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Assessing the microscale heterogeneity in Standard Reference Material 4600 Surrogate Post-detonation Urban Debris

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ABSTRACT

Nondestructive microbeam X-ray fluorescence (μXRF) spectrometry has been used to investigate the elemental microheterogeneity in a nuclear forensics reference material (RM), NIST SRM 4600 Surrogate Post-detonation Urban Debris. Using a principal component analysis (PCA) model, results indicate the majority of elements appear homogeneous; however, zinc (Zn) exhibits microscale heterogeneity for this SRM. To minimize contributions to the measurement uncertainty from elemental microheterogeneity, a minimum sample mass of 24 mg is recommended for analysis.

1. Introduction

Microanalytical techniques can be powerful tools in forensic investigations because the analysis of distinct chemical signatures of trace elements and contaminants in materials may provide information for source attribution. For applications in nuclear forensics investigations however, to date, limited reference materials (RMs) exist for users in this community to validate the microanalytical approaches for such measurements. This community requires Standard Reference Materials (SRMs) with suitable elemental microscale heterogeneity. The production of SRM 4600 Surrogate Post-detonation Urban Debris may offer a RM for the post-detonation nuclear forensics community to validate their microanalytical instruments/techniques. SRM 4600, produced by the National Physical Laboratory (NPL), UK through collaboration with National Institute of Standards and Technology (NIST) and the Federal Bureau of Investigation (FBI) Laboratory, USA, contains a natural uranium (U) composition in a vitrified material, with a total mass fraction of natural U of approximately 60 μg/g. The primary objective of this SRM is to offer a material that provides the ability for laboratories to develop and validate their methods for the measurement of the activation products that result from exposure to neutron irradiation of a nuclear detonation. Thus, the elemental composition of this SRM simulates the minerals and metals representative of building materials (e.g., concrete, glass, and steel) that would be exposed to a nuclear detonation and whose resulting activation products would be found in rubble samples collected as forensic evidence. Upon neutron irradiation from a nuclear event, the natural U could also yield fission products (Mann et al., 2016; Fallon et al., 2018).

The growing use of microanalytical techniques (e.g. laser ablation (LA)) inductively coupled plasma mass spectrometry (ICPMS),

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secondary ion mass spectrometry (SIMS), resonance ionization mass spectrometry (RIMS), etc.) for elemental and isotopic analysis of solid materials necessitates RMs to be evaluated and characterized for elemental microheterogeneity. Isolated microscale areas chemically enriched or depleted in the analyte of interest can result in increased measurement variability with decreasing sample mass. RMs, however, are typically issued with a minimum sample mass - at which the reported/certified concentration and/or isotope ratio values are considered valid. These minimum sample masses are typically 100 mg or higher, with recent work assessing microscale heterogeneity by microbeam X-ray fluorescence (μXRF) spectrometry yielding a methodology for reducing this quantity (Zeisler, 1999; Molloy and Sieber, 2008). To achieve comparability between measurement communities requires sample amounts of material spanning several orders of magnitude from single micrograms to milligrams (ISO Guide 35:2017(E); ISO 17034:2016(E)). RM suppliers for the increasingly used microanalytical techniques are faced with the challenge of producing and delivering RMs that are suitably homogeneous at sample masses at the level of analytical interest.

The intended use for SRM 4600 is for macroscale measurement techniques, primarily mass spectrometry for amount content and counting techniques for the measurement of massic activity. The homogeneity of this material was not prepared with the microscale analytical techniques in mind, but the potential interest in its use with microanalytical techniques prompted further investigation. In this work, we used a combined nondestructive μXRF spectrometry and principal component analysis (PCA) methodology developed by Molloy and Sieber, 2008, 2011 to assess the microheterogeneity of the SRM 4600 surrogate debris material. This methodology has been used for rapid detection and analysis of actinides in nuclear fallout debris and other nuclear forensic applications (Castro, 2016). Using this approach, we assess elements exhibiting potential microheterogeneity and provide an estimate of the minimum sample mass recommended for elemental microheterogeneity to have negligible contribution to the measurement uncertainty.

1.1. Experimental

The assessment of the elemental microheterogeneity of SRM 4600 was a collaborative endeavor between the NIST and the FBI Laboratory, with μXRF analyses carried out by the Counterterrorism and Forensic Science Research Unit (CFSRU) (now Research and Support Unit (RSU)) at the FBI Laboratory Division in Quantico, VA. PCA analysis of the μXRF data was performed by the Inorganic Chemical Metrology Group of the Chemical Sciences Division at NIST in Gaithersburg, MD.

Assigning certified values to NIST SRMs requires assessment of the capabilities of collaborating laboratories participating in the SRM characterization process (Beauchamp et al., 2020). In this case, NIST provided two well-characterized SRMs – 2702 Inorganics in Marine Sediment and 2703 Sediment for Solid Sampling (Small Sample) Analytical Techniques (Molloy and Sieber, 2008) – to test the analysis methodology and the FBI Laboratory CFSRU's capabilities to measure materials similar to the surrogate debris SRM 4600 using μXRF instrumentation in their laboratory (Horiba XGT-7000 X-ray analytical microscope). These two SRMs are the same marine sediment material; however, SRM 2703 has been further homogenized for microscale elemental measurement technique validation. The purpose of this capabilities assessment was to identify if the difference in microheterogeneity of the two SRMs could be detected using the instrumentation and analysis approach. It was not intended to assess the accuracy of quantitative analysis nor to positively identify either material.

Once the analysis approach was determined to be consistent with results observed at NIST and that the FBI Laboratory CFSRU met the NIST criteria for analysis capability, eight bottles of SRM 4600 were selected randomly from the production lot of 100 bottles and provided for elemental microheterogeneity characterization.

1.2. Sample preparation

1.2.1. Testing SRMs 2702 & 2703

Duplicate samples of 2.0 g–2.5 g from single bottles of SRMs 2702 and 2703 were taken for μXRF capability and methodology analysis. Samples were dried overnight in a 105 °C oven and pressed into pellets with a stainless steel die at 10 tons for 20 s using a SPEX 3650 X-Press (SPEX SamplePrep, Metuchen, NJ) (Fig. 1) (Watson, 1996). Pellet diameters were approximately 32 mm and pellet thicknesses were about 2 mm.

1.2.2. SRM 4600

Because SRM 4600 is vitrified material (Fig. 2) and limited quantity was available, pressing the samples into pellets similar to that for SRM 2702 and SRM 2703 proved difficult. Therefore, a "sandwich" method was developed and tested for this application. Duplicate samples of approximately 1.5 g were taken from the eight bottles of SRM 4600 and were prepared into a "sandwich" configuration to limit loss of sample (Fig. 3) (Fallon et al., 2018). For this approach, the sample cup is inverted and used as a platform to hold the sample between two Mylar® film sheets. The sample cup is lined with a sheet of SPEX 6 μm (0.25 mil) Mylar® film and secured in place with a thin plastic ring. A small well is pushed into the Mylar® and the sample is gently added. A second piece of Mylar® film is placed over the sample and secured with a thicker plastic ring. Both the bottom and top films are gently pulled taut, starting with the lower film and taking care to ensure that the entire area of the Mylar® film is covered by the sample and as flat as possible. The well formed in the bottom sheet of mylar in addition to ensuring the Mylar pieces are taught and flush against the sample has a self-leveling effect, giving a degree of uniform thickness to the sample. The resulting samples were 25 mm in diameter and approximately 1 mm in thickness (Fig. 4), infinitely thick to the X-rays based on the nominal mass fractions of elements in the material (Henke et al., 1993). Preparing a

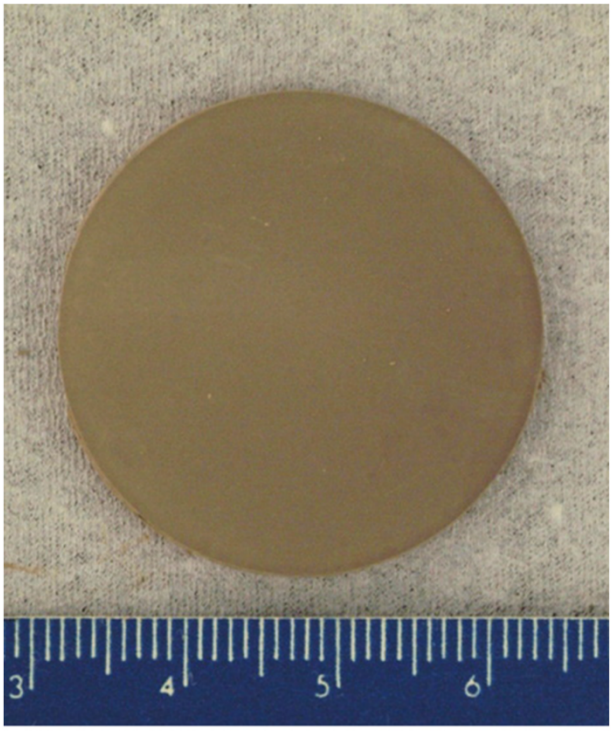

Fig. 1. Pressed pellet sample of SRM 2702 with approximate dimensions of 32 mm diameter x 2 mm thick and approximate sample mass of 2.5 g.

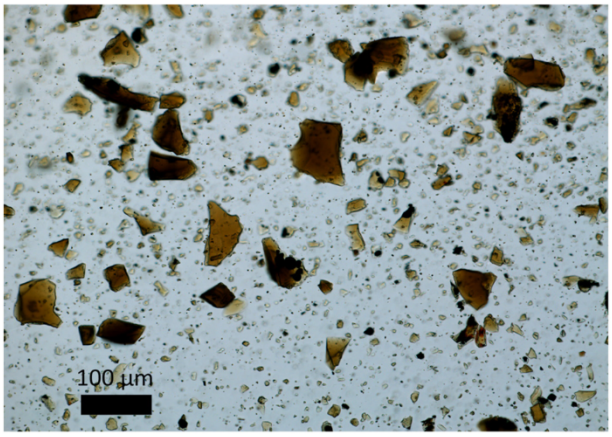

Fig. 2. Photomicrograph of the vitrified SRM 4600× in transmitted plane polarized light, 100× magnification. The particulate material is mounted in Permount™, which has an approximate refractive index of 1.52.

sample of infinite thickness, as well as preparing the "sandwich" on the top of an inverted sample cup (Figs. 2 and 3) to elevate the sample from the instrument sample platform, ensures that the X-rays being measured are those emitted from the sample and not from the platform. Consistent thickness and density across the sample can be checked using an x-ray fluorescence line of an abundant element with uniformity indicated by consistent intensity across the sample. The line chosen should also be of high enough energy to penetrate through the sample if infinite thickness is not achieved. If this measurement indicates areas that are not infinitely thick, then those areas of the sample should not be used.

The "sandwich" method was also evaluated using NIST sediment SRM 2702 and SRM 2703 to compare results obtained from the pressed pellets using the same µXRF instrument. This comparison revealed no statistical difference between the "sandwich" and pressed pellets for elemental homogeneity.

1.3. Data collection

The background-corrected counts from integrating each X-ray emission line for each element of interest were obtained for both the test SRMs and the surrogate debris SRM 4600 using a Horiba XGT-7000 X-ray analytical microscope. The analytical conditions for the µXRF spectrometer are listed in Table 1. X-ray tube settings of 50 kV and 1 mA, corresponding to an approximate 25% detector dead time, were used in conjunction with a 5 s detector live time acquisition per sample location. The nominal diameter spot size measured was 400 µm using a

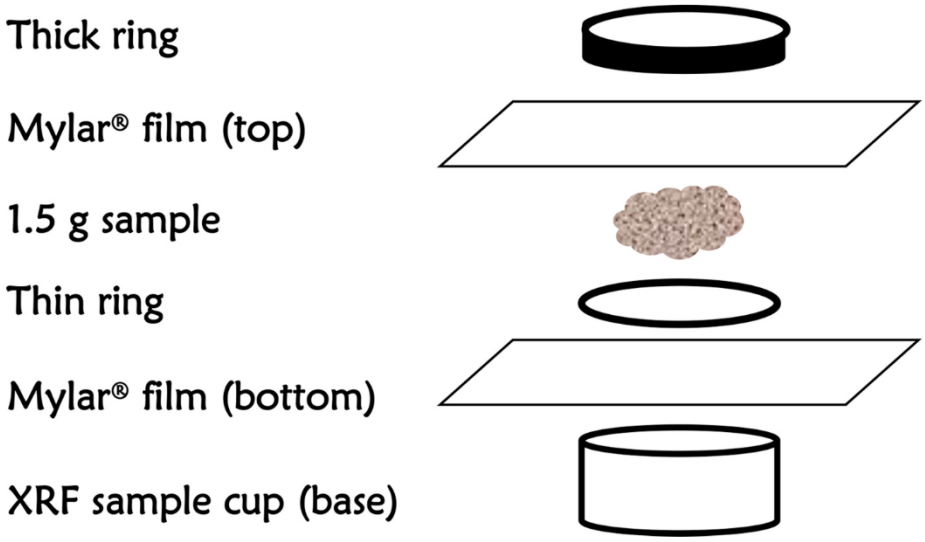

Fig. 3. Schematic showing the 'sandwich' sample preparation approach.

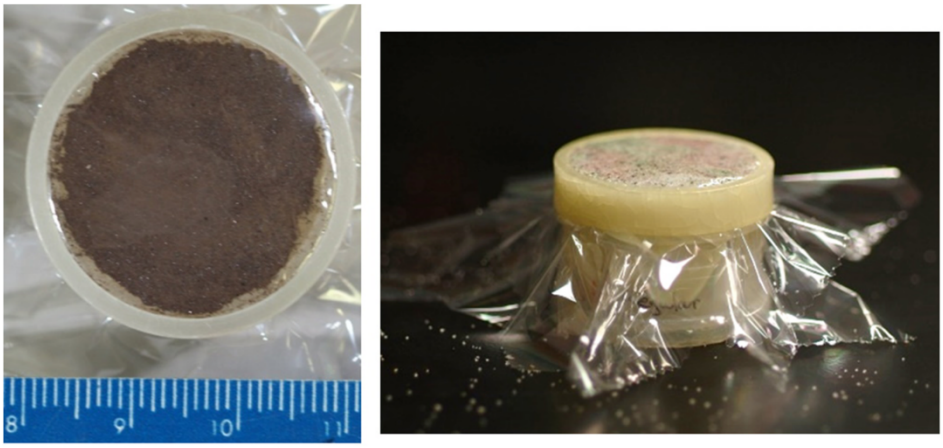

Fig. 4. Images (top view (l) and side view (r)) of the 'sandwich' assembly used for SRM 4600. 'Sandwich' sample dimensions were roughly 25 mm in diameter and 1 mm thick.

Table 1
Instrument parameters used for data acquisition for all runs with the HORIBA XGT-7000 X-ray Analytical Microscope.

Instrument Settings	
X-ray tube	
Target Material	Rhodium
Voltage (kV)	50
Current (mA)	1
X-ray Optic	
Capillary	Mono
Diameter Size (μm)	400
X-ray detector	Silicon
Data Acquisition	
Detector Live Time (s)	5

monocapillary X-ray optic. Depending on the depth of X-ray penetration, the amount of sample interrogated at each spot location is in the range of nanograms to micrograms (Henke et al., 1993).

For the PCA analysis method, extensive X-ray maps are required. For the tests of SRM 2702 and SRM 2703, 2000 points per sample were measured, whereas 5000 points per sample were measured for SRM 4600. Fewer points were collected for SRM 2702 and SRM 2703 because these materials have known levels of heterogeneity from previous published studies (Molloy and Sieber, 2008) and the Certificates of Analysis. This indicated that 2000 points were sufficient for the PCA models for SRM 2702 and SRM 2703. The lower number of measured points allowed for a significant reduction in analysis time (>5 h) for this portion of the study.

Instrumental drift was noted after the fact for most runs due to an apparent delay in the stabilization of the X-ray source at the start of the run. This appeared to be caused by the software lowering the power of the X-ray source between runs, requiring some time for the X-ray source to "warm up". It was determined that 50 points (at a 5 s detector live time acquisition) were a conservative estimate of this stabilization time so the first 50 points were removed from every run to eliminate this artifact in the data.

1.4. PCA data evaluation

The X-ray map data obtained was evaluated using a PCA approach developed by Molloy and Sieber (2008) for other solid matrix SRMs. In brief, the PCA evaluation requires:

- a 'stability' run (repeated μXRF measurements at one location on the sample), where any variance observed is related to sources (e.g. instrument and measurement sources) other than sample heterogeneity, and
- a 'random' run (μXRF measurements taken randomly within a designated map area) similar to the method used by Molloy and Sieber (2011), where the variability observed is due to not only instrument and measurement sources but also sample heterogeneity.

The 'stability run' represents an essentially homogenous sample and can be used as a homogeneity standard to build the PCA model. The PCA model is then built upon comparison of the 'stability run' to the 'random run' using factors describing the dataset, such as mean counts, standard deviation of counts, expected counting statistical error, dataset kurtosis, and skew of the data away from normal shape. These factors were calculated by taking the integrated counts under each fluorescence peak at each analysis location; for example, the mean counts factor was the mean counts for that fluorescence peak at all measured locations in the sample. Other factors were calculated in a similar manner using the fluorescence peak data at each location and calculated using formulas in Microsoft Excel (2016). Once tabulated for a given sample or group of samples, the factors were imported into MATLAB 2013a, with PCA analysis done using the PLS Toolbox 5.0 add-in for MATLAB with 'autoscale' data pretreatment, which mean centers the data set and scales the variance.

2. Results & discussion

2.1. SRMs 2702 & 2703 test

The purpose of the test sample measurements was to assess the ability of the FBI Laboratory CFSRU to identify that SRM 2703 is measurably less heterogeneous than SRM 2702. These two SRMs are the same marine sediment material; however, SRM 2703 has been further treated to be less heterogeneous on the microscale relative to SRM 2702, with a smaller particle size (centered around 7 μm) for SRM 2703 (Molloy and Sieber, 2008). This smaller particle size results in an overall improvement of the homogeneity for the elements in this material.

Two histogram plots (Fig. 5a and b) of the counts per second data are shown for iron (Fe) for both the 'stability' runs and the 'random' runs for SRM 2702 (Fig. 5a) and SRM 2703 (Fig. 5b). The 'stability' run and the 'random' run were measured back-to-back to maintain constant instrument conditions for the two runs. For a perfectly homogeneous sample, it is expected that both histograms ('stable' and 'random') would overlap and be nearly identical. The distribution observed for the 'random' run relative to the 'stable' run for SRM 2702 shows much greater dispersion, suggesting this material is heterogeneous or contains enriched areas ("nuggets") for Fe. The histogram plot for SRM 2703 shows much less dispersion in the 'random' run data relative to the 'stability' run, suggesting that SRM 2703 is more homogeneous for Fe particularly relative to SRM 2702. The Fe intensity distributions in Fig. 5 are slightly different between the 'stable' and 'random' runs in both SRM 2702 and SRM 2703. Although there is not a significant difference for the Fe intensity distributions for the SRM 2703 runs, the significant difference for SRM 2702 runs could be indicative of the 'stable' run being measured at a point in the sample that is relatively deficient in Fe. Fortunately, it is the distribution shape that matters more than the signal magnitude as outlined by Molloy and Sieber (2008) previously. If the signal magnitude was critical in this analysis, the location for the 'stable' run would have been chosen more carefully, after characterization of the entire sample surface. The apparent departure from a normal distribution shape, as seen in the SRM 2702 'random' run, is indicative of material heterogeneity.

The same Fe data used in the histogram plots was also plotted as Quantile-Quantile (QQ) plots (Fig. 6a (SRM 2702) and 6b (SRM 2703)) with the first 50 data points being removed due to instrumental drift as described previously. QQ plots are useful for assessing whether data is following a normal distribution. Elemental microheterogeneity tends to present itself as a deviation from the normal distribution (Molloy and Sieber, 2008). The data for the 'stability' runs plot on the line for both test SRMs and show no significant deviation from normal. This is as expected as there should be no observable deviation measuring at one location on the sample as long as the sample is not changing due to the X-ray beam during measurement. The plot of the 'random' data for SRM 2702 shows a significant deviation from normal at the top tail of the plot, which indicates elemental heterogeneity. The 'random' run for SRM 2703 shows minimal deviation from normality suggesting that, for Fe, this material is comparatively homogeneous and is, with respect to Fe, more homogeneous than SRM 2702. A full PCA evaluation of the heterogeneity of the two SRMs was not performed as this had been done previously (Molloy and Sieber, 2008), and the goal to demonstrate the FBI Laboratory CFSRU's capability of performing the end-to-end analysis and detecting microheterogeneity differences between SRM 2702 and SRM 2703 was successfully accomplished.

2.2. SRM 4600 surrogate debris

For SRM 4600, the following elements were measured: magnesium

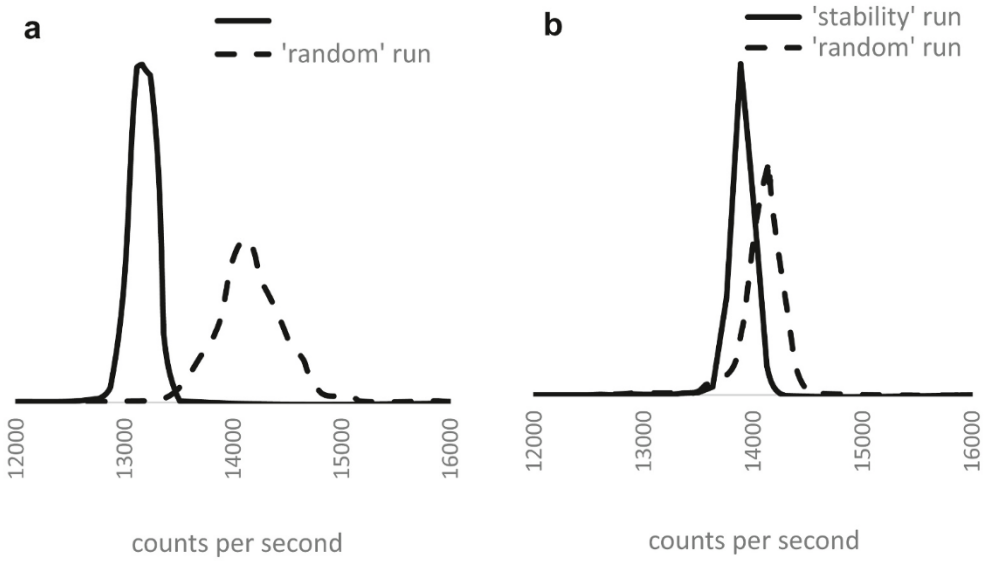

Fig. 5. Histogram plots of the counts per second data for iron (Fe) for the 'stability' runs and the 'random' runs for SRM 2702 (a) and SRM 2703 (b).

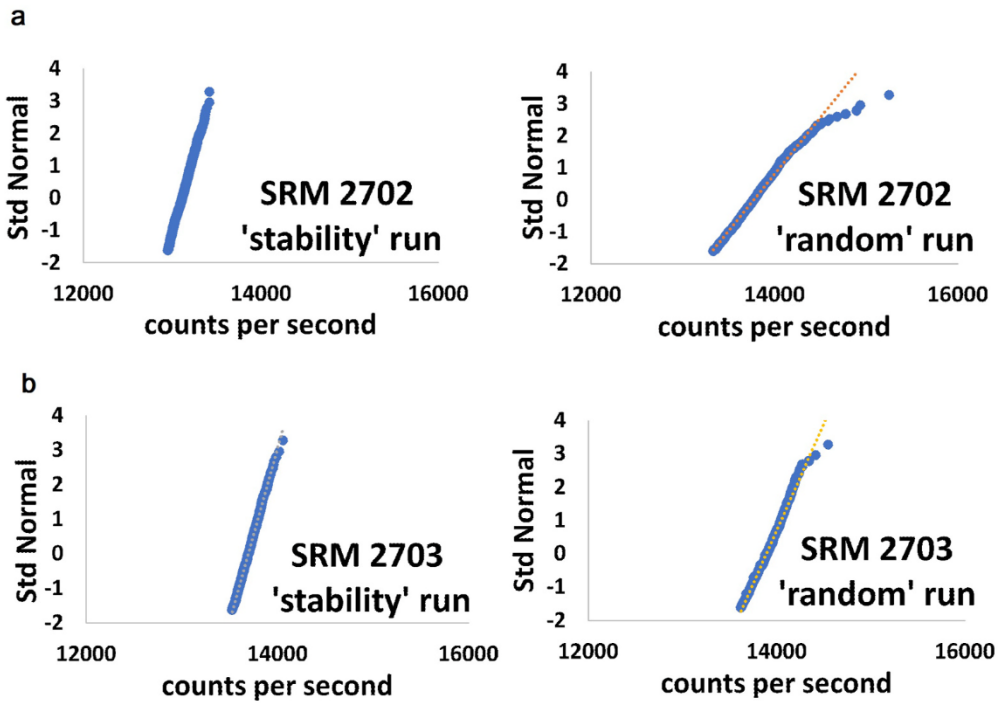

Fig. 6. Quantile-Quantile (QQ) plots showing the iron (Fe) fluorescence counts data for both the 'stability' and 'random' runs for SRM 2702 (a) and SRM 2703 (b) with the first 50 data points removed due to observed instrumental drift. The standard normal distribution was used to normalize the mean of the data to 0 and standard deviation to 1 in order to minimize effect of the magnitude of the fluorescence line in favor of the shape of the distribution.

(Mg), aluminum (Al), silicon (Si), phosphorous (P), sulfur (S), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), Fe, nickel (Ni), copper (Cu), Zn, rubidium (Rb), strontium (Sr), barium (Ba), cerium (Ce), and lead (Pb). U was below the limit of detection for these short spectral collection times and was not assessed. An example μXRF spectrum is shown in Fig. 7; in the linear scale, the differences in major and minor are apparent. The spectra are taken and integrated (integration was performed using The Microanalysis Suite Issue 17b, XGT-7000 Suite Version 1.84, Oxford Instruments Analytical, Inc., Horiba Limited software) under the peaks to provide the data necessary for the PCA analysis. Using the methodology described previously (Molloy and Sieber, 2008), PCA was used to determine which elements appeared heterogeneous for a 400 μm diameter analysis area. Fig. 8 shows the results of the PCA analyses for successive summations of up to 300 analysis locations for a sample of SRM 4600. The confidence ellipses shown in these plots are 99.5% confidence ellipses, a confidence level that corresponds to 3 standard deviations. Three standard deviations above a blank signal is a traditional definition for limit of detection, so these confidence ellipses serve as detection limits for heterogeneity, with the measured samples' elements located outside the confidence ellipses having detectable levels of heterogeneity. Due to insufficient sensitivity of these short collection times, neither Ce nor V could be assessed for heterogeneity. Based on an approximated elemental composition provided by the producers of the material, a

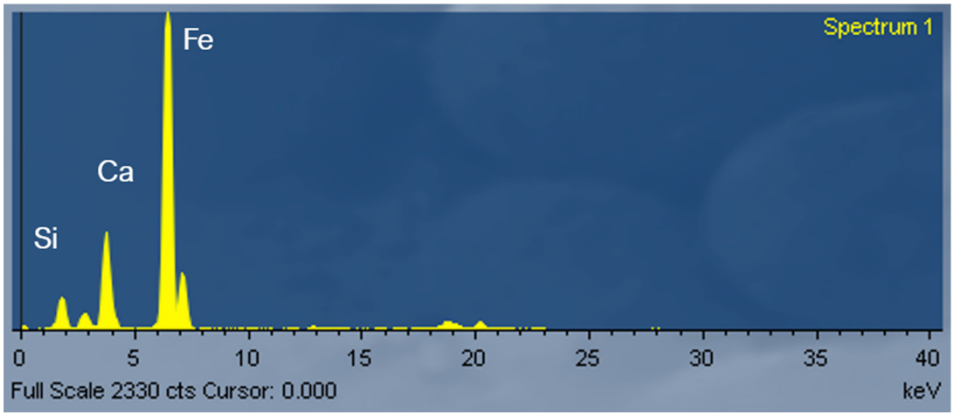

Fig. 7. Example μXRF spectrum of SRM 4600. High intensity X-ray fluorescence peaks are labeled. Other visible peaks are due to the rhodium (Rh) X-ray tube.

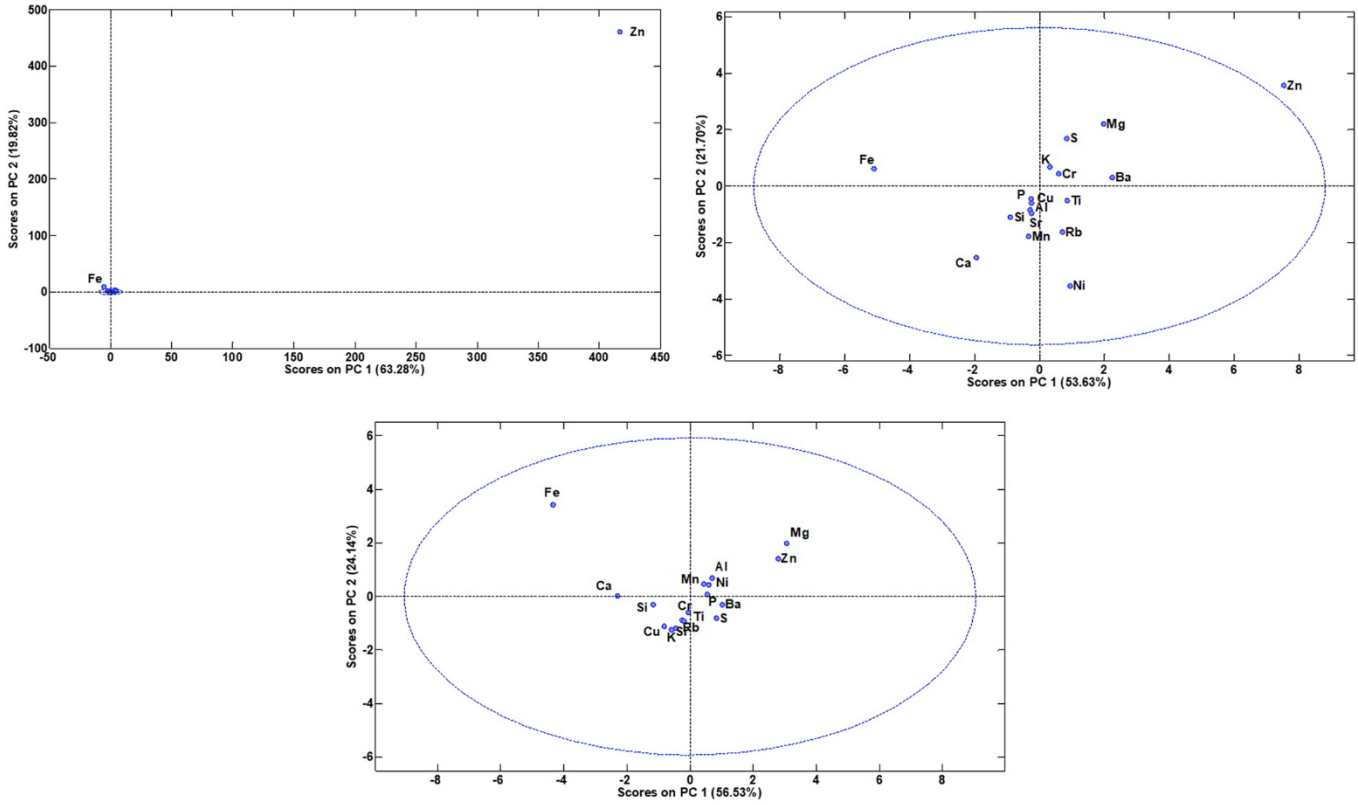

Fig. 8. PCA results showing heterogenous elements for a) 1 analysis location, b) 100 analysis locations summed together, and c) 300 analysis locations summed together. Dashed confidence ellipses are indicative of 99.5% confidence intervals from the model built from single location 'stability' runs and serve as a limit of detection for heterogeneity within the sample above the variability of the measurement process.

calculated penetration depth (233 μm for Zn, the most heterogeneous element) (Henke et al., 1993) and sample density (1.36 g/cm^3) can be used to determine that each 400 μm diameter analysis location is indicative of approximately 40 μg of sample. For one sample, the material appears to be homogenous after summing together 300 analysis locations, indicative of 12 mg of sample.

Although it is useful to have an assessment of elemental heterogeneity for a particular sample, it is more useful for users of a RM to have an idea of the elemental heterogeneity across the entire population of material produced. A method for applying the PCA protocol used above for one sample has been described and was repeated on samples from seven bottles of the production lot of SRM 4600. Results for the replicate sample analyses, with duplicate analyses from all bottles and triplicate analyses from two bottles, are shown in Fig. 9. The data in Fig. 9 was not averaged between samples, and no averaging of data was made for samples taken from the same bottle, resulting in 16 total samples displayed. The ellipse shown represents a 99.5% confidence ellipse based on the variation of the 'stability' run. A 99.5% confidence level is consistent with a variation of 3 standard deviations, which is also a traditional definition of limit of detection. Therefore, the confidence ellipse represents a limit of detection for heterogeneity within the sample given the variability of the model due to instrumental effects. The heterogeneity results for the entire population of material are a bit more complex than for a single sample. Once again, Ce and V could not be assessed due to insufficient signal, but Fe also could not be assessed even though it had the most intense signal of all elements measured. Unfortunately, there appeared to be a high degree of drift in the instrumental response over time in many samples even when measuring

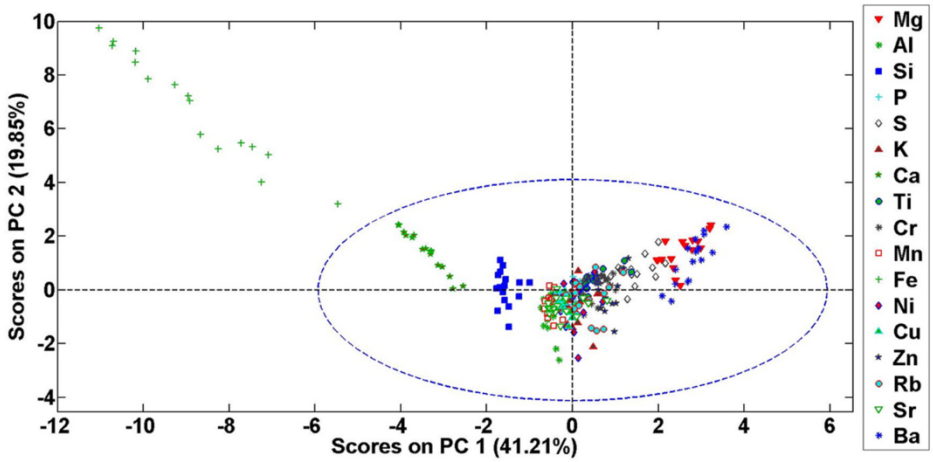

Fig. 9. PCA results for analysis representative of entire population of SRM 4600 bottles. Sixteen samples of approximately 1.5 g were taken from 7 bottles with duplicate analyses from all bottles and triplicate analyses from two bottles. Green + symbols are indicative of Fe results across all samples appearing heterogeneous due either to material heterogeneity or long-term instrumental drift. Percent values shown for each principal component identify the percent of total variance that component accounts for.

a single location on a sample. This high degree of uncertainty due to instrumental drift meant a reliable PCA model using the Fe signal could not be constructed. The instrument variation could not be separated from Fe variation within and between samples. Additionally, the drift observed during the 'stability' runs where the x-ray beam measured the sample at one location yielded a distribution that was not a normal distribution. Because the departure from normality is the largest indicator of microscale heterogeneity using this methodology (Molloy and Sieber, 2008), no determinations for Fe could be made. For the remaining elements (Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Ba, and Pb), 400 analysis locations summed together gave an estimate of the minimum sample mass required for the entire SRM, where sample heterogeneity is not a significant contributor to the uncertainty of assigned values. The minimum sample mass determined is approximately 16 mg, but the uncertainty from this calculation (50% relative (Molloy and Sieber, 2008)) is significant; therefore, a conservative estimate of the minimum sample size recommended for use is 24 mg. This conservative estimate is the result of adding the uncertainty to the minimum sample mass calculated using the PCA methodology. It is important to point out that this minimum sample size is a threshold for determining fitness for use, not a certified value. Thus, the minimum sample size provided (24 mg) does not have any sort of confidence interval associated with it, but is a single number that should be easily compared to the sample size candidate analysis method for use with SRM 4600.

3. Conclusions

Based on the PCA analysis, a minimum sample of 24 mg is recommended. The results from the PCA analysis indicate that heterogeneity exists for Zn (<400 μg) at the microscale for SRM 4600; users must consider this when employing microanalytical techniques. Further analysis might be possible to assess Ce, V, Fe, and U for heterogeneity; however, this will require extensive additional analysis time due to detection and stability limitations.

Disclaimer

The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or the FBI or are recommended by NIST or the FBI or that they are necessarily the best materials, instruments, software, or suppliers for the purpose described.

This is publication number 20–66 of the Laboratory Division of the Federal Bureau of Investigation (FBI). The views expressed are those of the authors and do not necessarily reflect the official policy or position of the FBI or the U.S. Government. Names of commercial manufacturers are provided for identification purposes only, and inclusion does not imply endorsement of the manufacturer or its products or services by the FBI.

CRediT authorship contribution statement

Jacqueline L. Mann: Conceptualization, Resources, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **John L. Molloy:** Methodology, Software, Formal analysis, Visualization, Supervision, Writing – review & editing. **JoAnn Buscaglia:** Conceptualization, Methodology, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Kevin P. Pfeuffer:** Formal analysis, Investigation, Data curation, Writing – review & editing, Visualization. **Barbara L. Fallon:** Investigation, Writing – review & editing. **Mark A. Tyra:** Conceptualization, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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