Characterization of Three Berry Standard Reference Materials for Nutrients

Laura J. Wood,* Katherine E. Sharpless, Monique Pichon, Barbara J. Porter, and James H. Yen

National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Stefan Ehling

Grocery Manufacturers Association, Washington, D.C. 20005, United States

ABSTRACT: The National Institute of Standards and Technology (NIST) has been working with the National Institutes of Health Office of Dietary Supplements to produce Standard Reference Materials (SRMs) of interest to analysts of dietary supplements. Some of these SRMs are traditional foods including SRM 3281 Cranberry (Fruit), SRM 3282 Low-Calorie Cranberry Juice Cocktail, and SRM 3287 Blueberry (Fruit), which have been characterized for nine nutritional elements and sugars. The blueberries have also been characterized for proximates, two water-soluble vitamins, and amino acids. These new materials are intended for use in method development and validation as well as for quality assurance and traceability in the assignment of values to in-house control materials. Foods can be difficult to analyze because of matrix effects. With the addition of these three new SRMs, it is now possible to more closely match controls to matrices and analyte levels for fruit and vegetable test samples. Several nutritional elements in these three SRMs are present at lower levels than in other food-matrix SRMs.

KEYWORDS: berries, referece material, dietary supplements, cranberries, blueberries

INTRODUCTION

The Nutrition Labeling and Education Act of 1990 requires that processed foods sold in the United States be labeled with specific nutrition information, whereas labeling of raw fruits and vegetables is voluntary as long as at least 60% of the industry provides nutrition information on labels or at the point of sale.[1] In continued support of this legislation, the National Institute of Standards and Technology (NIST) is developing several new food Standard Reference Materials (SRMs) for laboratories to use to ensure the quality of the information they provide on their labels. This paper describes the value assignment of nutritional elements and sugars in SRM 3281 Cranberry (Fruit), SRM 3282 Low-Calorie Cranberry Juice Cocktail, and SRM 3287 Blueberry (Fruit) as well as proximates, two water-soluble vitamins, and amino acids in SRM 3287. A separate publication[2] describes preparation of these three materials and characterization of organic acid content. These SRMs are intended for use as primary control materials in the assignment of nutrient and organic acid values to in-house (secondary) control materials and for validation of analytical methods for the measurement of these analytes in similar matrices.

Foods can be difficult to analyze for elemental content because matrix effects result from the presence of easily ionized elements (e.g., sodium and potassium) as well as elements that are more difficult to ionize.[3] These effects can be minimized by using the method of standard additions. At low concentrations, the detection of an element becomes subject to interferences, which may not be apparent when the element is at a higher concentration.[4] Spectral background shifts are more evident when trace levels of analytes are measured and can cause enhancement or suppression of the signals of the analytes of interest. Differences in spectral background can cause poor repeatability if an unsuitably matched sample is associated with a control that has a particularly high concentration of a spectral interferent.[5] Therefore, it is important to analyze a control material that is compositionally similar to the test samples being analyzed.

AOAC International developed a food composition triangle to demonstrate the applicability (or lack thereof) of an analytical method to foods; if the method provided reliable results for one or two foods with a certain fat, protein, and carbohydrate composition, the method was expected to do the same for foods of similar composition.[6,7] NIST extended this model to reference materials:[8] a reference material of a certain composition is expected to be useful as a control material for other foods of similar compositions. Food-matrix SRMs distributed across the nine sectors of the triangle were produced to meet the need for reference materials of these various compositions. The food and dietary supplement SRMs that have been characterized for fat, protein, and carbohydrate content are shown in the AOAC triangle in Figure 1. SRM 3287 Blueberry (Fruit) is located in sector 5, with its high carbohydrate content and low fat and protein contents. SRM 3281 Cranberry (Fruit) and SRM 3282 Low-Calorie Cranberry Juice Cocktail have not been placed in one of these sectors because proximate analysis was not performed on either of these materials. On the basis of USDA nutrition data,[9] the locations of both are also expected to be in the lower left corner of sector 5.

EXPERIMENTAL PROCEDURES

Phillips et al. describe the preparation of the SRMs.[2] Briefly, SRM 3281 Cranberry (Fruit) and SRM 3287 Blueberry (Fruit) consist of
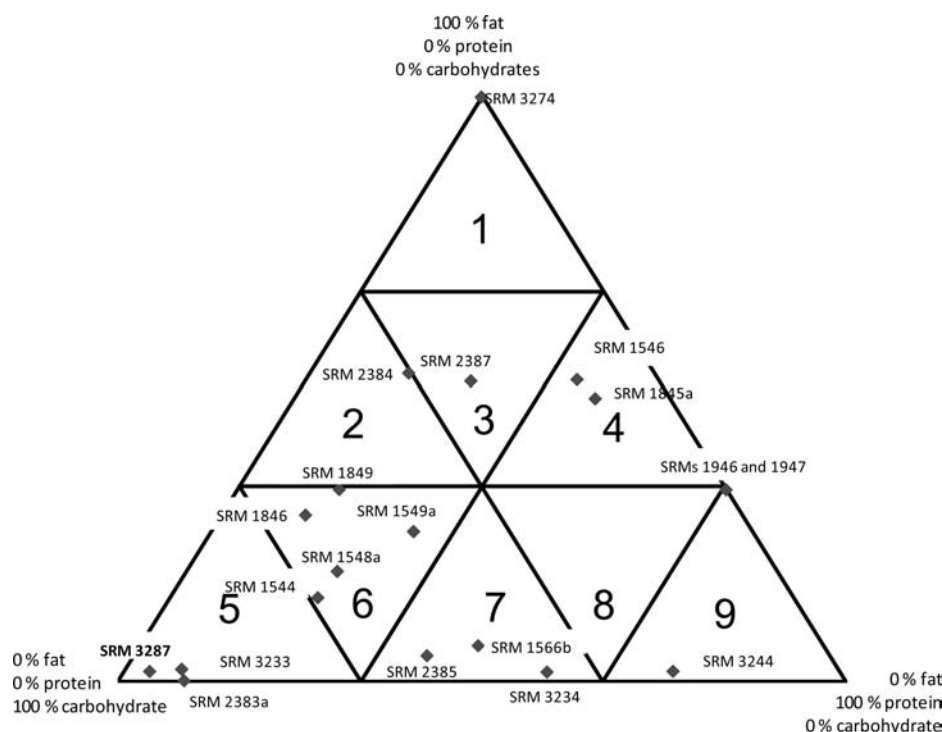
Figure 1. Location of SRM 3287 Blueberry (Fruit) in the AOAC fat−protein−carbohydrate triangle. Other materials in sector 5 are SRM 3233 Fortified Breakfast Cereal (in preparation), SRM 2383a Baby Food Composite (in preparation), and probably SRM 3281 Cranberry (Fruit).

Table 1. Laboratories Reporting Data for Their Analysis of One or More of the Three SRMs Described in This Paper

Campbell Soup Co., Camden, NJ	Krueger Food Laboratories, Billerica, MA
ConAgra Foods Analytical Laboratory, Omaha, NE	Silliker Inc., Chicago Heights, IL
Covance, Inc., Madison, WI	The Coca-Cola Co., Apopka, FL
Eurofins Scientific, Inc., Des Moines, IA	The J. M. Smucker Co., Orrville, OH
General Mills, Inc., Minneapolis, MN	The National Food Laboratory, Livermore, CA
Hormel Foods Corp., Austin, MN	The Schwan Food Co., Salina, KS

freeze-dried, ground, and sieved cranberries and blueberries, respectively. Low-calorie cranberry juice cocktail was used to produce SRM 3282.

Value assignment of the mass fractions of nine nutritional elements (calcium, copper, iron, potassium, magnesium, manganese, sodium, phosphorus, and zinc) in the blueberry and cranberry fruit SRMs was based on the combination of NIST determinations using inductively coupled plasma optical emission spectrometry (ICP-OES) and determinations by collaborating laboratories (Table 1). (Phosphorus was not detected in SRM 3282 by NIST using ICP-OES.)

In preparation for ICP-OES measurements at NIST, duplicate 0.5 g portions were taken from each of six packages of SRMs 3281 and 3287 and single 1.5 g portions were taken from each of six ampules of SRM 3282 and placed into Teflon microwave vessels along with either concentrated HNO_3 or a concentrated HNO_3/HF mixture (90:10 volume fractions). Weighed amounts of SRM 3124a Indium Spectrometric Solution and SRM 3148a Scandium Spectrometric Solution were added to each vessel for use as internal standards. Samples were digested using a microwave sample preparation system. Four instrumental measurements

were made and averaged for each sample and each spiked solution. Analyte mass fractions were calculated using single-point standard additions.

The Grocery Manufacturers Association's (GMA) Food Industry Analytical Chemistry Committee (FIACC) laboratories (Table 1) measured nutrient element, proximates, total dietary fiber, amino acids, sugars, and vitamins in the blueberries in a semiannual interlaboratory comparison exercise. A subset of these laboratories measured elements and sugars in the cranberry and low-calorie cranberry juice cocktail SRMs. The laboratories were asked to use their usual methods and to make two measurements on test portions taken from each of two packets or ampules of each SRM. The medians of the means of the collaborating laboratories' data were used to assign reference values for proximates, vitamins, and sugars. Methodological information for the laboratories' analysis of the blueberries was not collected. For measurement of the sugars in the cranberries and cranberry juice cocktail, four laboratories used liquid chromatography (LC) with refractive index detection, one used LC with evaporative light scattering detection, and one used gas chromatography.

For measurement of calcium, iron, magnesium, potassium, and sodium in the cranberries, three laboratories used inductively coupled plasma optical emission spectrometry (ICP-OES), one laboratory used direct current plasma optical emission spectrometry (DCP), and one laboratory used flame atomic absorption spectrometry (FAA). For measurement of phosphorus, three laboratories used ICP-OES, two used colorimetry, and one used ICP with mass spectrometric detection (ICP-MS). For measurement of copper in the cranberries, two laboratories used FAA, two used ICP-OES, one used DCP, and two used ICP-MS. For measurement of manganese, one laboratory used FAA, two used ICP-OES, and one used ICP-MS. For measurement of zinc, one laboratory used FAA, three used ICP-OES, one used DCP, and one used ICP-MS.

For measurement of calcium, potassium, and sodium in the cranberry juice cocktail, two laboratories used FAA, one used ICP-OES, and one used DCP. For measurement of iron and magnesium, two laboratories

Table 2. Comparison of Element Content in Food-Matrix SRMs Arranged by AOAC Fat−Protein−Carbohydrate Triangle Sector[a]

sector[b]	SRM no.	SRM name[c]	Ca	Cu	Fe	Mg	Mn	P	K	Na	Zn
2	2384	Baking Chocolate	**840**	23.2	132	2570	20.3	3330	8200	40	36.6
3	2387	Peanut Butter	**411**	**4.93**	**16.4**	**1680**	**16.0**	3378	**6070**	**4890**	**26.3**
4	1546	Meat Homogenate	**323**	0.60	10.1	**163**	0.23	**1530**	**2370**	**9990**	**18.3**
4	1845a	Whole Egg Powder; in prepration	2388	2.395	84.27	412.4	1.2468	8925	4309	4543	57.53
(5)	1567a	Wheat Flour	**0.0191**[d]	2.1	14.1	**0.040**[d]	9.4	**0.134**[d]	**0.133**[d]	6.1	11.6
(5)	1568a	Rice Flour	**0.0118**[d]	2.4	7.4	**0.056**[d]	20.0	**0.153**[d]	**0.1280**[d]	6.6	19.4
5	3233	Fortified Breakfast Cereal; in preparation	36497	3.90	739	1062	32.26	2549	3010	6741	621
(5)	3281	**Cranberry (Fruit)**	528	3.52	27.7	446	21.9	835	8020	259	6.9
(5)	3282	**Low-Calorie Cranberry Juice Cocktail**	26.3	0.23	0.54	**12.97**	0.493		247	**201**	0.15
5	3287	**Blueberry (Fruit)**	323	2.22	12.2	313.7	8.47	671	4490	16.39	**6.49**
5	2383a	Baby Food Composite; in preparation	342.5	0.719	4.164	213.9	0.9309	451.8	3018	181.05	2.098
6	1549	Non-Fat Milk Powder	**1.30**[d]	**0.7**	1.78	**0.120**[d]	0.26	**1.06**[d]	**1.69**[d]	**0.497**[d]	**46.1**
6	1849	Infant/Adult Nutritional Formula	**4900**	20.29	177.1	1578	51.00	3782	8860	4150	152.3
6	1548a	Typical Diet	1967	2.32	35.3	580	5.75	3486	6970	8132	24.6
7	2385	Slurried Spinach	624	0.90	17.1	368	3.81	323.7	3650	47	8.37
7	3234	Soy Flour; in preparation	2970	14.39	75.16	3251	34.41	7682	23560	2.37	45.39
7	1566b	Oyster Tissue	**0.0838**[d]	**71.6**	**205.8**	**0.1085**[d]	18.5		**0.652**[d]	**0.3297**[d]	1424
7	1570a	Trace Elements in Spinach Leaves	**1.527**[d]	12.2			75.9	**0.518**[d]	**2.903**[d]	1.818	82
(9)	1577c	Bovine Liver	**131**	**275.20**	**197.94**	620	10.46	1.175[c]	**1.023**[d]	**0.2033**[d]	**181.1**

[a] Certified mass fraction values (bold) and reference values (normal typeface) are mg/kg unless otherwise noted. [b] Determination of locations in sectors shown in parentheses are based on USDA nutrition information.[9] [c] Values for materials currently in preparation are estimated from NIST ICP-OES data. [d] Mass fraction values are %.

used FAA, one used ICP-MS, and one used DCP. For measurement of copper and zinc, one laboratory used FAA, one used DCP, and two used ICP-MS. For measurement of phosphorus, one laboratory used ICP-OES, one used ICP-MS, and two used colorimetry. For measurement of manganese, one laboratory used FAA and two used ICP-MS.

■ DISCUSSION

To determine whether an analytical method is generating reliable results, it is important to choose a quality control material that is a good match to both the test sample matrix and the analyte levels. The lines that define the nine sectors of the AOAC triangle are guides, and a material near the border of a sector may be a good matrix match to materials in an adjacent sector, as well. Elemental analyses typically involve a complete digestion in concentrated acids. Matching the fat, protein, and carbohydrate contents of controls and samples becomes important for elemental analyses to minimize differences in matrices. Matching analyte concentrations becomes especially important at lower concentration levels, when analytes approach method detection limits (MDLs). There is the potential for differences in spectral background if an unsuitably matched sample has a particularly high concentration of a spectral interference.

To compensate for matrix effects, the method of standard additions is used. ICP-OES responses may differ for the samples and the calibration standards. A portion of the sample is spiked with a known amount of standard, which will be subjected to the same matrix effects as the analyte that is naturally occurring in the sample. The increase in signal will be due to the standard that was added; the original signal is due to the analyte only. Extrapolation gives the naturally occurring concentration of the analyte in the material. Additionally, use of an element that is not being determined as an internal standard increases the precision of the instrumental measurements. A ratio of the two elemental signals,

Table 3. Comparison of Final NIST Results to Method Detection Limits (MDLs) and Limits of Quantification (LOQs) for SRMs 3281, 3282, and 3287

	mass fraction (mg/kg)								
	Ca	Cu	Fe	K	Mg	Mn	Na	P	Zn
MDL	1.4	0.27	2.0	74	0.83	0.75	4.2	20	0.58
LOQ	4.5	0.90	6.8	246	2.8	2.5	14	68	1.9
SRM 3281	528	3.52	27.7	8020	446	21.9	259	835	6.9
SRM 3287	329	2.23	12.6	4593	312	8.8	16.4	663	6.4
MDL	0.74	0.0036	0.33	0.99	0.11	0.0050	0.10	5.1	0.087
LOQ	2.5	0.012	1.1	3.3	0.36	0.017	0.34	17	0.29
SRM 3282	25.5	0.20	0.53	247	13.0	0.486	210		0.15

measured simultaneously, is used to overcome the effects of instrumental drift.[10] A summary of the elemental compositions of selected food-matrix SRMs available from NIST is provided in Table 2. As has been observed previously, some laboratories have difficulty measuring low concentrations of elements in foods, for example, sodium in SRM 2384 Baking Chocolate and iron in SRM 1546 Meat Homogenate.[11,12] Contamination in the laboratory is the probable cause of the problem.

To identify contamination issues, it is important to prepare and analyze several procedural blanks using all reagents and steps that were used in the dissolution method. MDLs typically are estimated as 3 times the standard deviation of the measurements of procedural blank solutions prepared along with the samples. The MDL is the level at which an analyte can be seen above the signal of the blanks and determines whether an analyte can be measured. Limits of quantification (LOQs), typically estimated

7248

dx.doi.org/10.1021/jf200883e |J. Agric. Food Chem. 2011, 59, 7246–7252

Table 4. Reference Mass Fractions (Milligrams per Kilogram) for Selected Elements in SRM 3281 Cranberry (Fruit)[a]

| element | collaborating laboratories | | | NIST ICP-OES | | | |
	median	mean (s)	range	mean	U	assigned value	U
Ca	393	434 (95)	338–580	528.1	8.1	528	7
Cu	2.48	2.84 (0.93)	1.95–3.97	3.52	0.13	3.52	0.09
Fe	21.0	25 (17)	7.38–91.5	27.7	0.95	27.7	0.7
Mg	347	313 (111)	151–467	446.0	3.8	446	4
Mn	18.1	15.8 (7.3)	4.59–21.7	21.91	0.29	21.9	0.2
P	767	868 (290)	641–1437	835	18	835	17
K	7256	7366 (1034)	5891–9056	8015	145	8020	130
Na	299	372 (214)	229–821	259.2	3.6	259	3
Zn	6.79	34 (71)	3.1–199	6.89	0.26	6.9	0.2

[a] Each reference value, expressed as a mass fraction for the material on a dry-mass basis is the mean of results from analyses by NIST. The uncertainty in the reference value, calculated according to the method described in the ISO Guide,[12] is expressed as an expanded uncertainty, U. This expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-laboratory and within-laboratory components of uncertainty. The coverage factor, k, is determined from Student's t distribution corresponding to the appropriate associated degrees of freedom and 95% confidence level for each analyte. Values in SRM 3281 are reported on a dry-mass basis.

Table 5. Certified (Bold) and Reference (Normal Typeface) Mass Fractions (Milligrams per Kilogram) for Selected Elements in SRM 3282 Low-Calorie Cranberry Juice Cocktail[a]

| element | collaborating laboratories | | | NIST ICP-OES | | | |
	median	mean (s)	range	mean	U	assigned value	U
Ca	27.0	24.8 (6.0)	15.9–29.1	25.52	0.82	**26.3**	**1.6**
Cu	0.26	0.29 (0.11)	0.202–0.513	0.2020	0.0075	**0.23**	**0.06**
Fe	1.30	2.69 (3.27)	0.65–7.5	0.54	0.18	0.54	0.14
Mg	12.9	13.1 (1.5)	12–16	13.04	0.16	**12.97**	**0.84**
Mn	0.50	0.51 (0.03)	0.486–0.54	0.4859	0.0037	**0.493**	**0.016**
P	14.48	19.99 (13.71)	11–41				
K	247	234.9 (37.4)	181–303	246.8	1.9	**247**	**12**
Na	192.5	187.4 (30.2)	132–214	209.8	1.7	**201**	**20**
Zn	0.42	1.18 (1.70)	0.16–3.95	0.153	0.069	0.15	0.06

[a] Each certified value, expressed as a mass fraction for the material as received, is the mean from the combination of the mean of results from analyses by NIST and the median of the mean results provided by collaborating laboratories. Each reference value, expressed as a mass fraction for the material as received, is the mean of results from analyses by NIST. The uncertainty in the certified and reference values, calculated according to the method described in the ISO Guide,[12] is expressed as an expanded uncertainty, U. This expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-laboratory and within-laboratory components of uncertainty. The coverage factor, k, is determined from Student's t distribution corresponding to the appropriate associated degrees of freedom and 95% confidence level for each analyte. Values in SRM 3282 are reported on an as-received basis.

by taking 10 times the standard deviation of the measurements of the procedural blank solutions, is the level at which mass fractions of an analyte begin to be accurately determined.[4] The content of each analyte in these procedural blanks is crucial to accurately determining trace analyte levels. For example, if there is a high level of sodium in the procedural blank, then clearly the analyses of the real samples will be affected. It is better to identify and to eliminate sources of contamination than it is to try to compensate for them. If a low-level quality control material can be accurately measured, it can be reasonably assumed that mass fractions in the unknown sample have been accurately measured. Table 3 shows both MDLs and LOQs for analyses of juice SRM 3282 and berry SRMs 3281 and 3287 compared to analyte mass fraction levels. The MDL and LOQ for the cranberries and blueberries are the same because these materials were analyzed together. SRM 3282 Low-Calorie Cranberry Juice Cocktail was analyzed separately and has different MDLs and LOQs.

As the mass fraction values of the working solutions approach the LOQ, the ability to accurately measure an analyte in an unknown decreases and an appropriately chosen quality control material becomes more important. As can be seen in Table 3, both zinc and iron mass fractions are above the MDLs for SRM 3282, but are not above the LOQs. Relative expanded uncertainties are high for these two elements; therefore, reference values are assigned. The range of mass fractions reported for iron is 0.53–7.5 mg/kg and includes the NIST values. The range of mass fractions reported for zinc is 0.16–3.95 mg/kg. The procedural blank solutions for both iron and zinc were nearly 10% of the analyte mass fraction. A high level of between-laboratory variability was seen in collaborating laboratories' data for sodium in SRM 3287: 14–292 mg/kg. The sodium mass fraction in the blueberries is just slightly above the LOQ determined by NIST, and the reference value is assigned using only NIST data. Once all sources of contamination have been

7249

dx.doi.org/10.1021/jf200883e |J. Agric. Food Chem. 2011, 59, 7246–7252

Table 6. Certified (Bold) and Reference (Normal Typeface) Mass Fractions (Milligrams per Kilogram) for Selected Elements in SRM 3287 Blueberry (Fruit)[a]

| | | collaborating laboratories | | NIST ICP-OES | | | |
element	median	mean (s)	range	mean	U	assigned value	U
Ca	317	323 (36)	254–384	329.3	5.5	**323**	**16**
Cu	2.2	2.3 (1.2)	0.6–5.4	2.23	0.11	**2.22**	**0.16**
Fe	11.8	12.4 (3.0)	8.6–27.1	12.55	0.95	**12.20**	**0.74**
Mg	315	309 (19)	266–329	312.4	2.5	**313.7**	**7.2**
Mn	8.2	7.6 (0.9)	5.9–8.6	8.76	0.34	**8.47**	**0.59**
P	678	753 (274)	599–1527	663	14	**671**	**21**
K	4397	4353 (440)	3490–4980	4593	92	**4490**	**220**
Na	92	111 (103)	14–296	16.39	1.50	**16.39**	**0.74**
Zn	6.5	6.2 (1.8)	1.1–9.1	6.43	0.22	**6.49**	**0.61**

[a] Each certified value, expressed as a mass fraction for the material, is the mean from the combination of the mean of results from analyses by NIST and the median of the mean results provided by collaborating laboratories. Each reference value, expressed as a mass fraction for the material on a dry-mass basis, is the mean of results from analyses by NIST. The uncertainty in the certified and reference values, calculated according to the method described in the ISO Guide,[12] is expressed as an expanded uncertainty, U. This expanded uncertainty is calculated as $U = k u_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-laboratory and within-laboratory components of uncertainty. The coverage factor, k, is determined from Student's t distribution corresponding to the appropriate associated degrees of freedom and 95% confidence level for each analyte. Values in SRM 3287 are reported on a dry-mass basis.

Table 7. Reference Mass Fraction Values (Percent) for Sugars in the Three Berry SRMs[a]

| | SRM 3281 Cranberry (Fruit) | | SRM 3282 Low-Calorie Cranberry Juice Cocktail | | SRM 3287 Blueberry (Fruit) | |
	reference value	U	reference value	U	reference value	U
total sugars	26.2	2.1	2.86	0.05	60.4	3.3
fructose	4.51	0.53	2.08	0.10	30.5	1.5
glucose	21.6	1.1	0.85	0.06	30.5	1.4

[a] The uncertainty provided with each value is an expanded uncertainty about the median to cover the measurand with approximately 95% confidence, consistent with the ISO Guide.[12] The uncertainty incorporates within-method uncertainty and a component related to moisture correction for SRMs 3281 and 3287. The expanded uncertainty is calculated as $U = k u_c$, where u_c is intended to represent, at the level of one standard deviation, the effects of the combined components of uncertainty, and k is a coverage factor corresponding to approximately 95% confidence for each analyte. Values in SRMs 3281 and 3287 are reported on a dry-mass basis. Values in SRM 3282 are reported on an as-received basis.

eliminated and low-level control materials can reliably be measured, it is reasonable to assume that the unknown is being measured accurately.

Assigned values for SRMs 3281, 3282, and 3287 are provided in Tables 4–6, respectively, and are compared to the data used for value assignment. The median of the means of the GMA FIACC laboratory data was combined with the mean result of the NIST data for calculation of the certified values and estimates of uncertainty for elements in SRMs 3282 and 3287. GMA FIACC results were not used for value assignment of elements in SRM 3281 (see below). A NIST certified value is a value in which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account.[13] Certified values in the berry SRMs were provided for analytes measured by both NIST and the collaborating laboratories. NIST reference values represent a best estimate of the true value where all known or suspected sources of bias have not been fully investigated or taken into account. Reference values have associated uncertainties that may not include all sources of uncertainty and may represent only the precision of the measurement method(s).[13] Reference values may be assigned if no NIST data are available or if sources of bias in NIST measurements have not been fully resolved.[14]

Whereas certified values were provided for the majority of the nutrient elements in SRM 3282 and SRM 3287, the elements in SRM 3281 are provided as reference values because the relative expanded uncertainties are high, with relative expanded uncertainties ranging from 10 to 35% in comparison to the other two SRMs, for which the relative uncertainties ranged only from 2 to 10% with one exception. Copper in SRM 3282 had a relative

uncertainty of 26%. A comparison of NIST data and data provided by collaborating laboratories is provided in Table 4. The between-laboratory variability in the collaborating laboratories' data is higher than expected as shown by the range provided for each element in Tables 4–6. Two laboratories specifically reported seeing greater variability in their own results for this material than usual; however, this variability was not observed at NIST. Although specific digestion techniques were not reported from outside laboratories for this study, observations from previous studies led to assumptions that the poor repeatability observed by collaborating laboratories may have been caused by incomplete digestion of the cranberries.

Reference values for sugars, proximates, two water-soluble vitamins, and amino acids are provided in Tables 7 and 8. Sugars and organic acids are typically included in the suite of tests used to demonstrate adulteration and verify authenticity of juice and juice products (see, for example, http://www.tcjjp.org/normdb.html). SRM 3282 is the first "juice" material available from NIST. Multielemental[15−18] and amino acid analyses[19] can be used to demonstrate geographic origin, which can also be used to support a demonstration of authenticity. These analyses typically include 18–20 elements, some of which are the traditional "nutrition" elements and some of which are associated with the compositions of the soils on which agricultural products were grown.[20] Although it may be possible to determine a berry's geographical origin, it has also been demonstrated that berry species can be determined by their chemical composition.[21] Compositions of organic acids and sugars differ among species of blueberries and can be used for identification. Highbush blueberries contain fructose, glucose, and traces of sucrose, whereas the smaller lowbush blueberries contain only fructose and glucose.[21] Thus, the certified values for organic acids[2] and the reference values for sugars should be a valuable quality assurance resource for laboratories measuring species differences.

NIST has been working with the National Institutes of Health, Office of Dietary Supplements (NIH-ODS) to produce SRMs of dietary supplement matrices. Some dietary supplements contain conventional foods, such as berries, and their extracts as ingredients. New food-matrix SRM 3281 Cranberries (Fruit), SRM

Table 8. Reference Mass Fraction Values (Percent, Except Where Noted) for Proximates, Amino Acids, Niacin, and Vitamin B$_6$ in SRM 3287[a]

	SRM 3287 Blueberry (Fruit)	
	reference value	U
solids	98.59	0.65
ash	1.126	0.084
fat	1.40	0.37
protein	3.43	0.30
carbohydrate	91.92	0.83
total dietary fiber	18.4	1.3
calories	392 kcal/100 g	10 kcal/100 g
niacin	20.1 mg/kg	9.2 mg/kg
vitamin B$_6$	2.79 mg/kg	0.35 mg/kg
alanine	0.167	0.095
arginine	0.342	0.037
aspartic acid	0.279	0.087
cysteine	0.056	0.023
glutamic acid	0.402	0.079
glycine	0.165	0.006
isoleucine	0.11	0.034
leucine	0.211	0.022
lysine	0.149	0.022
methionine	0.061	0.007
phenylalanine	0.134	0.012
proline	0.121	0.019
serine	0.141	0.019
threonine	0.121	0.015
tyrosine	0.088	0.020
valine	0.147	0.060

[a] The uncertainty provided with each value is an expanded uncertainty about the median to cover the measurand with approximately 95% confidence, consistent with the ISO Guide.[12] The uncertainty incorporates within-method uncertainty and a component related to moisture correction for SRMs 3287. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the effects of the combined components of uncertainty, and k is a coverage factor corresponding to approximately 95% confidence for each analyte. Values in SRM 3287 are reported on a dry-mass basis.

3282 Low-Calorie Cranberry Juice Cocktail, and SRM 3287 Blueberries (Fruit) will provide a broader selection for matrix-matched controls with appropriate analyte concentrations for the food industry as well as for dietary supplement manufacturers interested in demonstrating method applicability and providing quality assurance for their products.

Funding Sources

REFERENCES

(1) Nutrition Labeling and Education Act. Public Law 101-535, H.R. 3562, Nov 8 1990.

(2) Phillips, M. M.; Case, R. J.; Rimmer, C. A.; Sander, L. C.; Sharpless, K. E.; Wise, S. A.; Yen, J. H. Determination of organic acids in *Vaccinium* berry standard reference materials. *Anal. Bioanal. Chem.* **2010**, published on-line 27 June.

(3) Todoli, J. L.; Gras, L.; Hernandis, V.; Mora, J. Elemental matrix effects in ICP-AES. *J. Anal. At. Spectrom.* **2002**, *17*, 142–169.

(4) Thomsen, V.; Schatzlein, D.; Mercuro, D. Limits of detection in spectroscopy. *Spectroscopy* **2003**, *18*, 112–114.

(5) Poussel, E.; Mermet, J.-M. Simultaneous measurements of signal and background in inductively coupled plasma atomic emission spectrometry: effects on precision, limits of detection and limit of quantitation. *Spectrochim. Acta Part B* **1995**, *51*, 75–85.

(6) Wolf, W. R. *Methods of Analysis for Nutrition Labeling*; Sullivan, D. M., Carpenter, D. E., Eds.; AOAC International: Arlington, VA, 1993; pp 111−122.

(7) Wolf, W. R.; Andrews, K. W. A system for defining reference materials applicable to all food matrices. *Fresenius' J. Anal. Chem.* **1995**, *352*, 73–76.

(8) Sharpless, K. E.; Thomas, J. B.; Christopher, S. J.; Greenberg, R. R.; Sander, L. C.; Schantz, M. M.; Welch, M. J.; Wise, S. A. Standard reference materials for foods and dietary supplements. *Anal. Bioanal. Chem.* **2007**, *389*, 171–178.

(9) USDA Agricultural Research Service National Nutrient Database for Standard Reference, http://www.nal.usda.gov/fnic/foodcomp/search/.

(10) Salit, M. L.; Turk, G. C.; Lindstrum, A. P.; Butler, T. A.; Beck, C. M., II; Norman, B. Single-element solution comparisons with a high-performance inductively coupled plasma optical emission spectrometric method. *Anal. Chem.* **2001**, *73*, 4821–4829.

(11) Sharpless, K. E.; Thomas, J. B.; Bryant, C. N.; Phinney, C. S.; Sieber, J. R.; Wood, L. J.; Yen, J. H.; Howell, D. W. Value assignment of nutrient concentrations in Standard Reference Material 2384 Baking Chocolate. *J. Agric. Food Chem.* **2002**, *50*, 7069–7075.

(12) Welch, M. J.; Colbert, J. C.; Gill, L. M.; Phinney, C. S.; Sharpless, K. E.; Sniegoski, L. T.; Wood, L. J. The certification of SRM 1546 Meat Homogenate, a new reference material for nutrients in a high protein, high fat matrix. *Fresenius' J. Anal. Chem.* **2001**, *370*, 42–47.

(13) JCGM 100:2008. *Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); International Bureau of Weights and Measures, Joint Committee for Guides in Metrology: Sèvres Cedex, France, 2008; available at www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf/. See also: Taylor, B. N.; Kuyatt, C. E. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; National Institute of Standards and Technology: Gaithersburg, MD, 1994; available at http://www.nist.gov/pmL/Pubs.

(14) May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B. *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Gaithersburg, MD, 2000; http://www.nist.gov/srm/publications.

(15) Smith, R. G. Determination of the country of origin of garlic (*Allium sativum*) using trace metal profiling. *J. Agric. Food Chem.* **2005**, *53*, 4041–4045.

(16) Baxter, M. J.; Crews, H. M.; Dennis, M. J.; Goodall, I.; Anderson, D. The determination of the authenticity of wine from its trace element composition. *Food Chem.* **1997**, *60*, 443–450.

(17) Heaton, K.; Kelly, S. D.; Hoogewerff, J.; Woolfe, M. Verifying the geographical origin of beef: the application of multi-element isotope and trace element analysis. *Food Chem.* **2008**, *107*, 506–515.

(18) Coetzee, P. P.; Steffens, F. E.; Eiselen, R. J.; Augustyn, O. P.; Balcaen, L.; Vanhaecke, F. Multi-element analysis of South African Wines by ICP-MS and their classification according to geographical origin. *J. Agric. Food Chem.* **2005**, *53*, 5060–5066.

(19) Arvanitoyannis, I. S.; Katsota, M. N.; Psarra, E. P.; Soufleros, E. H.; Kallithraka, S. Application of quality control methods for assessing wine authenticity: use of multivariate analysis (chemometrics). *Trends Food Sci. Technol.* **1999**, *10*, 321–336.

(20) Kelly, S.; Baxter, M.; Chapman, S.; Rhodes, C.; Dennis, J.; Brereton, P. The application of isotopic and elemental analysis to determine the geographical origin of premium long grain rice. *Eur. Food Res. Technol.* **2002**, *214*, 72–78.

(21) Bremer, V.; Crisosto, G.; Molinar, R.; et al. San Joaquin Valley blueberries evaluated for quality assurance. *Calif. Agric.* **2008**, *62*, 91–96.