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Twenty five years of reference material activity at Agriculture and Agri-Food Canada

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Abstract In the mid 1970s, the available RMs, notably Bowen's Kale and Orchard Leaves and Bovine liver from National Bureau of Standards (NBS), although of great benefit, were overwhelmingly insufficiently representative, in respect of matrix and elemental composition, of the wide range of natural products submitted for analysis and in worldwide commerce. To provide additional coverage, an RM development project was initiated with input from cooperating analysts leading to an Agriculture and Agri-Food Canada/National Institute of Standards and Technology (NIST) cooperative venture and development of a total of 12 different agricultural/food RMs. With a total of 303 concentration values for 34 elements and a wide range of matrix components such as ash, silica, protein, fat, carbohydrate and fiber, these RMs significantly augment the world repertoire of biological control materials. A final material under consideration is a highly reliable, discrete, synthetic RM for quality control and calibration. This paper summarizes the research and developmental activities undertaken during the past quarter of a century related to RM development at Agriculture and Agri-Food Canada and includes a short historical background, conceptual considerations, preparation, physical characterization, homogeneity estimation, chemical characterization, calculation of recommended reference values and associated uncertainties, methodology development and application, and performance of inorganic analytical methods in a multi-element, multilaboratory, collaborative characterization campaign.

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Introduction

A cost-effective approach to monitoring and maintaining reliability of analytical procedures is the incorporation of appropriate, compositionally-similar reference materials (RM) into the scheme of analysis. Agricultural and food commodities encompass an extremely wide range of composition in respect of measurand and supporting material (matrix), which were not fully reflected in the biological RMs (BRMs) available a quarter of a century ago when the author's interest in RMs crystallized. It was with the intention of filling some of these gaps with suitable products that experimental work was initiated to deal with the selection, preparation and characterization of 12 agricultural/food RMs for inorganic constituents. This paper summarizes the research and developmental activities undertaken during the past quarter of a century related to BRM development at Agriculture and Agri-Food Canada (AAFC). These activities are recorded in the complete list of references referring to AAFC RM development and related activities [1–61], participation in other RM undertakings and intercomparisons [62–66], and relevant analytical method development [67–77].

Background and conceptual considerations [1–3, 6, 9, 12, 14–16, 19, 20, 43, 45, 46, 57]

The beginning of the author's interest in RMs can be traced to the early 1970s, with his need to monitor method development and application activities during development of a fluorimetric method for Se [67, 68]. SRM 1571, Orchard Leaves, and SRM 1577, Bovine Liver, from the National Institute of Standards and Technology (NIST), then fondly known as National Bureau of Standards (NBS), were used to complement other dry food products prepared on a small scale, for example beef steak, potato, skimmed-milk powder, oat cereal, carrot, flour, and various fish. This interest advanced with ideas of augmenting the then very small world repertoire of natural matrix BRMs and sub-

stantive discussions were had with R.W. Dabeka, Health and Welfare Canada and W.R. Wolf, USDA. Wolf and his laboratory assisted with preliminary and final analyses in the early stages for several of the first materials; Dabeka made highly skilled contributions to homogeneity and certification with reliable analyses of many products. Early contact with NBS was via R. Alvarez and a meeting with J.P. Cali, Chief, Office of Standard Reference Materials in October 1978 at which the author expressed his interest in supplementing NBS's limited stock of BRMs. Discussions over the following years with subsequent Chiefs, G.A. Uriano, S. Rasberry, and W.P. Reed led to acceptance of AAFC products by NIST for distribution as RMs by the Standard Reference Materials Program, SRMP.

The history of BRMs [12] indicates an interesting but limited array of materials at the time of initiation of this activity, with the better known products being Kale produced by Bowen in the UK, and SRM 1577, Bovine Liver, SRM 1571, Orchard Leaves, SRM 1570, Spinach, SRM 1573, Tomato Leaves and SRM 1575, Pine Needles from NBS. Other RMs were available or coming on stream from the Commission of the European Community and the IAEA. The rationale for additional RMs included the non-concordance of the limited existing BRMs with materials being analyzed in AAFC laboratories and with the wide range of food and agricultural commodities in commerce with respect to matrix and measurand levels [9, 16, 73]. If the premise is accepted that there should be a reasonably close correspondence, in respect of measurand and matrix composition, between RMs and test samples, a variety of RMs must be available; the AAFC program was formed to help fill the gap.

Preparation and physical characterization [1, 2, 4–6, 9, 12, 15, 20, 22–31, 34, 37, 42, 49–55, 58]

Preparation refers to all the physical steps necessary to bring the starting material to candidate material status. It includes acquisition of commercially available or custom-prepared starting material, and steps dealing with collection, cleaning, component separation, comminution, drying, sieving, blending, and packaging. Selection, testing and assessment of preparative procedures, control and monitoring of contamination, assessment of stability expected during long-term storage, and steps for stability enhancement are other details in the preparative effort.

Sources of materials were either in-house production (RM 8412 Corn Stalk, RM 8413 Corn Kernel, RM 8414 Bovine Muscle Powder) or commercial suppliers (RM 8415 Whole Egg Powder, RM 8416 Microcrystalline Cellulose, RM 8418 Wheat Gluten, RM 8432 Corn Starch, RM 8433 Corn Bran, RM 8435 Whole Milk Powder, RM 8436 Durum Wheat Flour, RM 8437 Hard Red Spring Wheat Flour, RM 8438 Soft Winter Wheat Flour). Codes are NIST designations, and this list includes all 12 RMs brought to completion and marketed by NIST.

The processing of all 12 RMs was performed at the facilities of AAFC, Ottawa. Most processing steps were con-

ducted in a specially prepared, moderately clean preparation room equipped with preparation equipment, utensils, furniture, and necessary accessories. Where possible, construction was from plastic or wood and laboratory personnel were clothed in low-linting clothes and footwear to minimize contamination of the materials with metal and dust. Particle size reduction was effected by ball milling using Teflon equipment. Sieving was through nylon monofilament sieve cloths. Blending of sieved materials was typically accomplished in a custom-manufactured V-configuration blender with a poly(methyl methacrylate) mixing chamber.

Once prepared, RMs were packaged into nominally 60-mL or 120-mL clear glass bottles fitted with pulp/Saran® or Triseal® (polyethylene)-lined polypropylene caps. Filling was performed manually by weighing. During this operation, units were randomly removed and set aside for physical and chemical characterization. Four materials, bovine muscle powder, whole egg powder, whole milk powder and, later, durum wheat flour were also individually sealed in aluminum–nylon pouches to enhance long-term stability.

Physical characterization included sieving, macroscopic (visual) and microscopic examination, assessment of particle-size distribution, moisture loss/pickup, and moisture determination techniques. Observations were made of the physical appearance, flow characteristics, and color of the originally-acquired or prepared materials. Small-scale test sieving was performed on representative portions of the starting materials to ascertain particle-size distribution for decisions about preparatory sieve sizes and the requirement for additional particle-size reduction. Sieve sizes were chosen to encompass the expected ranges of particle sizes in initial and final candidate reference material preparation.

In addition to the twelve materials selected as candidate RMs, many other products were subjected to cursory visual examination and some were subjected to detailed visual and microscopic examination and test sieving to aid selection. Table 1 lists all such materials considered and examined; the 12 brought to completion are indicated in the table by their NIST codes.

Chemical characterization [1, 2, 4–12, 17, 18, 20, 22–31, 33–35, 37–44, 46, 49–57, 59, 60]

Chemical characterization deals with the establishment of measurand concentration values, in accordance with an appropriate protocol, to establish material homogeneity and to provide data for certification. Certification implies the assignment of a reliable, unassailable numerical value to a property of material. It deals with the assessment of analytical information, selection of data and computation, and assignment of certified (recommended) values and associated uncertainties or confidence limits.

Chemical characterization (certification) was the most demanding component of this undertaking. It encompassed measurand (element) selection based on nutritional, toxicological, and environmental significance and the availability of suitable analytical methodologies and analysts.

Table 1 Repertoire of agricultural/food starting materials acquired, prepared, considered, and investigated at Agriculture and Agri-Food Canada for development into reference materials for elemental content quality control

Material name	Working code ^a	Final status ^b
Corn (Zea Mays) Leaves	131	PC/CC
Corn (Zea Mays) Stalk	CS 132	NIST RM 8412
Corn (Zea Mays) Cob	133/135	PC/CC
Corn (Zea Mays) Kernel	CK 134	NIST RM 8413
Bovine Muscle Powder	BMP 136	NIST RM 8414
Rapeseed Flour (defatted)	137	PC
Rapeseed Hull Powder	138	PC
Yellow Mustard Flour (defatted)	139	PC
Yellow Mustard Hull Powder	140	PC
Blood Meal (Feed grade)	141	C
Ground Paprika	142	PC
Spray Dried Cheddar Cheese Powder	143	C
Dried Torula Yeast	144	PC
Tomato Powder	145	PC
Whey Powder	146	C
Edible Gelatin	147	C
Soybean Meal (44% protein)	148	C
Soybean Meal (48% protein)	149	C
Soybean Hulls	150	C
Canola Meal	151	C
Polished Long Grain Rice	152	C
Ground Paprika	153	C
Sesame Seed (whole)	154	C
Caraway Seed (whole)	155	C
Cocoa Powder	156	C
Desiccated Coconut	157	C
Ground Coffee	158	C
Corn Bran (G-regular)	159	C
Skim Milk Powder	160	C
Corn Germ	161	C
Corn Starch	CS 162	NIST RM 8432
Corn Gluten Meal	163	PC
Corn Germ Cake	164	C
Hard Red Spring Wheat Flour	HRSWF 165	NIST RM 8437
Soft Winter Wheat Flour	SWWF 166	NIST RM 8438
Hard Red Spring Wheat Bran	167	C
Soft Winter Wheat Bran	168	C
Oat Groats	169	C
Oat Hulls	170	C
Barley (Leger)	171	C
Frederick Winter Wheat	172	C
Oats (breeder seed)	173	C
Barley (Massey)	174	C
Fall Rye Seed	175	C
Rye Straw Powder	176	C
Black Spruce Wood Flour (Powder)	177	PC
White Birch Wood Flour (Powder)	178	PC
Spray Dried Brewer's Yeast	179	C
Casein	180	C
Peanut Meal	181	C
White Fine Granulated Sugar	182	PC
Whole Milk Powder	WMP 183	NIST RM 8535

Table 1 (continued)

Material name	Working code ^a	Final status ^b
Wheat Gluten	WG 184	NIST RM 8418
Potato Starch	185	PC
Corn Bran	CB 186	NIST RM 8433
Durum Wheat Flour	DWF 187	NIST RM 8436
Whole Egg Powder	WEP 188	NIST RM 8415
Microcrystalline Cellulose	MC 189	NIST RM 8416

^aCode assigned at Agriculture and Agri-Food Canada during development

^bProducts with NIST codes were brought to final RM status and are available from Standard Reference Materials Program, NIST, Gaithersburg, MD 20899, USA. Other materials were not brought to RM status for reasons of physical and/or chemical unsuitability or inhomogeneity, or lack of resources; they were, however, either considered and cursorily examined visually (C), subjected to preliminary physical characterization (PC), or subjected to more complete physical and chemical characterization (PC/CC)

It also included: selection of certification protocols based on definitive, reference, and validated methodologies; selection of expert analysts applying conceptually different approaches; selection, development, assessment, and validation of methodologies; and adaptation of statistical protocols for data treatment and calculation. The characterization philosophy adopted for the generation of reference concentration values was measurement by the 'selected expert laboratory – different method' route making use of at least two but typically several analytical methods, independent in theory and experimental procedure, applied by different analysts, thoroughly validated, and yielding sufficiently precise and accurate results. Additional input was by the initiating laboratories whose contributions served both homogeneity assessment and certification. Material homogeneity was measured in three ways:

1. at the micro level by use of solid-sampling graphite-furnace atomic absorption spectrometry (SSGFAAS);
2. precision of analysis; and
3. intra- and inter-bottle analysis of variance (ANOVA).

SSGFAAS measurements for Cu and Pb were carried out by M. Stoeppler and U. Bagschik at the Research Center, Jülich, Germany, using typically 0.0005 g sub-samples of material from several different units. Homogeneity assessment using precision was based on coefficients of variation (CVs) from analyses of sub-samples from randomly selected units performed by the two initiating laboratories (M. Ihnat at Agriculture and Agri-Food Canada, R.W. Dabeka at Health and Welfare Canada) and by the cooperating analysts participating in the certification campaign. The third estimation of homogeneity was based on ANOVA statistical calculations and comparisons of within- and between-unit variance components.

For chemical characterization, analysis was by the two initiating laboratories and outside analysts in two interlaboratory characterization campaigns. The two initiating laboratories performed analyses simultaneously for homogeneity and characterization. Analyses were performed at Agriculture and Agri-Food Canada by careful application

of a reliable (high precision/high accuracy) acid-digestion flame atomic absorption spectrometry (ADFAAS) method for Al, Ca, Cu, Fe, K, Mg, Mn, Na, Sr, and Zn. Cd, Co, Pb, and Ni were determined at Health and Welfare Canada by reliable graphite-furnace atomic absorption spectrometry (GFAAS) after acid digestion, coprecipitation with ammonium pyrrolidine dithiocarbamate, and isolation of the precipitate by filtration followed by dissolution in nitric acid. Lead was also determined by nitric-perchloric acid digestion, coprecipitation from perchloric acid with palladium carrier, and GFAAS. Cd was directly determined in nitric acid digests of some materials by GFAAS. Fluoride was determined by an acid-facilitated diffusion ion-specific electrode (EISE) procedure.

The bulk of the chemical characterization of the 12 materials for a wide range of elements involved a large number of selected outside analysts in the two interlaboratory characterization campaigns. A total of approximately 75 laboratories with 160 analysts participated in the final chemical characterization using a variety of reliable methods. The principal classes of methods applied were: atomic absorption spectrometry, atomic emission spectrometry, mass spectrometry, neutron activation analysis, X-ray emission spectrometry, molecular light absorption spectrometry, molecular fluorimetry, electrochemistry, the Kjeldahl method for nitrogen, combustion elemental analysis, volumetry, ion chromatography, and gravimetry. A concerted attempt was made to obtain results from wide-ranging measurement techniques and different sample-preparation approaches, including methods not requiring decomposition – as for instrumental neutron activation analysis and particle-induced X-ray emission spectrometry. Total measurand contents (the sum of all forms of the element in all phases of the material) were sought.

Calculation of reference concentration values [4, 5, 7, 8, 12, 22–31, 38–43, 49–55, 59, 60]

Overall, the chemical characterization campaigns involved 14,275 elemental analytical determinations on sub-sample masses ranging from 0.0005 to 10 g, typically 0.5 g. Data treatment and calculation led to 303 reference and information concentration values for 34 elements of nutritional, toxicological, and environmental interest at major, minor, and trace levels. Before final calculation of reference and information values, the analytical results were carefully inspected, using technical, statistical, and judgmental criteria to remove aberrant, outlying or unrepresentative data. Outlying data were rejected in three steps:

1. deletion of obviously erroneous data;
2. deletion of data with excessive imprecision or systematic errors (bias); confirmation of rejection by noting performance with appropriate certified RMs; and
3. rejection of additional outliers when their retention would have a serious impact on final uncertainty.

Outlier rejection criteria included:

1. within-laboratory precision;
2. within-sub-sample precision (within-laboratory instrumental precision);
3. laboratory systematic error;
4. accuracy (based on performance with certified RMs);
5. within-laboratory precision with certified RMs;
6. technical merit of the analytical procedure;
7. number of sub-samples analyzed.

Reference concentrations were calculated from the accepted data-set as the mean of equally-weighted individual laboratory means retaining determinations by as many independent, diverse methods as possible to strengthen the accuracy of the final values. The associated standard deviations (SD) were calculated from the three variance components representing within-unit (σ_w^2), among-unit (σ_u^2), and among-laboratory/method (σ_L^2) variation according to the equation:

$$SD = (\sigma_w^2 + \sigma_u^2 + \sigma_L^2)^{1/2}$$

where each σ indicates the estimates of the associated variance component obtained from a type-I (hierarchical) variance component analysis. Reference concentrations, weight percent or mg kg⁻¹ (ppm), presented in Reports of Investigation [4, 5, 22–31, 49–54] are based on the dry material and are equally-weighted means of results from, generally, at least two, but typically several, different analytical methods applied by analysts in different laboratories. Uncertainties are estimates expressed either as 95% confidence intervals or occasionally as intervals based on ranges of accepted results for a single future determination based on a sample weight of at least 0.5 g. These uncertainties, based on among-method and laboratory, among-unit and within-unit estimates of variances, include measures of analytical method and laboratory imprecision and bias, and of material inhomogeneity. In instances with limited data, only ‘information concentration’ values were assigned.

Distribution

Adequate documentation was produced in respect of the numerical values assigned to the products, instructions on use, and information on production and characterization in the Reports of Investigation and in the many scientific and technical publications issued with this endeavor. A distribution/marketing strategy with the related infrastructure of storage, pricing, marketing, handling, and shipping is effectively being managed by NIST under a Technology Licensing Agreement between AAFC and NIST signed in 1993.

Methodology development and application [62–77]

Preceding and concurrently with the RM activity, development of analytical methodologies [67–77] and their ap-

plications in a variety of cooperative research and technology-transfer activities was another major activity. These highly reliable methods consisted, principally, of an acid digestion fluorimetric method (ADF) for selenium [67, 68] and acid-digestion flame atomic absorption spectrometry (ADFAAS) for approximately 12 elements [69–77]. They were relevant to the RM undertaking and extensively used in-house for RM homogeneity testing and contribution to certification.

Invitations were received from many agencies to participate in RM characterization and intercomparison exercises for major, minor, and trace elements. Participation in several permitted additional application of developed methods [62–66]: NBS, Gaithersburg, MD (Standard Reference Material 1572 Citrus Leaves, Ca, Cu, Fe, K, Mg, Mn, Na, Zn by ADFAAS, 1981); National Research Council of Canada, First Marine Analytical Chemistry Standards Program Intercomparison Exercise for Trace Metals in Marine Biological Tissues (Cu, Zn in Dogfish, Scallops, Swordfish by ADFAAS, 1984); Department of Internal Medicine, University Hospital, Ghent, Belgium, (Dr. Jacques Versieck's 2nd generation human serum: Se by ADF, Cu, Zn by ADFAAS, 1985); Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, Warszawa, Poland (Dr. Rajmund Dybczynski, Collaborative Study on the Determination of Trace Elements in Oriental Tobacco Leaves CTA-OTL-1 and Virginia Tobacco Leaves CTA-OTL-2: Ca, Fe, K, Mg, Mn, Na, Sr, Zn by ADFAAS, 1989); Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, Warszawa, Poland (Dr. Rajmund Dybczynski, Intercomparisons for Certification of Tea Leaves INCT-TL-1 and Mixed Polish Herbs INCT-MPH-2: in progress 2000). Leading and participating in the characterization of human blood serum, Seronorm 102 and 103, for Se under auspices of IUPAC is covered under RM development [7, 8, 10, 11]. Performance of inorganic analytical methods in a multielement, multilaboratory, collaborative characterization campaign is recorded elsewhere [44, 56].

Future developments [43]

Although great strides have been made in the past three decades with elemental composition biological RMs, there is still a shortage of elemental concentration data for a wide range of nutritionally, toxicologically, clinically, and environmentally pertinent elements (e.g. Al, Ba, B, Be, Br, Cs, F, I, Li, Mo, N, Pt, S, Sb, Si, Sn, Th, Ti, Tl, U, V, W, rare earth elements, and radionuclides). Little information is available about bioavailable, extractable, or leachable levels of elements and elemental chemical forms or species.

Very few, if any, soil and related RMs certified for extractable elemental concentrations are available for monitoring of the usual procedures in soil science based on extraction. Extractable concentrations are *method-dependent*, an idea which has to be rationalized with the fundamental *method-independent* concept in RM certification work; ex-

perimental, practical and conceptual issues must be resolved. It will be a challenge to develop soil materials for extractable elemental nutrients and toxicants applicable to soil and environmental science.

Naturally-occurring matrices to be considered in continuing and future developments include animal tissues, sewage sludges, wastes of various kinds, soils representative of various important agricultural areas, marine tissues and oils, fresh full-fat food and marine products, waters (drinking, fresh surface, ground, sea, waste), human tissues, and plastics.

In all endeavors, the selection of required, but poorly-represented matrices and measurands is, however, tempered by the need for, and possible shortage of, highly competent analysts required for analysis and certification, the difficulties of accurate work at trace and ultratrace levels, and methodological deficiencies for specific measurands.

RMs based on pure basic standards, either pure calibration preparations or synthetic calibrants or 'synthetic RMs' are in use but it would be of interest to take synthetic RMs further. Consideration is being given to the concept and development of a 'high reliability Synthetic Reference Material' to complement natural matrix products.

Development of a comprehensive multielement flame atomic absorption spectrometric method for the determination of elements in food and biological materials is in progress. Scientific and technical information relating to the 12 Agricultural/Food Reference Materials will continue to be disseminated and the author continues to serve as the scientific authority. This includes participation with work at NIST to characterize some of these RMs for other nutritional parameters such as proximate constituents, fatty acids, and caloric value and issuance of revised Reports of Investigation [49–54]. Final scientific publications on the RM endeavor, high-reliability atomic spectrometric method, and a joint NIST/AAFC Technical Report, comprehensively documenting the entire Reference Material development venture, are in preparation.

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