

# Assessment of stability of trace elements in two natural matrix environmental standard reference materials: NIST-SRM 1547 Peach leaves and NIST-SRM 1566a Oyster Tissue

E. A. Mackey · R. O. Spatz

Received: 19 April 2009 / Published online: 12 June 2009  
© Akadémiai Kiadó, Budapest, Hungary 2009

**Abstract** The NIST program for environmental Standard Reference Materials (SRM) includes materials covering a range of matrices, mass fraction values and analytes. For many SRMs, mass fraction data are accumulated, incidentally, over time, as these are used routinely for quality assurance purposes. Although these are not formal stability studies, data generated may be useful in assessing stability. To evaluate the potential for assessing material stability from incidental use of SRMs, results of neutron activation analysis performed from 1992 through 2008 were compiled for SRM 1547 Peach Leaves and SRM 1566a Oyster Tissue. Results indicate that incidental use of SRMs yields useful information on SRM stability.

**Keywords** Certified Reference Material · Element analysis · Neutron activation analysis · Oyster tissue · Peach leaves · Stability

## Introduction

NIST provides a wide variety of Standard Reference Materials (SRMs) that are certified for chemical composition or element content. Production and certification of SRMs are covered by the scope of the NIST Quality System (<http://ts.nist.gov/qualitysystem/>) which conforms with International Standards Organization (ISO/IEC) Guide 17025[1] and relevant portions of ISO/IEC Guide 34[2]. Therefore, the concept of assuring material stability is

considered throughout the entire lifetime of the SRM. Methods of material acquisition, processing and packaging are designed to help assure material stability. After production, the recommended material handling and storage conditions are intended to preserve the material and the final product is monitored to evaluate stability during the SRM shelf life.

ISO Guide 30[3] defines stability as the “ability of a reference material, when stored under specified conditions, to maintain a stated property value within specified limits for a specified period of time.” ISO/IEC Guide 35[4] further distinguishes between short- and long-term stability, referring to times and conditions for shipping the material in the former case and times and conditions for storage over the material shelf-life in the latter case. The classically designed long-term stability study involves measurement of selected samples, over time and relevant storage conditions following a statistical design. This rigorous approach is essential for the evaluation of new matrices and materials of unknown stability. However, a large amount of data is generated during routine use of SRMs and these may provide adequate evidence of material stability.

This work presents an evaluation of the stability of two freeze-dried, irradiation-sterilized, environmental reference materials, SRM 1547 Peach Leaves and SRM 1566a Oyster Tissue. These SRMs were collected, prepared and stored using techniques and conditions previously demonstrated to provide stability for the prescribed shelf life for the elements of interest (see, e.g., Anderson and Cunningham [5]). In each case, experience with nearly identical matrices justified the methods used for material preparation and storage. SRM 1547 Peach Leaves is one of a series of botanical SRMs, and SRM 1566a Oyster Tissue was the replacement material for SRM 1566 Oyster Tissue. This present evaluation was undertaken to determine whether

---

E. A. Mackey (✉) · R. O. Spatz  
Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8395, USA  
e-mail: lmackey@nist.gov

the incidental use of these SRMs as routine quality control materials provides sufficient evidence of the stability of these two SRMs, and whether those results may be used to justify expiry dates for similar materials prepared and stored under the same conditions.

## Experimental

Instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA) and prompt gamma-ray activation analysis (PGAA) were performed using comparator methods. For each technique, element standards prepared from chemicals or solutions containing known amounts of each element of interest were used. As this work compares results acquired over the past 10–16 years, the details of each analysis, for a given technique, necessarily differed as new element standards were used for each analysis, irradiation times may have differed, and detection systems differed as older systems were replaced with newer ones.

The following references describe the general methods or instruments. A description of the PGAA instrument and general analytical procedures used for analyses performed prior to 2003 has been published elsewhere [6]. Descriptions of the newer PGAA instrument [7] and procedures [8] used for PGAA experiments performed after 2003 have also been published elsewhere. Although specific details such as irradiation and decay times, and detection systems vary for the different individual analyses performed over the years, the typical INAA scheme used at NIST for multi-element analysis using the comparator method has been described by Greenberg et al. [9]. The RNAA procedure used for a subset of the results presented for As, Cd, Cu, Cr and Se has been described by Greenberg [10]. Note that bottles of these SRMs were stored in the laboratory on the shelf at room temperature and that any given bottle of SRM may have been used multiple times. For each analysis the dry mass basis was determined on one or more separate portions of the SRM from the same bottle(s) at the time of use, by following the instructions for drying given on the Certificates of Analysis [11, 12].

## Results and discussion

Results from analyses of SRM 1547 and SRM 1566a performed during the past 16 years were evaluated using two criteria. The first of these criteria, described in Eq. 1, determines whether each individual value deviates from the certified value. Measured values,  $X_m$ , were reported with uncertainties ( $U_m$ ) that over the years were calculated using different approaches, typically either a value representing a

95% confidence interval or an expanded uncertainty  $U$  with a  $k$  value of 2, calculated according to Taylor and Kuyatt [13]. This stability evaluation is based on comparison of the measured value ( $X_m$ ) and its reported uncertainty ( $U_m$ ) with the certified value,  $X_c$  with its uncertainty,  $U_c$ , described on the Certificates of Analysis: [11, 12]

$$(X_c - U_c) < (X_m \pm U_m) < (X_c + U_c) \quad (1)$$

As non-certified or information values are not accompanied by uncertainties, no statistical evaluation was possible, so comparison with information values was based on agreement to one significant figure.

The second criterion follows the recommendations of ISO Guide 35 Appendix B [4], and determines whether any significant linear trend has been observed. This evaluation, described in Eq. 2, compares the absolute value of the slope,  $b$ , of the linear regression line, with the error in the slope ( $s_b$ ) multiplied by the “ $t$ ” value for a two-tailed distribution, at the 95% confidence level (see ISO Guide 35 Appendix B for a complete description of this model):

$$|b| < t_{n-2,95\%} s_b \quad (2)$$

Ratios of measured values to certified or information values were also calculated. Average values for each element in each material were evaluated to determine if there were consistently low or high biases for either material that might indicate changes in the mass basis.

Evaluated data included 41 individual results for 15 elements in SRM 1547 and 166 individual results for 29 elements in SRM 1566a. The elements covered mass fraction ranges from a few 0.01 mg/kg to several 0.1% and covered wide differences in potential for volatility and chemical speciation. Data were evaluated to determine whether any deviations from certified values were observed and where sufficient data existed, to determine whether there were any trends as a function of time. Only elements for which three or more results were available were included for temporal trend analysis. Results of these evaluations for SRMs 1547 and 1566a are shown in Tables 1 and 2, respectively.

For SRM 1547, data for seven elements (As, B, Cd, Cl, Cr, Cu and Se) obtained from measurements performed from 1992 through 2008 were evaluated for trends. As these data were collected from incidental use of SRMs rather than from a formal stability study, the ranges of years covered differed for each element (see Table 1). For SRM 1566a a larger data set was available with data for 29 elements determined at various times between 1996 and 2007 evaluated. Again, the range of years covered differs for each element and is shown in Table 2.

Results for SRM 1547 showed no significant linear trends over time for the seven elements for which there was sufficient data to evaluate trends. In all cases values for

**Table 1** Summary of the number of determinations (n), number of results within the certified value (C) or consistent with the information value (I), and parameters of linear trend analysis as a function of time (year) for 16 elements in SRM 1547 Peach Leaves

Element	Certified or information value (mg/kg)	Certified (C) or information (I)	n	Time (year)	Number of values consistent with C or I	Slope (b; mg/kg/year)	$t_{95\%, n-2} \times s_b$	Trend	Average ratios (range) measured to C or I
As	0.060 ± 0.018	C	4	1992-2001	4	-0.52	3.2	None	1.06 (0.95-1.16)
B	29 ± 2	C	4	1998-2008	4	0.003	0.55	None	0.96 (0.93-1.00)
Cd	0.026 ± 0.003	C	3	1999-2001	3	1.7	7.6	None	1.12 (1.05-1.23)
Cl	360 ± 19	C	5	1998-2005	4	-4.2	4.3	None	0.96 (0.91-1.01)
Cr	I	I	3	1992-2001	3	0.007	0.07	None	1.0 (1.0-1.0)
Cu	3.7 ± 0.4	C	3	1992-2001	3	-0.003	0.16	None	1.01 (1.00-1.03)
Se	0.120 ± 0.009	C	4	1992-2001	4	0.31	2.5	None	0.96 (0.92-0.99)
Element	Certified or information value	Certified (C) or information (I)	n	Time (year)	Number of values consistent with C or I	Ratio(s) of measured values to C or I			
Ba	124 ± 4 mg/kg	C	2	1997, 2001	2	1.07, 1.03			
Co	0.07 mg/kg	C	2	1997, 2001	2	1.05, 1.01			
Fe	218 ± 14 mg/kg	C	2	1997, 2001	2	1.00, 1.03			
K	2.43 ± 0.03%	C	2	1998, 2001	2	1.00, 1.02			
Rb	19.7 ± 1.2 mg/kg	C	1	1997	1	0.99			
S	0.2%	I	2	1998, 1999	1	1.0			
Sc	0.04 mg/kg	I	1	2001	1	1.0			
Th	0.05 mg/kg	I	1	1997	1	1.2			
Zn	17.9 ± 0.2 mg/kg	C	2	1997, 2001	2	1.01, 1.02			

**Table 2** Summary of the number of determinations (n), number of results within the certified value (C) or consistent with the information value (I), and parameters of linear trend analysis as a function of time (year) for 29 elements in SRM 1566a Oyster Tissue

Element	Certified or information value	Certified (C) or information (I)	n	Time (year)	Number of values consistent with C or I	Slope (b mg/kg/year)	t <sub>95%</sub> b	Trend	Average (range) ratios measured to C or I
Ag	1.68 ± 0.15 mg/kg	C	10	1996–2007	10	0.00028	0.014	None	1.05 (0.99–1.12)
Al	202.5 ± 12.5 mg/kg	C	4	1996–2002	4	-1.1	1.4	None	1.05 (1.04–1.07)
As	14.0 ± 1.2 mg/kg	C	15	1996–2007	15	0.012	0.043	None	0.98 (0.95–1.01)
Ca	0.196 ± 0.019%	C	8	1996–2002	8	-26	34	None	1.00 (0.94–1.07)
Cd	4.15 ± 0.38 mg/kg	C	4	1997–2007	4	0.026	0.061	None	1.01 (0.98–1.06)
Cl	0.829 ± 0.014%	C	9	1996–2002	9	-34	44	None	0.99 (0.97–1.02)
Co	0.57 ± 0.11 mg/kg	C	8	1996–2006	8	-0.000045	0.0066	None	0.92 (0.89–0.97)
Cr	1.43 ± 0.46 mg/kg	C	7	1996–2007	7	-0.010	0.026	None	1.11 (1.01–1.19)
Cu	66.3 ± 4.3 mg/kg	C	7	1996–2002	7	-0.13	2.6	None	0.98 (0.92–1.10)
Fe	539 ± 15 mg/kg	C	10	1996–2006	10	1.3	1.4	None	0.99 (0.97–1.00)
K	0.790 ± 0.047%	C	8	1996–2002	8	-15	115	None	1.03 (0.97–1.07)
Mg	0.118 ± 0.017%	C	8	1996–2002	8	3.9	8.4	None	0.99 (0.97–1.03)
Mn	12.3 ± 1.5 mg/kg	C	9	1996–2002	9	0.016	0.082	None	1.00 (0.98–1.02)
Na	0.417 ± 0.013%	C	9	1996–2002	9	-12	47	None	1.02 (0.98–1.05)
Rb	3 mg/kg	I	3	1997–2000	3	0.065	0.52	None	1.0 (1.0, 1.0, 1.0)
Sc	0.06 mg/kg	I	3	1998–2000	3	-0.00069	0.019	None	0.9 (0.8, 0.8, 1.0)
Se	2.21 ± 0.24 mg/kg	C	12	1996–2007	12	-0.00032	0.025	None	0.98 (0.94–1.17)
V	4.68 ± 0.15 mg/kg	C	9	1996–2002	9	0.012	0.034	None	1.04 (1.00–1.06)
Zn	830 ± 57 mg/kg	C	11	1996–2006	11	3.7	5.4	None	1.02 (0.95–1.07)
Element	Certified or information value (mg/kg)	Certified (C) or information (I)	n	Time (year)	Number of values consistent with C or I	Ratio(s) of measured value(s) to C or I			
Ce	0.4	I	1	2000	0	-			
Cs	0.02	I	1	2006	1	1			
Eu	0.01	I	1	1998	1	1			
Hg	0.0642 ± 0.0067	C	2	1996	2	1.00, 1.00			
I	4.46 ± 0.42	C	1	1996	1	0.9			
La	0.3	I	1	2000	1	1			
Sb	0.01	I	2	2000	2	1, 1			
Sm	0.06	I	1	2000	1	0.8			
Th	0.04	I	1	2000	1	1			
U	0.132 ± 0.012	C	1	2000	1	0.9			

$t_{0.95}S_b$  were greater than the values for the slopes; and although all slopes were insignificant they were roughly equally split between positive and negative values. The  $l_b$  value for Cl was approximately equal to the  $t_{n-2, 0.95}S_b$  value so this element will be closely monitored to determine whether a trend is developing.

Results for these seven elements and for an additional eight elements (for which only one or two measurement results were available) were evaluated to determine whether any differences from certified values have been detected. For 39 of 41 measured mass fraction values, results agreed with the certified or information values within the stated uncertainties. The exceptions were one value (of five) for Cl, and one value of two for S. The value for S ( $0.320 \pm 0.006\%$ ) was higher than the information value of 0.2%. The Cl value [ $(330 \pm 10)$  mg/kg] was lower than the certified value [ $(360 \pm 19)$  mg/kg] and was also the most recent determination (this value was reported in 2005). The mass fraction of Cl in this material will be closely monitored to determine whether this one value for Cl is significant and if so, whether the lower value indicates any trend. The ratio of measured values to certified values shows no overall trend (four values were  $<1.0$ , seven values  $>1.0$ ) and the overall average for the eleven certified elements was 1.015. These results indicate that, to date, no significant trends have been observed in 11 of 24 certified or in 4 of 19 information values.

Results of data evaluation for SRM 1566a are summarized in Table 2. Of the 166 individual values evaluated, all but four agreed with the certified values within the stated uncertainties, or with non-certified information values (to one significant figure). The exceptions were: one low value (of one) for Ce, one low value (of nine) for Cl, one low value (of three) for Sc and one high value (of nine) for V. The one low Cl value ( $8,050 \pm 80$ ) mg/kg, compared with a certified value of ( $8,290 \pm 140$ ) mg/kg was obtained in 2000, and subsequent results obtained in 2000 and 2002 were not low. It is possible that this low value was erroneous or that the uncertainty reported (1% relative) was not an accurate estimate of the total expanded uncertainty (U). An increase in the reported U value from 1% relative to 1.25% relative would result in a value that would overlap the range defined by the certified value.

Similarly, the cause of the high value for V ( $4.95 \pm 0.09$ ) mg/kg (compared with a certified value of  $4.68 \pm 0.15$  mg/kg) is not known, but a small increase in the U value from 1.8% relative to 2.4% relative would provide overlap with the range defined by the certified value. The cause of the low value for Ce (0.2 mg/kg compared with the information value of 0.4 mg/kg) is not known, and this element is not determined routinely, so there are no other values with which to compare this result. The cause for the low Sc value ( $0.051 \pm 0.001$ ) mg/kg,

compared with an information value of 0.06 mg/kg is also not known, as previous results ( $0.061 \pm 0.002$ ) mg/kg and ( $0.055 \pm 0.004$ ) mg/kg, are consistent with the information value. No overall trend is suggested by any of the four values that represent only 2.4% of the 166 values that were part of this evaluation.

Results for 19 of the elements in SRM 1566a were evaluated as a function of time. The slopes were insignificant for all elements investigated, and there were roughly the same number of positive and negative slopes. These data provide verification of material stability (within stated uncertainties) for 20 of 25 certified values and for 9 of 16 non-certified (information) values. SRM 1566a is no longer available at NIST; it has been replaced by SRM 1566b, prepared and stored in the same manner. However, evidence on the stability of SRM 1566a provides justification for assigning similar expiry dates for SRMs of similar matrices prepared and stored in the same manner.

## Conclusions

Results from analyses of SRM 1547 Peach Leaves provide evidence for the stability of representative elements over a 10-year period for botanical SRMs prepared from dried leaves, that have been prepared by air jet-milling, blending and radiation sterilization and that have been stored at room temperature. Similarly, results for SRM 1566a provide evidence for stability of this matrix type (also, dried, air jet-milled, blended and radiation sterilized, and stored at room temperature) for most or all elements of interest for nearly 20 years. Although all natural matrix SRMs will continue to be monitored for stability, the use of 10-year expiration dates for these materials under these conditions appears justified based on these results.

## References

1. ISO Guide 17025 General requirements for the competence of calibration and testing laboratories. ISO/IEC 17025:1999(E) Geneva (1999)
2. ISO Guide 34:2000 General requirements for the competence of reference material producers. Ref. No.: ISO GUIDE 34:2000(E) Geneva (2000)
3. ISO Guide 30:1992 Terms and definitions used in connection with reference materials. ISO GUIDE 30:1992 (E/F) Geneva (1992)
4. ISO Guide 35:2006 Reference materials—general and statistical principles for certification. Ref. No.: ISO GUIDE 35:2006(E) Geneva (2006)
5. Anderson, D.L., Cunningham, W.C.: Revalidation and long-term stability of National Institute of Standards and Technology Standard Reference Materials 1566, 1567, 1568, and 1570. *J. AOAC Int.* **83**, 1121–1134 (2000)

6. Anderson, D.L.: Neutron capture prompt gamma-ray activation analysis of meat homogenates. *J. Radioanal. Nucl. Chem.* **244**, 225–229 (2000)
7. Mackey, E.A., Anderson, D.L., Liposky, P.J., Lindstrom, R.M., Chen-Mayer, H., Lamaze, G.P.: New thermal neutron prompt  $\gamma$ -ray activation analysis instrument at the National Institute of Standards and Technology Center for Neutron Research. *Nucl. Instr. Meth. Phys. Res. B* **226**, 426–440 (2004)
8. Mackey, E.A., Paul, R.L., Lindstrom, R.M., Anderson, D.L., Greenberg, R.R.: Sources of uncertainties in prompt gamma activation analysis. *J. Radioanal. Nucl. Chem.* **265**, 273–281 (2005)
9. Greenberg, R.R., Mackey, E.A., Becker, D.A.: The application of instrumental neutron-activation analysis for the certification of the new NIST fly-ash SRM. *J. Radioanal. Nucl. Chem.* **193**, 7–14 (1995)
10. Greenberg, R.R.: Element characterization of the National Bureau of Standards Milk Powder Standard Reference Material by instrumental and radiochemical neutron activation analysis. *Anal. Chem.* **58**, 2511–2516 (1986)
11. Certificate of analysis SRM 1547, NIST Technology Services. [http://smors.nist.gov/certificates/view\\_cert2gif.cfm?certificate=1547](http://smors.nist.gov/certificates/view_cert2gif.cfm?certificate=1547) (1993). Accessed Sept 2008
12. Certificate of analysis SRM 1566a, NIST Technology Services. [http://ts.nist.gov/MeasurementServices/ReferenceMaterials/archived\\_certificates/archived\\_certificates.htm](http://ts.nist.gov/MeasurementServices/ReferenceMaterials/archived_certificates/archived_certificates.htm) (1989). Accessed Sept 2008
13. Taylor, B. N., Kuyatt, C.E.: NIST technical note 1297: guidelines for evaluating and expressing the uncertainty of NIST measurement results. <http://physics.nist.gov/Pubs/guidelines/contents.html> (1994). Accessed Jan 2009