NIST Special Publication 260-200

Certification of Standard Reference Material® 2859 and Standard Reference Material® 2861
Restricted Elements in Polyvinyl Chloride

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Standards and Technology
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Abstract

The National Institute of Standards and Technology has issued its first Standard Reference Materials for elemental analysis of polyvinyl chloride (PVC). The custom designed PVC blends contain elements regulated in consumer products by the United States, the European Union, and other governments worldwide. The regulated elements are antimony, arsenic, barium, bromine, cadmium, chromium, lead, mercury, and selenium. Also, present in the PVC blend are elements from performance additives: calcium, sulfur, and tin; and from contaminants: copper, and iron. The development and certification project was designed and coordinated by NIST with technical assistance from the U.S. Consumer Product Safety Commission, Underwriters' Laboratories and the University of Washington Physics Department. This report describes how the PVC blends were designed, manufactured, packaged, analyzed, and value-assigned. Users will find descriptions of material heterogeneity testing and information from several test methods used for quantitative analyses of the PVC blends. The SRMs are available for purchase with one unit consisting of a single bottle containing 25 g of extruded pellets. In addition to describing the development of these SRMs, this report describes a process for creating calibrations for X-ray fluorescence spectrometry with mass fraction values traceable to the International System of Units using NIST SRM 3100 series, single element, spectrometric solutions. After the issuance of the SRMs, they were analyzed to obtain the mass fraction values for hexavalent chromium using a new, high-resolution X-ray emission method. The new method is described briefly with reference given to a detailed journal publication.

Keywords

Technical Information Contact for these SRMs

Please address technical questions about these SRMs to srms@nist.gov, where they will be assigned to the appropriate Technical Contact responsible for support of this material.
For sales and customer service inquiries, please contact srminfo@nist.gov.

NOTICE: This document contains test results obtained during development of the SRMs. The reader shouldAuf keep in mind that the only official values for the measurands for these SRMs are those presented in the Certificates of Analysis. It is not appropriate to use any other values in place of the certificate values.

This extensive report provides an account of the work performed to develop SRM 2859 and SRM 2861. It is one unique example of SRM development practices in compliance with the NIST Quality System for Measurement Services. Other development projects may use different practices and equipment to characterize the material(s) and set(s) of measurands.

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1. Introduction

Polyvinyl chloride (PVC) formulations are widely used in industrial applications, construction, plumbing, and consumer products. For many years, PVC and other polymers have been subject to restrictions on the amounts of hazardous constituents that may be used in them. In 1989, the Coalition of Northeast Governors (CONEG) developed legislation to reduce hexavalent chromium, cadmium, lead and mercury in municipal waste, including packaging. In 2005, the European Union implemented a directive known by the acronym RoHS to regulate hexavalent chromium, lead, mercury, cadmium, and brominated flame retardants in selected classes of manufactured products imported into and sold in EU nations. Soon thereafter, similar regulations were implemented in numerous countries. In 2008, the United States enacted the Consumer Product Safety Improvement Act of 2008 (CPSIA) that gives the Consumer Product Safety Commission (CPSC) authority to restrict the amounts of certain elements in consumer products [1]. The CPSIA incorporates ASTM International F963 Standard Consumer Safety Specification for Toy Safety. In addition to chromium, cadmium, lead, and mercury, F963 covers antimony, arsenic, barium, and selenium. In most cases, manufacturers, importers, retailers, and regulators concern themselves with restricting the mass fractions of the nine elements As, Ba, Br, Cd, Cr, Hg, Pb, Sb, and Se; so, they need not worry about the chemical forms present.

In 2011, NIST and CPSC began design and development of a PVC SRM for Pb content. In time, this project grew to development of two PVC SRMs – SRM 2859 for the RoHS elements and SRM 2861 for the F963 elements. SRM 2859 contains high levels of Br, Cr, Cd, Pb, and Hg, and SRM 2861 contains the F963 elements at lower levels closer to those listed in the standard. The blends were prepared by weighing organometallic compounds and SRM 3100 series solutions into virgin PVC powder to create concentrated master blends. These master blends were thoroughly mixed. Then, they were weighed together with a commercially provided dry blend, and finished by melt extrusion and chopping into pellets. The finished pellets were blended and bottled at NIST.

NIST procedures for certification of values [2] require the use of two or more independent methods of analysis. In this case, the methods were X-ray fluorescence (XRF) spectrometry performed by NIST and inductively coupled plasma atomic emission spectrometry (ICPOES) performed at the CSPC and at Underwriters' Laboratories (UL). An incentive to use XRF is that polymer manufacturers use XRF methods for a variety of virgin polymers. ASTM international publishes F2617−15 Standard Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry [3]. The approach in F2617 can be extended to additional elements using appropriate calibration standards and measurement conditions. Therefore, the SRM materials must work well with XRF measurement technologies, and limitations due to heterogeneity and sample preparation must be investigated and reported to the SRM user.

In addition to describing the development and creation of the PVC blends, this publication reports the development of simple procedures for formulating and preparing disk form PVC calibration standards for XRF. The preparation procedures produce disks that are homogeneous at the micrometer scale. By using NIST SRM spectrometric solutions as the sources of the elements, the assigned values for mass fractions of elements are directly traceable to the International System of Units (SI). The more direct are the links of traceability; the more defensible is the validation of a test method.

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The collaborators, whose results are summarized herein, have considerable experience with elemental analyses of plastics, including PVC. The CPSC published an ICPOES test method used worldwide for elements in plastic [4], and they analyze products on a constant basis. Underwriters' Laboratories participated in an international pilot comparison involving analysis of polypropylene for the elements Cd, Cr, Hg, and Pb. They also analyze plastics on a regular basis. The NIST Technical Project Leader provided samples, spectrometric solution SRMs, quality assurance materials, and instructions for sampling and reporting, per the requirements of the NIST Quality system for Measurement Services.

When SRM 2859 and SRM 2861 were issued in 2017, NIST became aware of laboratory-based X-ray emission spectrometry (XES) technology that appeared capable of quantitative determinations of amounts of elemental oxidation states in materials. In collaboration with the Physics Department of the University of Washington, a test method was developed and used to quantify the mass fractions of Cr(VI) in plastics. The project results [5] included a value now assigned as a reference value for Cr(VI) in SRM 2859.

2. Manufacture and Acceptance Testing

The two PVC blends were formulated using master blends and a commercial dry blend that contained performance additives. The master blends were prepared at NIST using SRMs as the sources of the elements of interest. Master blends and the dry blend were combined at a research scale blending and extrusion facility.

In an ideal situation, the PVC formulations would be prepared gravimetrically from reference materials and high-purity compounds and manufactured such that the values for element contents in the ingredients and the weights of those ingredients could be used as a source of reliable mass fraction values in value assignment through combination with results from one or more instrumental test methods. The manufactured PVC formulations would be highly homogeneous, if it is possible to completely mix the ingredients with the PVC resin. Two approaches were envisioned to obtain sufficient homogeneity. First, a finely divided PVC powder would be coated by wetting with solutions of the elements. If necessary, a detergent could be used with aqueous solutions. After the H_2O was removed by drying, the PVC powder particles should be coated with the compounds dissolved to make the solutions. Second, the elements could be introduced as organometallic compounds that would become thoroughly blended with the PVC resin during melt extrusion of the final formulation. That way, the compounds would more likely be distributed within the PVC matrix than be present as discreet particles as has been observed with inorganic compounds. The NIST SRMs numbered 1050 through 1080 are organometallic compounds that provide an excellent opportunity to use this approach with certified mass fractions of the metals. Although these SRMs are more than 40 years old, the remaining materials have been monitored and are known to be stable with valid certified values.

This multiple step process was designed with the goal of improving on approaches used by other developers of reference materials for plastics. Earlier attempts all appear to have used a single step approach with the base polymer and all ingredients blended just prior to extrusion. This approach has been applied to PVC with, for example, powder-form inorganic and organometallic compounds [6, 7], PVC with powder form oxides [8], and polycarbonate with powder form

inorganic compounds [9]. In one case for polypropylene [10], NIST analyses by micro X-ray fluorescence spectrometry (microXRF) identified localized regions of the inorganic compounds. Small regions of HgS were discovered to be volatile under X-irradiation.

2.1 Preparation of Master Blends

With those goals, the two PVC formulations were begun by creating master blends consisting of virgin PVC powder to which the organometallic compound SRMs and SRM 3100 series, single element, spectrometric standard solution SRMs were added. The combined ingredients were thoroughly mixed by stirring and shaking. Then, the master blends were dried to constant mass in a convection oven at 85 ºC and in a box desiccator at room temperature ($\approx$ 22 ºC) with additional, intermittent mixing. By design, SRM 2859 contains the elements Br, Cd, Cr, Hg, and Pb at high levels with all introduced as organometallic compounds in powder form, except Cr, which was added as a solution of $Na_2Cr_2O_7$ to incorporate Cr in its hexavalent oxidation state. SRM 2861 contains Cd, Cr, Hg, and Pb from the same ingredients at lower levels, Ba from an organometallic compound, and the elements As, Sb and Se from SRM 3100 series solutions.

For the master blends, the ingredients and masses are given in Table 1. For solution SRMs, the mass of each solution was recorded, then the mass of the element of interest was calculated and listed under compound mass. Because the SRM 3100 series solutions contain acids, a neutralizing solution of LiOH (6.7 %) in H_2O was added to the master blend for SRM 2861. The source of the high-purity $Na_2Cr_2O_7$ is unknown. The powder was dried for 2 h at 105 ºC and dissolved in distilled and deionized H_2O to obtain a nominal 6.7 % solution as Cr. The copper phthalocyanine green 36 is a commercial[1] dye compound (Landers-Segal Color Co., Inc., Warwick, RI) containing highly brominated organic chains coordinated to the Cu atoms. It was analyzed using semiquantitative XRF to determine the approximate mass fractions of Cu and Br. The octanoic acid compounds of Ca, Pb, Cd, Ba, and Hg were used directly from the SRM bottles.

Some limitations to the master blend approach were observed. The phthalocyanine green dye compound is extremely colorful and sticky. It stained the plastic jar in which the master blend was prepared. All ingredients introduced as solutions will have coated the container inside surfaces and the utensils used for mixing. All ingredients introduced as organometallic compounds were more likely to become incorporated into the PVC matrix, but there is no data on how complete the incorporation may be. It was not known how effectively the master blends were dried, which could bias the final weights of the blends and weights used when combining the master blends with the commercial dry blend.

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[1] Certain commercial equipment, instrumentation, or materials are identified in this document to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Ingredients and Prepared Element Mass Fractions in PVC Master Blends for SRM 2859 and SRM 2861

Ingredient	SRM Number or Source	Element	Mass Fractions SRM 2859 (%)	SRM 2861 (%)
Calcium 2-ethylhexanoate	1074b	Ca	1.141	0.266
Lead cyclohexanebutyrate	1059c	Pb	2.161	0.096
Cadmium cyclohexanebutyrate	1053a	Cd	0.215	0.080
Barium cyclohexanebutyrate	1051	Ba	-	0.909
Mercury cyclohexanebutyrate	1064	Hg	2.167	0.066
Sodium dichromate solution	Unknown	Cr	2.040	0.062
Arsenic solution	3103a	As	-	0.028
Antimony solution	3102a	Sb	-	0.076
Selenium solution	3149	Se	-	0.197
Copper Phthalocyanine Green 36	Lansco Colors	Br	2.170	-
Virgin PVC powder	Aldrich	-	-	-
LiOH (6.7 %) neutralizing solution	Aldrich	-	-	-

2.2 Formulation and Extrusion

A commercial PVC manufacturer provided a sufficient quantity of a so-called dry blend of PVC, $CaCO_3$, plasticizer and the stabilizer methyltin mercaptide ($C_{22}H_{44}O_4S_2Sn$) into which the master blends could be mixed prior to extrusion. The dry blend was not intended to represent specific compositions of commercial PVC products.

Blending was performed at Polymers Center of Excellence, Charlotte, NC. Each PVC formulation was prepared by combining the master blend and dry blend in a Henschel mixer (Fig. 1) heated to 84 ºC water jacket temperature. Because this mixer is small, each formulation was blended in three parts, which were added serially to the twin-screw extruder. For the SRM 2859 blend, each charge was about 109 g of master blend with 2.67 kg of dry blend. For the SRM 2861 blend, each charge was about 282 g of master blend with 2.66 kg of dry blend. Each charge was blended for 5 min to 10 min until the internal temperature was approximately 60 ºC. For all six charges, free moisture was observed on the interior surfaces of the mixer. A possible reason is that the master blend, the dry blend or both were not completely dry. It is also possible incomplete neutralization between HNO_3 and LiOH in the SRM 2861 master blend was driven to completion with release of H_2O. However, that was not possible with the SRM 2859 master blend, because no acids or bases were added. Last, the humid laboratory environment may have contributed moisture.

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Fig. 1. Henschel mixer (left) and interior of mixer (right) with remnants of blended SRM 2859 ingredients. A water heater (not shown) maintains mixer jacket temperature.
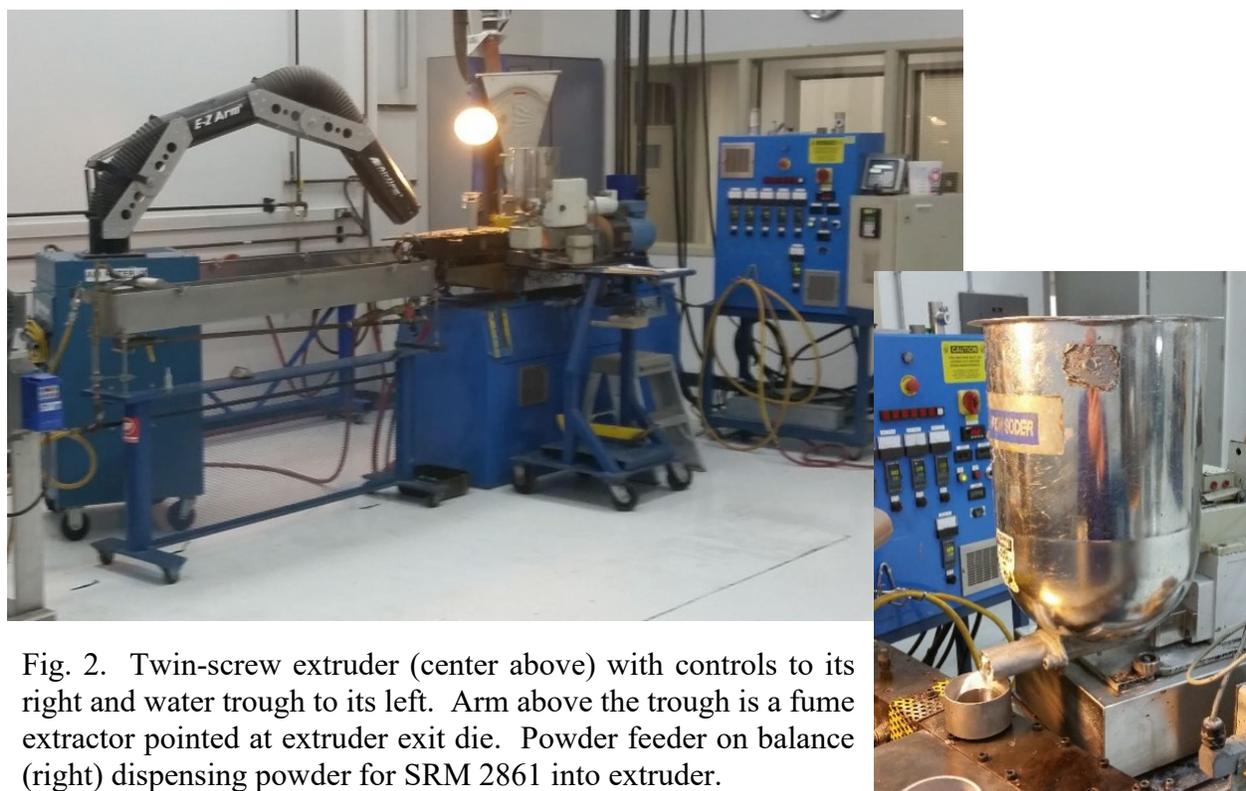
Fig. 2. Twin-screw extruder (center above) with controls to its right and water trough to its left. Arm above the trough is a fume extractor pointed at extruder exit die. Powder feeder on balance (right) dispensing powder for SRM 2861 into extruder.

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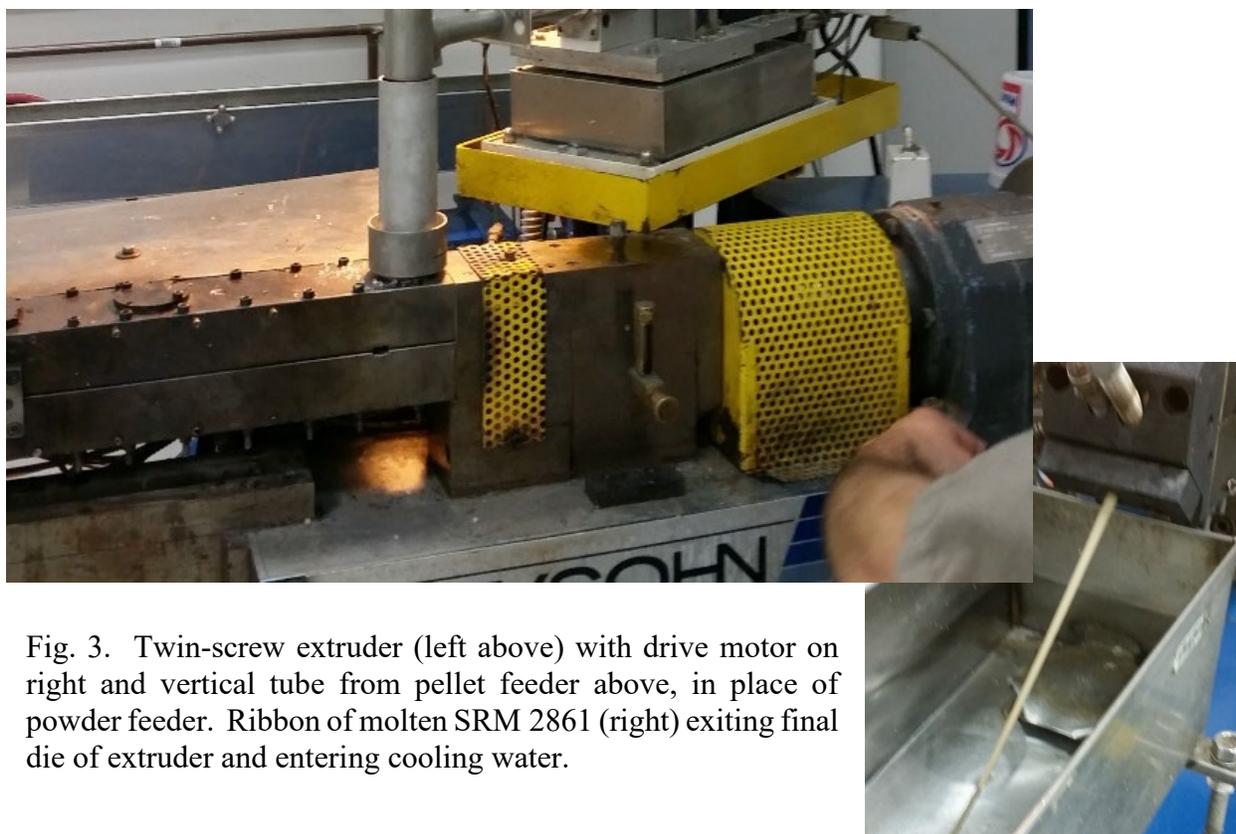
Fig. 3. Twin-screw extruder (left above) with drive motor on right and vertical tube from pellet feeder above, in place of powder feeder. Ribbon of molten SRM 2861 (right) exiting final die of extruder and entering cooling water.

Fig. 4. Chopper (left) with thin, tan ribbon of SRM 2861 entering on left and blue can to collect pellets. Cover removed (right) shows black feed spindle, chopping block and rotating knife (l to r).

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Fig. 5. Chopped and bagged pellets of PVC SRM 2861.

Fig. 6. Melt-pressed disk made from pellets of SRM 2861 heated to 175 ºC for 1.5 h. Darker regions are outer surfaces of individual pellets.

Melt extrusion was performed in a K-Tron Twin (Fig. 2 and Fig. 3) twin-screw, top-feed extruder run at 21.3 rad/s (203 rpm (revolutions per minute)) to 22.3 rad/s (213 rpm) with a single, large bore exit die. Powder feed rate was controlled by a mass sensor and balance. The melt temperature and five extruder zones were held between 172 ºC and 174 ºC with the exit die held constant at 165 ºC. The hot, extruded PVC was routed through a 180 cm water bath before being chopped into small pellets by a rotating knife (Fig. 4). After mixing the pellets by hand stirring, each formulation was extruded and chopped a second time, under the same operating conditions. Pellets were collected in polypropylene bags and sealed into plastic pails for transport.

As shown in Fig. 5, the pelletized material for SRM 2861 is tan, because the only colored compound it contains is $Na_2Cr_2O_7$. The pelletized material for SRM 2859 is dark green from a small amount of brominated dye compound and $Na_2Cr_2O_7$. The pellets of SRM 2859 are larger in diameter and have a greater average mass (0.057 g) than the pellets of SRM 2861 (0.037 g per pellet). At NIST, the pellets were bottled in amber glass with ≥ 25 g per bottle yielding a total of 291 bottles of SRM 2859 and 302 bottles of SRM 2861

3. Analytical Methods

The PVC formulations underwent homogeneity assessment using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry to study sample amounts normally used in testing production quantities of plastics and using microXRF spectrometry to study material heterogeneity at the 100 μm level. Quantitative analyses were performed using WDXRF for all constituent elements, except Ba, which was quantified using energy dispersive X-ray fluorescence (EDXRF) spectrometry, because the EDXRF spectrometer was capable of measuring Ba $K-L_{2,3}$ X-rays. Every 20th bottle was selected for testing, along with the first and last bottles of each SRM material,

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for 16 bottles of each PVC composition. For WDXRF, each bottle was sampled twice for melt pressing of disks. Each bottle was tumbled a few times by hand prior to taking each sample of nominally 6.2 g with bottles sampled at random until all 16 bottles were sampled twice. A subset of the WDXRF samples was used for EDXRF determinations. Additional samples were taken from selected bottles to test the melt pressing procedure and for microXRF measurements.

3.1 Disk Preparation by Melt Pressing

For each specimen, approximately 6.2 g of pellets was placed into a pressing cap that had been flared and inserted into a die designed for pressing of powders into briquettes. The pressing cap sits directly on the bottom die pellet and acts as a mold for the softened PVC. The second die pellet is placed on top of the pellets, followed by the ram. A #64 rubber band is placed around the die to cover the gap where the upper and lower pieces meet. Later, the rubber band seals the die so a vacuum can be obtained during pressing. The loaded die was inserted into the press, and the screw was tightened by hand as much as possible. Then, the press was pumped until the pressure stayed just greater than zero to create greater contact among PVC pellets and metal parts. The die was carefully placed into a forced air oven to roast at 175 ºC for 1.5 h. After roasting, the hot die was carefully placed into the press and a vacuum pulled on the side port by a mechanical pump. The hydraulic press was hand pumped to between 12 tons and 13 tons. As the PVC cooled, the pressure slowly decreased. When the die was cool enough to handle, the vacuum was removed, and the hydraulic pressure was released. After the disk and Al cap were removed from the die, the cap was cut away and the PVC disk was placed in a small, zip-closure plastic bag for storage in a plastic jar, until measured.

An example disk of SRM 2861 is shown in Fig. 6. The disk is 30 mm diameter and 6.3 mm thick. The lighter and darker shades of tan come from the different colors of the interior of each extruded pellet and the exterior of each pellet, respectively. The exterior surfaces of pellets were in contact with hot extruder parts and cooled in air just after the boule exited the extruder. When subjected to higher heat or high levels of ionizing radiation, PVC formulations darken due to chemical damage in the polymer. The melt-pressing process happens in a vacuum with the PVC in contact with metal surfaces. There is little opportunity for oxidation or other chemical damage as the PVC cools inside the evacuated die. Even so, virgin PVC darkens on heating above 100 ºC inside the die. In contrast, the stabilized blends for SRM 2859 and SRM 2861 did not change appearance inside the heated die. In a similar manner, the SRM formulations show only a small amount of damage after X-irradiation, while virgin PVC disks darken extensively.

3.2 WDXRF Measurements

The WDXRF spectrometer (Model Axios mAX, Malvern Panalytical, Almelo, The Netherlands) was used to measure the $K\text{-}L_{2,3}$ characteristic X-ray lines of the elements As, Br, Ca, Cl, Cr, Cu, Fe, Na, S, and Se, the $L_3\text{-}M_{4,5}$ lines of the elements Ba, Cd, Hg, Sb, and Sn, and the $L_2\text{-}M_4$ line of the element Pb. Background measurements were obtained for all elements, except Cl. All measurements were performed in a vacuum environment with the generator operated at a low 600 W of power to minimize X-ray induced damage to the PVC. The disks were measured in two batches for each SRM. After being measured on one side, each disk was flipped and measured on its opposite side in a second batch job. The mask between the sample and the collimator was set to view a 27 mm circular area of the sample. Counting times were chosen to obtain relative counting statistical uncertainty ranging from 0.1 % to 1 % depending on the X-ray count rate for

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each element and the number of measurements of background. The Rh K-L Compton scatter line from the X-ray tube was measured for use as a drift monitor. The resulting measurements were used in analysis of variance calculations and quantitative analysis.

3.3 EDXRF Measurements

The EDXRF spectrometer (Model PW5000, PANalytical, Almelo, The Netherlands) was used to measure Ba K-$L_{2,3}$ X-rays for quantitative analysis of SRM 2861. Measurement conditions were set manually: W/Sc tube, 80 kV, 7.5 mA, Al_2O_3 Barkla scatter target, standard energy resolution, 100 s live time ($\approx$ 16 % dead time), and vacuum ($\approx$ 1 Pa), with spinner. Although only Ba K-$L_{2,3}$ count rates were needed for quantification, all measurable elements were added to the spectrum fitting procedure, because the program is designed to use all available information to improve the accuracy of fitting. Ba count rates were reported as cps/mA, i.e. counts per second per milliampere of X-ray tube current. As with WDXRF measurements, disks were measured in random order and on both sides. However, only a subset of the disks measured by WDXRF was remeasured using EDXRF.

3.4 MicroXRF Measurements

Because there are numerous options in commercial spectrometers for X-ray beam size, and because analysts use techniques based on sample digestion and either atomic spectrometry or mass spectrometry, it is necessary to study material heterogeneity at very low masses. The microXRF spectrometer (Model Eagle 3, Ametek EDAX, Mahwah, New Jersey), equipped with a 0.05 mm diameter viewed spot, was programmed to cover a rectangular region on one circular face of a melt-pressed briquette or across the cross-section of a disk that was cut in half along a diameter chord. The same X-ray lines were used as given above for WDXRF measurements. Dwell time per location was set to just a few seconds live time to allow the entire chosen area to be covered in four days or less, which is the limit provided by a full Dewar of LN_2. For all measurements, the primary beam from the Rh tube was filtered using a 25 μm Al foil to remove the Rh L-series X-rays.

3.5 Density

For experiments involving calculations of X-ray attenuation, reliable estimates of density are needed [11]. Estimates were obtained by measuring the dimensions and masses of two melt-pressed disks of each PVC blend. For SRM 2859, the calculated density is 1.310 g/cm^3. For SRM 2861, the calculated density is 1.292 g/cm^3. The combined standard uncertainty for both values is estimated to be 0.013 g/cm^3 (1 % relative) based on uncertainties of measurements of mass and length. It was expected that the density of SRM 2861 would be lower, because it contains less dry blend, and therefore, less $CaCO_3$ and methyltin mercaptate. For calculated estimates of measured mass per element, the compositions of both PVC blends were modeled as C_2H_2Cl, ignoring the added elements and compounds. This simplification may cause X-ray attenuation lengths to be overestimated, but the error is not important with respect to the intended use of the values to estimate measured mass of each element in each blend and to choose from that data a recommended minimum mass for sampling the PVC blends.

3.6 XES Measurements

The Seidler group at the University of Washington recently developed laboratory-based (i.e., non-synchrotron) X-ray emission spectroscopy (XES) instrumentation that provides signal-to-noise, energy resolution, and stability fully comparable to synchrotron-based instrumentation. These features make the instruments well-suited for studies of element oxidation state in dilute samples. A detailed presentation of method development and performance is provided elsewhere [5], along with further references providing details of the instrument and its development. The instrument used for method development employed an X-ray tube (Moxtek Au anode) operated at 40 kV and 200 μA, i.e. only 8 W total tube power, a Ge (422) spherically bent crystal analyzer (SBCA) from XRS Tech, and an energy-dispersive silicon drift detector (Amptek SDD-X123), yielding exceptionally low backgrounds. As a means of minimizing the potential for radiation damage to the PVC, specimens were mounted on a spinner to rotate them so that a greater area of material was exposed to the primary X-ray beam.

4. Homogeneity Results for SRM 2859

Tables 2 through 13 contain the analyses of variance [12] of the measured count rates from elements in SRM 2859 as determined from the NIST XRF data. The measurements from each side of each disk were treated as independent samples, because most of the measured X-rays do not penetrate all the way through a disk of PVC. Each table contains information for one element, including an average value for the count rate (in kilocounts per second (kcps)) from the duplicate specimens from each bottle along with an average and estimate of the standard deviation of the set of bottles. Control chart tests [13] were used to determine whether any individual bottle exhibited a statistically significant difference from the set or if the variance of measurements multiple specimens from a single bottle exhibited a statistically significant difference from the remaining bottles. Any positive findings are marked with an X in each column.

The findings for within-bottle heterogeneity indicated that, at the 95 % confidence level, zero to as many as three bottles were flagged for each element. A finding of a statistically significant result only indicates that the four measurements of the two disks were somehow different. It is not proof the material itself is heterogeneous in that bottle. At the 95 % confidence level, it is reasonable to expect to flag two bottles in a population of 16 bottles just due to the nature of the statistical analysis, including the assumption that all data sets have normal distributions. Chlorine and mercury were flagged for three bottles, but the relative standard deviation (%RSD) estimates for individual measurements were 1.1 % and 0.82 %, respectively. Therefore, these measurements provide evidence that heterogeneity was sufficiently low to meet project goals. Sodium and iron had %RSD values > 2 %, but these elements were not intended for certification.

The findings for among-bottle variability indicated that, at the 95 % confidence level, zero or one bottle was found to be significantly different from the average of the set for all analytes. For all elements, except Hg and Pb, there were no statistically significant differences between the within-bottle variance and the among-bottle variance because none of the elements failed the F-test. While Hg and Pb failed the F-test, %RSD values for individual measurements were 0.82 % and 1.2 %, respectively, and the %RSD values for bottle means were 0.55 % and 0.82 %, respectively, none of which were cause for concern about heterogeneity.

Table 14 contains a summary of the statistical F and P values for the analytes measured in SRM 2859, along with the relative standard deviation (%RSD) of individual count rates, the counting statistical standard uncertainty (%CSE), and an estimate of measured mass for each element. In cases where the %RSD was much greater than the %CSE, there may have been cause for concern, and possibly a need to account for material heterogeneity in the estimation of uncertainty for an assigned mass fraction value. Of concern were the elements Na, S, Fe, Cu, and Cd for which the %RSD values were all > 2 %. Of these elements, Na and Cu were published as information values. Iron came from contamination at mg/kg levels in the dry blend, and S was associated with the methyltin mercaptide and at least one additional sulfur-containing compound, possibly an oil or wax, which was observed as a deposit on glassware used to prepare custom samples by hand. Sulfur, iron and cadmium were to be certified. Therefore, these three elements required that a variance component for heterogeneity be included as a component of the uncertainty assessment.

5. Homogeneity Results for SRM 2861

Tables 15 through 27 contain the analyses of variance [12] of the measured count rates from elements in SRM 2861 as determined from the NIST XRF data. The measurements from each side of each disk were treated as independent samples, because most of the measured X-rays do not penetrate all the way through a disk of PVC. Each table contains information for one element, including an average value for the count rate from the duplicate specimens from each bottle along with an average and estimate of the standard deviation of the set of bottles. Control chart tests [13] were used to determine whether any individual bottle exhibited a statistically significant difference from the set or if the variance of measurements from a single bottle exhibited a statistically significant difference from the remaining bottles. Any positive findings are marked with an X in each column.

The findings for within-bottle heterogeneity indicated that, at the 95 % confidence level, zero to as many as three bottles were flagged for each element. A finding of a statistically significant result only indicates that the four measurements of the two disks were somehow different. It is not proof that the material itself is heterogeneous in that bottle. At the 95 % confidence level, it is reasonable to expect to flag two bottles in a population of 16 bottles just due to the nature of the statistical analysis, including the assumption that all data sets have normal distributions. Sulfur was flagged for three bottles, and the relative standard deviation (%RSD) estimate for individual measurements was 2.8 %. Therefore, it was necessary to add an additional uncertainty component for S heterogeneity to the calculations of an uncertainty estimate for the certified value.

The findings for among-bottle variability indicated that, at the 95 % confidence level, zero or one bottle was found to be significantly different from the average of the set for all analytes. For all elements, there were no statistically significant differences between the within-bottle variance and the among-bottle variance because none of the elements failed the F-test.

Table 2. Analysis of Variance for Sodium in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	Significant Difference from set of samples
1	4	0.1615	0.00029		
20	4	0.1632	0.00037		
40	4	0.1586	0.00044		
60	4	0.1582	0.00005		
80	4	0.1579	0.00019		
100	4	0.1567	0.00029		
120	4	0.1543	0.00020		
140	4	0.1574	0.00006		
160	4	0.1620	0.00030		
180	4	0.1533	0.00003		
200	4	0.1507	0.00034		
220	4	0.1658	0.00017		
240	4	0.1499	0.00011		
260	4	0.1487	0.00009		
280	4	0.1570	0.00008		
291	4	0.1644	0.00056		

Average	0.1575
Standard Deviation	0.0052	3.3%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0016	15	0.00011	0.479	0.940	1.880
Within Samples	0.0106	48	0.00022			
Total	0.0122	63				

Table 3. Analysis of Variance for Sulfur in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	Significant Difference from set of samples
1	4	2.630	0.0067		
20	4	2.583	0.0005		
40	4	2.589	0.0029		
60	4	2.594	0.0037		
80	4	2.589	0.0020		
100	4	2.662	0.0334		
120	4	2.584	0.0026		
140	4	2.583	0.0004		
160	4	2.658	0.0328		
180	4	2.753	0.0502	X	X
200	4	2.623	0.0242		
220	4	2.626	0.0018		
240	4	2.724	0.0572	X	
260	4	2.618	0.0032		
280	4	2.617	0.0071		
291	4	2.596	0.0019		

Average	2.627
Standard Deviation	0.050	1.9%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.15	15	0.010	0.708	0.764	1.880
Within Samples	0.69	48	0.014			
Total	0.84	63				

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Table 4. Analysis of Variance for Chlorine in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	97.49	0.027		
20	4	97.69	0.161		
40	4	97.89	0.056		
60	4	97.76	0.013		
80	4	98.04	0.150		
100	4	96.93	3.685	X	
120	4	97.78	0.045		
140	4	97.62	0.068		
160	4	97.11	2.609		
180	4	95.95	3.758	X	
200	4	96.26	5.076	X	
220	4	97.71	0.101		
240	4	96.87	2.955		
260	4	97.64	0.017		
280	4	97.52	0.149		
291	4	97.51	0.091		

Average	97.36	
Standard Deviation	0.59	0.60%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	21	15	1.4	1.167	0.329	1.880
Within Samples	57	48	1.2			
Total	78	63				

Table 5. Analysis of Variance for Calcium in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	10.934	0.002		
20	4	10.943	0.026		
40	4	11.002	0.010		
60	4	10.991	0.032		
80	4	10.967	0.003		
100	4	10.975	0.041		
120	4	10.922	0.003		
140	4	11.002	0.004		
160	4	11.077	0.075	X	
180	4	11.125	0.057		
200	4	10.963	0.028		
220	4	10.868	0.017		
240	4	10.991	0.103	X	
260	4	10.962	0.002		
280	4	10.883	0.002		
291	4	10.910	0.016		

Average	10.970	
Standard Deviation	0.065	0.60%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.257	15	0.017	0.648	0.819	1.880
Within Samples	1.267	48	0.026			
Total	1.524	63				

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Table 7. Analysis of Variance for Iron in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	0.1754	0.000001		
20	4	0.1668	0.000025		
40	4	0.1777	0.000056		
60	4	0.1867	0.000294	X	
80	4	0.1728	0.000045		
100	4	0.1764	0.000049		
120	4	0.1766	0.000019		
140	4	0.1759	0.000081		
160	4	0.1733	0.000057		
180	4	0.1750	0.000011		
200	4	0.1735	0.000040		
220	4	0.1788	0.000069		
240	4	0.1740	0.000003		
260	4	0.1764	0.000186		
280	4	0.1801	0.000498	X	
291	4	0.1784	0.000048		

Average	0.1761	
Standard Deviation	0.0042	2.4%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0010	15	0.000070	0.752	0.720	1.880
Within Samples	0.0044	48	0.000092			
Total	0.0055	63				

Table 6. Analysis of Variance for Chromium in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	1.0477	0.00002		
20	4	1.0498	0.00003		
40	4	1.0434	0.00008		
60	4	1.0475	0.00001		
80	4	1.0487	0.00008		
100	4	1.0507	0.00016		
120	4	1.0461	0.00001		
140	4	1.0454	0.00003		
160	4	1.0465	0.00017		
180	4	1.0583	0.00032	X	
200	4	1.0367	0.00007		
220	4	1.0460	0.00008		
240	4	1.0568	0.00011		
260	4	1.0400	0.00002		
280	4	1.0480	0.00001		
291	4	1.0425	0.00004		

Average	1.0471	
Standard Deviation	0.0054	0.52%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0018	15	0.000118	1.518	0.137	1.880
Within Samples	0.0037	48	0.000078			
Total	0.0055	63				

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Table 8. Analysis of Variance for Copper in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	0.1871	0.000024		
20	4	0.1896	0.000012		
40	4	0.1875	0.000019		
60	4	0.1905	0.000008		
80	4	0.1898	0.000015		
100	4	0.1917	0.000014		
120	4	0.1916	0.000007		
140	4	0.1904	0.000004		
160	4	0.1900	0.000018		
180	4	0.1893	0.000007		
200	4	0.1885	0.000064	X	
220	4	0.1915	0.000034		
240	4	0.1926	0.000017		
260	4	0.1921	0.000032		
280	4	0.1904	0.000006		
291	4	0.1924	0.000017		

Average	0.1903		
Standard Deviation	0.0017	0.87%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.00017	15	0.000011	0.599	0.861	1.880
Within Samples	0.00089	48	0.000018			
Total	0.00105	63				

Table 9. Analysis of Variance for Bromine in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	8.374	0.0017		
20	4	8.394	0.0038		
40	4	8.388	0.0020		
60	4	8.358	0.0008		
80	4	8.341	0.0023		
100	4	8.396	0.0003		
120	4	8.413	0.0013		
140	4	8.387	0.0010		
160	4	8.403	0.0048		
180	4	8.383	0.0003		
200	4	8.281	0.0142	X	
220	4	8.357	0.0041		
240	4	8.399	0.0021		
260	4	8.372	0.0003		
280	4	8.383	0.0007		
291	4	8.407	0.0035		

Average	8.377		
Standard Deviation	0.032	0.39%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.063	15	0.0042	1.551	0.12	1.880
Within Samples	0.129	48	0.0027			
Total	0.192	63				

Table 10. Analysis of Variance for Cadmium in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	0.05453	0.0000012		
20	4	0.05183	0.0000028		
40	4	0.05358	0.0000029		
60	4	0.05298	0.0000019		
80	4	0.05348	0.0000014		
100	4	0.05318	0.0000007		
120	4	0.05238	0.0000028		
140	4	0.05163	0.0000014		
160	4	0.05300	0.0000002		
180	4	0.05165	0.0000009		
200	4	0.05228	0.0000085	X	
220	4	0.05225	0.0000021		
240	4	0.05275	0.0000029		
260	4	0.05383	0.0000005		
280	4	0.05345	0.0000013		
291	4	0.05323	0.0000035		
Average		0.05287			
Standard Deviation		0.00083	1.6%		

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.000041	15	0.0000027	1.245	0.274	1.880
Within Samples	0.000105	48	0.0000022			
Total	0.000146	63				

Table 11. Analysis of Variance for Tin in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	from set of samples
1	4	7.220	0.0004		
20	4	7.232	0.0052		
40	4	7.215	0.0005		
60	4	7.208	0.0004		
80	4	7.222	0.0005		
100	4	7.195	0.0055		
120	4	7.255	0.0004		
140	4	7.217	0.0030		
160	4	7.160	0.0152		
180	4	7.132	0.0078		
200	4	7.065	0.0424	X	
220	4	7.242	0.0023		
240	4	7.194	0.0174		
260	4	7.226	0.0022		
280	4	7.247	0.0022		
291	4	7.203	0.0015		
Average		7.202			
Standard Deviation		0.048	0.67%		

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.14	15	0.0092	1.376	0.198	1.880
Within Samples	0.32	48	0.0067			
Total	0.46	63				

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Table 12. Analysis of Variance for Mercury in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	Significant Difference from set of samples
1	4	3.712	0.00034		
20	4	3.693	0.00059		
40	4	3.711	0.00005		
60	4	3.690	0.00047		
80	4	3.700	0.00186	X	
100	4	3.746	0.00026		
120	4	3.718	0.00014		
140	4	3.725	0.00059		
160	4	3.755	0.00053		
180	4	3.735	0.00009		
200	4	3.687	0.00138		
220	4	3.745	0.00212	X	
240	4	3.721	0.00008		
260	4	3.729	0.00016		
280	4	3.720	0.00019		
291	4	3.732	0.00204	X	

Average	3.720		
Standard Deviation	0.021	0.55%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.025	15	0.00169	2.493	0.0085	1.880
Within Samples	0.033	48	0.00068			
Total	0.058	63				

Table 13. Analysis of Variance for Lead in SRM 2859

SUMMARY

Bottle Number	Count	Average kcps	Variance	Significant Difference between replicates	Significant Difference from set of samples
1	4	2.840	0.00167		
20	4	2.823	0.00090		
40	4	2.834	0.00122		
60	4	2.827	0.00038		
80	4	2.819	0.00229	X	
100	4	2.883	0.00088		
120	4	2.856	0.00097		
140	4	2.863	0.00063		
160	4	2.875	0.00023		
180	4	2.864	0.00014		
200	4	2.807	0.00120		
220	4	2.858	0.00113		
240	4	2.849	0.00053		
260	4	2.865	0.00030		
280	4	2.876	0.00009		
291	4	2.877	0.00014		

Average	2.851		
Standard Deviation	0.023	0.82%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.033	15	0.00220	2.765	0.0038	1.880
Within Samples	0.038	48	0.00079			
Total	0.071	63				

Table 14. Summary of Results for Homogeneity Testing of SRM 2859

Element	$F^{(a)}$	Passed F Test	P-value	%RSD[b]	%CSE[c]	Estimated Mass (g)
Na	0.479	Yes	0.940	8.8	0.94	0.006
S	0.708	Yes	0.764	4.4	0.48	0.095
Cl	1.167	Yes	0.329	1.1	0.23	0.14
Ca	0.648	Yes	0.819	1.4	0.68	0.046
Cr	1.518	Yes	0.137	0.89	0.28	0.13
Fe	0.752	Yes	0.720	5.3	0.99	0.21
Cu	0.599	Yes	0.861	2.1	0.67	0.39
Br	1.551	Yes	0.125	0.66	0.35	1.2
Cd	1.245	Yes	0.274	2.9	0.96	0.030
Sn	1.376	Yes	0.198	1.2	0.30	0.038
Hg	2.493	No	0.0085	0.82	0.20	0.73
Pb	2.765	No	0.0038	1.2	0.31	0.86

[a] Critical F value, $F_{crit} = 1.880$.
[b] of Individual Measurements of disks.
[c] %CSE = relative counting statistical uncertainty ($1s$).
[d] of PVC measured in each disk.

Table 15. Analysis of Variance for Sulfur in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average *kcps*	Variance	Significant Difference *among replicates*	Significant Difference *from set of samples*
1	4	2.376	0.0008		
20	4	2.382	0.0008		
40	4	2.391	0.0021		
60	4	2.382	0.0000		
80	4	2.380	0.0009		
100	4	2.394	0.0009		
120	4	2.411	0.0005		
140	4	2.450	0.0012		
160	4	2.377	0.0035		
180	4	2.395	0.0009		
200	4	2.393	0.0008		
220	4	2.419	0.0010		
240	4	2.427	0.0123	X	
260	4	2.408	0.0053		
280	4	2.483	0.0241	X	
302	4	2.462	0.0167	X	

Average	2.408		
Standard Deviation	0.033	1.3%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.063	15	0.0042	0.942	0.527	1.880
Within Samples	0.215	48	0.0045			
Total	0.279	63				

Table 16. Analysis of Variance for Chlorine in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average *kcps*	Variance	Significant Difference *among replicates*	Significant Difference *from set of samples*
1	4	101.91	0.020		
20	4	101.98	0.005		
40	4	101.90	0.025		
60	4	101.93	0.021		
80	4	101.86	0.175		
100	4	101.88	0.078		
120	4	101.78	0.129		
140	4	101.69	0.018		
160	4	101.98	0.024		
180	4	101.90	0.065		
200	4	101.89	0.139		
220	4	101.75	0.100		
240	4	101.75	0.216		
260	4	101.26	0.830	X	
280	4	101.70	0.278		
302	4	101.32	1.355	X	

Average	101.78		
Standard Deviation	0.21	0.21%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	2.7	15	0.18	0.828	0.643	1.880
Within Samples	10.4	48	0.22			
Total	13.1	63				

Table 17. Analysis of Variance for Calcium in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference among replicates	from set of samples
		kcps			
1	4	10.047	0.009		
20	4	9.941	0.008		
40	4	10.056	0.006		
60	4	10.141	0.005		
80	4	10.035	0.033		
100	4	10.029	0.000		
120	4	10.017	0.019		
140	4	10.138	0.007		
160	4	10.064	0.002		
180	4	10.012	0.004		
200	4	10.023	0.001		
220	4	10.033	0.025		
240	4	10.168	0.001		
260	4	9.987	0.036	X	
280	4	10.031	0.024		
302	4	10.053	0.019		

Average	10.048		
Standard Deviation	0.058	0.58%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.20	15	0.013	1.078	0.400	1.880
Within Samples	0.60	48	0.012			
Total	0.80	63				

Table 18. Analysis of Variance for Chromium in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference among replicates	from set of samples
		kcps			
1	4	0.07860	0.0000042		
20	4	0.07490	0.0000021		
40	4	0.07638	0.0000012		
60	4	0.07695	0.0000105		
80	4	0.07693	0.0000005		
100	4	0.07578	0.0000166	X	
120	4	0.07620	0.0000014		
140	4	0.07608	0.0000041		
160	4	0.07573	0.0000011		
180	4	0.07765	0.0000073		
200	4	0.07648	0.0000046		
220	4	0.07578	0.0000022		
240	4	0.07610	0.0000039		
260	4	0.07710	0.0000032		
280	4	0.07645	0.0000009		
302	4	0.07590	0.0000056		

Average	0.07644		
Standard Deviation	0.00087	1.1%	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.000046	15	0.0000030	0.703	0.769	1.880
Within Samples	0.000208	48	0.0000043			
Total	0.000254	63				

Table 20. Analysis of Variance for Arsenic in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference	
				among replicates	from set of samples
		kcps			
1	4	0.252	0.00021		
20	4	0.258	0.00003		
40	4	0.245	0.00042		
60	4	0.249	0.00028		
80	4	0.252	0.00054		
100	4	0.270	0.00027		
120	4	0.275	0.00050		
140	4	0.260	0.00012		
160	4	0.252	0.00028		
180	4	0.283	0.00015		
200	4	0.264	0.00003		
220	4	0.273	0.00083	X	
240	4	0.272	0.00019		
260	4	0.267	0.00007		
280	4	0.258	0.00044		
302	4	0.263	0.00037		

Average	0.262	
Standard Deviation	0.011	4.1%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0071	15	0.00047	1.600	0.109	1.880
Within Samples	0.0142	48	0.00030			
Total	0.0213	63				

Table 19. Analysis of Variance for Iron in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference	
				among replicates	from set of samples
		kcps			
1	4	0.1616	0.000017		
20	4	0.1635	0.000028		
40	4	0.1635	0.000076	X	
60	4	0.1665	0.000010		
80	4	0.1673	0.000002		
100	4	0.1654	0.000007		
120	4	0.1695	0.000022		
140	4	0.1655	0.000011		
160	4	0.1648	0.000034		
180	4	0.1661	0.000030		
200	4	0.1672	0.000008		
220	4	0.1681	0.000031		
240	4	0.1669	0.000026		
260	4	0.1608	0.000005		
280	4	0.1695	0.000009		
302	4	0.1655	0.000012		

Average	0.1657	
Standard Deviation	0.0025	1.5%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.00037	15	0.000025	1.208	0.299	1.880
Within Samples	0.00098	48	0.000020			
Total	0.00135	63				

Table 21. Analysis of Variance for Selenium in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference	
		kcps		among replicates	from set of samples
1	4	1.9510	0.00035		
20	4	1.9615	0.00035		
40	4	1.9731	0.00043		
60	4	1.9697	0.00016		
80	4	1.9604	0.00013		
100	4	1.9639	0.00008		
120	4	1.9593	0.00036		
140	4	1.9703	0.00016		
160	4	1.9636	0.00023		
180	4	1.9711	0.00014		
200	4	1.9752	0.00019		
220	4	1.9663	0.00043		
240	4	1.9595	0.00006	X	
260	4	1.9615	0.00078		
280	4	1.9640	0.00021		
302	4	1.9707	0.00015		

Average	1.9651	
Standard Deviation	0.0063	0.32%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0024	15	0.00016	0.610	0.852	1.880
Within Samples	0.0126	48	0.00026			
Total	0.0150	63				

Table 22. Analysis of Variance for Cadmium in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference	
		kcps		among replicates	from set of samples
1	4	0.04683	0.0000005		
20	4	0.04768	0.0000021		
40	4	0.04570	0.0000025		
60	4	0.04553	0.0000015		
80	4	0.04468	0.0000027		
100	4	0.04808	0.0000014		
120	4	0.04635	0.0000018		
140	4	0.04690	0.0000017		
160	4	0.04688	0.0000039		
180	4	0.04690	0.0000019		
200	4	0.04598	0.0000006		
220	4	0.04625	0.0000032		
240	4	0.04665	0.0000073	X	
260	4	0.04685	0.0000008		
280	4	0.04618	0.0000008		
302	4	0.04570	0.0000021		

Average	0.04644	
Standard Deviation	0.00084	1.8%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.000042	15	0.0000028	1.295	0.242	1.880
Within Samples	0.000104	48	0.0000022			
Total	0.000146	63				

Table 24. Analysis of Variance for Antimony in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average (kcps)	Variance	Significant Difference among replicates	from set of samples
1	4	0.3108	0.00010		
20	4	0.3164	0.00025		
40	4	0.3144	0.00004		
60	4	0.3208	0.00016		
80	4	0.3143	0.00005		
100	4	0.3147	0.00011		
120	4	0.3091	0.00018		
140	4	0.3309	0.00001		
160	4	0.3225	0.00028		
180	4	0.3239	0.00019		
200	4	0.3187	0.00016		
220	4	0.3164	0.00019		
240	4	0.3269	0.00007		
260	4	0.3211	0.00022		
280	4	0.3152	0.00013		
302	4	0.3229	0.00007		

Average	0.3187	
Standard Deviation	0.0059	1.8%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0021	15	0.00014	1.004	0.467	1.880
Within Samples	0.0066	48	0.00014			
Total	0.0087	63				

Table 23. Analysis of Variance for Tin in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average (kcps)	Variance	Significant Difference among replicates	from set of samples
1	4	6.977	0.0031		
20	4	6.984	0.0007		
40	4	6.949	0.0070		
60	4	6.976	0.0016		
80	4	6.952	0.0024		
100	4	6.997	0.0005		
120	4	6.972	0.0082		
140	4	7.031	0.0005		
160	4	7.016	0.0016		
180	4	6.965	0.0020		
200	4	6.989	0.0028		
220	4	6.986	0.0052		
240	4	7.007	0.0057		
260	4	6.951	0.0225	X	
280	4	6.970	0.0036		
302	4	6.962	0.0031		

Average	6.980	
Standard Deviation	0.024	0.34%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.034	15	0.0022	0.510	0.923	1.880
Within Samples	0.211	48	0.0044			
Total	0.244	63				

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Table 26. Analysis of Variance for Mercury in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference among replicates	Significant Difference from set of samples
		kcps			
1	4	0.2638	0.00008		
20	4	0.2681	0.00008		
40	4	0.2700	0.00006		
60	4	0.2710	0.00007		
80	4	0.2661	0.00001		
100	4	0.2702	0.00006		
120	4	0.2685	0.00014		
140	4	0.2754	0.00014		
160	4	0.2648	0.00007		
180	4	0.2657	0.00018		
200	4	0.2702	0.00010		
220	4	0.2650	0.00002		
240	4	0.2713	0.00006		
260	4	0.2726	0.00009		
280	4	0.2737	0.00024		
302	4	0.2698	0.00015		

Average		0.2691	
Standard Deviation		0.0034	1.3%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.00068	15	0.000045	0.470	0.945	1.880
Within Samples	0.00465	48	0.000097			
Total	0.00533	63				

Table 25. Analysis of Variance for Barium in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average	Variance	Significant Difference among replicates	Significant Difference from set of samples
		kcps			
1	4	0.0952	0.000000		
20	4	0.1003	0.000004		
40	4	0.0987	0.000008		
60	4	0.1007	0.000000		
80	4	0.0977	0.000007		
100	4	0.0978	0.000003		
120	4	0.0999	0.000030		
140	4	0.1006	0.000008		
160	4	0.0969	0.000023		
180	4	0.1003	0.000032	X	
200	4	0.0995	0.000002		
220	4	0.0971	0.000004		
240	4	0.0985	0.000007		
260	4	0.1000	0.000019		
280	4	0.1005	0.000024		
302	4	0.0987	0.000010		

Average		0.0989	
Standard Deviation		0.0016	1.6%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.00016	15	0.000010	0.915	0.554	1.880
Within Samples	0.00054	48	0.000011			
Total	0.00070	63				

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Table 27. Analysis of Variance for Lead in Candidate SRM 2861

SUMMARY

Bottle Number	Count	Average kcps	Variance
1	4	0.3293	0.00015
20	4	0.3305	0.00006
40	4	0.3376	0.00015
60	4	0.3394	0.00009
80	4	0.3318	0.00027
100	4	0.3246	0.00006
120	4	0.3258	0.00014
140	4	0.3266	0.00011
160	4	0.3345	0.00005
180	4	0.3166	0.00007
200	4	0.3309	0.00001
220	4	0.3194	0.00030
240	4	0.3201	0.00006
260	4	0.3252	0.00006
280	4	0.3331	0.00018
302	4	0.3326	0.00004

Average	0.3286	
Standard Deviation	0.0065	2.0%

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Samples	0.0025	15	0.00017	1.474	0.153	1.880
Within Samples	0.0054	48	0.00011			
Total	0.0079	63				

Significant Difference: among replicates / from set of samples

Table 28 contains a summary of the statistical F and P values for the analytes measured in SRM 2861, along with the relative standard deviation (%RSD) of individual count rates, the counting statistical standard uncertainty (%CSE), and an estimate of measured mass for each element. In cases where the %RSD was much greater than the %CSE, there may have been cause for concern, and possibly a need to account for material heterogeneity in the estimation of uncertainty for an assigned mass fraction value. Of concern were the elements S, Cr, Fe, As, Cd, Sb, Ba, Hg, and Pb for which the %RSD values are all > 2 %. Iron came from contamination at mg/kg levels in the dry blend, and S is associated with the methyltin mercaptide and at least one additional sulfur-containing compound, possibly an oil or wax, which was observed as a deposit on glassware used to prepare custom samples by hand. All nine elements were to be certified. Therefore, these nine elements required that a variance component for heterogeneity be included as a component of the uncertainty assessment.

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Table 28. Summary of Results for Homogeneity Testing of SRM 2861

Element	$F^{(a)}$	Passed F Test	P-value	%RSD[b]	%CSE[c]	Estimated[d] Mass (g)
S	0.942	Yes	0.527	2.8	0.50	0.095
Cl	0.828	Yes	0.643	0.45	0.22	0.14
Ca	1.078	Yes	0.400	1.1	0.71	0.046
Cr	0.703	Yes	0.769	2.6	0.70	0.13
Fe	1.208	Yes	0.299	2.8	1.0	0.21
As	1.600	Yes	0.109	5.5	0.27	0.85
Se	0.610	Yes	0.852	0.78	0.37	1.0
Cd	1.295	Yes	0.242	3.3	0.99	0.030
Sn	0.510	Yes	0.923	0.89	0.30	0.038
Sb	1.004	Yes	0.467	3.7	0.18	0.043
Ba	0.915	Yes	0.554	3.4	1.0	0.076
Hg	0.470	Yes	0.945	3.4	0.36	0.73
Pb	1.474	Yes	0.153	3.4	0.53	0.86

[a] Critical F value, $F_{crit} = 1.880$.
[b] of Individual Measurements of disks.
[c] %CSE = relative counting statistical uncertainty ($1s$).
[d] of PVC measured in each disk.

6. Micrometer Scale Heterogeneity of PVC Blends

The microXRF spectrometer was used to qualitatively image the variability of each element within the PVC blends. Measurements were made across one circular face of melt-pressed disks of both PVC compositions and across the cross-section of one melt-pressed disk of SRM 2861. Net count rates were plotted as a function of location in rectangular grids covering a large portion of the circular face or covering the cross-section from face-to-face. It was observed that some elements are spread relatively uniformly throughout the PVC with no sharply higher or lower count rate locations. Other elements show a uniform, low count rate level across a mapped region peppered with numerous, discrete high count rate locations. Examples of the latter type were the elements Ba, Fe, and Se. Figure 7 gives a small map of Ba L_3-$M_{4,5}$ X-ray count rates in a disk of SRM 2861. Similar maps resulted for Fe and Se.

In Fig. 7, there are 32 locations of Ba count rates that are in the top 10 % of all measured locations. These count rates are from 10 times to 100 times the mean count rate of the other 90 % of locations. The red circle is 3 mm diameter, and it is representative of the aperture of a handheld XRF

spectrometer. Among known handheld spectrometers, the 3 mm aperture option is the smallest currently available. Within the circle are a few high Ba locations. If the circle is moved to simulate measurement of a different 3 mm spot, it may cover as many as eight to 10 high Ba locations. The result would be a significant difference between the count rates from the two 3 mm spots. Even greater contrast is seen when considering commercial, bench top spectrometers known to use a 1 mm diameter aperture. With such a small aperture, it is possible to measure two discrete locations with one count rate being 15 times greater than the other. In the extreme case of the microXRF spectrometer having a 0.05 mm aperture, the ratio of maximum to minimum count rates is 534, in this data. Figure 8 illustrates that when a disk was cut in cross section, the Ba map appeared similar to the map in Fig. 7.

As an example of a uniformly distributed element in SRM 2861, Fig. 9 shows a map of Hg count rates. In this case, the maximum count rate was just 1.7 times the mean count rate, and the minimum count rate measured by the microXRF was 50 % of the mean rate. So, the microXRF observed a maximum ratio from two discrete locations of only 3.3. In this map, the highest 10 % of count rates and the lowest 10 % are uniformly distributed across the mapped region. The elements As, Pb, Cd, and Sb showed the same behavior. The remaining elements were somewhat more heterogeneous, but much better than Ba, Fe, and Se.

To attempt to improve homogeneity, 6.2 g of pellets of SRM 2861 were cryogenically ground by freezing with LN_2 and pulverizing in a ball mill. Shaking at 15 Hz for 3.5 min reduced the PVC to a fine powder. A melt-pressed disk was prepared from this powder and mapped for Ba using the L_3-$M_{4,5}$ line. Figure 10 shows the heterogeneity remains with small regions of concentrated Ba present in the disk. In this case, red circles show two alternate measurement locations for a 1 mm aperture X-ray spectrometer. The left-most location contains four of the 13 highest Ba count rates out of 2500 locations in the measured region. The adjacent location contains zero points with high Ba. Even after grinding, the PVC continues to exhibit heterogeneity that will result in high variance among measurements made using a small aperture spectrometer.

7. Calibration of XRF Spectrometers

To calibrate the quantitative XRF methods with at least three points for each element, a series of synthetic PVC disks were prepared using a new approach to impart direct traceability of values through NIST primary reference materials. To obtain mass fraction values for all elements of interest, it was necessary to develop a process to spike PVC with sources of the elements that provide traceable values. For all calibrated elements, the SRM 3100 single element solutions were used, except Br for which NaBr in aqueous solution was used. For additional calibration standards, PVC reference materials from commercial sources were included for the elements for which their assigned values appeared to be accurate by comparison to the NIST calibration standards.
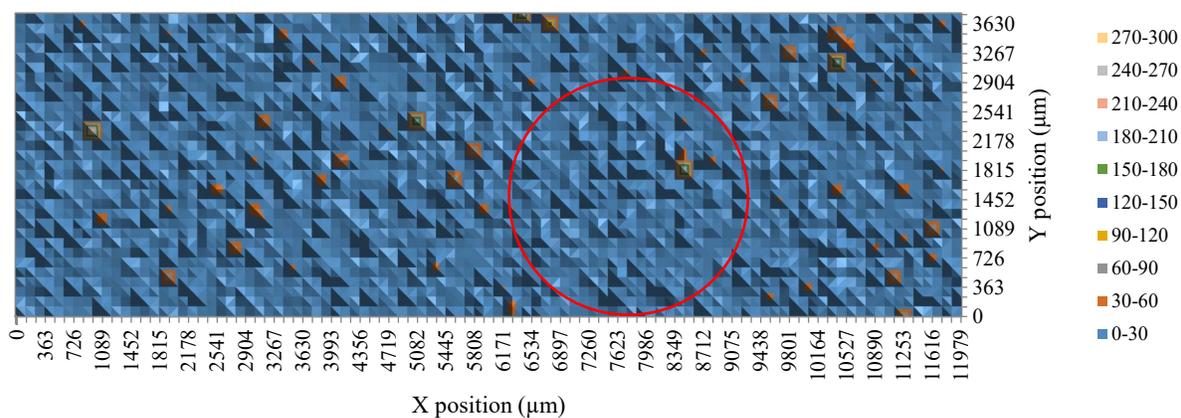
Fig. 7. Map of Ba L₃-M₄,₅ count rates in the surface of a melt-pressed disk of candidate SRM 2861. The red circle represents a 3 mm X-ray aperture of a handheld spectrometer.
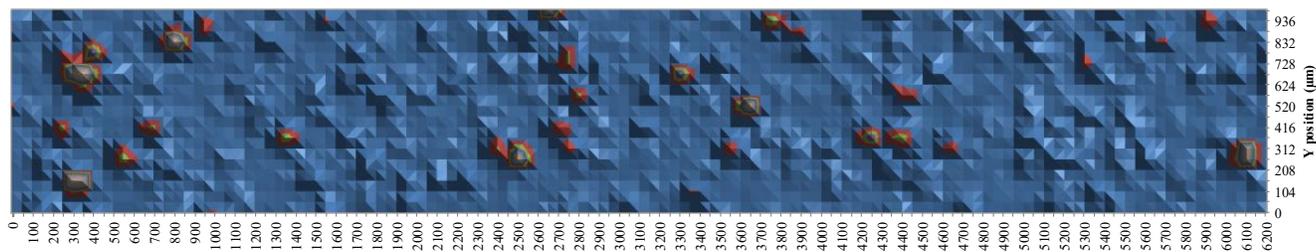
Fig. 8. Map of Ba L₃-M₄,₅ count rates in the cross-section of a melt-pressed disk of SRM 2861. In the X axis, positions of 0 µm and 6200 µm are the faces of the disk. Data were collected using a 0.05 mm spot size.
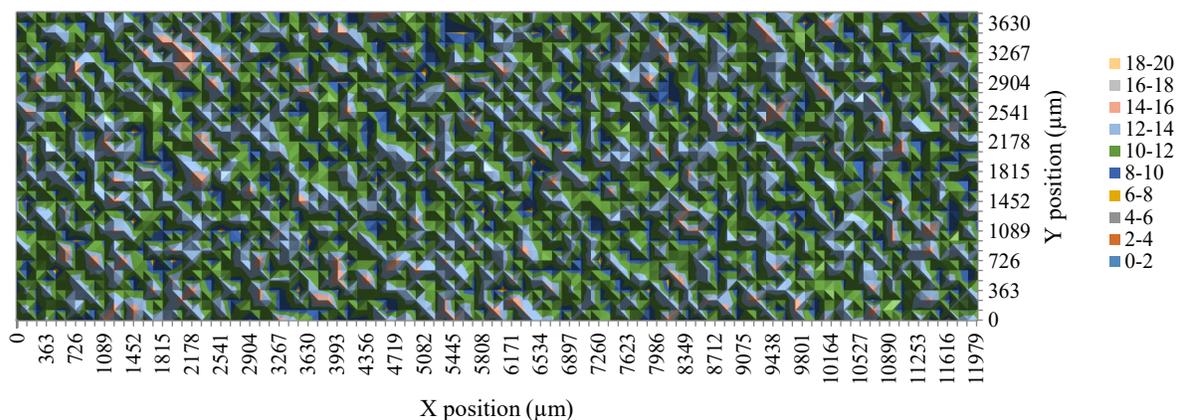
Fig. 9. Map of Hg L$_3$-M$_{4,5}$ count rates in the surface of a melt-pressed disk of SRM 2861. Data were collected using a 0.05 mm spot size.
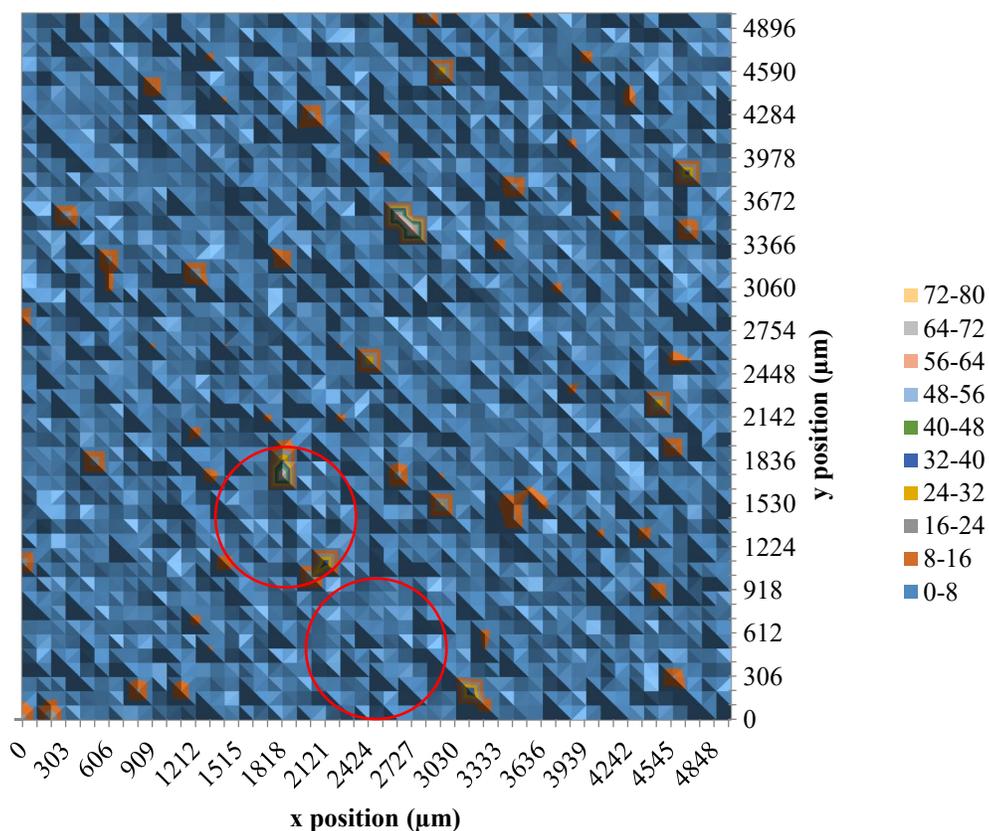
Fig. 10. Map of Ba L$_3$-M$_{4,5}$ count rates in the surface of a melt-pressed disk of SRM 2861 after cryogenic grinding to a fine powder. The red circles represent an X-ray beam from a 1 mm aperture aimed at two locations. Data were collected using a 0.05 mm spot size.

7.1 Equipment

The following equipment was used in this work, including sample preparation and XRF measurements.

Top load balance (Sartorius model LP1200S) was used for weighing detergent and LiOH solutions during preparation of calibration standards.

Analytical balance (Sartorius model MC210S) was used for weighing ingredients and beakers during preparation of calibration standards.

Labware for weighing and mixing calibration standards:
- Beakers, 50 mL; ingredients were weighed into beaker and mixed,
- Bottle, narrow mouth, low density polyethylene, 30 mL (Thermo Scientific Nalgene® Products); used for SRM 3100 solutions transferred from ampoules, LiOH solution, and detergent solution,
- Plastic bags, 6.4 cm x 7.6 cm, clear polypropylene (PP) with zip closure and writing area,
- Desiccator, glass with vacuum capability and charged with $Mg(ClO_4)_2$; house vacuum was used,
- Spatulas, 20 cm long with flat blade and round end (45 mm long x 7 mm wide), stainless steel with mirror finish,
- Disposable transfer pipets, polyethylene, 7 mL capacity (Taylor Scientific cat. # 13-5950-20); tips stretched to a fine diameter and cut at an angle to get smaller drops,
- Parafilm® M wrap (Pechiney Plastic Packaging, Menasha, WI); used to cover beakers during weighing of solutions and to seal bottles of SRM 3100 solutions between uses; 1 square per beaker or bottle.

7.2 Reagents

The following chemicals were used in creation of calibration standards for the XRF spectrometers.

Dry Blend – Base PVC blend for the SRMs provided by a commercial PVC manufacturer, containing PVC, $CaCO_3$ filler [CAS 471-34-1], and the stabilizer methyltin mercaptide ($C_{22}H_{44}O_4S_2Sn$) [CAS 57583-35-4]. This blend was used as the matrix for calibration standards of elements known to be not present in the dry blend. This approach yielded calibration standards matrix matched to the PVC SRM blends. Plus, this stabilized blend was resistant to damage by X-irradiation.

Poly(vinyl chloride) – Aldrich 81388-1KG, Lot # BCBL2272V, low molecular weight [CAS 9002-86-2]. This PVC was not sold with an analysis of elemental contents. Therefore, it was analyzed using the PANalytical semiquantitative method UQ+ and found to be free of the elements of interest within the limits of detection of the method.

Polyethylene – Aldrich 332119-500G, Lot # MKBH2495V, medium density [CAS 9002-88-4].

The PVC and polyethylene (PE) were mixed in a mass ratio of 2:1, which was expected to yield a Cl mass fraction of approximately 30 % in finished calibration standards. The powders were

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weighed into a glass bottle and blended by capping, rotating and shaking the bottle. This blend of powders was the matrix for calibration standards for the elements present in the dry blend: S, Ca, Fe, and Sn.

SRM 3100 Series – The following spectrometric solution standards were used as sources of the elements.

SRM 3102a Antimony, Lot 140911   SRM 3103a Arsenic, Lot 100818
SRM 3104a Barium, Lot 140909   SRM 3108 Cadmium, Lot 130116
SRM 3109a Calcium, Lot 130213   SRM 3112a Chromium, Lot 030730
SRM 3126a Iron, Lot 140812   SRM 3128 Lead, Lot 101026
SRM 3133 Mercury, Lot 991304   SRM 3149 Selenium, Lot 100901
SRM 3154 Sulfur, Lot 892205   SRM 3161a Tin, Lot 140917

Sodium Bromide – Allied Chemical, NaBr 99.0 % minimum, dried at 107 ºC for 2 h [CAS 7647-15-6]. In a 30 mL bottle, a 1 % Br solution was prepared in deionized H_2O. This solution was used in place of SRM 3184, because the last lot of SRM 3184 was unavailable and the next lot had not been certified yet.

Triton X-100 – Union Carbide Chemicals and Plastics Corp., Lot # OO0573, nonionic, polyethylene glycol octylphenol ether ≥ 97 % [CAS 9036-19-5], poly(ethylene oxide) ≤ 3 % [CAS 25322-68-3]. In a 30 ml bottle, a 5 % solution was prepared in deionized H_2O. Detergent promoted wetting of PVC/PE powder by aqueous solutions for homogeneous mixing of plastic powder doped with SRM 3100 solutions and LiOH.

Lithium Hydroxide – Sigma Aldrich 450197-25G, Lot # 03098JC, LiOH·H_2O, 99.995 % [CAS 1310-66-3]. In 30 mL bottle, a solution of 6.7 % LiOH was prepared in deionized H_2O. Solution was used to neutralize the acids in SRM 3100 series solutions after doping of PVC/PE powder.

Magnesium perchlorate – Desiccant, $Mg(ClO_4)_2$ [CAS 10034-81-8].

Deionized Water – distilled, deionized H_2O, having conductivity < 20 μS.

7.3 Calibrant Preparation Steps

The following stepwise procedure was used to prepare a single element PVC disk calibration standard.
1. Select the mass fractions of the element of interest and of total Cl required in the finished disk.
2. Calculate the required quantities of PVC powder, polyethylene (PE) powder, SRM 3100 series solution (or other calibration source material), and LiOH neutralizing solution (if using an SRM 3100 solution) to prepare 8.0 g of doped powder.
3. Use the analytical balance to weigh a clean beaker to the nearest 0.01 mg.
4. Weigh the required mass of either dry blend or PVC/PE powder mix into the beaker.
5. Press fit a square of Parafilm to form a cover for the beaker. Then, return the covered beaker to the balance, and tare it.

6. Weigh the appropriate SRM 3100 series solution or other calibration source material into the powder and take the mass with the Parafilm in place to stop loss of H_2O.
7. Transfer the covered beaker to the top load balance and tare it.
8. Add the required mass of detergent solution, record the mass[2], and tare the balance.
9. Add the required mass of LiOH solution and record the mass[3]. The LiOH neutralizes the acid(s) from the 3100-series solution to promote stability during storage and measurement[3].
10. Promptly begin stirring and mixing the powder and solutions together. The correct technique is to push the mixture against the wall of the beaker to smear the ingredients together as you turn the beaker slightly. Continue to rotate the beaker in one hand while smearing together the ingredients[4] with the other hand.
11. Leave the spatula in the beaker, and place the beaker into the drying oven. At approximately 15 min intervals, stir and mix the contents. If the material has developed various colors, be sure to return it to a single, uniform color. When removing powder from the spatula, use care to prevent losses.
12. After a minimum of 2 h, remove the beaker from the oven and scrape all material from the spatula into the beaker by dragging the spatula horizontally across the rim of the beaker causing the particles to fall inside.
13. Place the beaker into the vacuum desiccator, and pump house or rough vacuum. Allow the powder mixture to continue drying overnight or at least 18 h. When the powder is dry, it will be free flowing.
14. Weigh the beaker and its contents in the analytical balance. Calculate the mass of the contents.
15. Use the mass of calibration source material from step 6, the mass fraction of the element in the calibration source material, and the mass of beaker contents from step 14 to calculate the mass fraction of the element of interest.
16. Prepare a melt-pressed disk by following the procedure in the section Disk Preparation by Melt-Pressing on page 11.
17. Place the disk into a PP bag, and store it in the vacuum desiccator. Nitrates in the PVC disk are hygroscopic. If the disk absorbs moisture, it cannot be used as a calibrant. With enough moisture, the disk may exude a liquid that is hazardous.

Because each calibrant is prepared in powder form to 8.0 g total mass, and the melt-pressed disks take only 6.2 g of powder, there is some powder left from each calibrant. Place this extra powder in a plastic vial, and store it in the vacuum desiccator.

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[2] The masses of detergent solution and LiOH solution are not used in calculations. Record the approximate mass of each for quality and review purposes.

[3] The nominal acid contents given for the SRM 3100 series solutions are approximate and may be very different from the stated value. For this project, the solutions were titrated with LiOH solution and pH indicator paper to obtain an estimate of the necessary mass of LiOH to neutralize the acid in 1 g of SRM solution.

[4] To learn the mixing procedure, it is instructive to substitute pure PVC powder for the matrix blend and substitute food coloring for the SRM 3100 series solution. As you try the mixing motion, the food coloring will indicate the amount of mixing achieved. Continue until the mixture has a completely uniform color. Do not add food coloring to calibrant mixtures, because food coloring compounds contain metals, sulfur and halogen atoms.

7.4 Additional Calibrants

One multi-element calibrant was prepared from the leftover powders. Each powder was weighed into a beaker, using the analytical balance. The contents of the beaker were stirred thoroughly before being transferred into the pressing die.

Blank disks were prepared from the dry blend and from the PVC/PE mixture. The dry blend is not blank for Ca, Fe, S, and Sn.

One unique calibrant was prepared by weighing cryogenically ground National Metrology Institute of Japan (NMIJ) CRM 8103-a and CRM 8113-a together with the dry blend. These two CRMs are acrylonitrile butadiene styrene (ABS) polymer certified for Cd, Cr, Hg, and Pb. The mixture of powders was melt pressed into a disk.

Resolve/PANalytical PVC Calibration Standards were acquired with the EDXRF spectrometer. They are disks of PVC containing compounds incorporating the elements Al, Br, Cd, Cr, Hg, Mg, Pb, Sn, and Zn. Di-octyl phthalate was used as plasticizer in increasing concentration from blank to standard PVC 4. Nominal mass fraction values are provided for total Cl in each of the five compositions. Because the disks are thin, they were stacked to obtain approximately the same thickness as the melt pressed PVC sample disks.

7.5 WDXRF Calibrations

Calibration calculations were performed using the PANalytical SuperQ regression software to fit the mass fractions and net count rates to Equation 1.

$$C_i = D_i - \sum_l L_l C_l + E_i \frac{R_i}{R_R} \tag{1}$$

In Eq. 1, C denotes mass fraction, D is the intercept, E is the inverse sensitivity, R is the net count rate, and L is the line overlap correction factor with i being the analyte element and l being the element with an overlapping X-ray line. In two cases, the term C_l was replaced with R_l, because it was necessary to calculate the line overlap correction using measured count rates for the overlapping element, instead of mass fractions. The term R_R is the gross count rate for an internal reference. Four corrections for line overlap were applied: As on Br using the mass fractions of As; Hg on Br using the mass fractions of Hg; Pb on As using the count rates for Pb; and Cd on Sb using the count rates for Cd. Calculations for Cr, As, Se, Cd, Pb, Sb, and Sn used internal reference ratios with R_R set equal to the Rh Compton scatter count rate for each sample. For Br and Hg, the background count rates for the Pb channel were used as R_R, because there are absorption edges between the Rh Compton peak energy and the analyte peak energies. For the Cr regression, weighting with the weighting factor set equal to the inverse Cr mass fraction was used to force the calculated curve to fit better the lower mass fraction calibration points. Weighting was not used for other elements.

As an example of the performance of the calibration approach, Fig. 11 presents the calibration of Pb in PVC. Of the 46 points in the graph, nine are single element Pb disks and disks containing both Pb and Cd with Pb from SRM 3128. Two points are from multielement disks prepared from

leftover powders of the single element calibration standards. Twenty-six points are calibration disks containing one of the other analytes in this project and blank for Pb. Four points are blends of PVC and PE powders that are blank for all analytes, except Cl. Six points are reference materials from a commercial source and NMIJ. In Fig. 11, the trendline represents the calibration curve from Eq. 1, where $y = C_i$, $x = R_i/R_{Rh}$, and no line overlap term was used. The actual calibration curve was calculated using the regression software of the WDXRF spectrometer operating system. There are numerous Pb calibrants, because the procedure for preparing these calibration standards was developed using Pb first Pb and later Pb and Cd. With so many points, the precision of the approach is evident. A curve of equivalent performance could be obtained with fewer points. In fact, most analytes in this project were calibrated using just two spiked disks and several blanks.

Calcium calibration was done with a single calibrant and several blanks. The mass fraction of Ca in the calibrant was ten times lower than the Ca in the SRMs. Therefore, Ca results may have been biased high because Ca self-absorption was not included in the calibration model.

Copper calibration was obtained using samples of PVC analyzed by the U.S. Consumer Product Safety Commission. All Cu results were considered approximate, and they have no clear traceability link to values for NIST SRMs or primary compounds.

Chlorine calibration was obtained using estimated Cl mass fractions for the calibrants, calculated from the theoretical amount of Cl in PVC and the amounts of dry blend or PVC/PE mix. Therefore, the Cl results were considered approximate. Because Cl and Ca were present at the highest mass fractions by far, Equation 2 was used to calibrate Cl, and absorption corrections, α_{ClCl}, for Cl absorption of Cl X-rays and α_{ClCa}, for Ca absorption of Cl X-rays, were applied.

$$C_{Cl} = D_{Cl} + E_{Cl}R_{Cl}\left(1 + \alpha_{ClCl}R_{Cl} + \alpha_{ClCa}R_{Ca}\right) \qquad (2)$$

Because the PVC blends for the SRMs were made using mostly NIST SRMs, there are estimated mass fractions for the analyte elements (see Quality Assurance). From the WDXRF calibration for Ba, the results for SRM 2861 were all near 300 mg/kg Ba, which is too low compared to the expected value of 869 mg/kg. No applied corrections of any type could cause a calculated calibration to yield results closer to 869 mg/kg Ba. Measurements by microXRF, discussed on page 15, show heterogeneity of Ba in SRM 2861, and lower amounts of Ba near the surfaces of a disk.

7.6 EDXRF Barium Calibration

With the erroneous results for Ba in SRM 2861 from the WDXRF Ba calibration of the Ba L_3-$M_{4,5}$ line (4.487 keV), the EDXRF spectrometer was used to measure the Ba K-$L_{2,3}$ line (32.065 keV). The hypothesis for the cause of erroneous results was that Ba was heterogeneously distributed in the sample disks such that the surface regions were depleted relative to the total Ba mass fraction. The information depth for Ba L_3-$M_{4,5}$ X-rays is approximately 80 μm, whereas for Ba K-$L_{2,3}$ X-rays, it is > 18 mm, which is much greater than the 6 mm thickness of a disk sample. So, measurement of the high-energy K lines enables measurement of the entire disk thickness, eliminating concerns about heterogeneity and matrix effects.

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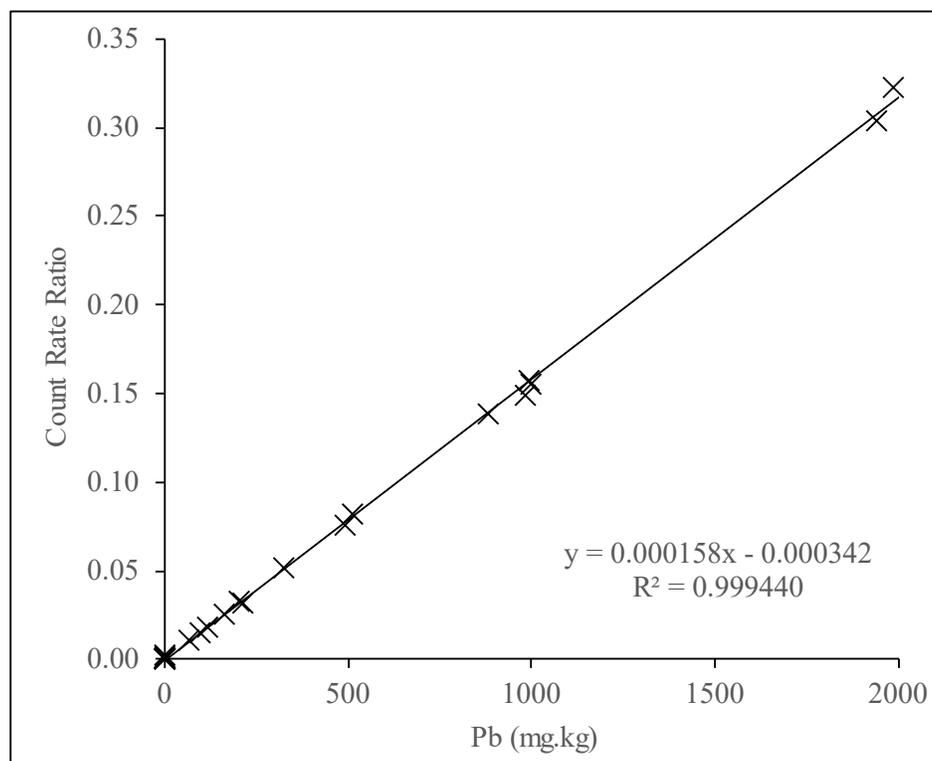
Fig. 11. Calibration graph for Pb L$_3$-M$_{4,5}$ by WDXRF. The value R^2 is the correlation coefficient, used as a simple measure of goodness of fit.

Three calibrants were measured, and a linear regression was performed. The calibrants were a dry blend blank, Ba100, and Ba900. The calibration data are shown in Table 29, and Fig. 12 is the graphical calibration fit. The measured count rates from the two sides of each disk were treated as separate specimens for the linear regression. As expected, the duplicate points were nearly indistinguishable. The calibration equation is shown in Fig. 12, where y is the measured count rate, and x is the mass fraction of Ba. A high-quality regression fit for such high energy X-rays is only possible with specimens of highly uniform thickness.

Table 29. Data for EDXRF Barium Calibration

Calibrant	Ba (mg/kg)	Count Rates from Surfaces	
		Inside	Outside
		------ (cps/mA) ------	
Dry blend	0	1.51	1.29
Ba100	119.4	18.45	17.90
Ba900	904.3	129.00	129.21
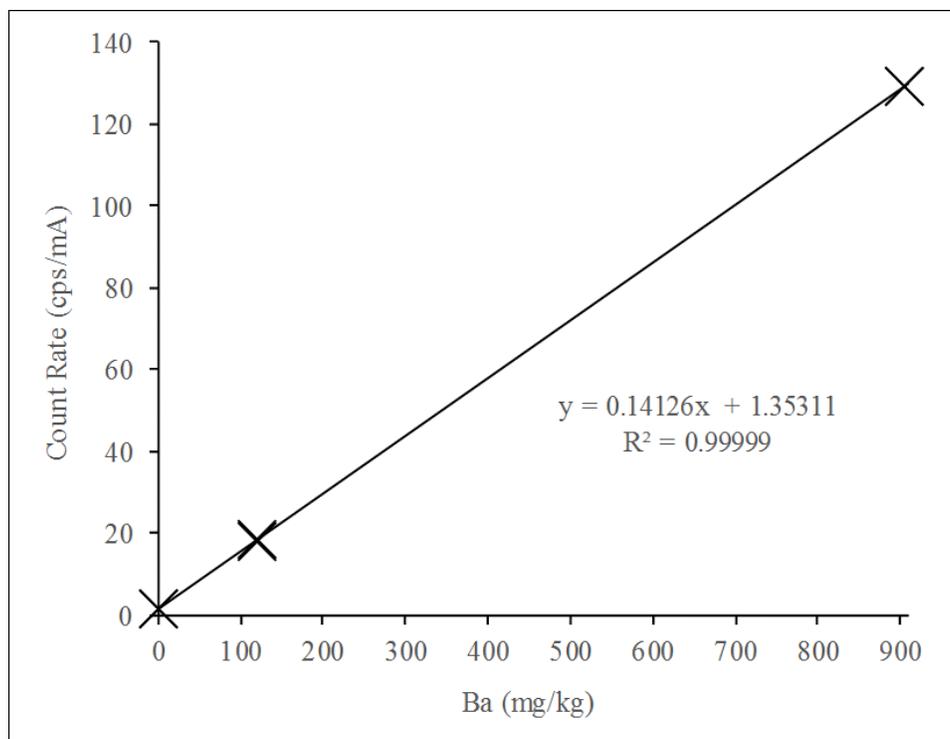
Fig. 12.   Calibration graph for Ba K-L$_{2,3}$ by EDXRF.   At each mass fraction, there are two measured points corresponding to the two faces of each calibrant disk in Table 29. The value R^2 is the correlation coefficient, used as a measure of goodness of fit.

8.   Quantitative XRF Results

8.1 SRM 2859

Calculated results for elements in SRM 2859 are summarized in Table 30.   All results were WDXRF results.   The table gives the overall mean, individual components of uncertainty (see Table 32), and the expanded uncertainty, $U_{k=2} = 2u_c$. The number of replicate determinations, n, is the total number of disk surfaces measured. For elements that were too low to be quantified, an estimate of the limit of detection, L_D, was obtained using Equation 3, where s is the estimated repeatability standard deviation and X is the mean of the mass fraction results.

$$L_D \approx 3s + |X| \tag{3}$$

This variation on limit of detection accounts for possible zero bias in the calibration curve. Table 32 contains definitions of the components of uncertainty for the analyses, which were combined using Equation 4.

$$u_c = \sqrt{\frac{s^2}{n} + \frac{u_m^2}{p} + u_s^2 + \frac{2u_b^2}{3}} \tag{4}$$

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8.2 SRM 2861

Calculated results for elements in SRM 2861 are summarized in Table 31. Results for Ba are EDXRF results, and the rest are WDXRF results. The table gives the overall mean, individual components of uncertainty (see Table 32), and the expanded uncertainty, $U_{k=2} = 2u_c$. The number of replicate determinations, n, is the total number of disk surfaces measured. For elements that were too low to be quantified, an estimate of the limit of quantification, L_Q, was obtained using Equation 3. Table 32 contains definitions of the components of uncertainty for the analyses, which were combined using Equation 4.

8.3 Quality Assurance

NMIJ CRM 8123-a is the only known PVC CRM from a national metrology institute. Two disks of CRM 8123-a were melt pressed and measured on both sides using WDXRF. Calculated results are given in Table 33. The table gives the overall mean, individual components of uncertainty (see Table 32), and the expanded uncertainty, $U_{k=2} = 2u_c$. For elements that were too low to be quantified, an estimate of the limit of quantification, L_Q, was obtained using Equation 3. Certified values and published uncertainty estimates are listed at the bottom of the table, along with recovery values.

The result for Cr agrees with the certified value, and there is no detectable bias for Cd. The recovery for Pb represents a detectable bias, and the recovery for Hg is significantly low. There are three possible causes for low Hg results: loss of the Hg compound during melt pressing, loss of the Hg compound during X-irradiation, and absorption of Hg L X-rays by an element not included in the calibration. All three possibilities were investigated. One was confirmed and one was found to be plausible.

CRM 8123-a was formulated with a Zn-containing stabilizer compound [14]. Zinc is not included in the WDXRF calibration. The K absorption edge for Zn is 9.660 keV, and the Hg L_3-$M_{4,5}$ X-ray energy is 9.987 keV. Therefore, the Zn in the PVC will strongly absorb Hg X-rays, and the use of an internal reference ratio will not compensate completely. In this situation, Hg results will be biased low. Using tabulated mass absorption coefficients for C, Cl, and Zn on Hg L_3-$M_{4,5}$ X-rays, an estimate can be made of the expected depression of Hg count rate by Zn absorption. With Zn present at approximately 1 % by mass and Cl at approximately 30 %, the Hg signal depression is estimated to be 10 %, compared to the observed bias of 21 %. This interference is a plausible reason for lower Hg results.

Because there is always concern about loss of Hg when samples are heated, in this case for melt pressing, the issuing laboratory was asked about stability of Hg. The project leader's response was that no evidence was observed that indicated Hg loss during the three extrusion passes at 200 ºC, which is higher than the NIST melt pressing temperature of 175 ºC. This possible cause of low Hg results is refuted.

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Table 30. Mass Fractions of Elements Quantified in Candidate SRM 2859 Using X-Ray Fluorescence Spectrometry

Element:	S (mg/kg)	Cl (%)	Ca (%)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Br (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
Mean	1048	32.8	3.590	712	59.6	56.2	<10	<7	853.6	72.3	1359	<15	<20	769	797.1
s	51	0.48	0.051	5.9	4.8	1.4			7.8	2.1	14			8.5	8.9
n	64	64	64	64	64	64			64	64	64			64	64
u_m	50	0.38	0.027	15	5.8				6.3	1.5	11			10	8.9
p	5	25	2	8	3				5	15	4			5	16
u_b	0.58	0.0008	0.0002	1.3	0.24				0.17	0.40	0.56			1.7	1.7
u_s	1.5	0.99	0.0035	0.82	0.072				0.85	0.099	1.7			1.9	0.56
u_c	23	0.58	0.020	5.4	3.4				3.0	0.57	5.8			5.1	2.9
$U_{k=2}$	47	1.2	0.041	11	6.9				6.0	1.1	12			10	5.7

Table 31. Mass Fractions of Elements Quantified in Candidate SRM 2861 Using X-Ray Fluorescence Spectrometry

Element:	S (mg/kg)	Cl (%)	Ca (%)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Br (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
Mean	951	34.7	3.288	49.25	54.2	<6	19.82	243.8	<10	62.1	1292	67.0	742.2	57.05	92.2
s	30	0.21	0.037	1.4	2.4		1.4	1.7		2.1	9.9	2.6	3.7	2.1	3.0
n	64	64	64	64	64		64	64		64	64	64	26	64	64
u_m	45	0.40	0.025	1.0	5.3		0.91	2.5		1.3	16	0.91	8.3	0.46	8.1
p	5	25	2	8	3		4	4		15	4	4	4	5	16
u_b	0.53	0.0009	0.0002	0.093	0.22		0.067	0.45		0.34	1.9	0.15	1.6	0.023	0.29
u_s	1.4	1.1	0.0032	0.056	0.065		0.015	0.61		0.085	1.6	0.064	0.91	0.14	0.064
u_c	21	0.61	0.018	0.41	3.1		0.49	1.4		0.51	8.3	0.57	4.4	0.35	2.1
$U_{k=2}$	41	1.2	0.037	0.82	6.2		0.98	2.8		1.0	17	1.1	8.9	0.69	4.2

Table 32. Standard Uncertainty Components of X-Ray Fluorescence Analysis

Uncertainty	Basis	Type	DF
Variability of Sample Preparation and Measurement, s	Standard deviation of the calculated mass fractions for n specimens.	A	$n-1$
Variability of Calibrant Preparation and Measurement and Performance of Calibration Model, u_m	Estimated from the fit of Equation 1 to the calibration data. The estimate is the r-m-s deviation of the calculated values from the chemical values. The estimate covers the calculated parameters D, L, E, and α, plus the inherent uncertainty of X-ray counting in R_i and R_{Rh} (if used). This component is assumed to have a uniform distribution. The variable p is the number of calibration points in the regression calculations.	A	p - 2
Assay of Primary Material, u_s	$u_s = U/k$, where U is the expanded uncertainty and k is the expansion factor from the Certificate of Analysis of each spectrometric solution SRM. For each high-purity compound, the combined standard uncertainty is used instead, and it is estimated to be 0.1 % relative.	B	∞
Uncertainty of Balance Calibration, u_b	The balance calibration and calibrated weights agreed to within 0.2 mg across the range of masses encountered in this work. The estimate was expressed as a relative uncertainty. The factor of 2 in Eq. 3 accounts for the solution mass and the total mass of mixture for each calibrant. The factor of 3 is due to the assumption of a uniform distribution.	B	∞
Combined Standard Uncertainty, u_c	See Equation 4.		

Because instability of HgS, the ingredient used by AIST [5], was observed during X-irradiation by NIST of polypropylene created for an international comparison study [9], the same microXRF experiment was run on extruded pellets of PVC CRM 8123-a. Over about 30 h, 804 measurements were made of a single location on a single pellet of the CRM, with generator settings of 40 kV and 0.5 mA ($\approx$ 1000 W/mm^2). The measured count rates for Hg L_3-$M_{4,5}$ are shown in Fig. 13. The fitted curve is a 4th order polynomial simply intended to show just the rate of change. The relative difference between the mean of the first 20 measurements and the mean of the last 20 measurements is 14.4 %, which is statistically significant. To demonstrate the stability of another element and of the spectrometer, the Pb L_3-$M_{4,5}$ measured count rates are included in Fig. 13. The slope of the fitted line for Pb measurements is not distinguishable from zero. Also included are count rates from Cr K-$L_{2,3}$, which appear to increase by a small amount with time, but the difference from start to finish is not statistically significant. Therefore, Hg is lost from CRM 8123-a under X-irradiation. The combined effects of volatilization under irradiation and absorbance by Zn explain the low results obtained for Hg.

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Table 33. Mass Fractions of Elements Quantified in CRM 8123-a Using X-Ray Fluorescence Spectrometry

Element:	S (mg/kg)	Cl (%)	Ca (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Br (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
Mean	<75	44.7	1839	937.9	<12	<5	<10	<5	85.09	86.8	<20	<25	<15	738	925.3
s		0.14	60	6.5					0.81	4.0				3.9	3.4
n		4	4	4					4	4				4	4
u_m		0.52	14	19					0.62	1.8				10	10
p		25	2	8					5	15				5	16
u_b		0.0011	0.11	1.8					0.017	0.48				1.7	1.9
u_s		1.4	1.8	1.1					0.085	0.12				1.8	0.65
u_c		0.79	31	7.7					0.49	2.1				5.2	3.5
$U_{k=2}$		1.6	63	15					0.98	4.2				10	7.0
Certified				949.0						95.62				937.0	965.5
U				9.7						1.39				19.4	6.6
Recovery (%)				99						91				79	96

Fig. 13. Measured count rates for Cr, Hg and Pb from a single location (nominally 50 μm diameter) on a single extruded pellet of CRM 8123a. The measurements were acquired in 30 h.

SRM 1648a Urban Particulate Matter was used as a quality assurance material by blending it with PVC powder and melt pressing a disk. SRM 1648a was chosen because it has assigned values for elements not certified in CRMs of plastic formulations, and because the very fine powder was easily mixed with powder PVC. The melt pressed mixture adhered to the aluminum mold, and the inside surface was broken so much it could not be measured. Therefore, the one good side was measured twice, and the results are listed in Table 34 on both the diluted basis and the original sample basis. Because there are only two measurements, the expanded uncertainty was calculated using $k = 3$ as the expansion factor.

Results for this diluted SRM 1648a material are reasonably accurate given that its composition is considerably different from the calibrants and SRMs. Results for Fe, As, Br, and Pb are accurate within the expanded uncertainty estimates for the found and assigned values. The results for Cd and Se are acceptable, if not technically in agreement with assigned values. Under most circumstances, selenium is sensitive to heating, which may explain the low results. The results for Sb and Hg are poor because there is insufficient sensitivity to measure the low mass fractions in the disk. Results for S, Ca and Cr are high with no explanation evident. The elements Ba and Sn have no assigned values in SRM 1648a. Consequently, there is no way to use a CRM to check on validity of results for Ba and Sn in the SRMs.

Table 34. Mass Fractions of Elements Quantified in SRM 1648a (Diluted in PVC) Using X-Ray Fluorescence Spectrometry

	S	Ca	Cr	Fe	Cu	As	Se	Br	Cd	Sn	Sb	Ba	Hg	Pb
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Mean	6584	7597	56.1	3183	45.31	11.0	1.91	50.0	6.27	13.59	2.2	55.9	15.6	640.3
s	79	342	1.2	55	0.81	1.4	0.00	1.9	0.26	0.10	5.6	3.1	2.0	3.1
n	2	2	2	2	2	2	2	2	2	2	2	2	2	2
u_m	76	57	1.2	312	1.4	0.50	0.020	0.37	0.13	0.11	0.20	0.70	0.21	7.2
p	5	2	8	3	3	4	4	5	15	4	4	4	5	16
u_b	0.16	0.19	0.0014	0.080	0.0011	0.00027	0.00005	0.0013	0.00016	0.00034	0.00006	0.0014	0.00039	0.016
u_s	9.6	7.5	0.064	3.8		0.0082	0.0048	0.050	0.0086	0.017	0.0021	0.069	0.038	0.45
u_c	66	245	0.92	184	0.97	1.1	0.010	1.3	0.19	0.089	4.0	2.2	1.4	2.9
$U_{k=3}$	197	736	2.75	553	2.91	3.2	0.031	4.0	0.56	0.268	12.0	6.6	4.2	8.6
Original Sample Basis	(%)	(%)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
	6.58	7.59	561	3.18	453	110	19.08	499	62.6	135.7	<190	559	155	6395
$U_{k=3}$	0.20	0.73	27	0.55	29	32	0.31	40	5.6	2.7		66	42	86
SRM 1648a	5.51	5.84	402	3.92	610	115.5	28.4	502	73.7	-	45.4	-	1.323	6550
U	0.36	0.19	13	0.21	70	3.9	1.1	10	2.3	-	1.4	-	0.064	330

9. Stability of SRMs to X-Ray Exposure

For a better understanding of the stability of the SRM PVC blends under X-irradiation, the same microXRF experiment used on CRM 8123-a was performed on a pellet of SRM 2859. A map of the pellet showed no locations with high count rates for Hg. Therefore, a single location was chosen at random for 800 consecutive measurements at ≈ 1000 W/mm^2. Figure 14 shows the trends of count rates for Cr, Hg, and Pb. Like CRM 8123-a, Pb is stable throughout, and Cr count rates increase slowly with time. In this case, the change in Cr rates is statistically significant, because the difference between beginning and end count rates is $> 2s$ for the 800 measurements. In contrast to CRM 8123-a in Fig. 13, the Hg count rates from SRM 2859 increase by more than double.

Measured microXRF data for Cl in the PVC shows the matrix is changing in some way during exposure. Figure 15 shows Cl count rates from measurements of individual pellets of SRM 2859 and CRM 8123-a. In both cases, there is an initial increase in signal, followed by a decrease. The change for SRM 2859 is significant, but for CRM 8123-a, it is not statistically significant. Measurements of Cl K-series X-rays in PVC are relatively surface sensitive, while Cr, Hg, and Pb measurements are much less so. Breakdown of PVC by ionizing radiation could cleave C=C double bonds and C-Cl bonds. Either way, the integrity of the matrix is reduced as compounds are altered by the ionizing radiation.
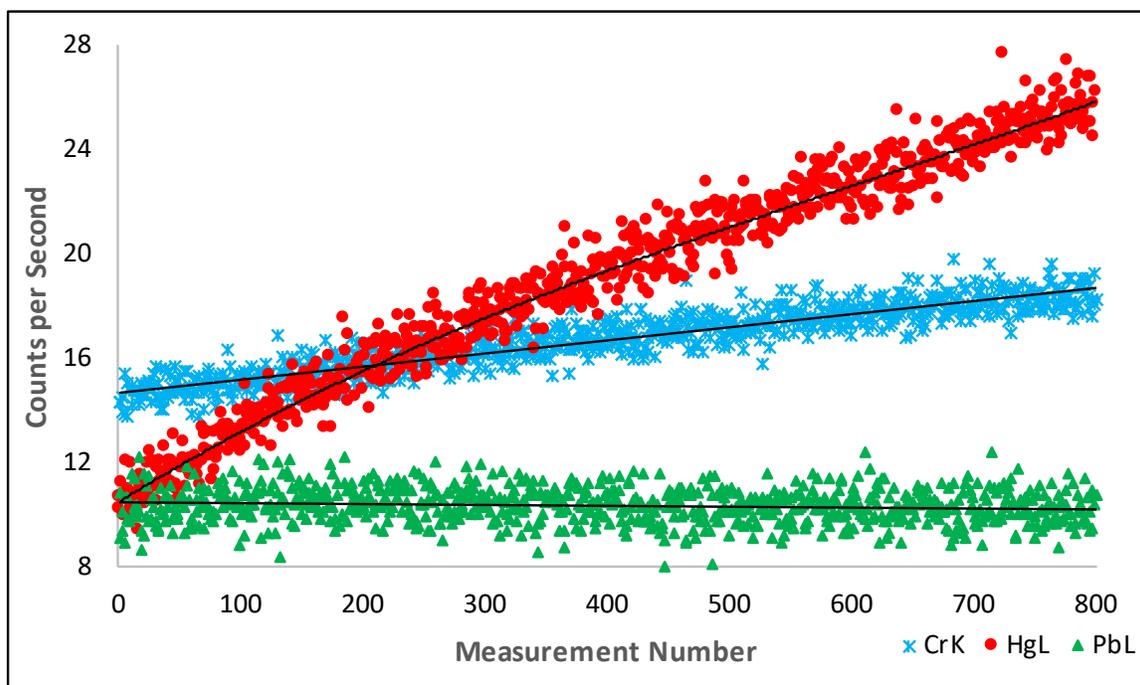
Fig. 14.   Measured count rates for Cr, Hg and Pb from a single location (nominally 50 μm diameter) on one extruded pellet of SRM 2859. The measurements were acquired in 30 h. Black curves are meant only to show trends.

Because homogeneity testing and quantitative analyses were done using WDXRF, a fresh disk of SRM 2859 was measured repeatedly under the same conditions (1200 W, 27 mm viewed diameter, ≈ 0.5 W/mm^2), except the time was reduced from the original 20 min to 10 min to get more measurements for elucidating any observed trends. In Fig. 16, both Hg and Cr count rates showed small increases during the 4 h period, which is 12 times longer than used for quantitative measurements. For Pb, the measured count rates did not change. The same is true for S, Br, Cd, and Sn, which are not shown here.

The disk of SRM 2859 was darkened considerably to almost black and made brittle by the 4 h exposure at 0.5 W/mm^2. The visible damage was accompanied by substantial changes in count rates for Cl and Ca as shown in Fig. 17 and Fig. 18, respectively, and by a mass loss of approximately 10 mg. The mass loss and 22 % reduction of Cl signal suggests loss of Cl from the near surface region of the disk, which could amount to 3×10^{-4} mol of Cl (1.8×10^{20} Cl atoms), if only Cl was lost. Ionizing radiation easily cleaves covalent bonds. Free Cl or small, chlorinated organic molecules would be expected to create a reducing environment. The most easily reduced species in the PVC formulation is any hexavalent Cr remaining from the $Na_2Cr_2O_7$ in the initial formulation. The loss of Cl was accompanied by a 48 % increase in the Ca count rate. A significant reduction in Cl concentration in the information volume near the sample surface would reduce the X-ray absorption of the matrix and have its greatest effect on Ca K-series X-rays.

10. Quantitative ICPOES Results

Both the U.S. CPSC and UL performed test methods using cryogenic grinding of PVC pellets followed by acid digestion, then measurement by ICPOES. Chosen wavelengths are listed in Table 35. The collaborators used essentially the same procedures to prepare samples, calibrate spectrometers, and quantify the elements. Both labs subjected samples to microwave-assisted acid digestion and diluted to concentrations targeted by calibration solutions. Both labs used NIST SRM 3100 solutions (listed below) and commercial single element solutions to create calibration standards.

> SRM 3102a Antimony, Lot 140911 SRM 3103a Arsenic, Lot 100818
> SRM 3104a Barium, Lot 140909   SRM 3108 Cadmium, Lot 130116
> SRM 3109a Calcium, Lot 130213 SRM 3112a Chromium, Lot 030730
> SRM 3126a Iron, Lot 140812   SRM 3128 Lead, Lot 101026
> SRM 3133 Mercury, Lot 991304   SRM 3149 Selenium, Lot 100901
> SRM 3154 Sulfur, Lot 892205   SRM 3161a Tin, Lot 140917

The CPSC published their method as *CPSC-CH-E1002-08.3 Standard Operating Procedure for Determining Total Lead (Pb) in Nonmetal Children's Products, Revision*, available at this link: https://www.cpsc.gov/s3fs-public/pdfs/blk_pdf_CPSC-CH-E1002-08_3.pdf [4]. Part II of this method addresses plastics by ICPOES. Measurements were made using an Agilent Technologies model 5100 ICPOES spectrometer.
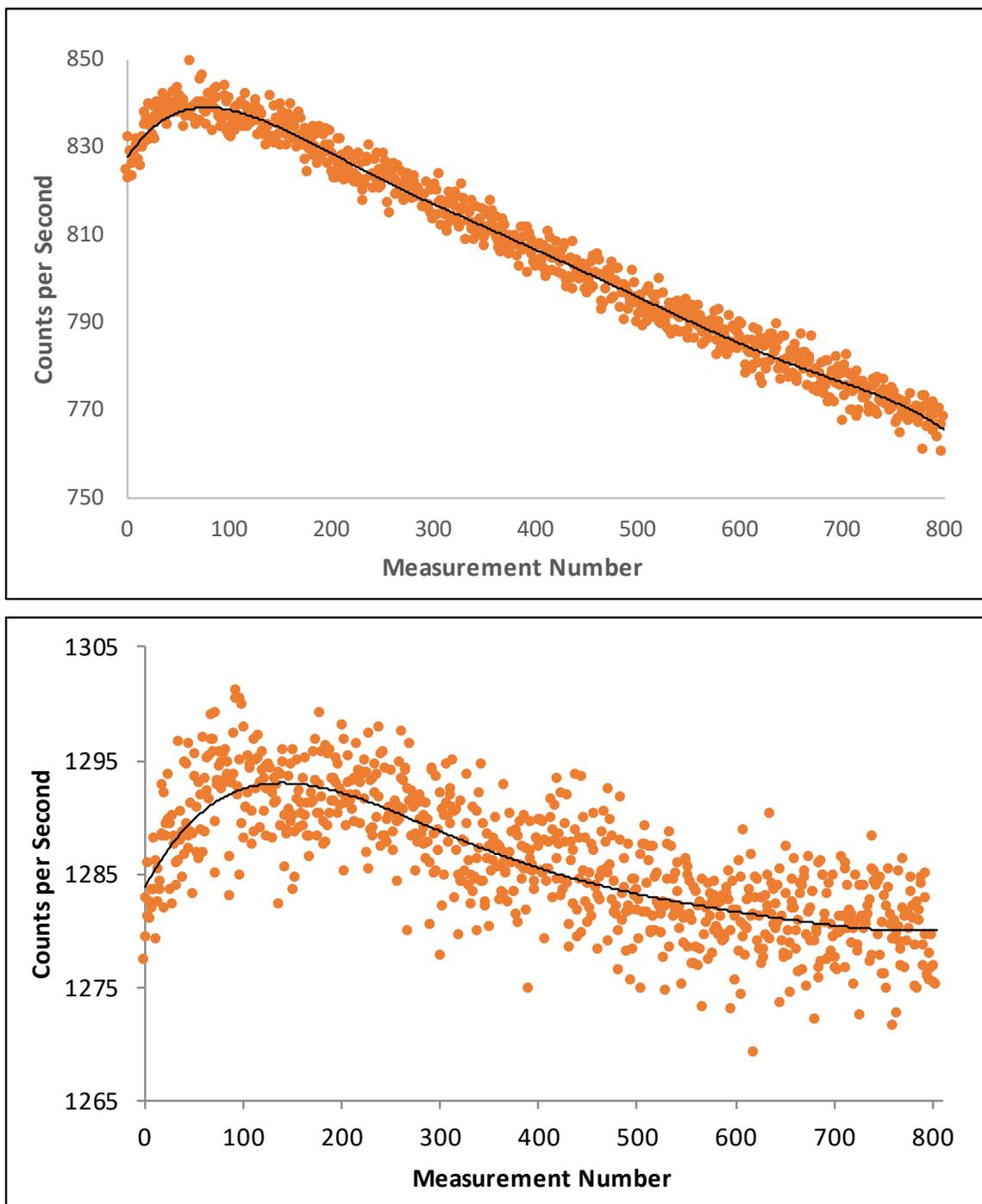
Fig. 15. Chlorine count rates as a function of exposure of a single location in the microXRF spectrometer. Top is SRM 2859; bottom is CRM 8123-a
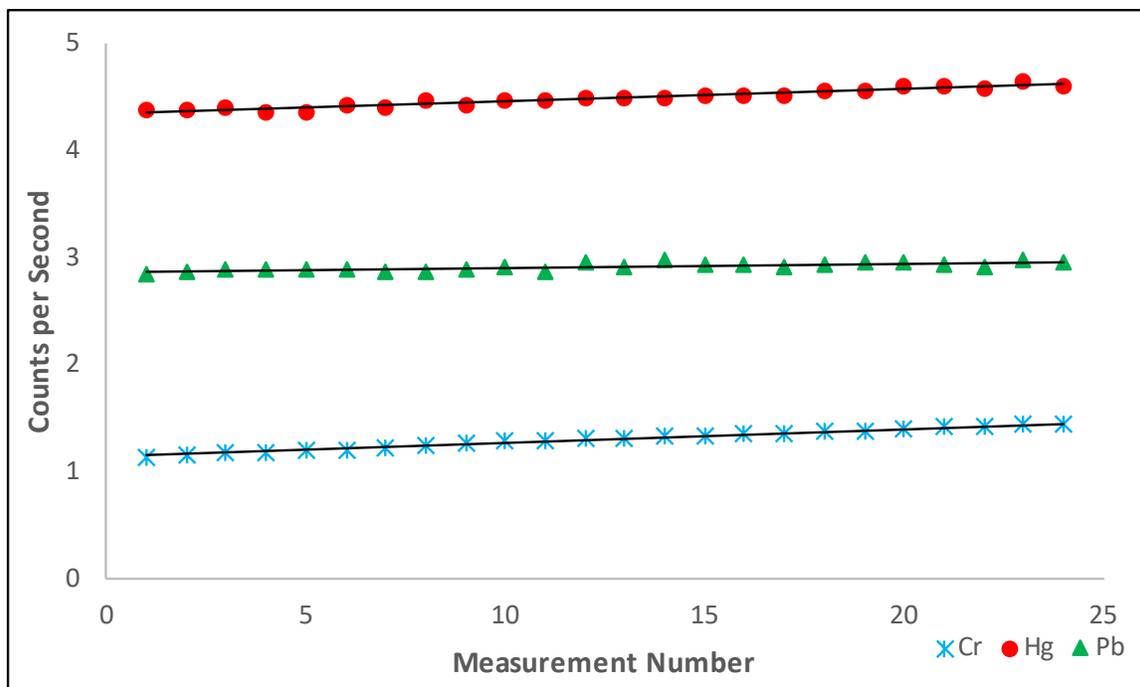
Fig. 16. Measured count rates for Cr, Hg and Pb from a single, melt-pressed disk of SRM 2859. The measurements were acquired in 4 h.
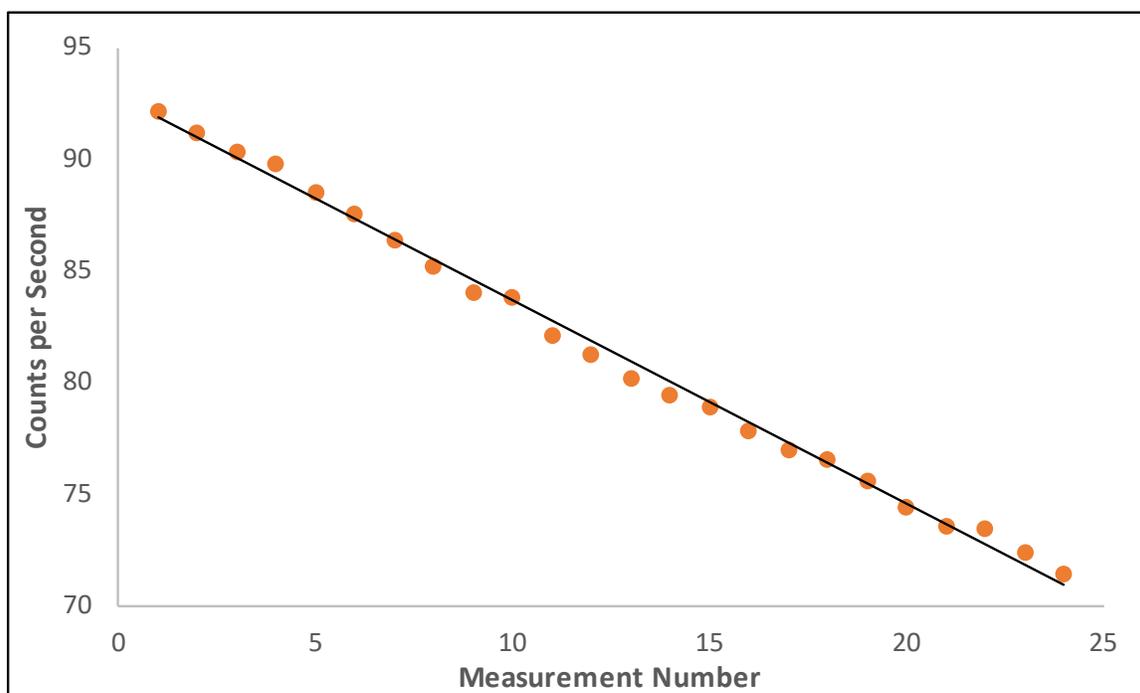
Fig. 17. Measured count rates for Cl in a melt-pressed disk of SRM 2859 at 1200 W generator power for 10 min per measurement.
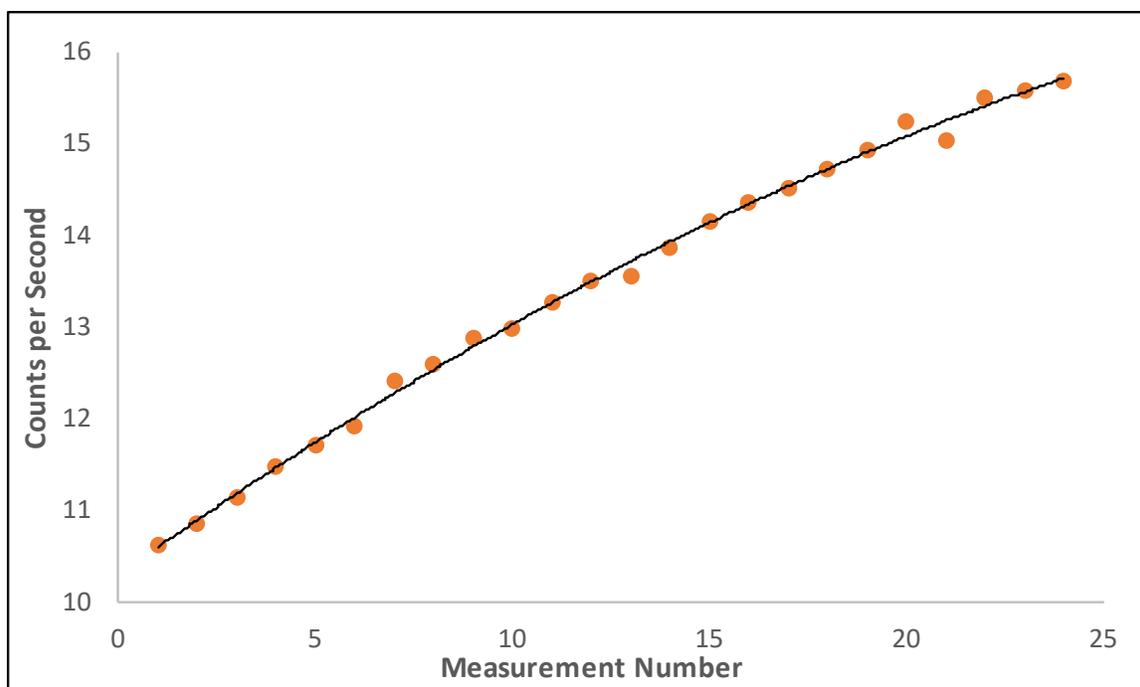
Fig. 18. Measured count rates for Ca in a melt-pressed disk of SRM 2859 at 1200 W generator power for 10 min per measurement.

Table 35. Wavelengths Chosen for ICPOES Measurements
Units are nanometers.

Element	UL		CPSC	
S[a]	180.731	182.034	180.669	181.972
Ca	315.887	422.673	396.847	
Cr	205.618	283.563	267.716	
Fe	238.204	239.562	238.204	
As	189.042	193.759	188.980	
Se	196.090		196.026	
Cd	226.502	214.438	228.802	
Sn	140.045	242.949	189.925	
Sb	206.833	217.581	217.582	
Ba	455.404	230.424	230.424	
Hg	184.950		194.164	
Pb	168.215	220.353	405.781	

[a] Where two wavelengths are listed, the lab reported the average of results from the two wavelengths.

At UL, milled samples (0.30 g) were digested in a microwave oven with an acid matrix of 7 mL HNO$_3$ and 3 mL HCl. Trace metal grade acids were used. The microwave program was 3 min at 120 ºC and 42 min at 215 ºC. Solutions were filtered over Whitman 451 paper into weighed 50 mL volumetric flasks and diluted to the target mass. Calibration standard solutions were prepared by weight to give three calibration points per element with acid matrix matching. All solutions were measured using a radial torch ICPOES spectrometer (Spectro Analytical).

Both laboratories used linear calibration models as in Equation 5, where y = measured signal, m = slope, x_s = mass fraction of the element in the measured solution, and b = intercept.

$$y = mx_s + b \tag{5}$$

Both laboratories converted results from sample solutions to the as-received basis for pellet samples using a dilution calculation as in Equation 6, where X = mass fraction result for the element in the original pellet sample, m_s = mass of the ground sample, and m_t = mass of total solution after digestion and dilution.

$$X = x_s\,{^{m_t}}\!/\!{_{m_s}} \tag{6}$$

Results for elements in SRM 2859 are given in Table 36. Results for elements in SRM 2861 are given in Table 37. For each laboratory, each table provides a summary giving the overall mean, $\bar{X}$, the repeatability standard deviation, s, the number of samples, n, the combined standard uncertainty, u_c, and the expanded uncertainty, $U_{k=2} = 2u_c$. The combined standard uncertainty includes standard uncertainty components for repeatability of measurement, the fit of calibration data to Eq. 5, uncertainty of weighing, and uncertainty of element mass fractions in the stock calibration solutions, i.e. the SRM 3100 series solutions. These uncertainty components were combined the same way as done for XRF results. See Table 32 and Eq. 4. For an element too low to be quantified, an estimate of the limit of detection, L_D, was obtained using Equation 7. For CPSC, the Ca result from one sample was declared an outlier.

$$L_D \approx 3s + \left| \bar{X} \right| \tag{7}$$

10.1 Quality Assurance

CPSC analyzed NMIJ CRM 8123-a in pellet form, and results are given in Table 38. At the bottom of the table, the summary gives the overall mean, individual components of uncertainty (for explanations, see Table 32), and the expanded uncertainty, $U_{k=2} = 2u_c$. For an element too low to be quantified, an estimate of the limit of detection, L_D, was obtained using Equation 3. Certified values and published uncertainty estimates are listed at the bottom of the table, along with recovery values. CPSC recoveries are excellent for Cr, Cd, Hg, and Pb. Results for Fe, As, Sn, and Sb are consistent with expectations, being either not detected or very low mg/kg values. The project leader at NMIJ [14] stated that CRM 8123-a was formulated with a Ca- and Zn-containing stabilizer compound. The result for Ca is consistent with this information. The PVC was also formulated with an oil, which is likely to contain sulfur. The result for S is consistent with this information.

Table 36. Mass Fractions of Elements Quantified in Candidate SRM 2859 Using Inductively Coupled Plasma Optical Emission Spectrometry at CPSC and UL

Element:	Na (mg/kg)	S (mg/kg)	Ca (%)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
CPSC														
Mean		1138	3.51	714.8	60		< 3	< 6	75.0	1387	< 6	8	745	808
s		6.3	0.044	4.1	1				1.5	13		2	17	13
n		12	11	12	12				12	12		12	12	12
u_c		24	0.11	10	1				1.2	23		1	12	12
$U_{k=2}$		48	0.21	21	2				2.3	46		1	24	23
UL														
Mean	371	1101	3.75	754	74.4	51.5	5.8	< 10	81.7	1408	9.4	< 7	803	833
s	12	20	0.054	15	4.4	0.64	0.6		1.4	22	1.2		12	15
n	8	8	8	8	8	8	8		8	8	8		8	8
u_c	6.5	16	0.052	11	1.8	0.70	0.2		1.2	20	0.5		11	12
$U_{k=2}$	13	32	0.10	22	3.7	1.4	0.5		2.3	40	0.9		22	24

Table 37. Mass Fractions of Elements Quantified in Candidate SRM 2861 Using Inductively Coupled Plasma Optical Emission Spectrometry at CPSC and UL

Element:	Na (mg/kg)	S (mg/kg)	Ca (%)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
CPSC														
Mean		1099	3.44	48.6	53.8		23.34	231.2	65.0	1318	70.8	744	52.6	84.8
s		11	0.040	0.46	1.4		0.63	4.9	0.63	17	2.2	9	1.1	2.2
n		12	12	12	12		12	12	12	12	12	12	12	12
u_c		23	0.11	0.71	0.81		0.35	4.1	0.96	22	1.7	28	0.83	1.3
$U_{k=2}$		47	0.21	1.4	1.6		0.71	8.2	1.9	44	3.3	56	1.7	2.7
UL														
Mean	54.5	1028	3.48	54.7	70.9	< 6	28.7	271	68.4	1297	75.4	709	55.4	88.1
s	12	39	0.13	1.9	3.8		1.2	11	2.5	36	3.7	28	2.8	3.3
n	8	8	8	8	8		8	8	8	8	8	8	8	8
u_c	4.4	19	0.064	0.97	1.6		0.55	5.3	1.2	21	1.6	13	1.2	1.6
$U_{k=2}$	8.8	38	0.13	1.9	3.3		1.1	11	2.5	42	3.3	27	2.5	3.3

Table 38. Quantitative Mass Fraction Results for CRM 8123-a Using ICPOES at CPSC

Element:	S (mg/kg)	Ca (%)	Cr (mg/kg)	Fe (mg/kg)	As (mg/kg)	Se (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
Mean	183.1	0.5575	942	1.92	< 1	4.97	92.4	< 1	< 5	9.8	908	924
s	0.57	0.0058	0.50	0.11		0.71	0.25			0.87	2.7	0.49
n	3	3	3	3		3	3			3	3	3
u_m	8.1	0.038	15	0.012		0.14	1.61			0.85	17	12
p	7	6	7	7		7	7			6	7	7
u_b	3.7	0.011	19	0.038		0.099	1.8			0.20	18	18
u_s	1.8	0.0056	9.4	0.019		0.050	0.92			0.098	9.1	9.2
u_c	3.9	0.017	13	0.069		0.42	1.3			0.62	13	13
$U_{k=2}$	7.7	0.035	27	0.14		0.83	2.7			1.2	27	25
Certified			949.0				95.62				937.0	965.5
U			9.7				1.39				19.4	6.6
Recovery (%)			99				97				97	96

11. Critical Evaluation of Collected Results

Critical evaluation of all results starts with comparison of the XRF and ICPOES results, which also can be compared to the expected mass fractions from the manufacturing process. Starting with the Master Blends compositions in Table 1 and using the blending data from the extrusion process, the expected prepared mass fractions were calculated as shown in Table 39. Also shown are the collected mean values and expanded uncertainty estimates from XRF and ICPOES methods. With exceptions, all found results are close to or slightly less than the prepared values with recoveries from 75 % to 108 %. The most obvious exception is Se in SRM 2861, which is higher than the expected mass fraction by 23 % (CPSC) to 44 % (UL). For elements present in both blends *viz*. Cr, Cd, Hg, and Pb, ratios of found values between the two blends (2859/2861) agree with ratios of prepared values. This is evidence that the processes of PVC blending and quantitative analyses at three laboratories were under control, with the exception that small amounts of some ingredients were lost during manufacturing.

As additional evidence that all results for the SRMs are consistent among CPSC, UL and NIST, the results for all elements determined by the three laboratories are shown graphically in Fig. 19 for SRM 2859 and in Fig. 20 for SRM 2861. Although not all differences among results are covered by the expanded uncertainty intervals (error bars), the relative differences between labs are generally < 15 %, except Fe and As.

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Table 39. Prepared *vs*. Found Mass Fractions of Elements in PVC Blends for Candidate SRMs

Element:	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	Se (mg/kg)	Br (mg/kg)	Cd (mg/kg)	Sb (mg/kg)	Ba (mg/kg)	Hg (mg/kg)	Pb (mg/kg)
SRM 2859										
Prepared	797	58	0	0	848	84	0	0	847	844
NIST XRF	712	56	< 10	< 7	853.6	72.3	< 15	< 20	769	797
$U_{k=2}$	11	-	-	-	6.0	1.1	-	-	10	5.7
Recovery, %	89	97	-	-	101	86	-	-	91	94
CPSC ICPOES	714.8		< 3	< 6		75.0	< 6	8	745	808
$U_{k=2}$	21		-	-		2.3	-	1	24	23
Recovery, %	90		-	-		89	-	-	88	96
UL ICPOES	754	51.5	5.8	< 10		81.7	9.4	< 7	803	833
$U_{k=2}$	22	1.4	0.5	-		2.3	0.9	-	22	24
Recovery, %	95	89	-	-		97	-	-	95	99
SRM 2861										
Prepared	60	0	27	188	0	76	73	869	63	92
NIST XRF	49.25	< 6	19.82	243.8	< 10	62.1	67.0	742.2	57.05	92.2
$U_{k=2}$	0.82	-	0.98	2.8	-	1.0	1.1	8.9	0.69	4.2
Recovery, %	82	-	75	129	-	81	92	85	91	100
CPSC ICPOES	48.6		23.34	231.2		65.0	70.8	744	52.6	84.8
$U_{k=2}$	1.4		0.71	8.2		1.9	3.3	56	1.7	2.7
Recovery, %	81		88	123		85	97	86	84	92
UL ICPOES	54.7	< 6	28.7	271		68.4	75.4	709	55.4	88.1
$U_{k=2}$	1.9	-	1.1	11		2.5	3.3	27	2.5	3.3
Recovery, %	92	-	108	144		89	104	82	88	96
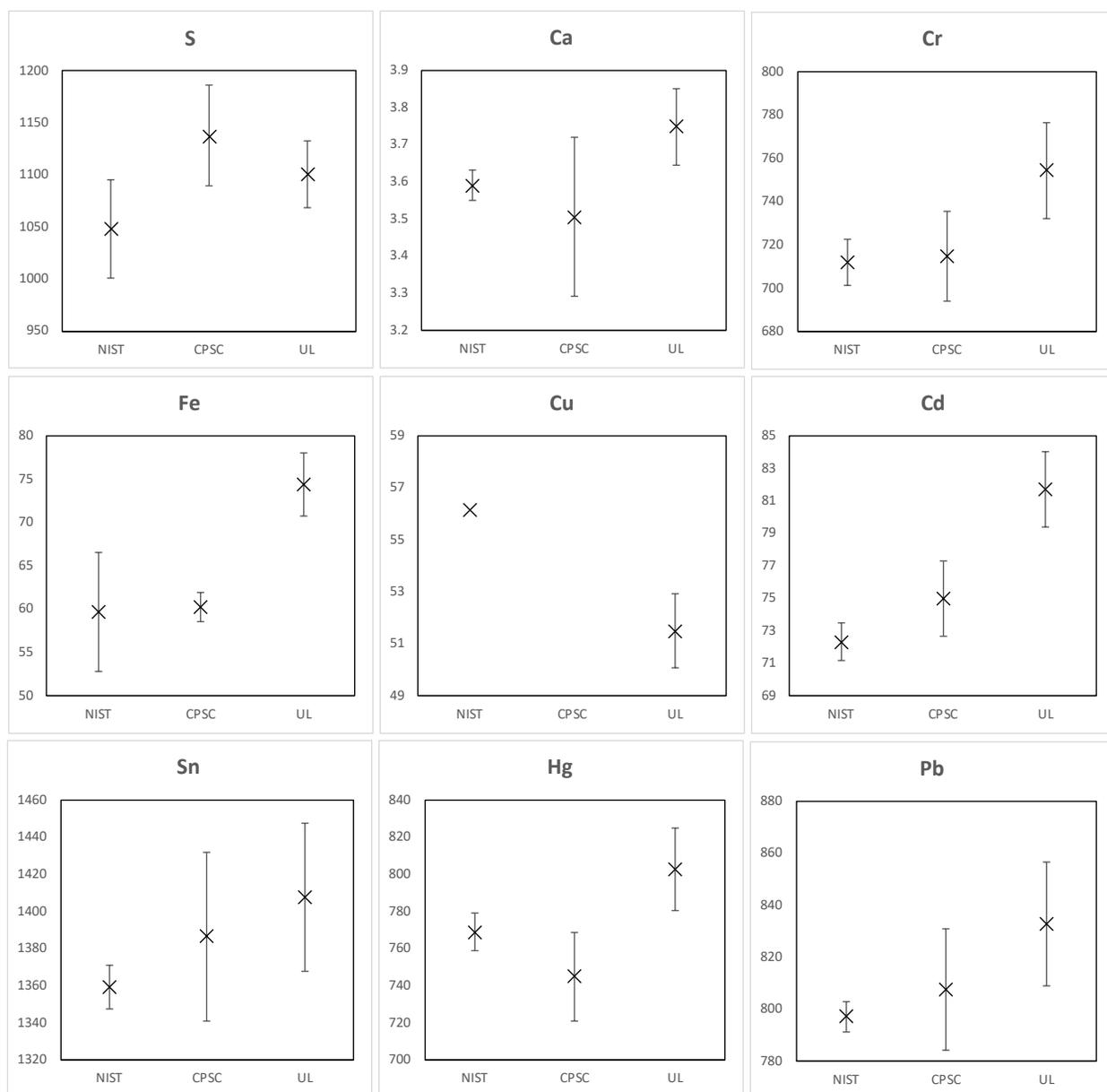
Fig. 19. Comparisons of mean results and expanded uncertainty estimates for elements found by collaborating labs in SRM 2859. Note, Cu by NIST is for information only, i.e. no uncertainty estimate was provided.
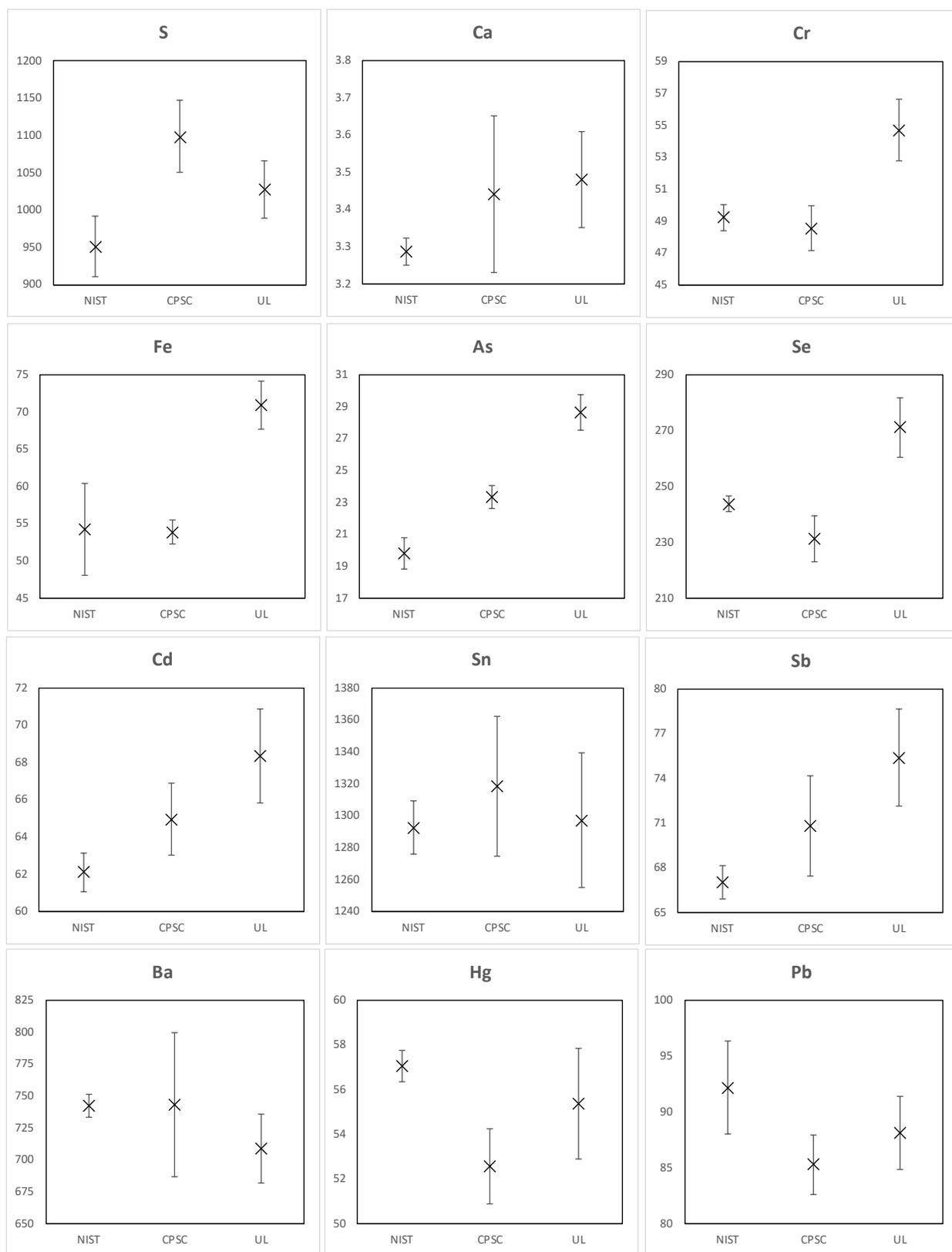
Fig. 20. Comparisons of mean results and expanded uncertainty estimates for elements found by collaborating labs in SRM 2861.

12. Statistical Consensus Analyses

SRM 2859 and SRM 2861 are PVC materials for which 13 constituents were measured with two to four methods. Three constituents were measured with a single method. Statistical approaches were applied to calculate estimates of the consensus values for the constituents. The method using the DerSimonian-Laird (DSL) consensus value estimator [15] and the Bootstrap uncertainty estimator [16] was chosen for certified and reference value assignments.

For measurements where multiple methods were used, the values and uncertainties (certified or reference) were calculated by combining the results from all measurement methods using the following model in Equation 9:

$$y_{ij} = \mu + m_i + \varepsilon_{ij}; \quad i = 1, 2, \ldots, n_{mm}; \quad j = 1, 2, \ldots, n_i \tag{9}$$

where i indexes measurement methods, j indexes replication within measurement method, n_{mm} represents the number of measurement methods, n_i represents the number of replications within measurement method, $m_i \overset{iid}{\sim} N(0,\sigma_m^2)$, and $\varepsilon_{ij} \overset{iid}{\sim} N(0,\sigma_i^2)$ independently of m_i. The values (certified or reference) are estimates of μ, say $\hat{\mu}$, in Eq. 9. The uncertainties were determined using the Bootstrap method. The certified consensus values, standard uncertainties, coverage factors, and expanded uncertainties are listed in Table 39 for SRM 2859 and Table 41 for SRM 2861. Tables 39 and 41 are based only on uncertainty components estimated using a type A (statistical) approach.

For some constituents, measurements from only a single measurement method were taken. The values and uncertainties were calculated using the following model in Equation 10:

$$y_i = \mu + \varrho_i; \quad i = 1, 2, \ldots, n \tag{10}$$

where i indexes replication, n represents the number of replications, and $\varepsilon_i \overset{iid}{\sim} N(0,\sigma^2)$. The reference value is an estimate of μ, say $\hat{\mu}$, in Eq. 10, which is just the mean of the y_i values. The expanded uncertainty is the half width of a 95 % Student's t confidence interval for μ. These single-method results are reported in Table 40 for SRM 2859 and Table 42 for SRM 2861. the mean values were assigned as reference values.

The reader must be aware that the values listed in these tables are not the official assigned values for the SRMs. The certificates of analysis are the only official documents for assigned values, uncertainty estimates, and instructions for use. Users are cautioned against relying on results from single methods given in this publication. Individual test methods are subject to biases however small, and their uncertainty estimates do not encompass all components of uncertainty associated with the best available estimate of the true value of each measurand.

Table 40. DSL-Bootstrap Results for Multiple Method Data for SRM 2859
Mean and uncertainty values are mass fractions in %.

Constituent	Consensus Mean	Bootstrap Uncertainty	Coverage Factor, k	Bootstrap Expanded Uncertainty
S	0.1130	0.0023	2.06	0.0048
Ca	3.651	0.033	1.98	0.065
Cr	0.0713	0.00079	1.92	0.0015
Fe	0.0064	0.0015	1.96	0.0029
Cu	0.0054	0.0016	1.97	0.0032
As	0.0031	0.0012	1.97	0.0024
Se	0.0043	0.00081	1.97	0.0016
Cd	0.0763	0.0020	1.96	0.0038
Sn	0.1366	0.0019	2.01	0.0039
Sb	0.0052	0.0010	1.96	0.0020
Ba	0.0053	0.0012	1.97	0.0024
Hg	0.0770	0.0015	2.09	0.0032
Pb	0.0799	0.0015	2.08	0.0032

Table 41: Results for Single Method Data for SRM 2859
Values for μ are mass fractions in %.

Constituent	Mean $\hat{\mu}$	Standard Uncertainty, μ_c	Coverage Factor, t	Expanded Uncertainty, $t\mu_c$
Na	0.037	0.004	2.31	0.010
Cl	32.80	0.06	2.00	0.12
Br	0.0854	0.0010	2.00	0.0002

Table 42. DSL-Bootstrap Results for Multiple Method Data for SRM 2861
Mean and uncertainty values are mass fractions in %.

Constituent	Consensus Mean	Bootstrap Uncertainty	Coverage Factor, k	Bootstrap Expanded Uncertainty
S	0.10334	0.00028	1.97	0.00055
Ca	3.391	0.035	1.96	0.069
Cr	0.0050	0.00060	1.97	0.0012
Fe	0.00590	0.00018	1.97	0.00035
Cu	0.00013	0.00017	1.99	0.00035
As	0.00239	0.00015	1.96	0.00030
Se	0.02440	0.00023	1.97	0.00045
Cd	0.00649	0.000091	1.97	0.00018
Sn	0.12941	0.00022	2.16	0.00048
Sb	0.00707	0.00013	1.96	0.00026
Ba	0.07422	0.00012	2.06	0.00026
Hg	0.00550	0.00013	1.96	0.00025
Pb	0.00884	0.00019	1.96	0.00037

Table 43. Results for Single Method Data for SRM 2861
Values for μ are mass fractions in %.

Constituent	Mean $\hat{\mu}$	Standard Uncertainty, μ_c	Coverage Factor, t	Expanded Uncertainty, $t\mu_c$
Na	0.0055	0.00044	2.31	0.0010
Cl	34.7	0.3	2.00	0.5
Br	0.00045	0.00002	2.00	0.00004

13. Quantitative XES Results for Hexavalent Chromium

Hexavalent and trivalent Cr compounds used in production of the PVC SRM materials and selected other plastics were measured to acquire reference spectra, as shown in Fig. 21. In addition, the Cr K-L$_{2,3}$ spectrum of a 25 μm thick stainless-steel shim was frequently collected to ensure a consistent energy scale throughout the study and to aid in the alignment of the plastic samples. Care was needed to determine the Cr(VI) species fraction for samples that exhibited radiation damage. This was addressed by spinning samples to distribute the radiation dose over a sample area approximately 28 times larger than that of a static sample. The scans averaged to represent the sample were then limited to those occurring before noticeable change in spectral shape or measured Cr(VI) content. The latter was assessed by examining the Cr(VI) fraction as a function of scan number and selecting consecutive points statistically consistent with no photoinduced reduction. As a result, the first eight scans were used for all PVC materials for which a quantitative result is reported.

Determination of the Cr(VI) fraction was accomplished via a least-squares regression analysis. First, the trivalent and hexavalent reference spectra were background corrected and normalized to the total number of counts in the integration range. The reference spectra were then fit to a pair of interpolating functions. Next, the spectrum of a sample with unknown chromium speciation was likewise background corrected and integral normalized. The portion of the unknown spectrum between 5400 eV and 5420 eV was fit by a linear combination of the interpolating functions representing the reference spectra with the Cr(VI) species fraction as the optimization parameter.

Sources of uncertainty affecting the fit were quantified, including the choices of reference spectra and the variability in the XES energy scale upon sample exchange. Bias introduced with the choice of reference compound was estimated by performing fits with all possible combinations of references and calculating a corresponding uncertainty in the result. Bias accompanying the imperfect reproducibility of the XES energy scale was estimated by sampling the maximal energy shifts introduced by sample exchange reported during instrument development. This was done by displacing an employed reference spectrum 10 meV lower, not at all, or 10 meV higher in energy. Displacements were done to both the trivalent and hexavalent references, and after considering all nine possible permutations, the standard deviation of the resulting fit parameters was taken as the resulting uncertainty.

The reference mass fraction value for Cr(VI) in SRM 2859 is 0.0480 % with an expanded uncertainty estimate of 0.0066 %. The information value for Cr(VI) in SRM 2861 is given as Not Detected. In this case, the mass fraction of total Cr in SRM 2861 is so low, it is near the detection limit. It was not possible to estimate the limit of detection for Cr(VI) under the circumstances [5]. Traceability of values is to the derived SI unit of mass fraction, expressed as %, established using values for high-purity compounds assayed by the suppliers and assumed to be stoichiometric in composition and the previously determined certified values for total Cr.
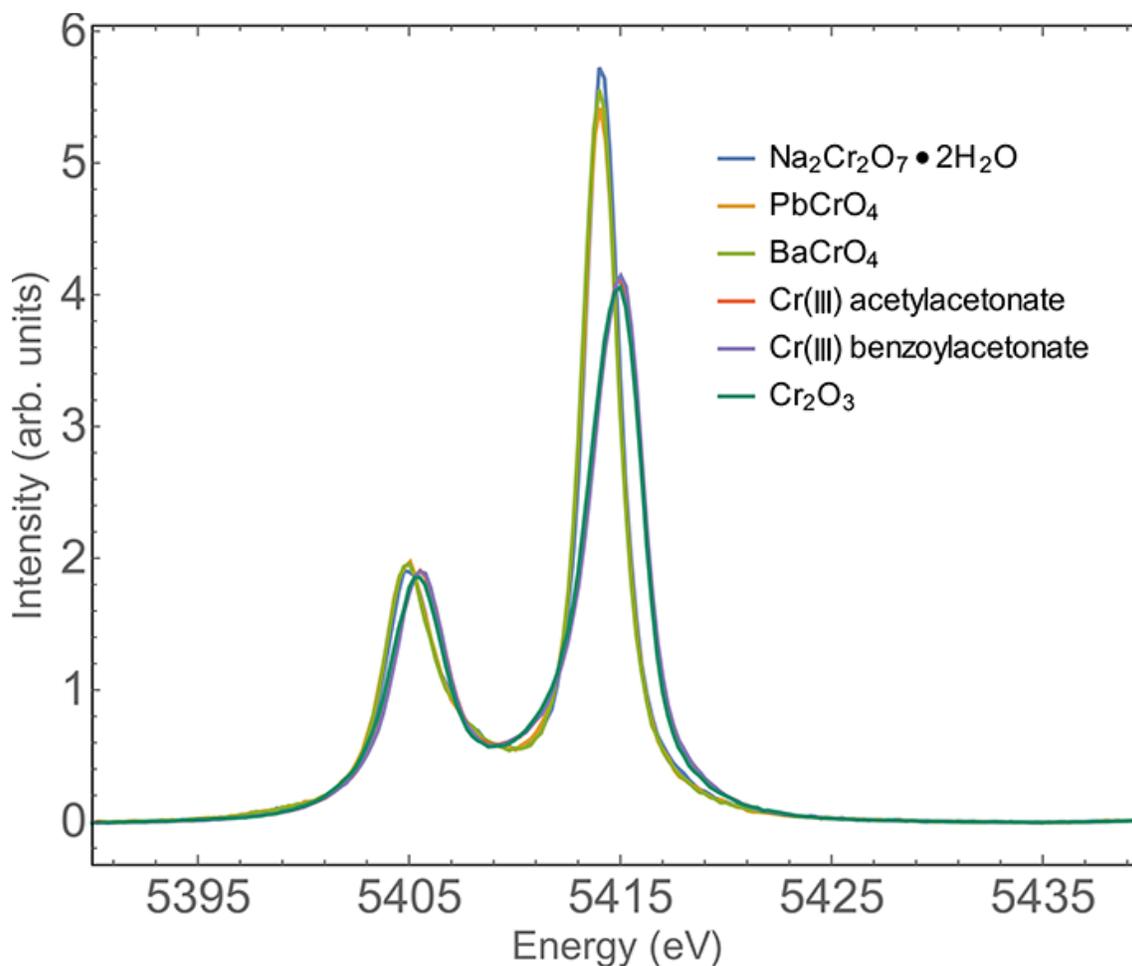
Fig. 21. Cr K-L$_{2,3}$ XES of selected trivalent and hexavalent reference Cr compounds after background correction and integral normalization. Note, the spectrum of Cr(III) acetylacetonate is nearly identical to that of Cr(III) benzoylacetonate and is hidden from view.

14. Conclusions

The materials for SRM 2859 and SRM 2861 exhibit sufficiently low levels of heterogeneity based on WDXRF measurements of melt pressed disks. Both within-bottle heterogeneity and among-bottle variance are acceptable within the limitations of the experimental design. Macro-scale heterogeneity was observed for certain elements, and it was considered as a source of uncertainty in the calculations of consensus values and estimated uncertainties for certified and reference values. The relatively wide area WDXRF measurements are insensitive to heterogeneity observed at the micrometer level, caused by insufficient mixing of ingredients. The microXRF measurements show the heterogeneity at masses much less than that of single pellets. However, for typical analyses by methods such as WDXRF, inductively-coupled plasma optical emission spectrometry and the like, the two PVC materials are acceptable when using multiple pellets. It was necessary to explain the different levels of macro-scale and micro-scale heterogeneity as part of the instructions for use of these PVC SRMs. See the Supplemental Information section at the end of this report for reproductions of the certificates.

A new process was developed to enable labs to calibrate XRF test methods for plastics and establish traceability of values to the International System of Units. The process works by mixing NIST Spectrometric Solution SRMs into virgin, powder polymers and melt pressing into disks. Samples are also melt pressed into disks. The calibration procedure can be used with ASTM international F2617-17 and similar standard test methods. It is also expected to work with other types of plastic that can be obtained as virgin powders and melt pressed.

Analytical results were obtained from NIST and two collaborating laboratories. The results agree sufficiently well for the purpose, and are consistent with the formulated values. All results were used in calculations of consensus values for assignment as certified or reference values.

A new test method for mass fraction of Cr(VI) was developed and applied to assign a reference value for the mass fraction of Cr(VI) in SRM 2859. No Cr(VI) was detected in SRM 2861. Some or all Cr(VI) was reduced in each PVC SRM.

New NIST SRM 2859 Restricted Elements in Polyvinyl Chloride and SRM 2861 Restricted Elements in Polyvinyl Chloride are available as extruded pellets supplied in bottles of 25 g each. The two SRMs cover elements restricted by the U.S. Consumer Product Improvement Act of 2008, the European Union RoHS Directive, and similar regulations worldwide.

Acknowledgements

References

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APPENDIX A: SUPPLEMENTARY INFORMATION

Unofficial copies of the Certificates of Analysis are provided below. The official certificates are issued with each unit of the SRM and can be obtained by free download from the NIST SRM catalog website at www.nist.gov/srm.

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2859

Restricted Elements in Polyvinyl Chloride

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis of polyvinyl chloride (PVC) and materials of similar matrix for restricted, additive and tramp element contents. It can be used to validate value assignment of in-house reference materials. A unit of SRM 2859 consists of one bottle containing approximately 25 g of PVC pellets.

Certified Mass Fraction Values: Certified values for constituents of SRM 2859 are reported in Table 1 as mass fractions of the elements in a PVC matrix [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been taken into account [2]. A certified value is the present best estimate of the true value. The certified values are the measurands and are metrologically traceable to the SI derived unit of mass fraction (expressed as percent). The expanded uncertainty estimates are expressed at a confidence level of approximately 95 %.

Table 1. Certified Mass Fraction Values for SRM 2859 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Cadmium (Cd)	0.00734	0.00044
Calcium (Ca)	3.603	0.065
Chromium (Cr)	0.0716	0.0016
Iron (Fe)	0.00635	0.00095
Lead (Pb)	0.07982	0.00096
Mercury (Hg)	0.07695	0.00069
Sulfur (S)	0.1087	0.0052
Tin (Sn)	0.1362	0.0018

Expiration of Certification: The certification of **SRM 2859** is valid, within the measurement uncertainty specified, until **01 July 2024**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). Reference values are expected also to remain valid within this period. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of technical measurements for certification was performed by J.R. Sieber of the NIST Chemical Sciences Division.

Statistical consultation for this SRM was provided by N.A. Heckert of the NIST Statistical Engineering Division.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 01 March 2019
Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

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Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Polyvinyl chloride pellets may be analyzed either in as-received form, cryogenically ground to powder for methods requiring dissolution, or melt pressed for methods that require a larger area of measurement, such as X-ray fluorescence spectrometry (XRF). To relate analytical determinations to the certified values in this Certificate of Analysis, a minimum test portion of 100 mg should be used when it has been prepared as powder. See below for additional information on melt pressing and exposure to X-rays. A bottle containing unused material should be recapped immediately and stored at room temperature away from light.

To use the uncertainty estimates given in this certificate, divide the expanded uncertainty by $k = 2$ to obtain the combined standard uncertainty. The effective degrees of freedom of the combined standard uncertainty are ≥ 60.

Heterogeneity of SRM 2859 is such that measurements of very small quantities will be subject to high variance. The element Fe is characterized by discrete locations of high concentrations. These locations range in size from approximately 50 µm to several hundred micrometers, and they may contain 10 times to 100 times the overall mass fraction of the element. Multiple measurements of small spots on a sample may exhibit widely varying results. To obtain a test result representative of the overall composition of SRM 2859, the user must make measurements of different locations until the mean of the measurements and the standard deviation no longer change.

CAUTION TO USERS

Polyvinyl chloride is damaged by exposure to X-rays of sufficient power density for a sufficient duration. When radiation damage is suspected, do not make repeat measurements of the same location of a specimen. Both microbeam XRF and high-power wavelength dispersive XRF spectrometers use direct excitation and cause sufficient damage to alter the composition of the PVC. An energy dispersive XRF spectrometer of the secondary target design may not damage the PVC. Damage from irradiation is characterized by discoloration of the PVC that may be accompanied by a faint odor of burned material. Sample mass loss may be observed. Excessive irradiation was observed to cause loss of Cl and Hg from SRM 2859 as well as reduction of the hexavalent Cr originally added as $Na_2Cr_2O_7$ prior to extrusion. Losses of Cl and Hg can be observed as decreasing X-ray count rates from repeat measurements. Increasing count rates for Ca were observed when Cl was lost.

ADDITIONAL CONSTITUENTS: Noncertified values are provided for the following additional constituents in SRM 2859.

Reference Mass Fraction Values: A reference value is a noncertified value that is the present best estimate of the true value based on available data; however, the value does not meet the NIST criteria for certification and is provided with associated uncertainties that may reflect only measurement repeatability, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [2].

A reference value for bromine in SRM 2859 is reported in Table 2 as the mass fraction of total Br in the PVC matrix. The reference value for Br in SRM 2859 was determined at NIST using XRF. The reference value is metrologically traceable to the SI derived unit of mass fraction (expressed as percent). The associated uncertainty is calculated as $U = k u_c$ where u_c is the combined standard uncertainty for the XRF test method, and the coverage factor, $k = 2$, was determined from the Student's t-distribution corresponding to the 95 % confidence level and to $(n - 1)$ degrees of freedom, where $n = 64$ is the number of determinations on which the mean value is based.

A reference value for hexavalent chromium in SRM 2859 is reported in Table 2 as a mass fraction of Cr^{+6} species in the PVC matrix. The reference value for hexavalent Cr in SRM 2859 was determined using laboratory-based, high-resolution XRF [6]. The reference value is metrologically traceable to the amount of Cr^{+6} species in commercially-available, high-purity $Na_2Cr_2O_7$ through measurements of the fluorescent X-rays in the energy region 5395 eV to 5435 eV attributable to atoms in the Cr^{+6} oxidation state. The associated uncertainty is calculated as $U = k u_c$, where u_c is the combined standard uncertainty for the XRF test method, and the coverage factor was chosen as $k = 2$ to approximate a 95 % confidence level.

Table 2. Reference Mass Fraction Value for SRM 2859 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Bromine (Br)	0.0854	0.0015
Hexavalent Chromium (Cr^{+6})	0.0480	0.0066

Information Mass Fraction Values: Information values for constituents in SRM 2859 are reported as mass fractions in Table 3. An information value is a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2]. Information values cannot be used to establish metrological traceability. The information values reported for Cl, Cu and Na were determined using a single test method at one laboratory: Cl by XRF; Cu and Na by inductively coupled plasma optical emission spectrometry (ICPOES). The values listed for As, Ba, Sb, and Se are the estimated limits of detection of the test methods. These four elements were not added intentionally to this PVC formulation.

Table 3. Information Mass Fraction Values for SRM 2859 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)
Antimony (Sb)	<0.001
Arsenic (As)	<0.001
Barium (Ba)	<0.001
Chlorine (Cl)	33
Copper (Cu)	0.0054
Selenium (Se)	<0.001
Sodium (Na)	0.037

PREPARATION AND ANALYSIS[5]

The material for SRM 2859 was prepared by combining a master blend with a dry blend in a mixer at 85 ºC, followed by extrusion at 175 ºC, cooling in a water bath, and chopping, then a second extrusion, cooling, and chopping. Blending and extrusion were performed by Polymers Center of Excellence (Charlotte, NC). The master blend was prepared from virgin PVC powder to which organometallic compounds of Ba, Cd, Hg, and Pb, an aqueous solution of $Na_2Cr_2O_7$ (containing a surfactant), and a copper phthalocyanine bromide dye were added. The dry blend consisted of PVC with added $CaCO_3$ and methyltin mercaptide. The approximate density of SRM 2859 is 1.3 g/cm^3. The PVC pellets were blended and bottled at NIST.

Homogeneity testing was performed at NIST using XRF to measure disks made from 6.2 g of pellets melt-pressed at 175 ºC. Additional evaluation of heterogeneity was performed using microXRF at NIST. Material heterogeneity was sufficiently low for value assignment. Quantitative determinations were done at NIST by XRF after melt pressing and at collaborating laboratories by ICPOES after cryogenic grinding and microwave-assisted acid digestion. Calibrations for all constituents, except Br and Cl, were created using NIST SRM 3100 series spectrometric solutions. Bromine by XRF was calibrated using high-purity NaBr, and Cl was calibrated using commercial reference materials for PVC.

Each certified value is a weighted mean of the results from the three methods [3]. The uncertainty listed with each certified value is an expanded uncertainty about the mean [4], with coverage factor, $k = 2$, calculated following the ISO/JCGM Guide [5].

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[1] Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Analyses leading to the certification of this SRM were performed at NIST by J.R. Sieber, J.L. Molloy, C. Bibb, and M. Boyce of the NIST Chemical Sciences Division. Analytical determinations were also performed by D. Cobb, U.S. Consumer Product Safety Commission (CPSC) (Rockville, MD); C.S. Helt and K. Leung, Underwriters Laboratories (Melville, NY); and E.P. Jahrman and G.T. Seidler, University of Washington (Seattle, WA).

NOTICE TO USERS

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REFERENCES

[1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at https://www.nist.gov/pml/pubs/sp811/index.cfm (accessed Mar 2019).

[2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition 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: Washington, DC (2000); available at https://www.nist.gov/srm/upload/SP260-136.PDF (accessed Mar 2019).

[3] DerSimonian, R. and Laird, N.; *Meta-analysis in Clinical Trials*; Control Clin. Trials, Vol. 7, pp. 177–188 (1986).

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[5] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Mar 2019); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Mar 2019).

[6] Jahrman, E.P.; Seidler, G.T.; Sieber, J.R.; *Determination of Hexavalent Chromium Fractions in Plastics Using Laboratory-Based, High-Resolution X-ray Emission Spectroscopy*; Anal. Chem., Vol. 90, pp. 6587-6593 (2018).

Certificate Revision History: 01 March 2019 (Added reference value for hexavalent Cr mass fraction; editorial changes); 10 August 2017 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2861

Restricted Elements in Polyvinyl Chloride

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis of polyvinyl chloride (PVC) and materials of similar matrix for restricted, additive and tramp element contents. It can be used to validate value assignment of in-house reference materials. A unit of SRM 2861 consists of one bottle containing approximately 25 g of PVC pellets.

Certified Mass Fraction Values: Certified values for constituents of SRM 2861 are reported in Table 1 as mass fractions of the elements in a PVC matrix [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been taken into account [2]. A certified value is the present best estimate of the true value. The certified values are the measurands and are metrologically traceable to the SI derived unit of mass fraction (expressed as percent). The expanded uncertainty estimates are expressed at a confidence level of approximately 95 %.

Table 1. Certified Mass Fraction Values for SRM 2861 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Antimony (Sb)	0.00678	0.00040
Arsenic (As)	0.00239	0.00051
Barium (Ba)	0.0740	0.0013
Cadmium (Cd)	0.00651	0.00036
Calcium (Ca)	3.33	0.14
Chromium (Cr)	0.00504	0.00031
Iron (Fe)	0.0058	0.0012
Lead (Pb)	0.00883	0.00047
Mercury (Hg)	0.00556	0.00030
Selenium (Se)	0.02441	0.00032
Sulfur (S)	0.1006	0.0090
Tin (Sn)	0.1294	0.0010

Expiration of Certification: The certification of **SRM 2861** is valid, within the measurement uncertainty specified, until **01 July 2024**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). Reference values are expected also to remain valid within this period. Periodic recalibration or recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 01 March 2019
Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

Coordination of technical measurements for certification was performed by J.R. Sieber of the NIST Chemical Sciences Division.

Statistical consultation for this SRM was provided by N.A. Heckert of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Polyvinyl chloride pellets may be analyzed either in as-received form, cryogenically ground to powder for methods requiring dissolution, or melt pressed for methods that require a larger area of measurement, such as X-ray fluorescence spectrometry (XRF). To relate analytical determinations to the certified values in this Certificate of Analysis, a minimum test portion of 100 mg should be used when it has been prepared as powder. See below for additional information on melt pressing and exposure to X-rays. A bottle containing unused material should be recapped immediately and stored at room temperature away from light.

To use the uncertainty estimates given in this certificate, divide the expanded uncertainty by $k = 2$ to obtain the combined standard uncertainty. The effective degrees of freedom of the combined standard uncertainty are ≥60.

Heterogeneity of SRM 2861 is such that measurements of very small quantities will be subject to high variance. The elements Ba, Fe, and Se are characterized by discrete locations of high concentrations. These locations range in size from approximately 50 μm to several hundred micrometers, and they may contain 10 times to 100 times the overall mass fraction of the element. Multiple measurements of small spots on a sample may exhibit widely varying results. To obtain a test result representative of the overall composition of SRM 2861, the user must make measurements of different locations until the mean of the measurements and the standard deviation no longer change.

CAUTION TO USERS

Polyvinyl chloride is damaged by exposure to X-rays of sufficient power density for a sufficient duration. When radiation damage is suspected, do not make repeat measurements of the same location of a specimen. Both microbeam XRF and high power wavelength dispersive XRF spectrometers use direct excitation and cause sufficient damage to alter the composition of the PVC. An energy dispersive XRF spectrometer of the secondary target design may not damage the PVC. Damage from irradiation is characterized by discoloration of the PVC that may be accompanied by a faint odor of burned material. Sample mass loss may be observed. Excessive irradiation was observed to cause loss of Cl and Hg from SRM 2861 as well as reduction of the hexavalent Cr originally added as $Na_2Cr_2O_7$ prior to extrusion. Losses of Cl and Hg can be observed as decreasing X-ray count rates from repeat measurements. Increasing count rates for Ca were observed when Cl was lost.

ADDITIONAL CONSTITUENTS: Noncertified values are provided for the following additional constituents in SRM 2861.

Information Mass Fraction Values: Information values for constituents in SRM 2861 are reported as mass fractions in Table 2. An information value is a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2]. Information values cannot be used to establish metrological traceability. The information values reported in Table 2 for Cl and Na were determined using a single test method at one laboratory: Cl by XRF and Na by inductively coupled plasma optical emission spectrometry (ICPOES). The values listed for Br and Cu are the estimated limits of detection of both test methods. These two elements were not added intentionally to this PVC formulation. The information provided for hexavalent Cr was determined using laboratory-based, high resolution XRF [6].

Table 2. Information Mass Fraction Values for SRM 2861 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)
Bromine (Br)	<0.001
Chlorine (Cl)	35
Copper (Cu)	<0.0003
Hexavalent Chromium (Cr^{+6})	Not Detected[a]
Sodium (Na)	0.006

[a] The term Not Detected indicates the test method is not capable of providing an estimate of the limit of detection for Cr^{+6} in this material. An explanation and demonstration are provided in the supplemental information for reference [6].

PREPARATION AND ANALYSIS[6]

The material for SRM 2861 was prepared by combining a master blend with a dry blend in a mixer at 85 ºC, followed by extrusion at 175 ºC, cooling in a water bath and chopping, then a second extrusion, cooling, and chopping. Blending and extrusion were performed by Polymers Center of Excellence (Charlotte, NC). The master blend was prepared from virgin PVC powder to which organometallic compounds of Ba, Cd, Hg, and Pb, an aqueous solution of $Na_2Cr_4O_7$ (containing a surfactant), and a copper phthalocyanine bromide dye were added. The dry blend consisted of PVC with added $CaCO_3$ and methyltin mercaptide. The approximate density of SRM 2861 is 1.3 g/cm^3. The PVC pellets were blended and bottled at NIST.

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REFERENCES

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