

## EDXRF of Light Elements in Water

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 concentration of low-Z ions (Si, P, S, Cl, and Ca) in water. This application is shown because it illustrates many of the basic concepts of EDXRF, because it illustrates some of the challenges of measuring light elements, and because it can easily be duplicated in a laboratory.

### 1 INTRODUCTION

*Characteristic X-rays* are emitted from elements when their electrons make transitions between the atomic energy levels. *X-Ray Fluorescence* is the emission of characteristic X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays.

Because each element has a unique set of atomic energy levels, it emits a unique set of X-rays which are characteristic of this element. The presence characteristic X-ray indicates the presence of the element. Moreover, the intensity of an X-ray line depends on the number of corresponding atoms which were excited. In EDXRF, the intensities of the characteristic X-rays are measured to determine the elemental composition of a sample,

EDXRF has some key advantages over other methods used in analytical chemistry. First, it is non-destructive, causing no damage to the sample tested. Second, it requires no sample preparation. Third, it can take as little as tens of seconds per item (though sensitivity improves with measurement time). Fourth, it can be carried out quickly by operators with minimal training. There are other methods used in chemical laboratories to analyze elemental concentration, some with far better

accuracy, but EDXRF is a powerful tool for quick and non-destructive screening of many products.

### 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<sup>2</sup> SDD X-ray detector, with a resolution of 128 eV at the Mn K<sub>α</sub> 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 with a W anode, at 12 kVp and 100 μA. No filter was used.
- 4) A mechanical fixture to hold the detector, tube, and sample, along with radiation shielding. In the measurements reported here, the fixture was attached to a ringstand and mounted vertically, pointing down towards an Al sample cup containing the solution to be measured.
- 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 samples used in this analysis were obtained by dissolving compounds, e.g. CaCl<sub>2</sub>, in deionized water.



Figure 1. Photograph of the prototype analyzer.

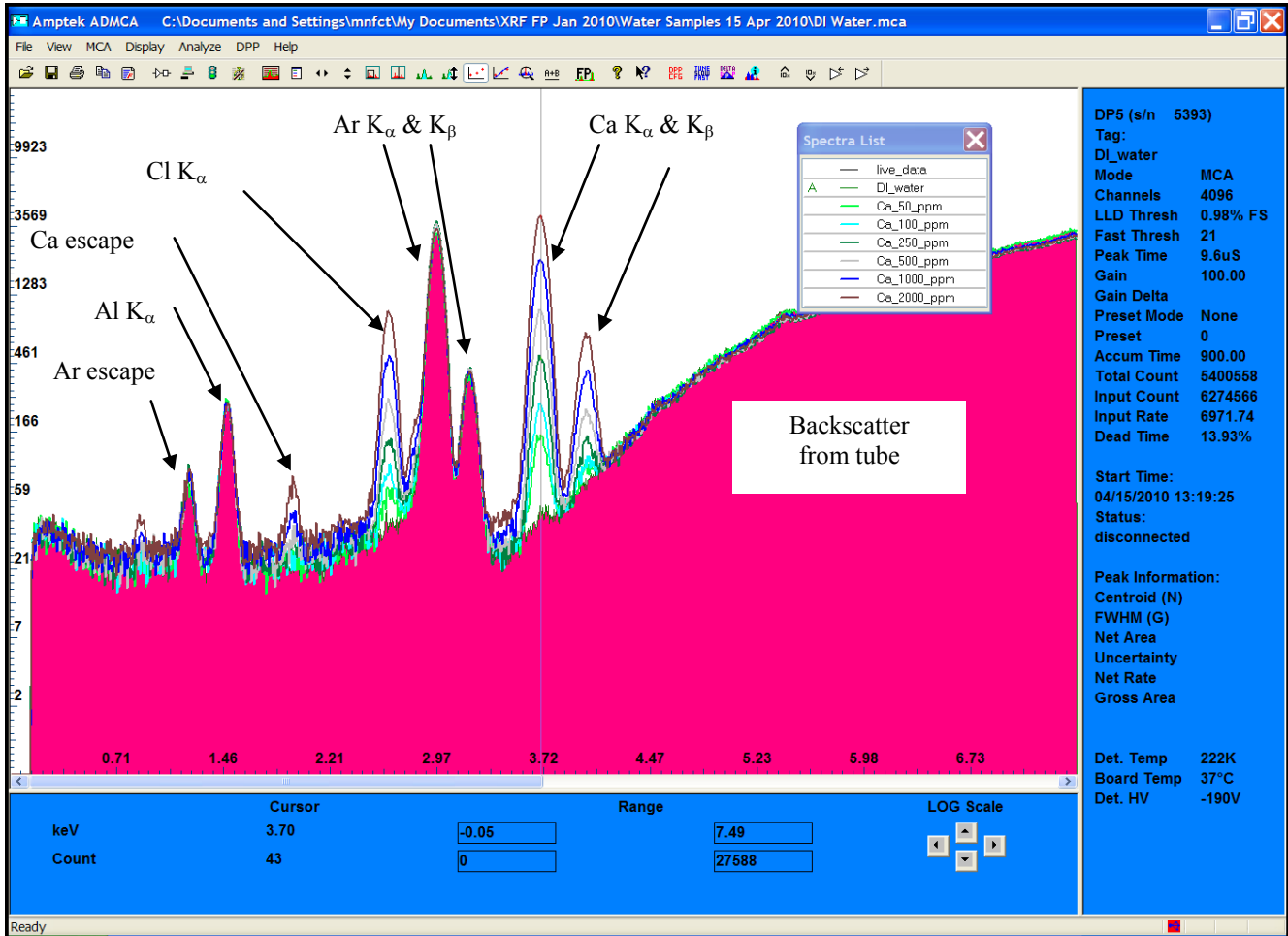


Figure 2. Plot showing spectra obtained from CaCl<sub>2</sub> dissolved in DI water with Ca concentrations of 50 to 2000 ppm. This plot is a screen capture from Amptek's ADMCA software, used for control, data acquisition, and display.

## SPECTRA

**Error! Reference source not found.** shows raw spectra taken on a set of samples with Ca at 50, 100, 250, 500, 1000, and 2000 ppm. The solid red trace shows the spectrum from deionized water. Each spectrum was measured for 15 minutes. There are some key features which are visible in this spectrum.

1. The Ca and Cl peaks are clearly visible, indicating the presence of these elements. The intensity of the peaks is proportional to the concentration of the CaCl<sub>2</sub>. This is the primary signal used in EDXRF analyses.
2. The Ca peaks are much more intense than the Cl peaks, even though there are two Cl atoms for each Ca. This will be discussed in more detail below, but in general, the intensity is lower for lighter elements.
3. There is a background continuum visible, due to X-rays from the tube which Compton scatter from

the water. The background must be removed to measure the X-rays of interest.

4. A pair of peaks can be seen at 3.0 and 3.2 keV in all the samples. This is due to Ar, a constituent of air. The Cl K<sub>β</sub> peak is a shoulder on the Ar peak. Separating such overlapping peaks is a challenge and requires good energy resolution. There is also an Al K<sub>α</sub> peak, arising from Al used in the detector construction. The Ar and Al peaks are examples of environmental interference.
5. There are escape peaks visible due to Ca, Ar, and Cl. These escape peaks arise because some of the X-rays scatter out of the detector, depositing less than their full energy in the detector. These secondary peaks can obscure lower energy characteristic X-rays. For example, the Ca escape peak (1.94 keV) is quite close to the P K<sub>α</sub> peak (2.02 keV).

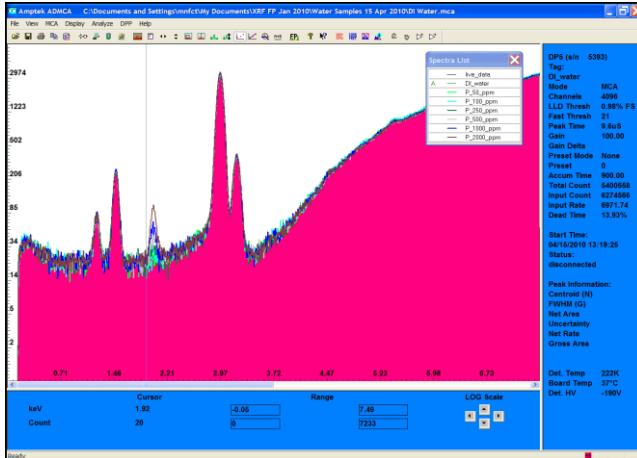


Figure 3. Plot showing P at 50, 100, 250, 500, 1000, and 2000 ppm .

Figure 3 shows similar results obtained with P. The intensity of the characteristic X-rays is much lower than was seen with Ca and Cl. Figure 4 shows a spectrum taken with a mixed sample. The presence of the elements of interest can clearly be seen.

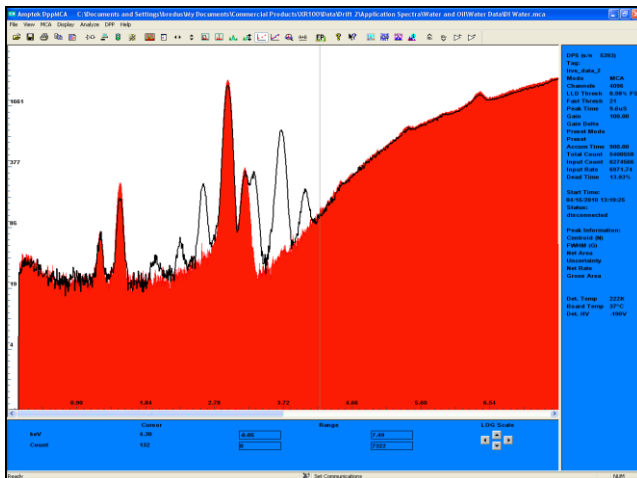


Figure 4. Plot showing spectrum taken with a mix containing 200 ppm P, 200 ppm S, 700 ppm Cl, and 400 ppm Ca.

## RESULTS

A set of 15 minute spectra were taken using samples with concentrations from 50 to 2000 ppm and these were used to calibrate the software, using a linear least squares method. Mixed samples were then measured using these calibrations. The results are shown in Table 1.

	Mix 1		Mix 2	
	Actual	Measured	Actual	Measured
P	200	70 ± 30	100	0 ± 5
S	200	210 ± 30	115	120 ± 30
Cl	710	630 ± 20	440	390 ± 25
Ca	400	430 ± 5	250	260 ± 5

Table 1. Summary of results obtained from mixtures.

## 2 DISCUSSION

### EFFICIENCY

As is clear from Figure 2 and Figure 3, light elements produce very low intensity X-ray lines. This establishes a limit on both the measurement uncertainty and on the measurement time. There are several reasons for this low intensity.

1. Lower energy X-rays have a lower fluorescent yield, i.e. fewer are produced for every photoelectric interaction in the atom.
2. Low energy X-rays are absorbed more efficiently by the sample matrix, in this case water. At 1.74 and 2.62 keV, the Si and Cl  $K_{\alpha}$  lines, the attenuation length is 10 vs 40  $\mu\text{m}$ . The Cl measurement essentially measures a greater depth into the sample.
3. Low energy X-ray are attenuated by the Be window used on the detector and by air between the detector and sample. Figure 5 shows the intrinsic efficiency of the detectors behind various window thicknesses and air paths (This plot is also shown in Amptek's application note AN-SDD-2 with more discussion. The note also include efficiency tables.) The air path is critical: for P, a 1/3 mil Be window transmits 80% of the X-rays, but 1 cm of air will transmit 50%. At low energies, the best results are obtained in vacuum, but this is not feasible with water. A He purge can also be used.

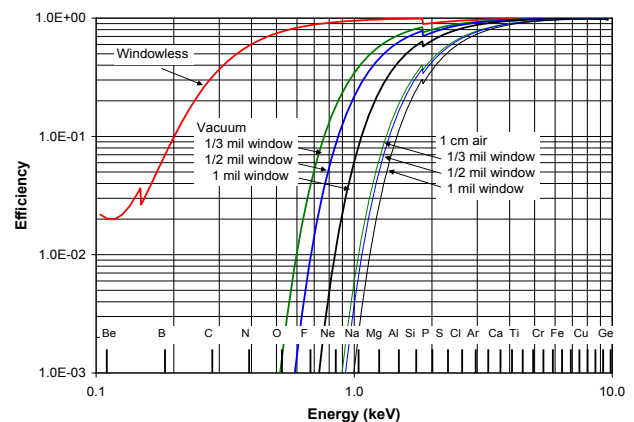
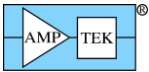


Figure 5. Plot showing the intrinsic efficiency of the detectors for light elements.

### SPECTRUM PROCESSING

There are two major steps involved in going from the raw spectra, i.e. Figure 4, to the quantitative results, i.e. Table 1. The first major step, spectrum processing, yields the intensities for the characteristic X-ray lines. There are several smaller steps which are required to



process the spectrum: correcting the spectrum for various artifacts (escape peaks, pulse pile-up), removing the background continuum, and then fitting the peaks to a sum of Gaussian functions. The second major step computes, from the intensities, the concentrations of the elements which are present.

Processing the spectrum is very important with these spectra, since the peak to background is low and there are several artifacts present, including the Ar, Al, and escape peaks. Figure 6 illustrates the processing. The black trace shows the raw spectrum from CaCl<sub>2</sub>. The data are smoothed, then escape peaks removed (the green trace shows the escape features which were removed and added to the correct channels). Next a function is fit to the background, yielding the blue curve, and this is subtracted, yielding the gray curve. Finally, the software fits a sum of Gaussians at the chose characteristics X-ray lines. Note that the Al and Ar peaks are not fit since they are not analyzed.

The Ca and Cl peaks are clearly visible. Note that the Gaussian deconvolution assigned a small number of counts to the Si and S peaks. There may have been some trace Si and/or S in the sample or this may be a numeric artifact, fluctuations in the processed result which can be removed with better processing.

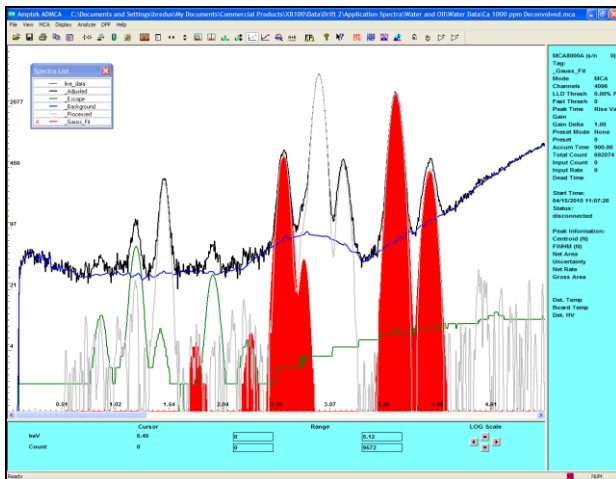


Figure 6. Plot showing raw and processed spectrum for CaCl<sub>2</sub>.

CALIBRATION TO STANDARDS

In the analysis shown here, the linear least squares analysis method was used. In other words, we assumed that the concentration of each element was linearly related to the intensity of the corresponding photopeak, i.e. the net count rate of the photopeak. This implies that each element can be analyzed independently. This is not a general property of X-ray fluorescence: in a water sample containing both Ca and Cl, the Cl atoms in the water will absorb some of the Ca characteristic

X-rays, and the Cl atoms will then fluoresce. This will decrease (increase) the measured count rate for Ca (Cl).

This is an example of a matrix effect. Matrix effects are not limited to XRF. One reference states

In chemical analysis, "matrix" refers to the components of a sample other than the analyte. The matrix can have a considerable effect on the way the analysis is conducted and the quality of the results obtained; such effects are called matrix effects...The most common approach for accounting for matrix effects is to build a calibration curve using standard samples with known analyte concentration and which try to approximate the matrix of the sample as much as possible.<sup>1</sup>

In this particular application, light elements at low concentrations in water, matrix effects are minimal. It is reasonable to neglect inter-element effects, and the dominant components of the matrix will have the same absorption properties for each measurement. Therefore, one can use a linear regression between the concentration and net count rate. Calibration spectra were used with a long accumulation time (1 hour each) to minimize statistical uncertainty in the calibrations.

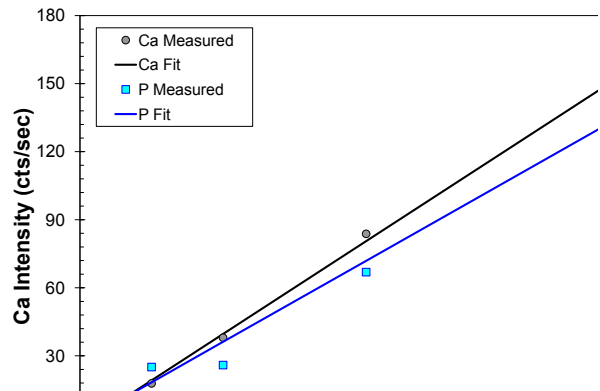
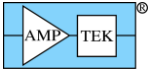


Figure 7. Plot showing linear regressions for Ca and P.

Figure 7 shows the calibration data and linear regressions for Ca and P. The correlation coefficients were >0.99 and the intercepts are <10 ppm. The net count rate from P is very low, only 1 s<sup>-1</sup> for 1000 ppm, but the it can be measured quite accurately. For this plot, the Ca data were fit to the samples with known Ca concentrations and the P data were fit to the samples with known P concentrations.

Calibration Challenges

In the XRS-FP software, the calibration files for all elements are combined. If we used the Ca and P data above, there are ten spectra. The Ca calibration would use the five P spectra as "blanks", assuming zero Ca, and so these will strongly impact the intercept of the calibration. Note that, in Figure 6, the processed CaCl<sub>2</sub> spectrum shows a small number of counts in the P peak. This small number of counts in the P peak, observed with Ca and S spectra, led to a non-zero



intercept in the regression used in XRS-FP for the P. This, in turn, led to the errors observed in Table 1.

Similar errors are observed for the other elements, due to small nonzero counts in the processed spectra, but the effect is largest in P due to its very low intensity. The origin of the P counts in CaCl<sub>2</sub> spectra is not clearly. They could be artifacts of the spectrum processing. They could be due to contamination in the CaCl<sub>2</sub> samples (trace amount of P). The sensor head may have become contaminated with small amounts of each compound (there were water spills and the some evaporation of the samples).

There are possible solutions to this issue which were not explored for this demonstration. First, better results may be obtained by tuning the parameters used for spectrum processing. For example, a linear and nonlinear deconvolution can give different results. The nonlinear option adjusts the centroids and FWHM of the peaks by a small amount to obtain a better fit, but as with any nonlinear optimization problem, it may converge on a local minimum. Changes to smoothing and background correction parameters may reduce false peaks. Second, rather than many pure element standards, it would be better to use a few standards, each with several elements. This would give fewer "zero" results to skew the intercept calculation. Third, independent verification of the calibration standards to ensure no cross-contamination would be useful.

### IMPROVING ACQUISITION TIME

These measurements were for a proof of concept demonstration and clearly showed the ability to measure the light elements in water down to tens of ppm. The measurement time, 15 minutes, is acceptable in many applications but is rather long. There are several changes that could be made to reduce the measurement time, or equivalently to reduce the detection limit for the same measurement time.

1. Increase the current on the X-ray tube. It was set to 100  $\mu$ A but can operate to 200  $\mu$ A. This would increase the dead time to 30%, which is quite acceptable.
2. Reduce the air path. The sensor head, designed for general laboratory use, had 1.7 cm of air from the sample to the detector. Reducing this distance would improve the low energy measurement considerably. Use of a He purge is more complex but would offer even more improvement.
3. Use a higher energy X-ray tube. Amptek's Mini-X is a small tube, designed primarily for portable instruments and with a 4 W limit. There are other X-rays tubes available which are not as compact but provide much higher power levels and hence higher count rates.

In many cases, the best analytical results are obtained at relatively high count rates with short peaking times. In this application, with many closely spaced peaks due to the analytes, the Ar and Al, and the escape peaks, high energy resolution is critical.

4. Sample preparation can be used. A key advantage of EDXRF is that sample preparation is not required, but many EDXRF users to prepare their samples and get more accurate results. With water, for example, laboratory methods can be used to concentrate the elements. These add to the cost and labor but will improve sensitivity.

### 3 CONCLUSIONS

This note shows one possible application of Amptek's EDXRF equipment, measuring the concentration of light elements in water in the tens to hundreds of ppm range. This note clearly demonstrates the feasibility of such a measurement. It shows how Amptek's "Experimenter's Kit" can be used, and provides an experiment one can easily reproduce in the laboratory.

This application also illustrates some interesting challenges in EDXRF. It shows some of the problems involved in measuring light elements, it illustrates the use of the linear least square analysis method, and it shows some of the challenges involved in calibration.

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<sup>1</sup> Wikipedia