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ORIGINAL PAPER

Development and certification of the new SRM 695 trace elements in multi-nutrient fertilizer

E. A. Mackey · M. P. Cronise · C. N. Fales · R. R. Greenberg · S. D. Leigh · S. E. Long · A. F. Marlow · K. E. Murphy · R. Oflaz · J. R. Sieber · M. S. Rearick · L. J. Wood · L. L. Yu · S. A. Wilson · P. H. Briggs · Z. A. Brown · J. Budahn · P. F. Kane · W. L. Hall Jr.

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Abstract During the past seven years, several states within the US have enacted regulations that limit the amounts of selected non-nutritive elements in fertilizers. Internationally, several countries, including Japan, China, and Australia, and the European Union also limit the amount of selected elements in fertilizers. The elements of interest include As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn. Fertilizer manufacturers and state regulatory authorities, faced with meeting and verifying these limits, need to develop analytical methods for determination of the elements of concern and to validate results obtained using these methods. Until now, there were no certified reference materials available with certified mass fraction values for all elements of interest in a blended, multi-nutrient fertilizer matrix. A new standard reference material (SRM) 695 trace elements in multi-nutrient fertilizer, has been developed to help meet these needs. SRM 695 has recently been issued with certified mass fraction values for seventeen elements, reference values for an additional five elements, and information values for two elements. The certificate of analysis includes an addendum listing percentage recovery for eight of these elements, determined using an acid-extraction inductively-coupled plasma optical-emission spectrometry (ICP–OES) method recently developed and tested by members of the Association of American Plant Food Control Officials.

Keywords Trace elements · Activation analysis · Fertilizers · Standard reference material · Nutrients

E. A. Mackey (✉) · M. P. Cronise · C. N. Fales · R. R. Greenberg · S. D. Leigh · S. E. Long · A. F. Marlow · K. E. Murphy · R. Oflaz · J. R. Sieber · M. S. Rearick · L. J. Wood · L. L. Yu
National Institute of Standards and Technology,
100 Bureau Drive, Mailstop 8395,
Gaithersburg, MD 20899, USA
e-mail: lmackey@nist.gov

S. A. Wilson · P. H. Briggs · Z. A. Brown · J. Budahn
US Geological Survey,
P.O. Box 25046, MS 973,
Denver, CO 80225, USA

P. F. Kane
Office of Indiana State Chemist, Purdue University,
175 S. University St.,
West Lafayette, IN 47907-2063, USA

W. L. Hall Jr.
The Mosaic Company,
3095 County Rd 640 West,
Mulberry, FL 33860, USA

Introduction

In the USA, the Environmental Protection Agency regulates the application of bio-solids used as fertilizers on land and is in the process of finalizing rules for waste-derived, zinc-based fertilizers; all other fertilizer products are regulated on a state-by-state basis. Until 1998, fertilizer manufacturers were generally required to guarantee only the nutrient content of their products. The discovery of high levels of arsenic in some iron-based fertilizer materials [1] and high levels of cadmium in some zinc-sulfate based fertilizer materials [2], however, prompted some states to enact regulations limiting the amount of selected non-nutritive (potentially toxic) elements in fertilizer materials. Washington was the first state to enact limits in the USA in 1998

[1]. Nine other states have since enacted or proposed regulations, and other states are expected follow suit. Elements for which limits have been set in the US and elsewhere are listed in Table 1.

When these non-nutritive metals were first limited by regulation in the US there were few certified reference materials (CRMs) available to assist manufacturing and regulatory laboratories in method development and measurement validation. There were many botanical and many soil CRMs with certified or reference values for the elements of interest, and a few bio-solid CRMs (e.g. NIST standard reference material (SRM) 2781 domestic sludge or Community Bureau of Reference (BCR)-144 sewage sludge) and phosphate rock CRMs (e.g. SRM 120 c phosphate rock and BCR-032 Moroccan phosphate rock). But there were no CRMs with matrices similar to typical agricultural or home-owner fertilizer blends. Typical blended fertilizers are identified by the percentage by mass of nitrates, phosphates and potash (commonly abbreviated as N-P-K) and often have micronutrient elements added also.

These types of fertilizer present special challenges for both reference-material producers and trace-element analysts. The materials often consist of a variety of components of different particle size and different density, making it difficult to produce a homogeneous material. Individual components of blended fertilizers may have different solubility characteristics leading to difficult sample digestion, and those with micronutrients contain percentage levels not only of N, P, and K but may also of other elements such as Ca or Fe, which present challenges for some element-detection techniques.

In this paper we describe the development of a new SRM intended for use in method development and measurement validation for determination of the regulated and nutrient element content of blended fertilizers. Details of material preparation and the experimental design, a brief description of the analysis methods, and discussion of the statistical evaluation of the results leading to the certified and reference values are included.

Table 1 Elements regulated in fertilizer materials

Country	Elements regulated in fertilizers
USA	As, Cd, Co, Hg, Mo, Ni, Pb, Se, Zn
Canada	As, Cd, Co, Hg, Mo, Ni, Pb, Se, Zn
Japan	As, Cd, Cr, Hg, Pb
Australia	Cd, Hg, Pb
European Union	Cd
China	Proposed: As, Cd, Cr, Hg, Pb

Materials and methods

SRM preparation

Approximately 180 kg of fertilizer was provided to NIST by The Mosaic Company. The material was derived from ammonium phosphate, various forms of urea, potassium nitrate, potash, borax, and various metal oxy-sulfates. It was ground into a powder at The Mosaic Company and shipped to NIST. At NIST the material was jet-milled and blended in a V-blender to produce approximately 160 kg of light gray powder with a floury consistency. The powder was apportioned into clean glass bottles each containing approximately 70 g. Approximately 2150 bottles were prepared.

Determination of the dry-mass basis

For many NIST SRMs the certified, reference, and information values that appear on a certificate of analysis are expressed on the basis of dry mass. Studies were therefore conducted to determine optimum drying methods and conditions. Results indicated the best drying procedure was desiccator drying of portions of the blended fertilizer at a sample depth of approximately 0.5 cm in (clean, oven-dried) glass containers, for two weeks, over fresh magnesium perchlorate. The average mass loss determined using this method for six portions of SRM 695 was 1.34% (1 s=0.06%). Note that the moisture content may change over time and as a function of local laboratory conditions, for example relative humidity. Oven drying was tested, but even at relatively low temperatures (85 °C) resulted in decomposition of the carbonate and ammonium (and possibly other) compounds in this blended fertilizer material. Oven drying is not recommended for this material.

Assessment of homogeneity

Bottle-to-bottle and within-bottle heterogeneity of SRM 695 was assessed before certification of the material by X-ray fluorescence spectrometry (XRF) measurement of 20 elements. Twenty-four bottles were selected in a stratified random manner from 2150 bottles, and the first and the last bottle were also included. Homogeneity testing measurements were made on briquettes pressed from the powder. From each bottle, two briquettes were prepared by pressing 4.1 g of the powder at 20 tons in a 31.5-mm steel die for 20 s. Gross count-rates were used, except for As and Mo for which net count rates were used. Measurement conditions were the same as described in the XRF section below. Gross count rates are used whenever possible to avoid including the counting statistical error associated with background measurements. Evaluation was based on the observed count-rate variation for each element, the effective

sampling mass for XRF, and the mass fraction present in the material.

Results for representative elements are shown in Table 2, in which the elements, estimated effective XRF sample masses, observed count rates, and associated results of statistical evaluation are listed. Analysis of variance (ANOVA, single factor) was performed to assess bottle-to-bottle heterogeneity; the results indicated that, at the 95% confidence level, only Mg in one bottle and S in another bottle differed significantly from the average results for the 24 bottles. The result for Mg differed from the average by 2%; that for S differed by 4%. The effective XRF sample mass for Mg was rather small, a few milligrams, and the relative standard deviation of the results from XRF of 24 bottles was <1%. The relative standard deviation (RSD) values were ≤1% for all elements. The *F*-test and *P*-values were used to compare within-bottle and between-bottle variance. Although the material failed the *F*-test for S, Na, and Ca, the observed variance for duplicates was <1% (relative) for both Na and Ca. For two of the 24 bottles variance for S was ≥8%. Although, subsequent analysis of three portions from one of these bottles revealed no significant variation, S was not certified in this material. The material was accepted for use as SRM 695 on the basis of these results.

Results from analyses performed for certification of SRM 695 were also used to assess material homogeneity. The relative standard deviation of the average value for a given element determined using a given technique did not usually exceed 2%. Exceptions were observed for Mn determined by using prompt gamma-ray activation analysis (PGAA), and Ca, Mg, and Na by instrumental neutron activation analysis (INAA). These analyses were limited by the uncertainties associated with counting statistics, which accounted for nearly all of the observed variation in the data. Two other exceptions were observed, Mo by ICP–OES (RSD=3.1%, n=12) and Co by INAA (RSD=3.2%, n=6); results obtained from XRF for both Mo and Co showed much less variation, however, with RSD values ≤1%. Because less variation was observed using XRF, it is likely that the observed variation from other techniques can be attributed to measurement reproducibility rather than material heterogeneity.

Experimental design

The experimental design for certification of SRM 695 was based on use of two or more independent analytical techniques performed at NIST with confirmation of these results by analyses performed at the USGS Denver Laboratories. The certification plan called for provision of certified values for all regulated elements and for the nutrient elements, when possible, and provision of reference or information values for elements for which there were results from only one NIST analytical technique. The elements and analytical techniques used to determine the mass fraction values are listed in Table 3. For each technique (except XRF), six bottles were selected in a stratified random manner from the entire batch of 2150 bottles of SRM 695. Eight bottles, also selected in a stratified random manner, were used for XRF analysis.

Analytical methods

INAA at NIST

For determination of As, Co, Cr, Fe, Se, and Zn using INAA, one 100-mg portion of SRM 695 was removed from each of six bottles. Disks were formed from the 100-mg portions of the powdered fertilizer by use of a stainless steel die and hydraulic press. Each disk was doubly encapsulated in bags formed from polyethylene film. Two portions of SRM 2709 San Joaquin soil and two of SRM 2781 domestic sludge were included in the analysis for the purpose of quality assurance (QA). These were prepared in the same manner as the fertilizer samples. Element standards consisted of metals of known purity or were prepared by depositing weighed portions of a standard solution

Table 2 Assessment of SRM 695 heterogeneity using XRF results

Element (mass fraction ± U)	Estimated XRF sample mass[a]	Average count rate ($\times 10^3$ s^{-1})	RSD (%)	P-value	F-test pass
Mo (19.95±0.35 mg kg^{-1})	1 g	2.577	1.03[b]	0.81	Yes
Ni (134.8±3.0 mg kg^{-1})	0.1 g	6.595	0.41	0.39	Yes
Cu (1230±18 mg kg^{-1})	0.1 g	43.34	0.31	0.30	Yes
Mn (0.304±0.007%)	0.1 g	49.66	0.34	0.50	Yes
Mg (1.80±0.02%)	0.01 g	94.91	0.67	0.20	Yes

[a] Effective sample masses are estimated on the basis of volume and density of the prepared target and the depth from which 99% of the X-rays would escape

[b] The relative standard deviation value for Mo is equivalent to the uncertainty associated with counting statistics

Table 3 Analytical techniques used to determine element mass fraction values in SRM 695

Element	Technique 1[a]	Technique 2[a]	Technique 3[a]
Al	XRF	INAA	
As	INAA		
B	PGAA		
Ca	XRF	INAA	
Cd	ID-ICP–MS	PGAA	
Cl	INAA		
Co	XRF	INAA	
Cr	XRF	INAA	
Cu	ICP–OES	ID-ICP–MS	INAA
Fe	INAA	PGAA	XRF
Hg	CV-ID-ICP–MS		
K	PGAA	XRF	
Mg	XRF	INAA	
Mn	PGAA	XRF	INAA
Mo	ICP–OES	XRF	
N	PGAA		
Na	XRF	INAA	
Ni	ICP–OES	XRF	
P	XRF		
Pb	ICP–OES	XRF	
Se	INAA		
Ti	XRF		
V	XRF	INAA	
Zn	INAA	XRF	

[a] CV-ID-ICP–MS, cold-vapor isotope-dilution inductively coupled plasma mass spectrometry; ICP–OES, inductively coupled plasma optical-emission spectrometry; ID-ICP–MS, isotope-dilution inductively coupled plasma mass spectrometry; INAA, instrumental neutron-activation analysis; PGAA, prompt gamma-ray activation analysis; XRF, X-ray fluorescence spectrometry

containing known amounts of the element of interest on to filter paper. Portions of SRM 695, the SRMs included for QA, iron foil neutron fluence monitors, and standards were packaged together in one polyethylene irradiation container and inserted into the NIST reactor, operating at a power of 20 MW, using a pneumatic tube facility (RT-4). Halfway through the irradiation, the irradiation container was removed, flipped end-over-end and reinserted in the reactor for the remaining half of the exposure. Because there is a linear drop-off of neutron flux within this irradiation facility, this procedure is used to minimize any differences in neutron exposure within the different locations in the irradiation container. After decay times of approximately 4 to 6 days, and again after decay times of two to three weeks, gamma rays from each portion were collected using a high-purity germanium detector and associated electronics—high-voltage supply, spectroscopy amplifier, and analog-to-digital converter (ADC). Data were acquired using a μVAX workstation connected to the ADC through an acquisition interface module. Mass fractions of elements in each sample and control material (SRM) were calculated by using a relative method based on comparison with element standards for each element determined.

For determination of Al, Ca, Cl, Cu, Mg, Mn, Na, and V using INAA, one 100-mg disk-shaped portion of SRM 695 from each of three bottles and two portions from each of three bottles were prepared as described above. Two portions of SRM 2709 San Joaquin soil, three portions of SRM 1577b bovine liver tissue, and one portion of SRM 1566a oyster tissue were prepared in the same manner and were included in the analysis for quality assurance. Standards for Al, Ca, Cl, Cu, Mg, Na, and V consisted of elements or compounds of known purity. The standard for Mn was prepared by depositing SRM 3132 manganese standard solution on to filter paper. Each portion of SRM was irradiated in the pneumatic tube irradiation facility (RT-1) together with one element standard and one neutron-flux monitor for 30 s. After a decay time of 10 min and again after a decay time of 15 min gamma rays were collected from each sample or standard using a spectrometry system consisting of a high-purity germanium detector and associated electronics—amplifier, loss-free counting module, and analog-to-digital converter (ADC). Data were acquired using a μVAX workstation connected to the ADC through an acquisition interface module. Again, mass fractions of elements in each sample and control material (SRM) were calculated on the basis of comparison with element standards.

PGAA at NIST

For determination of B, Cd, Fe, K, Mn, and N using PGAA, one 750-mg portion was removed from each of the six numbered bottles and individual disks were formed from each portion by use of a stainless steel die and hydraulic press. Each disk was placed in a bag formed from Teflon film and placed in a closed plastic Petri dish until needed for analysis. Three control SRMs were included in the analysis batch for the purpose of quality assurance. Two portions of SRM 2781 domestic sludge, two portions of SRM 2711 San Joaquin soil, and one portion of SRM 2710 Montana soil were prepared and packaged in the same way. Analysis of one Teflon bag was performed to determine the boron content of the bag and the background gamma-ray count-rates for the regions of interest. Standards consisted of pure elements, compounds of known purity, or mixtures containing known amounts of compounds (of known purity) containing the elements of interest and graphite. For analysis by PGAA, each sample, standard, or control material was irradiated individually in the vertical beam tube of the NIST reactor at a reactor power of 20 MW, which provides a thermal neutron fluence rate of approximately 3.0×10^{8} cm^{-2} s^{-1}. Once or twice each day, one Ti foil was irradiated to monitor small fluctuations in neutron

fluence over the course of the experiment. Count rates from these measurements were used to determine the correction factors needed to normalize all samples, standards, and controls to the same fluence rates. The neutron fluence rate does not vary appreciably during the time required for the irradiation of one sample, but over the course of the reactor fuel cycle increases gradually by 4% to 5%, relative to the fluence rate on the first day of the cycle. All count-rates were also corrected for the pile-up of pulses (which varies as a function of analyzer dead-time) and for neutron attenuation by the targets (3.0% for SRM 695, 0.4% for SRMs 2710 and 2711, 1.4% for SRM 2781, and from 4.7% to 5.8% for standards). Mass fractions of elements in each sample and control material (SRM) were calculated on the basis of comparison with standards.

XRF at NIST

For determination of Al, Ca, Co, Cr, Fe, K Mg, Mn, Mo Na, Ni, P, Pb, S, Ti, V, and Zn by quantitative XRF, samples were prepared by borate fusion. A platinum (5% Au) crucible was weighed empty and 7.50 g flux, a 67:33 (mass fraction) mixture of $Li_2B_4O_7$ and $LiBO_2$, was added. A 4.50-g sample was then weighed directly on to the flux. A Philips/SOLED Perl'x3 automated bead preparation machine was used to fuse and cast samples as 40-mm diameter beads in a single program. The fusion program consisted of a drying step at 200 °C for 2 min, a step at 600 °C for 6 min to calcine the specimen, a fusion step of 3 min at 975 °C without agitation to melt the flux and begin the fusion, followed by a step of 5 min at 975 °C with mixing. At this point, the melt was cooled to room temperature and two or three drops of LiI non-wetting agent (0.25 g LiI g^{-1} solution) were added. A final fusion step of mixing for 5 min at 975 °C was followed by casting. The resulting bead was cast in one of two platinum dishes, which were shown to produce identical beads before the start of this work. Because all beads had a flat, smooth surface, no additional preparations were required before measurement.

A Philips model PW2404 wavelength-dispersive XRF spectrometer was used to measure the K-$L_{2,3}$ characteristic X-ray lines of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Ti, V, and Zn and the L_2-M_4 line of Pb. All measurements for homogeneity and quantitative analyses were performed in a vacuum environment (<5 Pa) with the generator operated at 3.0 kW. Counting times were chosen to obtain relative counting statistical uncertainties of approximately 0.25% to 1.0% for each element. The quantitative analysis was performed using synthetic, bracketing standards prepared from high-purity compounds and NIST SRM spectrometric solutions. The compositions of the synthetic standards were closely matched to the unknown beads to make it possible to use straight-line calibration curves without introducing inter-element corrections. The Rh KL Compton scatter line from the X-ray tube was used as an internal reference for the elements Co, Cu, Fe, Mo, Ni, Pb, and Zn. The internal reference serves to compensate for effects of the matrix or effects which arise because the beads are not infinitely thick for the measured X-rays. Line-overlap corrections were made for the spectral overlaps I on Ti, Zn on Na, Ti on V, and Fe on Co. The correction for I on Ti was determined in a separate experiment. The other three corrections were calculated from the empirical data for this project. Corrections were made for the absorption by Cl of the X rays from P and K. These corrections were also calculated from the empirical data for this project. The calibrations were used to determine the mass fractions of constituents in the fused specimens. Mass fractions in the original fertilizer powder specimens were calculated by multiplying by the ratio of total borate glass formed by fusion to the mass of each specimen.

ICP–OES at NIST

For determination of Cu, Mo, Ni, and Pb using ICP–OES, two 0.4-g sub-samples were taken from each of six bottles and placed in Teflon microwave digestion vessels with 9 mL HNO_3 and 1 mL HF. For quality assurance, six reagent blanks and two or more portions of two different NIST SRMs (prepared in the same manner) were also included in the suite of samples. In the microwave oven the temperature was increased to 200 °C over a period of 15 min, and that temperature was held for 20 min. The power of the microwave was then set to zero and the samples were left to cool for 25 min. A 0.5-mL aliquot of internal standard solution containing 10.0 mg mL^{-1} In and 2 mL $HClO_4$ were then added to each sample, blank, and QA SRM. The beakers were covered and heated for 4 h at 200 °C. The covers were removed and the digests were evaporated to approximately 1 mL and transferred to 60-mL polyethylene (PE) bottles. Each was diluted to 50 g with 1.5% HNO_3.

Calibration was accomplished by using the method of standard addition. To determine Ni and Pb, 5-g aliquots from each original solution were transferred to weighed 30-mL PE bottles and diluted to 25 g with 1.5% HNO_3. Two 12.5-g aliquots were taken from each of these solutions and transferred to weighed 25-mL PE bottles. A 0.2-g spike containing a Ni mass fraction of 206.6 μg g^{-1} (prepared from SRM 3136 nickel standard solution) and a Pb mass fraction of 524.4 μg g^{-1} (from SRM 3128 lead standard solution) was added to one aliquot from each sample. To determine Mo, two 12.5-g aliquots were taken from each original solution and transferred to weighed 30-mL PE bottles. A 0.2-g spike containing a Mo mass fraction of 54.7 μg g^{-1} (prepared from SRM 3134 molybdenum standard solution) was added to one aliquot from each

sample. To determine Cu, 2-g aliquots were transferred from each original solution to weighed 30-mL PE bottles and diluted to 25 g with 1.5% HNO_3. Two 12.5-g aliquots were taken from each of these solutions and transferred to weighed 25-mL PE bottles. A 0.2-g spike containing a Cu mass fraction of 156.0 μg g^{-1} (prepared from SRM 3114 copper standard solution) was added to one aliquot from each sample. A Perkin-Elmer Optima 3300 Dual View instrument was used for analysis. The wavelengths used were: 324.752 nm for Cu, 202.031 nm for Mo, 231.604 nm for Ni, and 220.353 nm for Pb. Four instrumental measurements were taken and averaged for each sample and each spiked solution. Element mass fraction values were calculated by the method of standard addition.

ID-ICP–MS at NIST

For determination of Cu and Cd using ID-ICP–MS, 0.1 g to 0.2-g sub-samples were accurately weighed by difference into clean Teflon microwave vessels. A known amount of spike solution containing isotopically enriched ^{65}Cu and ^{111}Cd was added by mass difference to all SRM 695 samples, the SRMs included for QA, spike calibration samples, and procedure blanks. The concentration of ^{65}Cu and ^{111}Cd in each spike solution was calibrated by reverse isotope-dilution mass spectrometry against two gravimetrically prepared primary standard solutions for each element. The primary standard solutions were prepared from high-purity Cu metal, SRM 3114 Cu standard solution, SRM 746 Cd vapor pressure standard, and SRM 3108 Cd standard solution. Spike calibration samples were prepared in Teflon beakers from weighed aliquots of the primary standard solutions and spike solutions to have ratios similar to those of the analytical samples. SRM 695 samples, controls, and procedure blanks were digested with 9 g HNO_3 and 1 g HF in a high-throughput microwave oven using a single-stage procedure at 1200 W power. Vessels were heated to 205 °C over a 15-min period and held at 205 °C for an additional 20 min. Digests were transferred to clean Teflon beakers and heated on a hot-plate to evaporate the concentrated acids. Digests were re-dissolved in 15 g of 1 mol L^{-1} HNO_3 by heating gently for 24 h. Before ICP–MS analysis, samples, controls and spike calibration samples were diluted to 3.5 ng g^{-1} of the major isotope with 0.4 mol L^{-1} HNO_3. Procedure blanks were diluted to a minimum analysis volume with 0.4 mol L^{-1} HNO_3.

Mass ratios of Cu and Cd were measured in separate runs using a VG PlasmaQuad 3 quadrupole ICP–MS operated at 1350 W using standard gas flows. Measurement procedures for Cd have been described elsewhere [3]. In this work, solution was introduced using a peristaltic pump and 100-μL min^{-1} capillary nebulizer into a water-cooled (4 °C), low-volume cyclonic spray chamber. Signal intensities were measured using peak-jump data acquisition with one point per peak. Five blocks of data each 1 min in duration were acquired per sample and the mean ratio was used for computations. Typical dwell times were 10 to 20 ms. Copper concentrations were calculated from the $^{65}Cu/^{63}Cu$ ratio. Cadmium concentrations were calculated from the $^{111}Cd/^{114}Cd$ ratio after correction for isobaric interference from Sn. Results calculated with different Cd ratios (i.e. $^{111}Cd/^{112}Cd$ and $^{111}Cd/^{113}Cd$) were in excellent agreement with the $^{111}Cd/^{114}Cd$ results and only the latter were reported. In addition to correction for isobaric interference (for Cd only), measured ratios were corrected for drift, mass bias, and detector dead-time. The detector dead time of 21 ns was determined experimentally using natural Cd solutions with concentrations spanning the count-rate range from 1×10^5 to 9×10^5 counts s^{-1} of the major isotope. Isotopic standards composed of solutions of pure Cu or Cd metal were used to measure the mass-bias correction factors for Cu and Cd at the beginning of an analysis sequence. Samples were corrected for instrument drift every three samples by repeatedly measuring a spike calibration sample and applying a correction assuming linear change with time. Concentrations were calculated using the isotope-dilution equation described by Fassett and Paulsen [4].

CV-ID-ICP–MS at NIST

For determination of mercury by CV-ID-ICP–MS, approximately 0.25 g sample from each bottle was accurately weighed by difference into a clean 50-mL quartz microwave cell using a borosilicate glass transfer funnel. Then, the sample was spiked with an accurately weighed aliquot (approximately 2 g) of a stock solution of the ^{201}Hg-enriched isotope by means of a plastic syringe. Approximately 6 g high-purity HNO_3 was added to each cell. The cells were sealed and the contents digested in a high-pressure microwave oven (Anton PAAR) using a temperature program optimized for this type of matrix. The resulting digests were left to cool, the vessels pressure-vented, and the contents transferred to clean 50-mL polypropylene centrifuge tubes. The contents of the tubes were diluted to 15 mL with quartz-distilled H_2O. The tubes were placed overnight in a refrigerator at 4 °C to enable degassing of excess NO_2 and CO_2 resulting from the oxidation process. Analytical measurements were completed within one day of dilution to reduce the risk of external contamination or mercury losses from the solutions during storage. The contents of the tubes were further diluted to a concentration range suitable for measurement by the ICP–MS instrument. In addition to the samples and SRMs included for QA, three process blanks containing a small aliquot (0.05 g) of

the ^{201}Hg spike only were carried through the entire sample processing and measurement scheme.

Mercury measurements were made using cold-vapor Hg generation coupled with ICP–MS isotope-ratio measurements. The Hg vapor was generated using tin(II) chloride reductant (10% mass concentration in 7% volume fraction HCl) and separated from the liquid phase using a commercial (CETAC) glass reaction/separator cell. The vapor was transferred to a Thermo X7 ICP–MS system via 1/16" i.d. Viton tubing, using an Ar carrier gas flow rate of approximately 100 mL min^{-1}. This gas stream was mixed with the plasma injector gas stream using a plastic T connector. The ICP was operated in a dry plasma mode, which necessitated slight re-tuning of the ion lenses relative to an aqueous aerosol sample-introduction system. The ^{201}Hg and ^{202}Hg isotopes were monitored in a pulse-counting time-resolved-analysis mode to recover the individual ion-count rates. The isotope–time profiles were downloaded to a spreadsheet for calculation of background-corrected ^{201}Hg/^{202}Hg ratios. Instrument mass discrimination and instrument detector dead-time were measured by generation of Hg vapor from a calibration standard (SRM 1641d mercury in water). The instrument detector dead-time was 37 ns.

USGS analytical methods

At the USGS laboratories in Denver, CO, USA, several different analytical methods were used to determine mass fractions of 32 elements in SRM 695 [5]. The methods used were: cold-vapor atomic absorption spectrometry (CVAAS) for Hg; AAS with hydride generation for Se; a combustion method for total C and S; and ICP–OES for Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, P, La, Li, Mn, Mo, Ni,

Table 4 Average mass fraction values from each method, and certified values

Element	Method (*n*)	Mass fraction	Units	1 *s*	*U*	Certified values
As	INAA (8)	200.3	mg kg^{-1}	4.6	5.0	200±5 mg kg^{-1}
Ca	INAA (9)	2.238	%	0.097	0.080	2.26±0.04%
	XRF (12)	2.276	%	0.008	0.014	
Cd	PGAA (6)	17.03	mg kg^{-1}	0.14	0.36	16.9±0.2 mg kg^{-1}
	ID-ICP–MS (10)	16.81	mg kg^{-1}	0.07	0.11	
Co	INAA (8)	67.14	mg kg^{-1}	2.2	1.6	65.3±2.4 mg kg^{-1}
	XRF (16)	63.55	mg kg^{-1}	1.1	2.0	
Cr	INAA (8)	238.8	mg kg^{-1}	3.5	4.5	244±6 mg kg^{-1}
	XRF (16)	248.2	mg kg^{-1}	2.1	3.8	
Cu	ID-ICP–MS (10)	1223	mg kg^{-1}	5.4	8	1225±9 mg kg^{-1}
	ICP–OES (12)	1222	mg kg^{-1}	13	11	
	XRF (16)	1230	mg kg^{-1}	14	18	
Fe	INAA (8)	3.948	%	0.036	0.052	3.99±0.08%
	PGAA (6)	4.060	%	0.050	0.10	
	XRF (16)	3.971	%	0.015	0.018	
Hg	CV-ID-ICP–MS (6)	1.955	mg kg^{-1}	0.0055	0.036	1.955±0.036 mg kg^{-1}
K	PGAA (6)	11.66	%	0.06	0.23	11.65±0.13%
	XRF (16)	11.64	%	0.04	0.10	
Mg	INAA (9)	1.78	%	0.14	0.11	1.79±0.05%
	XRF (16)	1.80	%	0.01	0.02	
Mn	PGAA (6)	0.305	%	0.008	0.009	0.305±0.005%
	XRF (16)	0.304	%	0.004	0.007	
	INAA (9)	0.307	%	0.004	0.005	
Mo	ICP–OES (12)	20.12	mg kg^{-1}	0.51	0.48	20.0±0.3 mg kg^{-1}
	XRF (16)	19.95	mg kg^{-1}	0.25	0.35	
Ni	ICP–OES (12)	134.95	mg kg^{-1}	1.3	1.4	135±2 mg kg^{-1}
	XRF (16)	134.80	mg kg^{-1}	1.1	3.0	
Pb	ICP–OES (12)	286.2	mg kg^{-1}	3.2	5.1	273±17 mg kg^{-1}
	XRF (16)	260.6	mg kg^{-1}	4.0	15.3	
Na	INAA (9)	0.409	%	0.011	0.010	0.405±0.007%
	XRF (16)	0.400	%	0.001	0.004	
V	INAA (9)	123.5	mg kg^{-1}	2.4	3.1	122±3 mg kg^{-1}
	XRF (16)	119.9	mg kg^{-1}	1.7	1.6	
Zn	INAA (8)	0.3210	%	0.002	0.007	0.325±0.005%
	XRF (16)	0.3284	%	0.001	0.002	

Table 5 Average mass fraction values from each method, and reference values

Element	Method	Mass fraction	Units	1 s	U	Reference values
Al	INAA (9)	0.635	%	0.014	0.016	0.61±0.03%
	XRF (16)	0.593	%	0.002	0.003	
B	PGAA (6)	0.111	%	0.0006	0.002	0.111±0.002%
N	PGAA (6)	13.9	%	0.3	0.4	13.9±0.04%
P	XRF (16)	7.2	%	0.02	0.1	7.2±0.1%
Se	INAA (8)	2.1	mg kg^{-1}	0.09	0.1	2.1±0.1 mg kg^{-1}

Pb, Sc, Sn, Sr, V, Y, Yb, and Zn. Results from selected elements were used to confirm results from NIST.

Industry test method

The methods used at NIST and at USGS were either non-destructive (i.e. INAA, PGAA, and XRF) or involved complete dissolution of the material before performing measurements (e.g. ICP–OES, ID-ICP–MS, CV-ID-ICP–MS). For routine analysis of metals in fertilizer materials a method using microwave extraction with concentrated nitric acid followed by ICP–OES detection was developed and tested by members of the Association of American Plant Food Control Officials (AAPFCO). A complete description of this method and the results of the collaborative study can be found elsewhere [6]. As part of this collaborative study, portions of SRM 695 were distributed to ten laboratories for analysis by this test method. A summary of the results from the test method, compared with the NIST certified values appears as an addendum to the certificate of analysis (COA) for SRM 695.

Results and discussion

Average mass fraction values obtained from each NIST analytical technique are shown in Tables 4 and 5, together with the 1 s values, and the expanded uncertainties for each. Also shown in Table 4 are the final certified values for 17 elements, and in Table 5 the final reference values for five elements. Information values are provided for two additional elements, discussed below. A complete description of the terms "certified", "reference", and "information" is given in Ref. [7].

The reference value for Al and all certified values except those for As and Hg are the unweighted means of results from two or three analytical methods. The uncertainty, U, listed with each value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within-method variance [8], in accordance with the ISO Guide to the Expression of Uncertainty in Measurement and NIST Special Publication 1297 [9, 10]. The certified values for As and Hg are each results from a single NIST method (INAA for As and CV-ID-ICP–MS for Hg) for which a complete evaluation of all sources of uncertainty has been performed. Uncertainties for these certified values represent an expanded uncertainty with a coverage factor of 2, with each uncertainty component combined in accordance with Refs. [9] and [10].

Reference values for all elements (except Al) are based on results of one analytical method at NIST and the uncertainty values represent the expanded uncertainties which include the combined type-A and type-B uncertainties with a coverage factor of 2, in accordance with Refs. [9] and [10]. An average Cl mass fraction value of 4.6% was determined using INAA; a complete analysis of uncertainty was not performed, however, so this value is included on the certificate of analysis for information purposes. Similarly, a mass fraction value of 310 mg kg^{-1} Ti was determined using XRF and is included on the certificate of analysis for information purposes.

Where there are results from two or three NIST techniques, agreement is usually quite good. All results agree within the expanded uncertainties or within 2 s of the average values except those for Al and for Pb. The causes of these discrepancies are not known but are under investigation. For Al and Pb, estimates of between-method biases were 2.0% and 2.7%, respectively; an estimate of the uncertainty associated with between-method bias [8] was included in the combined uncertainty of the final certified

Table 6 Results from AAPFCO test method determination of selected elements in SRM 695

Element	Test method results (mg kg^{-1}): average mass fraction (1 s); range	Average recovery; range (%)	Certified element mass fraction (mg kg^{-1})
As	193 (19); 171–235	96; 85–117	200±5
Cd	16.1 (2.9); 12.4–23.2	95; 74–137	16.9±0.2
Co	47.5 (12.3); 27.4–65.7	73; 42–101	65.3±2.4
Cr	174 (19); 136–192	71; 56–79	244±6
Mo	14.0 (2.0); 10.2–16.8	70; 51–84	20.0±0.3
Ni	112 (15); 85–131	83; 63–97	135±2
Pb	257 (15); 231–281	94; 85–103	273±17

or reference value. Results from USGS confirmed NIST results for Ca, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Na, Ni, P, V, and Zn; agreement with NIST values was within ≤10%.

Results from AAPFCO-sponsored collaborative study

For this collaborative study many different materials were prepared as unknown test materials and sent to participating laboratories. Portions of SRM 695 were included in the sample set, also as unknown materials, and ten laboratories analyzed SRM 695 as part of this larger study. The results obtained using this method are shown in Table 6, together with total element content as determined at NIST for certification of this material and the percentage recovery defined as the ratio of the values obtained from the test method to the total element content determined for certification of SRM 695. Results indicate that some elements are completely extracted but that others are not. Average recovery ranges from approximately 70% to nearly 100%, indicating that this method may be useful for screening materials with a similar matrix to estimate levels of these elements.

Summary and conclusions

A new fertilizer reference material, NIST SRM 695 trace elements in multi-nutrient fertilizer, has been developed and is now available. Certified values are provided for 17 elements, reference values for five elements, and information values for two elements. This is the first blended, multi-nutrient fertilizer reference material and the first fertilizer material with certified or reference values for all elements of interest, both nutritive and non-nutritive.

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Disclaimer Commercial equipment and materials are identified in this paper for the purpose of adequately describing experimental procedures. Such mention does not imply endorsement by the National Institute of Standards and Technology.

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