Supporting Information for Determination of Hexavalent Chromium Fractions in Plastics Using Laboratory-Based, High-Resolution X-Ray Emission Spectroscopy

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Discussion of Uncertainties in XES Measurements and Supporting Values

In Table 1 and Table 2 of the paper, there are eight polymer samples used to demonstrate the performance of the X-ray emission spectrometric method. The assigned values for total Cr and Cr(VI) and the uncertainty estimates for those values are explained in this section.

In Table 1, the total Cr mass fractions are a mix of certified values for SRM 2859, SRM 2861, CRM EC681k, and CRM 8113a, consensus analysis results for P106 from an international comparison exercise, analysis results for E5 and F6 from NIST X-ray fluorescence spectrometry, and the value for Cr515 from gravimetric preparation using NIST SRM 1078a Tris(1-phenyl-1,3-butanediono)chromium(III), aka Cr(III)-benzoylacetonate, doped into clean, linear low-density polyethylene. The Cr(VI)/Cr fraction values were estimated using the preparation recipes provided by the suppliers in certification reposts, papers, and safety data sheets. It was not expected that all prepared Cr(VI)/Cr fractions would be preserved in the PVC materials, because PVC contains unsaturated C = C bonds, F6 and SRM 2861 formulations contain Sb, a suspected reducing agent for Cr(VI), and the two SRM formulations contain stabilizers and plasticizers that could also be reducing agents for Cr(VI).

Uncertainty estimates for the total Cr mass fractions in the plastics have several definitions. For P106, the uncertainty estimate is the median absolute deviation of the individual lab mean results from the median of those mean results. For materials E5 and F6, the uncertainty estimates are based on the professional judgement of the authors. For the certified reference materials, the uncertainty estimates are expanded uncertainties at approximately the 95 % confidence level. These estimates were divided by the estimated expansion factor $k = 2$.

In Table 2, all estimates of uncertainty are given as combined standard uncertainties based on the uncertainty estimates from Table 1 and the contributions of uncertainty from the XES test method. The individual components of uncertainty are listed in Table S1. The combined standard uncertainty values were calculated by adding the individual component estimates in quadrature. All components were assumed to have normal distributions with infinite degrees of freedom.

Table S1: The sources and magnitudes of uncertainty components characteristic of the XES test method are listed for each sample studied. In each case, the statistical uncertainty accompanying the regression fit, the choices of hexavalent and trivalent standard compounds, and the variance of the X-ray energy scale all contributed to the reported uncertainty. The uncertainties of total Cr mass fractions are listed, and are incorporated into the calculated uncertainty of the Cr(VI) mass fraction.

Sample	Source and Magnitude of Uncertainty (expressed as relative standard uncertainty)				Combined Standard Uncertainty	
	Fit Parameter (%)	Reference Choice (%)	Energy Scale (%)	Cr Mass Fraction (%)	Cr(VI)/Cr Fraction by XES (%)	Cr(VI) Mass Fraction (mg/kg)
P106	1.17	2.09	0.81	1.3	2.5	7.2
E5	3.01	2.29	0.65	10	3.8	180
F6	5.55	3.47	0.95	10	6.6	67
SRM 2859	3.84	2.30	0.60	1.1	4.5	33
EC681k	1.49	3.23	0.65	2.5	3.6	3.7
8113a	0.69	3.34	0.65	0.95	3.5	33
Cr515	1.12	4.10	0.73	0.21	4.3	22

Table S2: The Cr Kα XES spectra collected from Cr515, a plastic expected to contain strictly Cr(III), was fit to a linear combination of a hexavalent compound's spectrum and trivalent compound's spectrum. Below are the resulting Cr(VI)/Cr species fractions upon iterating all available combinations of references showing the strong dependence of the extracted Cr(VI)/Cr content on the choice of trivalent reference utilized in the fit.

Cr(VI) reference	Cr(III) reference	Determined Cr(VI)/Cr Fraction (%)
$PbCrO_4$	Cr_2O_3	0.697
$PbCrO_4$	Cr(III)-acetylacetonate	7.612
$PbCrO_4$	Cr(III)-benzoylacetonate	10.20
$BaCrO_4$	Cr_2O_3	0.673
$BaCrO_4$	Cr(III)-acetylacetonate	7.208
$BaCrO_4$	Cr(III)-benzoylacetonate	9.666
$Na_2Cr_2O_7 \bullet 2H_2O$	Cr_2O_3	1.243
$Na_2Cr_2O_7 \bullet 2H_2O$	Cr(III)-acetylacetonate	7.637
$Na_2Cr_2O_7 \bullet 2H_2O$	Cr(III)-benzoylacetonate	10.16

Table S3: The energy and intensity of the maxima of Cr $K\alpha_1$ and $K\alpha_2$ emission lines. Prior to calculation, XES spectra were background corrected and integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectrum. Spectra can be found in Fig. 1 of the manuscript.

Reference Compound	$K\alpha_2$ Maxima Energy (eV)	$K\alpha_2$ Maxima Intensity (arb. units)	$K\alpha_1$ Maxima Energy (eV)	$K\alpha_1$ Maxima Intensity (arb. units)
$PbCrO_4$	5405.03	1.97	5414.04	5.42
$BaCrO_4$	5404.93	1.96	5414.04	5.56
$Na_2Cr_2O_7 \bullet 2H_2O$	5404.85	1.91	5414.09	5.76
Cr_2O_3	5405.38	1.86	5414.94	4.06
Cr(III)-acetylacetonate	5405.52	1.90	5414.92	4.11
Cr(III)-benzoylacetonate	5405.60	1.90	5415.01	4.14

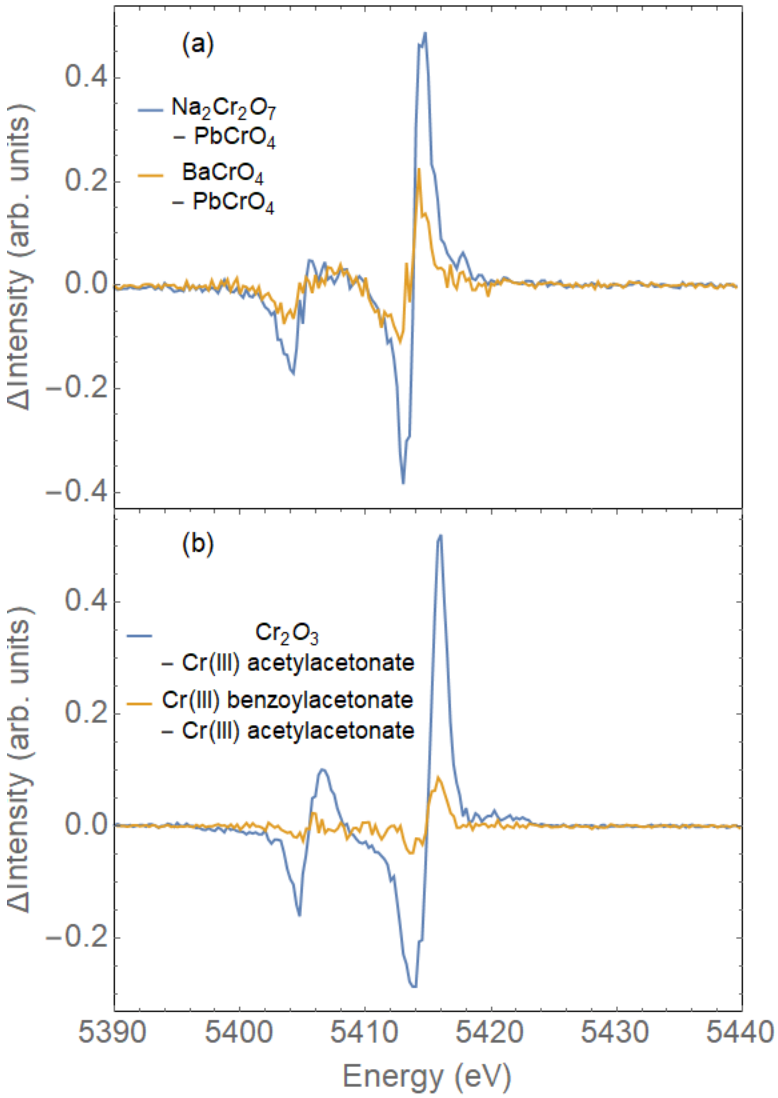

Figure S1: Residual plots Cr Kα XES of reference materials within the (a) hexavalent and (b) trivalent series. Prior to calculation of residuals, reference spectra were background corrected and integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectrum. The arbitrary units are consistent with those of Figure 1, allowing for assessment of relative variations.

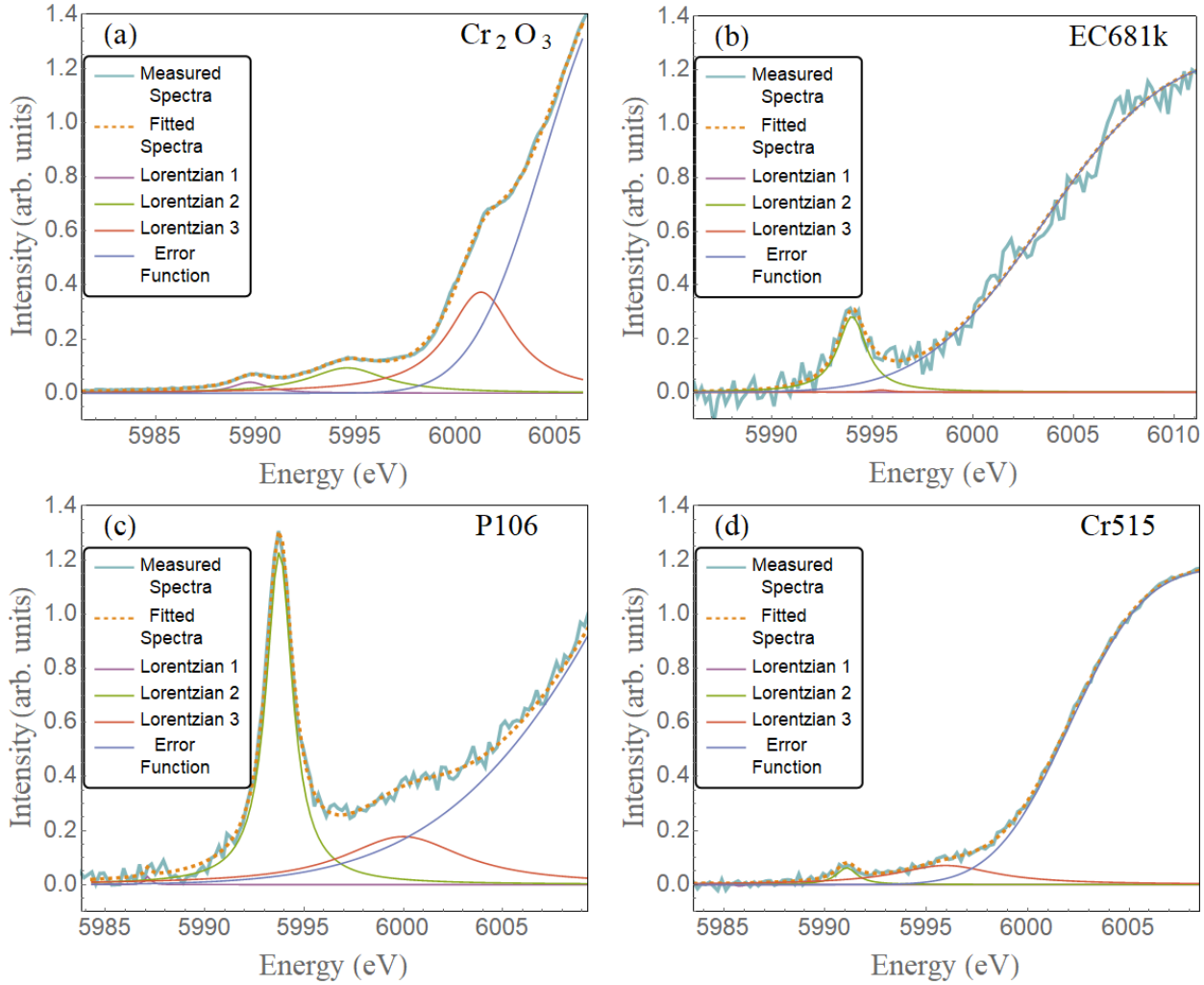

Figure S2: The near-edge region of the measured XAFS spectra of (a) chromium(III) oxide, (b) EC681k, (c) P106, and (d) Cr515 are shown along with the acquired fits and their components.

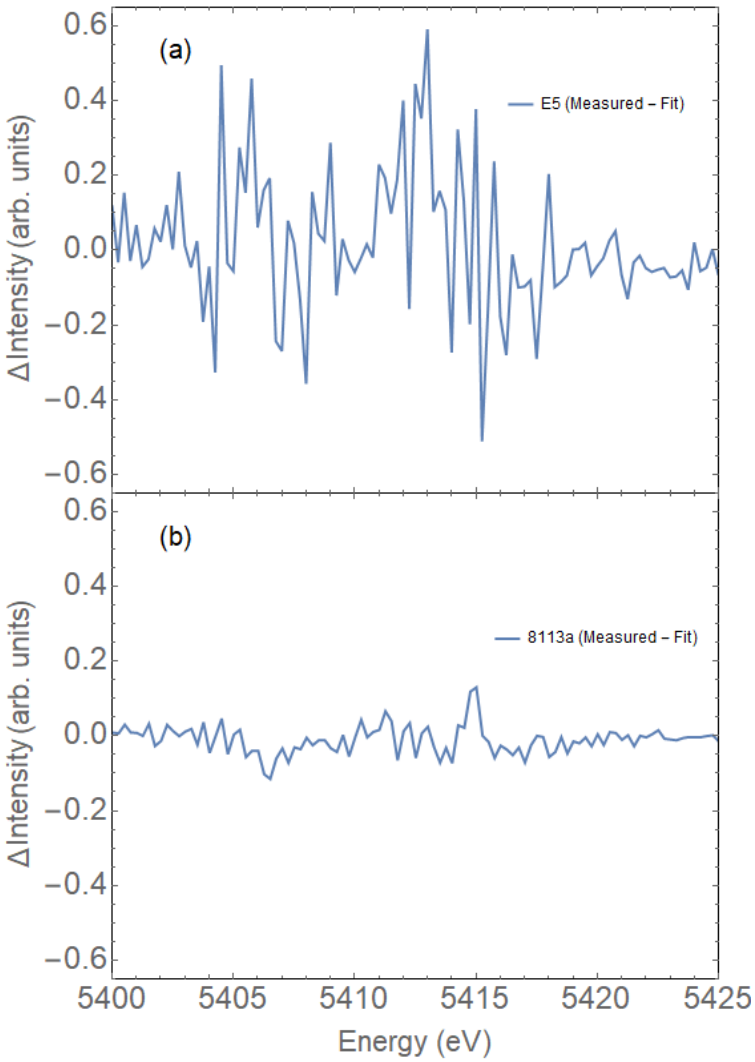

Figure S3: Example Cr Kα XES residual plots of the measured spectra relative to the fit produced by a least-squares regression analysis. Plastics selected to be shown here are (a) E5 and (b) 8113a. Prior to the calculation of fits and residuals, spectra acquired from the selected plastics were background corrected, integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectra.

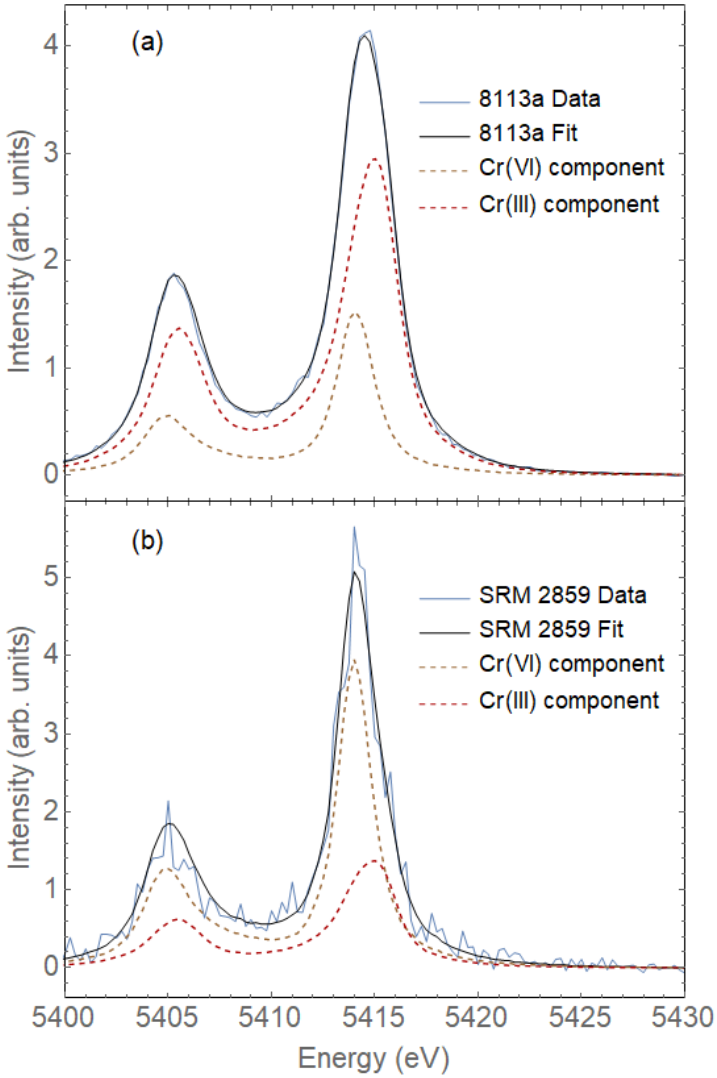

Figure S4: Example Cr Kα XES plots showing the measured spectra, its corresponding fit, and scaled contributions of the Cr(VI) and Cr(III) sources. Here the hexavalent and trivalent species fractions were found to be 28.1 % lead chromate with 71.9 % Cr(III) acetylacetonate (a) and 67.0 % barium chromate with 33.0 % Cr(III) oxide (b). Prior to the calculation of fits, spectra acquired from the selected plastics were background corrected, integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectra.

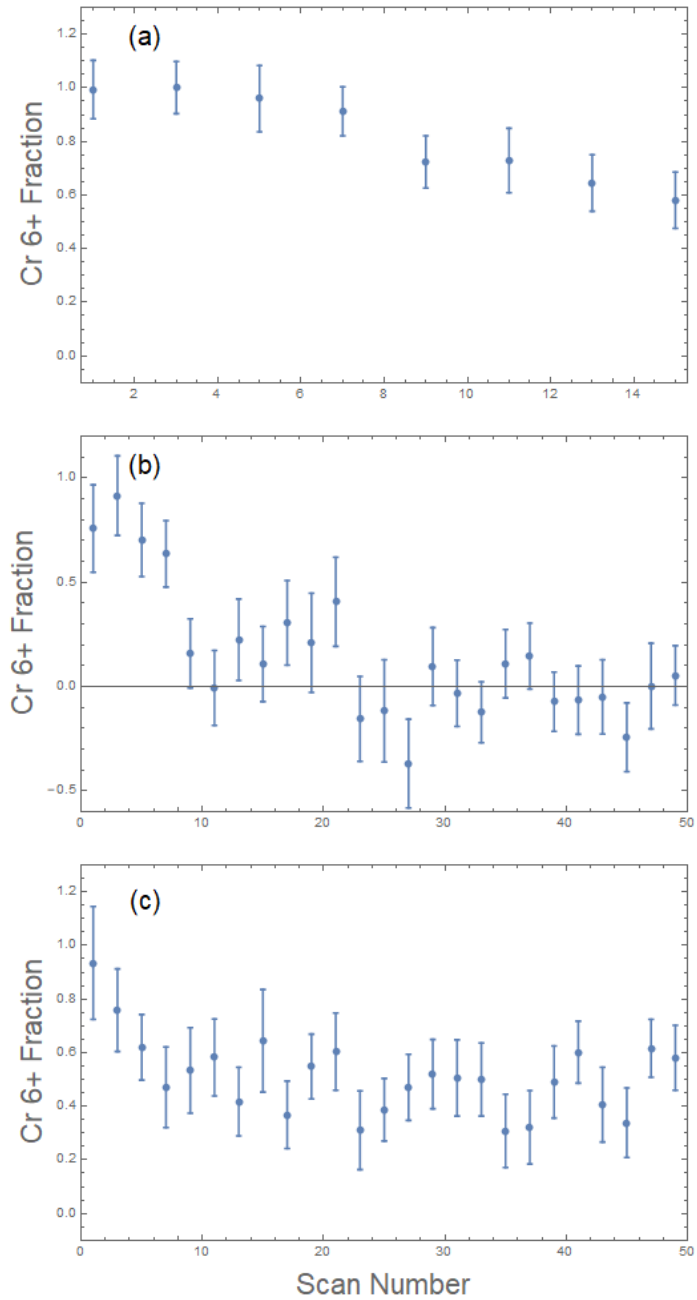

Figure S5: The Cr(VI) fraction found by a fit of the Cr Kα XES spectra is shown as a function of scan number. The plastics shown are E5 (a), F6 (b), and SRM 2859 (c). Every other scan is shown. Note that, prior to the calculation of fits, each scan was merged with the following scan and the result was background corrected, integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectra. For convenience, the data sets were truncated to the first 50 scans of F6 and SRM 2859, while 16 scans are shown for E5 as fewer scans were measured for plastic E5.

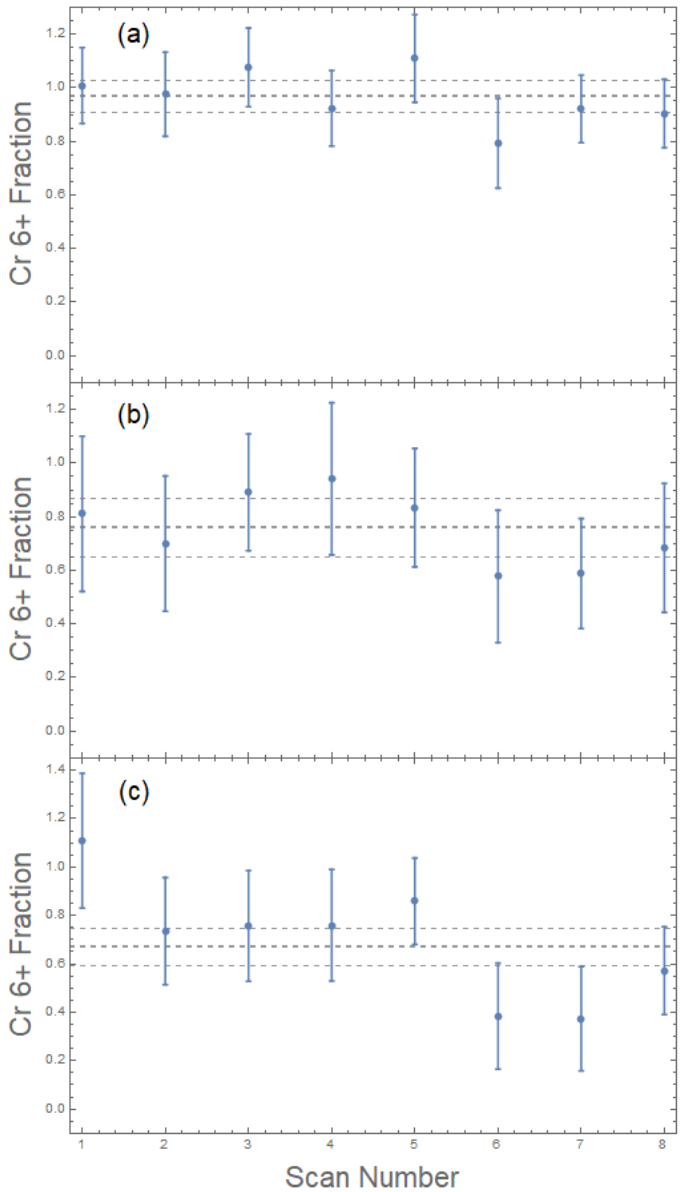

Figure S6: The Cr(VI) fraction found by a fit of the Cr Kα XES spectra is shown as a function of scan number. The plastics shown are E5 (a), F6 (b), and SRM 2859 (c). The error bars on each point encompass twice the standard error in the fit parameter on either side of the data point. The thick, dashed line corresponds to the value of the fit parameter attained from merging the first eight scans, while the thin, dashed lines encompass twice the standard error in the fit parameter above and below the value of the fit parameter. Prior to the calculation of fits, spectra were background corrected, integral normalized, and each point was scaled to its corresponding percentage of the total counts in the spectra. Note that the first scan of SRM 2859 contained two data points around the location of the Cr(VI) $K\alpha_1$ peak that were roughly two standard deviations above what would be expected for a purely Cr(VI) compound. When these points were removed, the resulting confidence interval overlapped with that of the merged spectra.

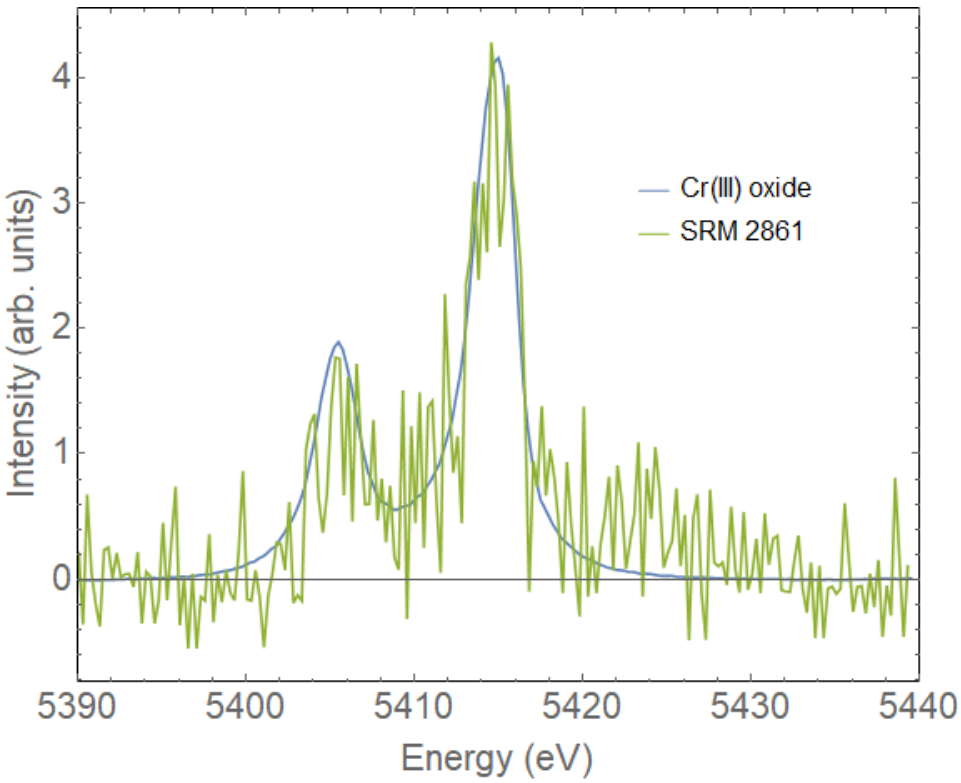

Figure S7: The XES spectrum collected from a sample of SRM 2861 shows poor signal-to-noise, and cannot be reliably fit with both the Cr(III) and Cr(VI) reference spectra. Here it is shown with only the Cr(III) reference, Cr_2O_3, to emphasize the high probability that only Cr(III) species are present and that all original Cr(VI) species were reduced to Cr(III) during preparation.

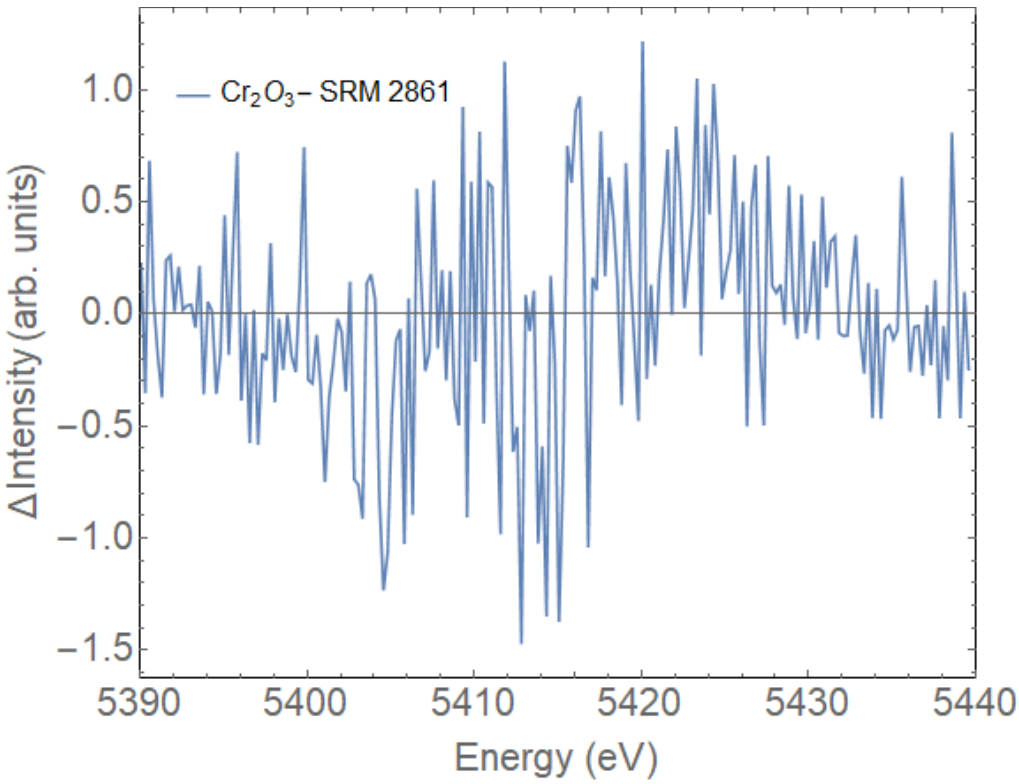

Figure S8: The residual spectrum for the fit shown in Fig. S7 for a trivalent reference compound and SRM 2861. The agreement between the general size of deviations and drift from zero difference provides further evidence of the trivalent character of Cr in SRM 2861. Qualitatively, the evidence indicates zero Cr(VI) present in SRM 2861.

Calculation of Cr(VI) Limit-of-Detection (LOD) by XES Method

An estimate of 1.3 µg for the Cr(VI) LOD by XES can be attained by the following steps. First the volume of sampled material is calculated. This involves assuming a 1 cm radius region being illuminated by the source. Given a sufficiently low concentration of Cr, the depth probed can then be taken as the absorption length of low-density polyethylene (assume a density of 0.92 g/cm^3) at the reported Kα_1 emission energy of 5414 eV for atomic Cr. An estimate of the exit angle can then be used to describe the photon's path length when exiting the sample, note that this factor is larger than for photon's entering the material given the polychromatic excitation source. Using the lowest mass fraction of chromium studied, along with the lowest Cr(VI)/Cr reported by XES in this work, an estimate of the Cr(VI) LOD is given by:

$$LOD_{Cr(VI)} \approx \frac{\pi r^2}{l_{abs}} \sin\theta_{exit}\, \rho_{LDPE} MF_{EC681k} SF_{Cr515} \quad (1)$$

$$\approx \frac{\pi(1\ cm)^2}{852.647\ \mu m} \sin(30°) \frac{0.92\ g}{cm^3} \frac{100\ mg}{kg}\ 0.102$$

$$\approx 1.3\mu g$$

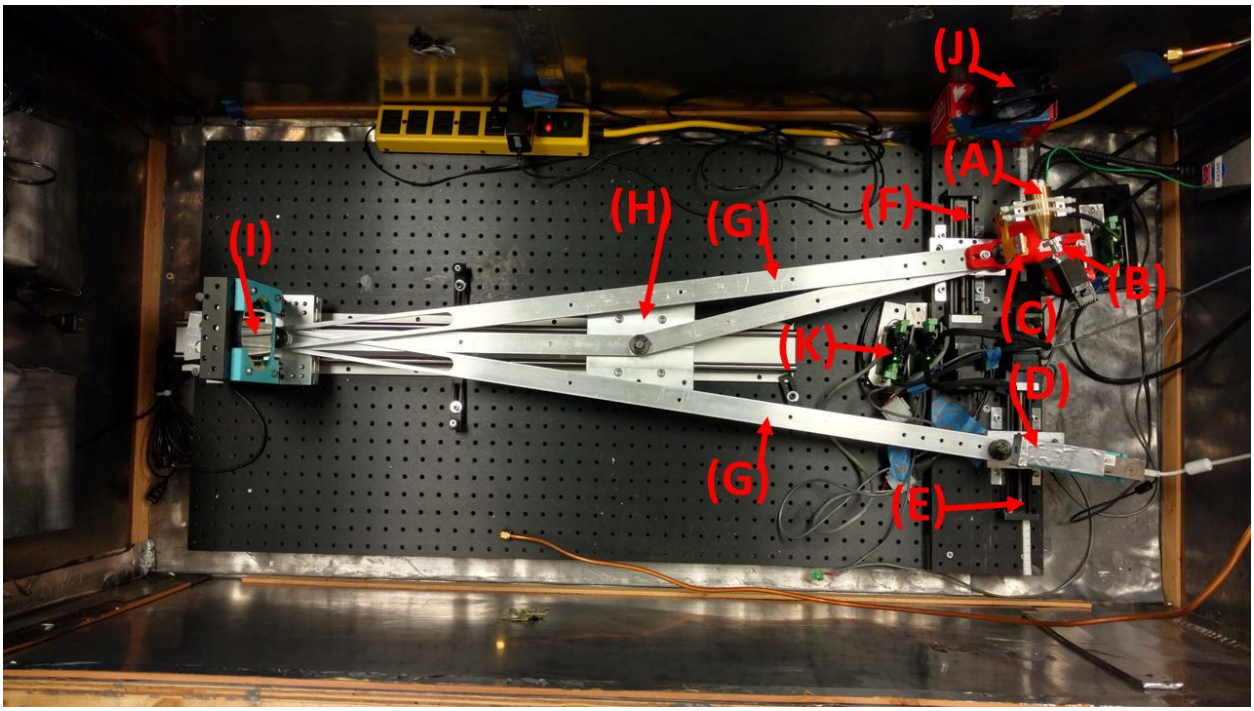

Figure S9: Top-view of the Rowland circle monochromator configured for XES measurements Cr in plastics using a motorized sample spinner. The helium box has been removed for clarity. For scale, the spacing of tapped holes in the optical table is 25.4 mm. (A) Moxtek X-ray tube source (10 W with Au anode); (B) NEMA 11 motor with attached aluminum adapter for sample mounting; (C) sample slit to dictate XES energy scale; (D) detector; (E) motorized detector stage; (F) motorized sample stage; (G) steering bars to enforce correct orientation of source and detector relative to the crystal analyzer; (H) carriage passively coupling source and crystal analyzer; (I) Ge (422) SBCA; (J) cooling fan; (K) motor controllers.