EDXRF of Used Automotive Catalytic Converters

Energy Dispersive X-Ray Fluorescence (EDXRF) is a very powerful technique for measuring the concentration of elements in a sample. It is fast, non-destructive, requires no sample preparation, and can be carried out in the field or on a factory floor by operators with minimal training. It is a very important complement to other methods in analytical chemistry.

Amptek, Inc. provides components used in many EDXRF systems. Amptek is an OEM provider of X-ray detectors, preamplifiers, signal processing electronics, X-ray tubes, and analysis software to many of the companies providing turnkey EDXRF analyzers. These components are also used in custom systems, when the requirements not met by turnkey analyzers.

This note illustrates an application of Amptek's products: measuring the composition of used automotive catalytic converters. This is a challenging measurement but important measurement for XRF. Used catalytic converters have a low concentration (hundreds of ppm) of valuable elements, generally Rh, Pd, and Pt. Accurate measurements of their concentrations are important for determining the value of a used converter. The challenge for XRF is that used catalytic converters also contain many other elements (Pb, Os, Ce, La, Ba, Zn, Zr, Fe) at much higher concentrations. Further complicating the measurement, these materials are in a low Z matrix (aluminum and silicon oxides). This application is shown here because it illustrates some of the important challenges one faces in measuring complex materials.

1   INTRODUCTION

Catalytic converters contain valuable materials. A typical automotive catalytic converter contains 2 to 7 grams of Pt and smaller quantities of Rh and Pd. With spot prices of $50, $60, and $25 per gram, respectively, both buyers and sellers of used catalytic converters need to know the concentration. A used catalytic converter typically sells for $20 to $30 with most of the value associated with these precious metals.

These precious metals are mounted on a ceramic substrate (silicon and aluminum oxides) at a concentration of tens to hundreds of ppm. Other metals may also be present: Ce, La, Fe, Ni, and Cu are also catalysts. Pb, Mn, and Zn are contaminants which may be found in gasoline additives, which poison the catalysts. These materials are often present at much higher levels than the precious metals one must measure.

There are many different methods in analytical chemistry which can be used to measure the concentration of precious metals in the catalytic converter. Many of the methods involve wet chemistry, so are destructive, must be carried out in a lab, require considerable time and labor, and produce a hazardous waste stream. EDXRF has some key advantages over other methods. First, it is non-destructive. Second, it requires no sample preparation. Third, it takes only tens of seconds per item. Fourth, it can be carried out in the field by operators with minimal training. EDXRF provides quick and non-destructive screening, with other methods available to validate the EDXRF results.

PROTOTYPE ANALYZER DESCRIPTION

The laboratory prototype used here is shown in Figure 1. It is not packaged for commercial use but contains all of the components necessary to carry out EDXRF analysis and is fully functional. Everything except the mechanical fixture and radiation shielding are standard products from Amptek, Inc. It includes

1) An Amptek 25 mm^2 SDD X-ray detector, with a resolution of 128 eV at the Mn K$_\alpha$ line.

2) An Amptek X-123-SDD incorporating a DP5 digital pulse processor and PC5 power supplies, operated here at a peaking time of 9.6 μs (shaping time of 4 μs), output count rate of 8 kcps, dead time of 15%.

3) An Amptek Mini-X X-ray tube at 40 kVp and 50 μA. Both Ag and W anodes were used, with different filters, discussed in the text.

4) A mechanical fixture to hold the detector, tube, and sample, along with radiation shielding.

5) Amptek's ADMCA software for data acquisition and control of the signal processor and software to control the X-ray tube. Both use a USB interface.

6) Amptek's XRS-FP software for spectrum processing and quantitative analysis.

The system was not fully optimized for this application but demonstrates key considerations. The samples were in powder form. They were Standard Reference Materials, 2556 and 2557 from NIST.
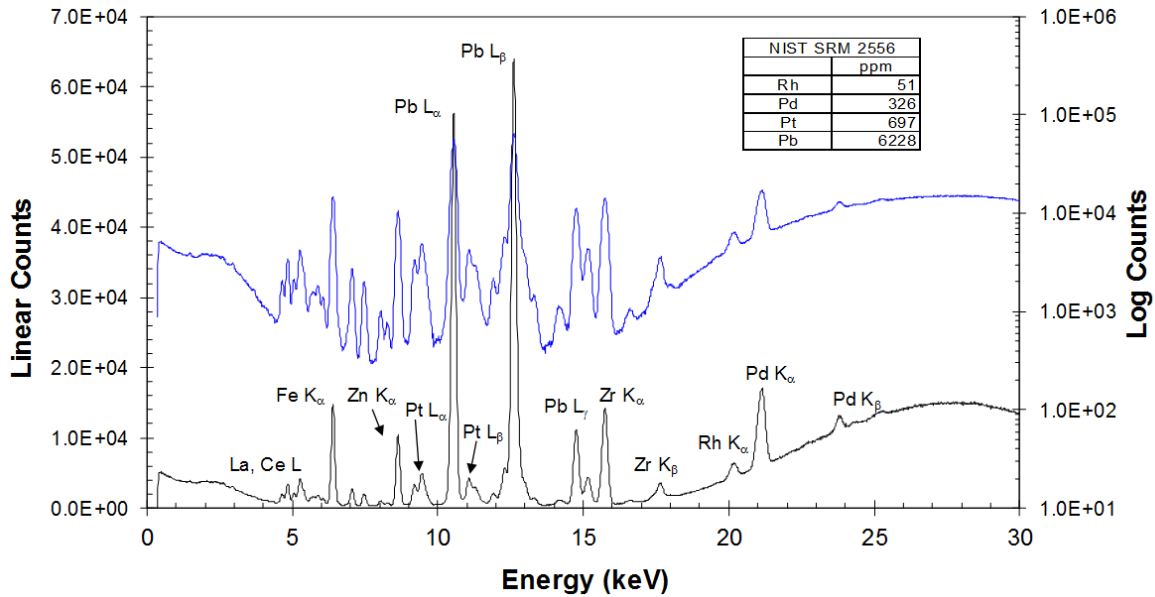

Figure 1. Photograph of the prototype analyzer.

Figure 2. Spectrum measured from one SRM 2556 plotted on a linear scale (black) and on a log scale (blue).

SPECTRA

Figure 2 shows a raw spectrum taken on SRM 2556. The same data are plotted on both linear and log vertical scales, in black and blue respectively. Figure 3 shows the same raw spectrum in black, along with the processed spectrum. The blue trace is the background continuum, while the gray trace is the result of correcting for escape peaks, pile-up, and background removal. The red filled trace shows the fit of the Pt L peaks to the (gray) corrected spectrum. The green lines mark the numerous Pb L lines.

Lead has a concentration of 0.6%, so the Pb L lines clearly dominate the spectrum. Spectral lines from the precious metals are easily seen but accurately quantifying their concentration presents some challenges.

The first measurement challenge is to properly process the spectrum to accurately determine photopeak areas. The Pt peaks exhibit overlap, e.g. Pt L_α overlaps the Zn K_β and Pb $L_{\lambda 1}$ peaks on either side. The Rh K_α line is superimposed on a large background continuum. La and Ce are not the most valuable components but are important, and only weak L lines are visible, superimposed on escape peaks and background.

The second challenge is addressing the matrix effects. One must account for both the low Z portion of the matrix, which attenuates the X-rays of interest, and the higher Z portion which exhibits both absorption and enhancement. The light elements, aluminum and silicon oxides, are not directly seen in the spectrum while the high Z elements overlap.
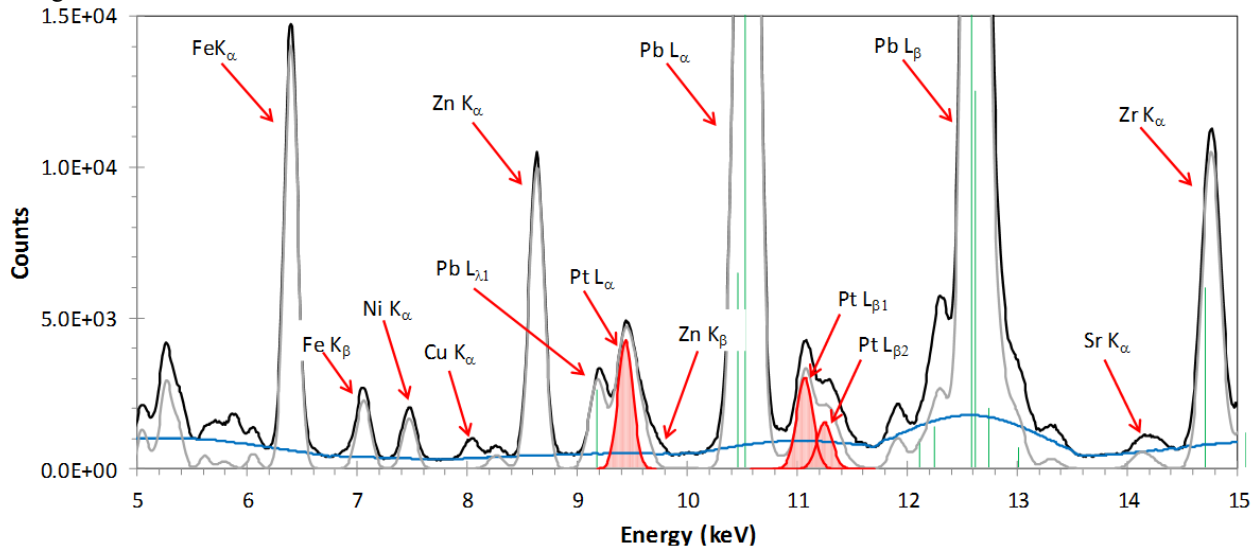

Figure 3. Detail of spectrum shown in Figure 2, showing both processed and raw spectra.

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	SRM 2556		SRM 2557	
	NIST Values	Measured	NIST Values	Measured
Fe	8,000	7,658 + 94	15,000	12,776 + 788
Ni		360 + 17	5,000	5,311 + 710
Zn	600	594 + 7	1,000	652 + 14
Zr	300	310 + 3	300	291 + 6
Rh	51 + 1	47 + 4	135 + 2	132 + 14
Pd	326 + 2	341 + 5	233 + 2	230 + 18
Cd		3 + 8	44	0 + 1
Ba	100	177 + 89	2,900	1,267 + 232
La	7,000	3,385 + 746	700	289 + 715
Ce	10,000	10,426 + 337	13,000	12,344 + 489
Pt	697 + 2	695 + 12	1,131 + 11	1,011 + 53
Pb	6,228 + 49	6,288 + 64	13.931 + 97	12,003 + 827

Table 1. Summary of measurement results, in ppm. Note that the NIST SRM only specified the measurement uncertainty for Pb, Pt, Rh, and Pd. The other concentrations of the other elements were "for reference only" and had no specified uncertainty, in part because of disagreements between the results of different chemical analyses.

RESULTS

Table 1 shows the results of the analysis. These results were obtained using a Mini-X with a W anode, using nonlinear deconvolution to fit the spectra and using a fundamental parameters (FP) analysis method, calibrated using these standards. A long duration (1 hour) reference spectrum was obtained with each sample and used to calibrate the FP parameters. A set of 50 spectra, of five minute durations, were then taken on each sample and analyzed using these parameters. The "measured" column shows the mean of the 50 measurements.

NIST reported certified values and a measurement uncertaintly only for the Pt, Pb, Rh, and Pd. The other elements are non-certified because there was not agreement between different analytical methods. The uncertainty listed in the "measured" columns is the one sigma standard deviation of the 50 results.

2   DISCUSSION

CONFIGURING THE SYSTEM

Detector and signal processing

It is important to choose the best detector and to select the best signal processing parameters. For this particular application, high energy resolution is very important to separate the many closely spaced spectral lines. This is why the 25 mm^2 SDD was chosen, with a peaking time of 9.6 μs, giving an energy resolution of 128 eV FWHM at 5.89 keV. In many EDXRF applications, in fact most applications, energy resolution is not the most critical parameters. The quality of the analytical results always depends on the number of counts in the spectrum, and for most cases, the optimum configuration is at a relatively short

peaking time (with degraded energy resolution) but high count rates (assuming the X-ray tube can provide enough flux). For this application, however, energy resolution is vital.

Excitation Source

The choice and configuration of the excitation source can have a major effect on the precision and accuracy of the measurement. Figure 4 shows four different spectra from the same sample, SRM 2556, with different configurations for the excitation source. These illustrate some of the major issues.

The green trace shows the same configuration as Figure 2, yielding the data shown in Table 1. This was a W anode tube, operated at 40 kVp, using a filter consisting of 25 μm W covered by 1000 μm Al. This is yields a low background continuum below 20 keV.
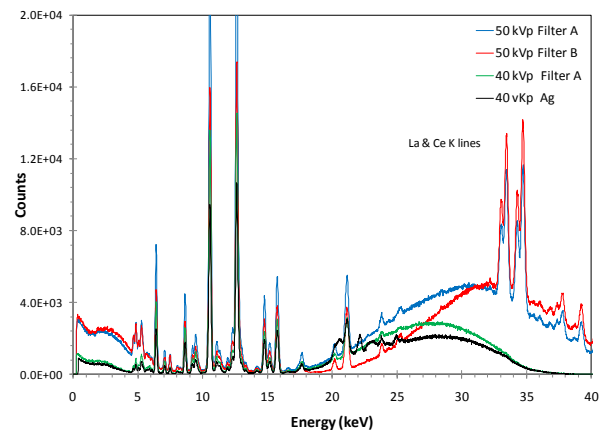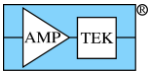

Figure 4. Spectra taken using different configurations for the X-ray tube, the excitation source.

The blue trace shows the spectrum with a prototype 50 kVp Au anode X-ray tube with the same filter, at

the same current. The most visible change is that the La and Ce K lines are excited. These K lines are strong and well separated from the background, unlike the L lines around 5 keV. This uncertainty of the La and Ce measurement with this configuration will be 25x better (everything else kept equal). The photopeak intensities and net count rate are about twice those of the green trace, simply because more X-rays exit the filter. There is more background continuum at low energy, below 5 keV. This continuum is due to incident X-rays which Compton scatter out of the detector.

The red trace shows the same 50 kVp Au anode tube but with more filtering (50 μm W behind 1000 μm Al) and twice the beam current. The heavier filtering reduces the background from 20 to 30 keV, thus improving the detection of Rh and Pd. The photopeak count rates and low energy background are comparable to the blue trace. The heavy filter improves the background, but for the same current reduces the photopeak intensities. The optimum will depend on the application.

The black trace was obtained with an Ag anode tube operated under the same conditions as the W anode tube yielding the green trace (40 kVp, same filter, same current). The major different is that scatter peaks from the Ag K lines at 22 and 25 keV are visible. This includes Rayleigh peaks at 22 and 25 keV and broader Compton peaks are lower energy. As will be discussed below, the relative intensity of the Rayleigh and Compton peaks indicates the mean Z of the matrix. This can be used in matrix correction to account for the low Z portion of the matrix. With this particular measurement, the Ag scattered lines overlap with the Rh and Pd K lines. The advantage of doing a scatter correction must be weighed against the need to separate these peaks.

The point of this discussion is that the choice of the X-ray tube, the kVp setting, and the tube filter are very important. Many instrument include multiple filters or a filter wheel. A single sample might be analyzed with two filters (and different kVp settings) which are optimized for different elements.

MATRIX EFFECTS

Quantitative analysis in EDXRF is based on the relationship

$$C_i = K_i \cdot I_i \cdot M_i \qquad [1]$$

where C_i is the measured concentration of element i, K_i is its calibration factor, I_i is the photopeak intensity for that element, and M_i represents a correction for matrix effects. In chemical analysis, "matrix" refers to the components of a sample other than the analyte. In the used automotive catalyst, when measuring the concentration of Pt, the matrix is everything but Pt.

Both absorption and enhancement effects are important. The Rh and Pd atoms in the matrix will emit K X-rays, some of which are then absorbed by Pb and Pt, resulting in additional characteristic X-rays from these elements. The count rates from Rh and Pd are reduced by the presence of Pb and Pt, while the count rates from Pb and Pt are enhanced by the presence of Rh and Pd. The photopeak intensity of every element in the sample is affected by the concentration of all the other elements. The accuracy of each element's measured concentration depends on all the others. In a complicated sample, like this used automotive catalytic converter, this is a challenge. Moreover, light elements (silicon, aluminum, oxygen, carbon) represent >95% of an automotive catalytic converter. These materials absorb X-rays from the elements of interest. The absorption depends on the relative amounts of the light elements but these light elements cannot be directly measured this system.

Figure 5 shows the measured photopeak intensity for Rh and Pt versus concentration for the two samples along with linear regressions. If matrix effects were negligible, the result would be a straight line through the origin. With only two samples, we will always get a straight, but notice that it does not go through the origin. The sample with high Rh and Pt concentration, SRM 2557, also has a high concentration of Pb, Ce, Ni, etc. These are presumably attenuating the Rh and Pt flux, leading to the error.
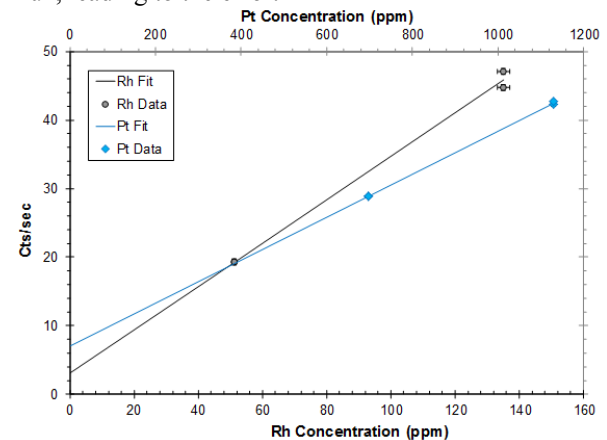

Figure 5. Plot showing the photopeak intensity vs concentration for Rh and Pt in the samples.

ANALYSIS METHODS

Amptek's XRS-FP software has several different choices for quantitative analysis which are different approaches to the solution of Eqn. [1]. Once the spectra were acquired and processed, we applied several different quantitative methods and compared the results. These will be discussed here.

The simplest option is the linear least-square approach. This method neglects inter-element effects. It assumes that M is unity so that each element can be
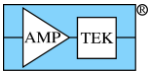
analyzed independently using a linear regression. It requires one to measure the photopeak intensities for known calibration standards and then applies the linear regression. As Figure 5 illustrates, for the case under consideration here, we will always get excellent results for a linear regression between the two points we have available (SRM 2556 and 2557) but this is not the appropriate method for these samples.

Fundamental Parameters

Sherman [1] wrote an equation which yields the intensity of the characteristic lines emitted by a sample of known composition. The Sherman equation considers primary and secondary fluorescence for a given incident X-ray spectrum and for a given configuration of the spectrometer. Inverting the Sherman equation lets one determine the concentrations of elements required to produce the measured set of intensities. The direct use of Sherman's equation is termed the Fundamental Parameters (or FP) method. Given the mathematical complexity of the true FP method, various simplified approximations are often used.

Amptek's XRS-FP software can implement the FP method in a "standardless" mode. This mode uses theoretical equations to estimate both the calibration coefficients K and the inter-element effects M in Eqn. [1]. This is very convenient but its accuracy will be limited, due to simplifying approximations that are required and to simple tolerances on the system.

Better accuracy is obtained if one calibrates the parameters. This can be done using multiple single element standards, by using a single multielement standard, or by using several multielement standard. If calibrations are only available for some of the elements, the other elements are analyzed using the standardless mode. The best analytical results are obtained when the calibration standards have a composition similar to that of the material to be measured. As mentioned previously, in this case one hour spectra were obtained from the two SRMs and used to calibrate the parameters, then a series of 5 min spectra from the sample SRMs were evaluated.

Scattered Intensity Ratio

Standard FP works well when all of the elements of interest have characteristic lines one can readily measure. However, in this case most of the sample is very low Z. The Al and Si lines cannot be measured very well so FP cannot accurately determine their concentration. But the ratio of backscatter peaks, scattered from the tube anode characteristic lines, is related to the mean Z of the target. By measuring this ratio, the software can estimate the mean Z and from this the attenuation. Two things are necessary for this approach. First, the tube has to create scattered K peaks, so the W anode will not work for this. For this

reason data were taken using a Mini-X with an Ag anode. Second, the XRS-FP software requires one to obtain a set of low-Z standards and measure the spectra. A set of ten standards were prepared using common materials such as polyethylene, graphite, water, and table salt. Spectra were taken for these standards and the XRS-FP software fit the ratio of the Compton to Rayleigh peak intensities (C/R ratio) to the mean Z of the standards. Figure 6 shows the spectra while Figure 7 shows the data and its fit, along with a list of the standards.
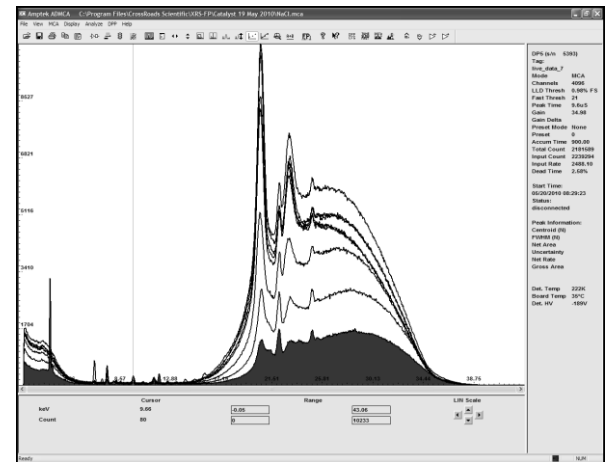

Figure 6. Spectra measured from low Z standards used to calibrate the SIR option of XRS-FP.

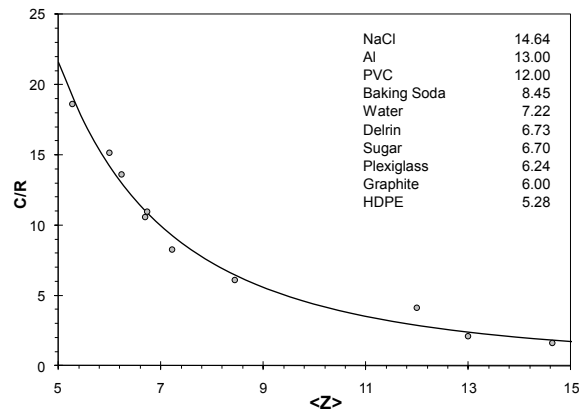|	
NaCl	14.64
Al	13.00
PVC	12.00
Baking Soda	8.45
Water	7.22
Delrin	6.73
Sugar	6.70
Plexiglass	6.24
Graphite	6.00
HDPE	5.28

Figure 7. Plot showing the relationship between the Compton to Rayleigh intensity (C/R) versus mean Z.

After the SIR calibration was carried out, one hour spectra were obtained to calibrate the FP parameters, then a set of 50, five minute spectra were obtained and were analyzed as with the W anode tube.

Comparison

Table 2 shows the results of the different FP methods with the error bars representing the standard deviation of the results, i.e. the precision of the measurements. The standardless method clearly demonstrates the worst accuracy. Its results are generally within a factor of two of the correct values. There can be applications where this is sufficient, for
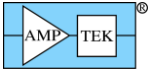
example screening materials to identify certain elements at the order of magnitude level.

The W anode tube gave much better results for Rh and Pd than the Ag anode tube, because the Rh and Pd K lines overlap the scattered Ag lines. The SIR analysis provides better accuracy for La, Cr, and Fe, which are the lowest energy lines analyzed here. The higher energy lines are comparable, for the two standards available here.

	NIST			Ag Anode									W Anode					
				FP - Standards			SIR FP - Stds			FP- Standardless			FP - Standards			FP- Standardless		
Fe	8,000			8,135	+	176	7,930	+	157	5,391	+	142	7,658	+	94	5,305	+	146
Ni				468	+	25	457	+	24	345	+	24	462	+	21	361	+	17
Zn	600			612	+	9	614	+	9	1,271	+	46	594	+	7	1,279	+	46
Zr	300			302	+	4	302	+	4	574	+	31	310	+	3	560	+	32
Rh	**51**	**+**	**1**	**65**	**+**	**17**	**65**	**+**	**17**	**141**	**+**	**37**	**47**	**+**	**4**	**101**	**+**	**12**
Pd	**326**	**+**	**2**	**348**	**+**	**23**	**344**	**+**	**22**	**814**	**+**	**67**	**341**	**+**	**5**	**783**	**+**	**47**
Cd				103	+	29	99	+	27	103	+	29	3	+	8	4	+	9
Ba	100			150	+	107	167	+	119	2,670	+	1,867	177	+	89	2,739	+	1,351
La	7,000			8,178	+	1,795	6,710	+	1,458	4,696	+	792	3,385	+	746	5,481	+	932
Ce	10,000			10,242	+	454	10,467	+	455	5,563	+	413	10,426	+	337	5,484	+	320
Pt	**697**	**+**	**2**	**726**	**+**	**17**	**724**	**+**	**17**	**1,131**	**+**	**51**	**695**	**+**	**12**	**1,115**	**+**	**44**
Pb	**6,228**	**+**	**49**	**6,366**	**+**	**70**	**6,300**	**+**	**69**	**9,772**	**+**	**409**	**6,288**	**+**	**64**	**9,723**	**+**	**413**

Table 2. Results of the different quantitative methods applied to SRM 2556.

3   CONCLUSIONS

This note shows one possible application of Amptek's EDXRF equipment: measuring the concentration of precious metals, particularly Rh, Pd, and Pt, in used automotive catalytic converters. This is a challenging measurement since it involves accurate measurement of elements present at tens to hundreds of ppm in a matrix which is mostly low Z but includes many higher Z elements. It is an example where the high energy resolution of the SDD is critical.

This application also illustrates some interesting challenges in EDXRF. It shows how important matrix effects can be, it shows some of the different quantitative methods which can be applied, and it shows the trade-offs involved in selecting the energy and filtering of the excitation source.

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[1]