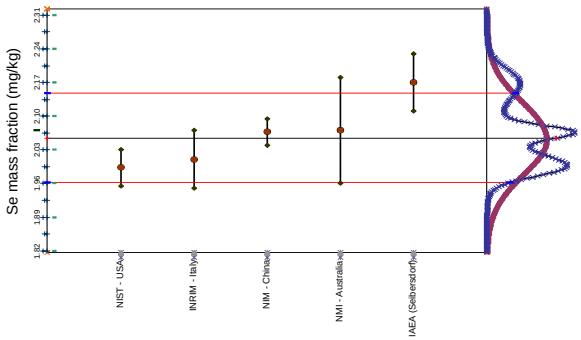

Fig.3 CCQM-K48 Toxic and essential elements in bovine liver

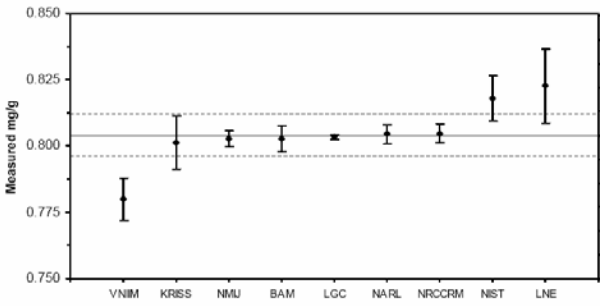

Fig.4 CCQM-K27a Ethanol in aqueous matrix
(NRCCRM refers to the result of NIM)

Table 2 CCQM key comparisons on food analysis

No.	Content	Date
CCQM-K5	p,p´-DDE in Fish oil	1999
CCQM-K21	p,p´-DDT in Fish oil	2000-2001
CCQM-K24	Cd in Rice	2001
CCQM-K27a,b	Ethanol in aqueous matrix	2002
CCQM-K38	PAHs in Solution	2004
CCQM-K39	Chorinated Pesticides in Solution	2004
CCQM-K40	PCB Congeners in Solution	2004
CCQM-K30	Lead in wine	2006
CCQM-K49	Essential and Toxic Elements in Bovine Liver	2006
CCQM-K43.1	As, Hg, Se and methylmercury in marine fish	2006
CCQM-K56	Cu、Zn、Ca、Fe in Nonfat Soybean Powder	2006
CCQM-K59	Nitrite and mitrate in calibration solution	2006-2007
CCQM-K60	Total Se and selenomethionine in selenised wheat flour	2008
CCQM-K62	Nutrients in infant formula	2007-2008

International comparisons organized by the CCQM within the framework of the CIPM-MRA are providing a transparent system for NMIs to demonstrate the comparability of their measurement capabilities intended for the assignment of values to CRMs or measurements, thereby providing a link to the global measurement infrastructure. Through good performance in CCQM comparisons and in claiming CMCs, the reliability and comparability of measurement methods and CRMs developed by NIM are validated. Meantime, we achieve and keep the international consistency in terms of chemical metrology study in the field of food analysis.

4. ORGANIZING PROFICIENCY TEST

Proficiency test (PT) schemes provide an independent and unbiased assessment of performance, which can be used by participants to assess the performance of their analytical methods and procedures [4]. In recent years, in response to the requirement of accurate measurement on food analysis, NIM have organized several proficiency tests in the field of food analysis, such as organochlorine pesticides analysis, Pb, Cd in corn, and Melamine in milk.

In this paper, PT for Pb,Cd in corn organized by NIM in 2008 is taken as an example to present the general PT procedure and the related results[5]. The aim of this PT is to assess the capability of laboratories of quality, checking measurement procedures, enhancing reliability of measurement results for foodstuff, and providing technique underpin for international trade.

70 laboratories including local metrological laboratories and food analysis laboratories from over 19 provinces plus Hongkong SAR in China participated in this PT. Wheat powder was selected as the test material candidate after the homogeneity and stability assessment in accordance with the technical specification of national reference materials. The PT samples along with an experiment protocol were then distributed to the participants. Each participant in the PT received only one sample and is free to use any method for the analysis. These laboratories are required to submit the measurement results 4 weeks after receiving the sample. After that, the statistical analysis was conducted followed by the report circulation.

Analytical methods including AAS, ICP-MS, ICP-OES and AFS were employed in this PT. The robust statistical procedure was used to statistically analyze all the submitted results. The end product of the performance assessment was a standardized statistic known as a z-score. z-scores between +2 and –2 were considered an indicator of satisfactory performance. Fig 5, 6 show the PT results for Pb, Cd in wheat powder, the real line refers to median value, and the broken line refers to the standard deviation. For Pb and Cd measurement, 90% and 86% of laboratories obtained a satisfactory z-score respectively.

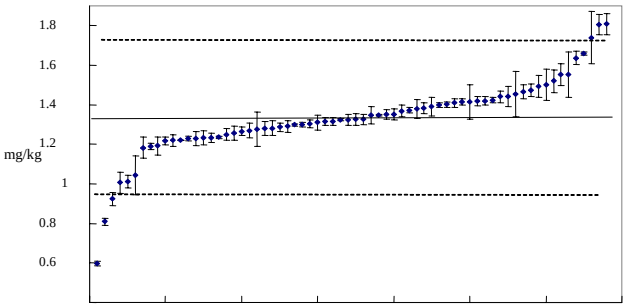

Fig.5 Result of Pb in wheat powder

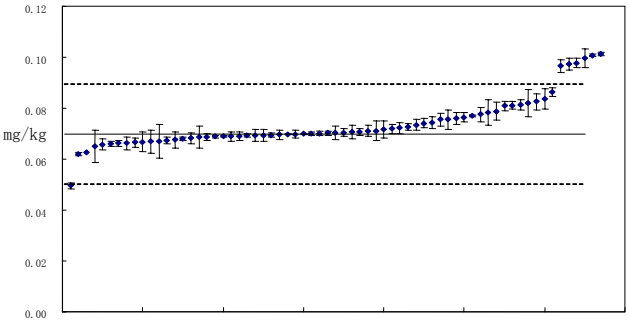

Fig.6 Result of Cd in wheat powder

Through organizing proficiency tests, NIM could to improve the ability of routine test laboratories on following aspects: 1) selecting appropriate traceable measurement methods, 2) using appropriate CRMs or reference materials, 3) establishing an operation process for traceability of measurement values, carrying out the evaluation of measurement uncertainty.

5. OUTLOOK FOR UNDERPINNING FOOD ANALYSIS

With the rapid growth of globalization of world economy, especially the extending of food trade, the issue of

food safety is more and more internationalization. The effect of food safety on human health has become a hot topic around the world. The new developments in food science and technology provide more opportunities and cchallenges to chemical metrology. In recent years, there are increasing requirements for metrology in the field of food safety. Such as assessment of safety of GM food, biotech food and crop, identification of new food or food components, evaluation of impact of functional food and health food, setting limit to contamination and additive in food[6-9]. Therefore, extending metrological field on food and feed analysis, studying and establishing measurement methods of higher order, and enhancing the quality of traceability are the arduous work for chemical metrology. As the foundation of the development of economy, technology and society, metrological research should possess foresight and impendency.

Food metrology is an emerging discipline. Facing the opportunity and challenge of the development of food arena, NIM will continue to engaged in promoting and perfecting the National System of Metrology in Chemistry to well meet the needs for food analysis through following activities: 1) further improving the quality assurance system, 2) researching and establishing new standard reference methods for specific property of food matrix materials and pure substance, 3) developing high level CRMs of food and feed matrix and calibrating solutions, and underpinning reference value assignment for PT schemes, 4) actively involving in international activities, strengthen international technique cooperation and communication in the field of food safety.

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