

# Lead in Solution

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## BRUKER TEST RESULTS

### Objective

The goal of the study was to identify the lower limit of determination for Lead (Pb) in an aqueous solution. The results for Lead would help assess the detection of other heavy elements such as Uranium, Thorium, and Mercury. The limitation of this approach is that the L-shell fluorescence was used, for Lead this has a fluorescence efficiency of ~11%.

### Method

A aqueous solution containing 10,000 mg/L (or ppm) of Lead was titrated down to a target of 1 mg/L using distilled water. This was done by first preparing a solution with 1,000 mg/L, then using this to prepare a solution with 25 mg/L used to generate lower values. 8 ml of each titrated solution was placed in a sample cup and sealed with 4  $\mu$ m of prolene. Titrations were performed twice to generate a better estimate of uncertainty in each.

Each sample cup was measured using two different parameters on a Bruker Tracer IIISD (T3S2376) portable electronic-dispersive x-ray fluorescence unit. The instrument uses a 4W bulb with a Rhodium target and a silicon-drift detector.

Data set 1: 40 keV, 25  $\mu$ A, 1 mil Cu/1 mil Ti/12 mil Al Filter (Red), 180 seconds

Data set 2: 40 keV, 25  $\mu$ A, 6 mil Cu/1 mil Ti/12 mil Al Filter (Green), 180 seconds

Spectra were analyzed using Spectra software version 7.4.0.0. Net photon counts from either the Pb L $\alpha$ 1 line (10.55 keV) and Pb L $\beta$ 1 line (12.61 keV) were normalized to the Compton peak (18.6 - 19.4 keV). These values were then regressed against target titration values using a first order polynomial model to generate quantitative estimates for the concentrations of lead in solution.

### Background

Heavy metal contaminants are of concern to the general public. In one famous example, elevated levels of Pb originating from lead pipes in municipal waters of Washington DC led to an increased infant mortality rate. For safety reasons such as these, heavy metals are typically regulated. However, the approach used here is applicable in other contexts - for example Uranium could be detected in smaller concentrations in solution as it fluoresces with greater energy (L $\alpha$ 1 = 13.6 keV)

## RESULTS

It is possible to measure in water at a greater depth for most elements (Figure 1) relative to most other matrices. Analysis of Lead using the  $L\alpha_1$  line (10.55) in a silicate typically occurs within a millimeter of the surface, whereas in water it takes place within a centimeter. This tenfold difference impacts the sensitivity to small concentrations of the element in aqueous solution.

Data were collected using a 1 mil Cu/1 mil Ti/12 mil Al (Red) filter and a 6 mil Cu/1 mil Ti/12 mil Al (Green) filter. The Red filter typically provides optimization for elements that fluoresce between 8 and 11 keV, while the Green filter provides optimization for elements which fluoresce between 13 and 16 keV. Lead, which fluoresces at 10.55 and 12.61 keV in its  $L\alpha_1$  and  $L\beta_1$  lines, falls within range of optimization for both filters. As such, both were used and assessed as to which conditions would be preferable. Both peaks were visible using the Green filter (Figure 2), however using the red filter provided a clearly visible peak (Figure 3). For qualitative determinations, the Red filter data were superior. At higher concentrations, both the Green (Figure 4) and Red (Figure 5) filters provided clear visualizations.

Given the difficulty of titrating down to 1 mg/L, a calibration curve was built to estimate uncertainty in the titration process. Using a second order polynomial regression against Compton normalized gross  $L\beta_1$  Pb counts (Green filter ) and Compton normalized net  $L\alpha_1$  counts (Red filter). The procedure used with Green filter data provided the closest match to titrated estimates (Figure 6, Table 1).

Based on the quantitative estimates, the lowest diluted samples were a little over 1 mg/L for Lead. This included two separate titrations from 1,000 mg/L for the purposes of replication. For the Lead L-shell fluorescence peaks, detection at levels of 1 mg/L (ppm) are possible, provided that other heavy metals are not present. The detection limit for heavier elements such as Uranium will be superior as they are analyzed at a greater depth (Figure 1).

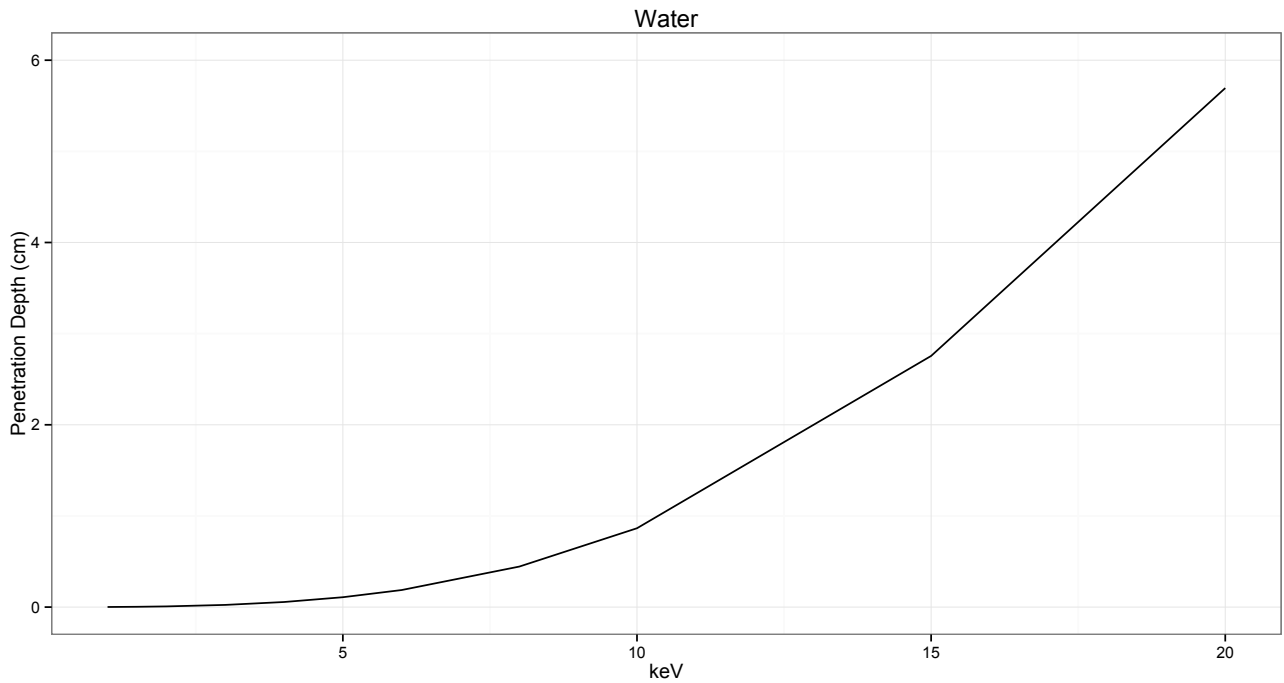


Figure 1: Depth of analysis in water  $I/I_0 = e^{-(\mu/\rho)\rho x}$ , where  $I$  is the quantity of photons returning from the sample,  $I_0$  is the quantity of photons entering the sample,  $\mu/\rho$  represents the mass attenuation coefficient of a given element for a particular matrix, and  $\rho$  represents the density of the object. Lead ( $L\alpha_1 = 10.55$  keV) is measured at a depth of 1 cm, while Uranium will be analyzed at a depth of 2 cm ( $L\alpha_1 = 13.61$  keV).

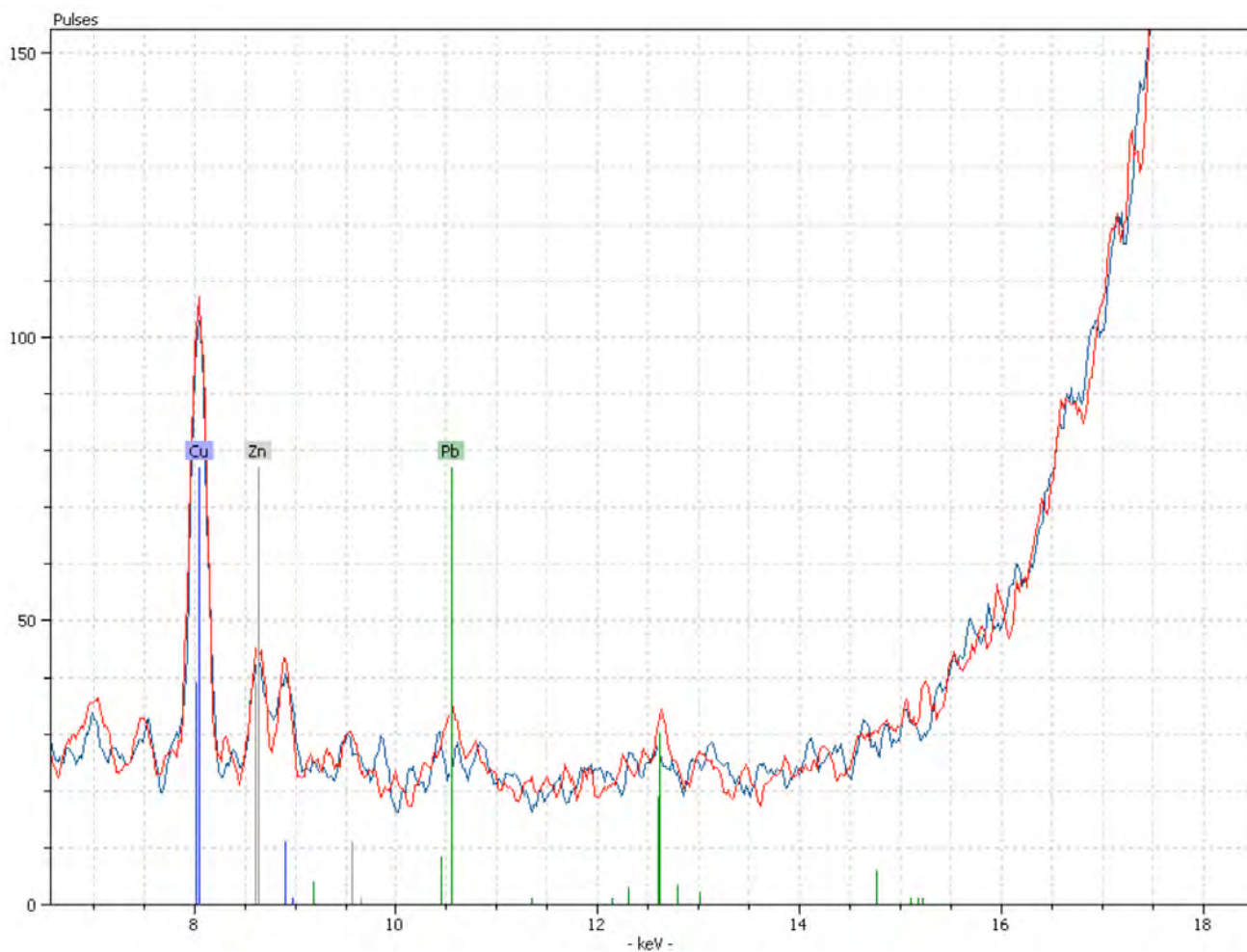


Figure 2: Solution with 1 mg/L of Pb (red) and distilled water (blue) collected using the Green filter. The L $\alpha$ 1 and L $\beta$ 1 peaks are only slightly detectible, but still clearly present. Cu and Zn are trace metals used in the instrument and vacuum grid.

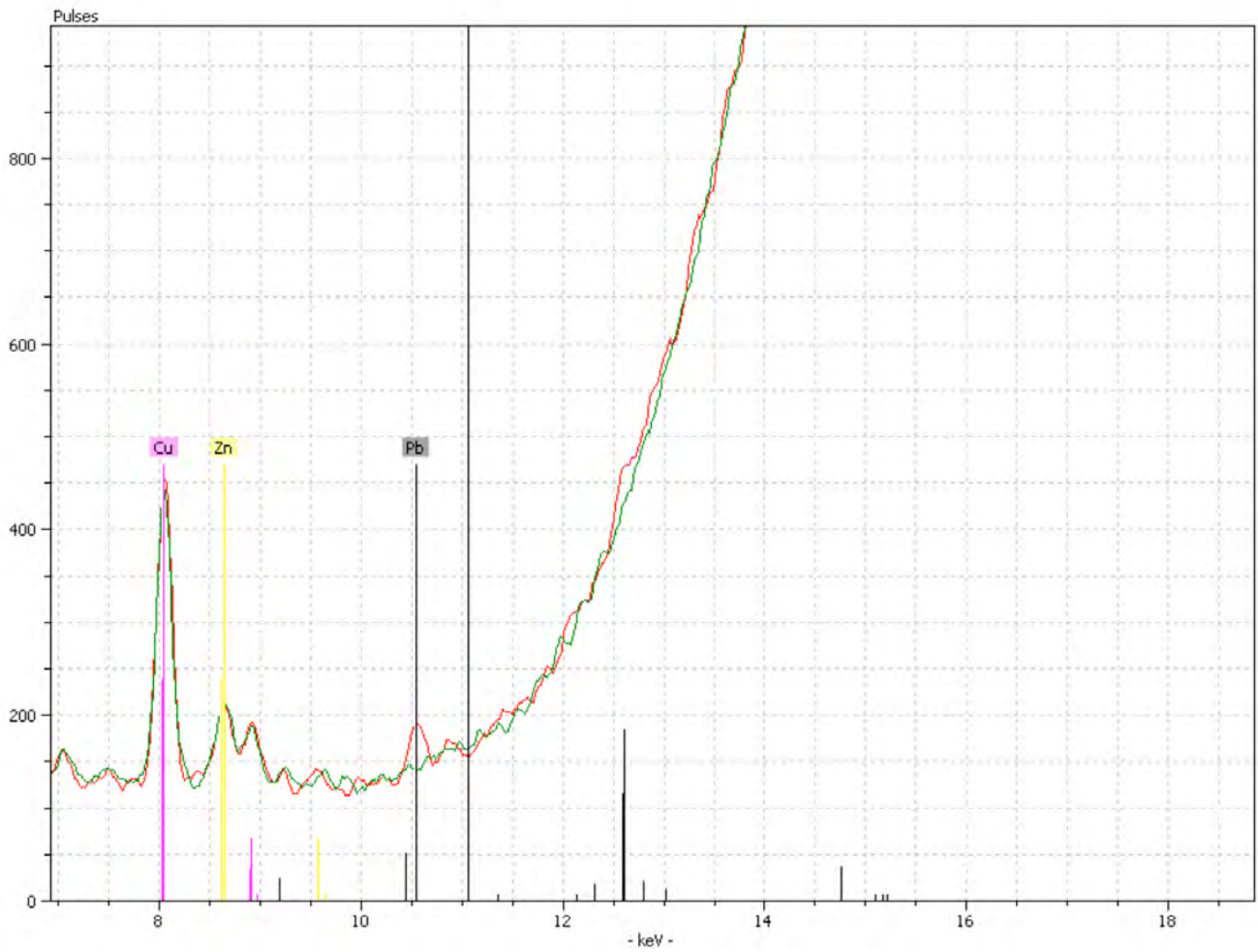


Figure 3: Solution with 1 mg/L of Pb (red) and distilled water (blue) collected using the Red filter. The La1 and L $\beta$ 1 peaks are only slightly detectible, but still clearly present. Cu and Zn are trace metals used in the instrument and vacuum grid.

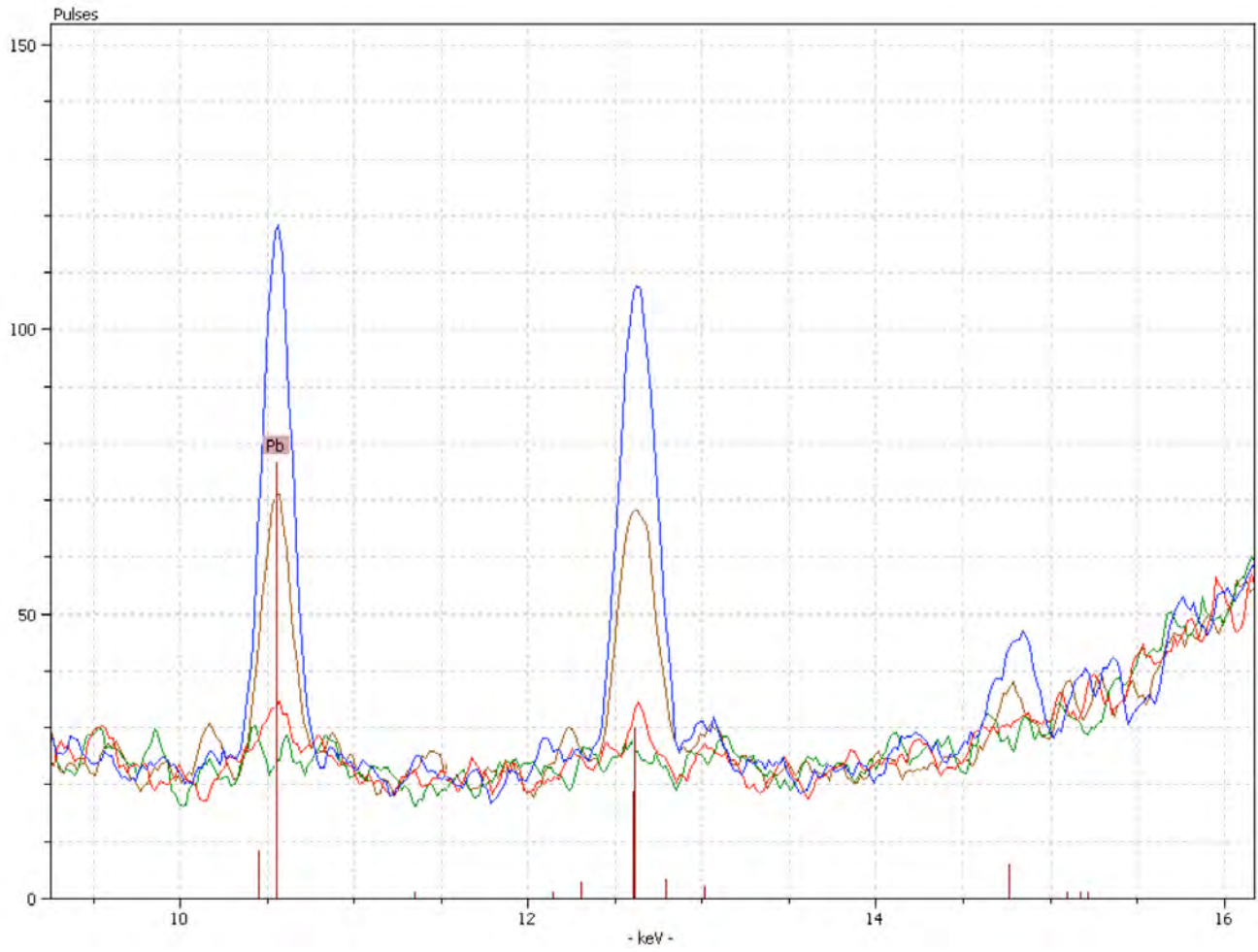


Figure 4: Lead concentrations of 1 mg/L (red), 12.5 mg/L (brown), and 25 mg/L (blue) using the green filter. The green line represents a spectrum from distilled water.



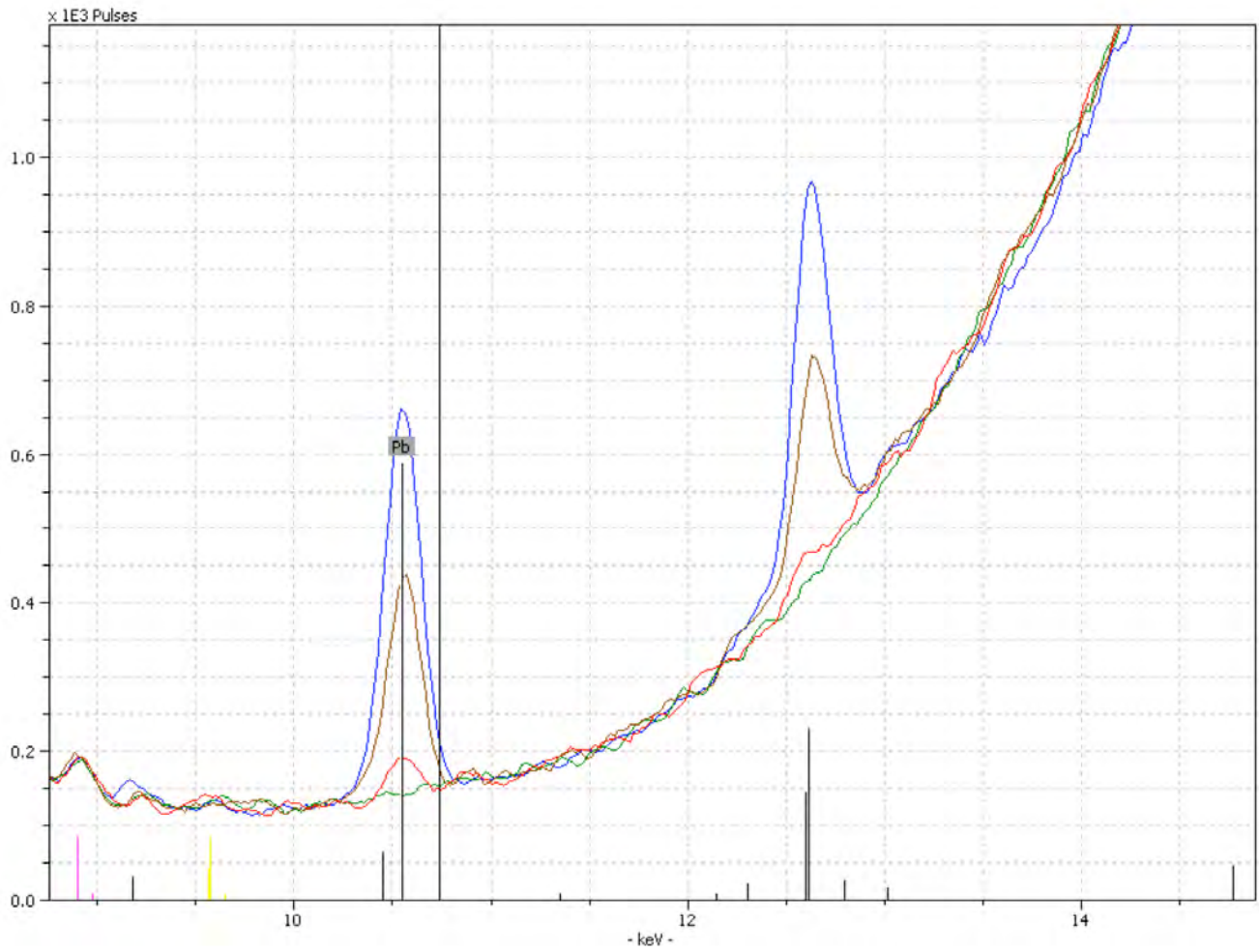


Figure 5: Lead concentrations of 1 mg/L (red), 12.5 mg/L (brown), and 25 mg/L (blue) using the red filter. The green line represents a spectrum from distilled water.



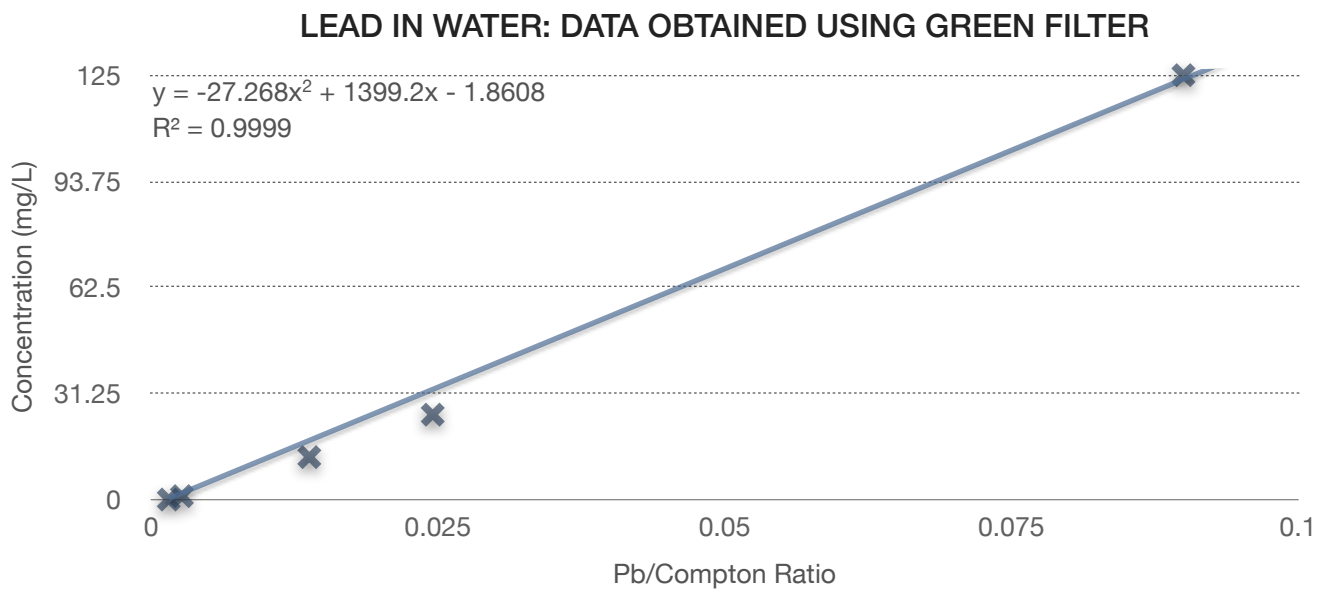
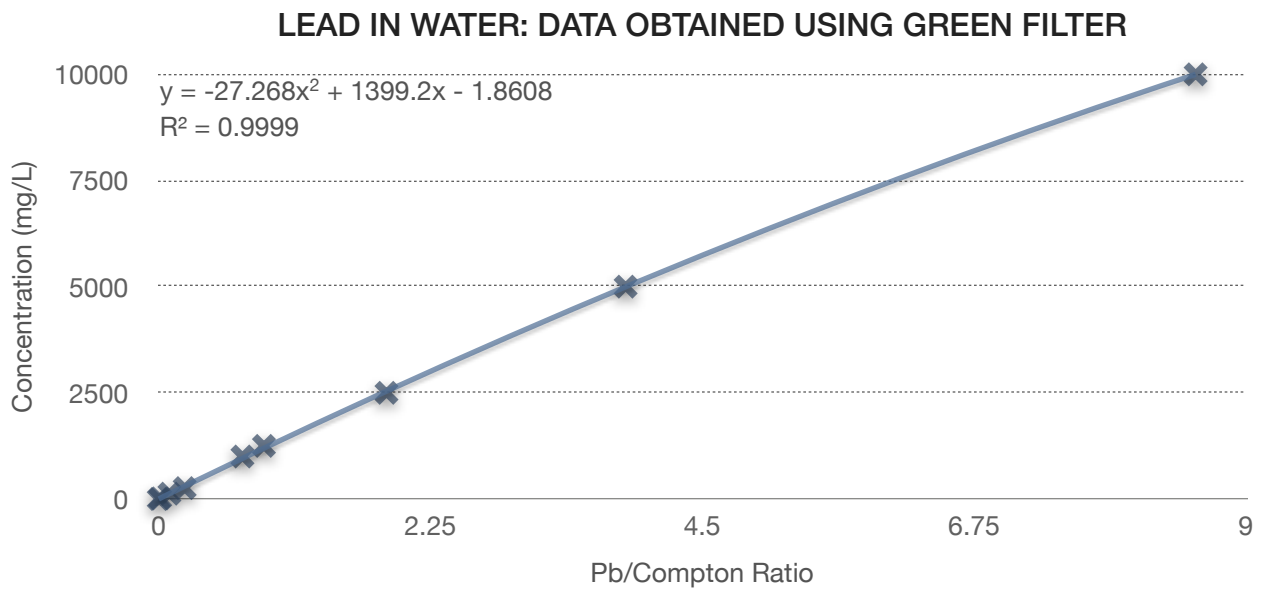


Figure 6: Calibration curves developed using green filter data. Net photons counts for Lead were normalized against the Compton peak and then regressed against concentrations to estimate uncertainty. The top graph shows the full range of concentrations (0 - 10,000 mg/L), the bottom graph shows a more limited range (0 - 125 mg/L)

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Concentration (mg/L)	Pb Cal Estimates Green (mg/L)	Pb Cal Estimates Red (mg/L)
0.00	0.00	0.04
1.00	1.58	2.43
1.00	1.43	1.80
6.25	5.68	5.45
12.50	17.62	14.91
25.00	21.15	21.64
125.00	124.93	117.17
256.00	300.64	275.32
1,000.00	957.31	902.67
1,250.00	1,198.96	1,124.61
2,500.00	2,542.88	2,472.75
5,000.00	4,998.63	5,118.20
10,000.00	9,999.65	10,611.17

Table 1: Quantification results from Green and Red filters. The green filter data produced stronger quantitative numbers than data collected using the red filter. Most error likely derives from titrating 10,000 mg/L solution to 1 mg/L. Two separate solutions of 1 mg/L Pb were titrated from 1,000 mg/L to provide replication.