Multi-Energy Radiography of Organic Materials

Krassimir STOEV 1, Eli SIMOVA 1

1 CNL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada
Phone: 613-584-3311, e-mail: Krassimir.Stoev@CNL.ca, Eli.Simova@CNL.ca

Abstract
Opioids and explosives are believed to present a significant threat to the public in Canada. For example, more than 12800 deaths in Canada were attributed to opioid overdoses in the period from 2016 to 2019, which is nearly twice the number of the deaths attributed to car accidents. Detection and neutralization of these substances is of significance to Canadian security organizations. X-ray radiography is a well-established technique which is already in use at many security checkpoints. A cost-effective approach to identify opioids and explosives could be to modify the x-ray radiography techniques currently in wide use. This work is aimed at evaluating the possibility of using multi-energy radiography for detecting and identifying organic materials. Comparison with the dual-energy approach as also presented.

Keywords: Multi-Energy Radiography, Opioids, Explosives

1. Introduction

Opioids and explosives present a significant threat to the public in Canada. More than 12800 deaths in Canada were attributed to opioid overdoses in the period from 2016 to 2019, which is roughly two times more than the deaths attributed to car accidents. Detection and neutralization of these substances is of great importance to the Canadian security organizations. X-ray radiography is a well-established technique which is used at many security checkpoints, so a cost-effective approach will be to evaluate if a modified x-ray radiography technique can be used for opioid and explosives detection. This work is aimed in evaluating the possibility of using multi-energy radiography for detecting organic materials. Currently, dual-energy x-ray radiography is widely used as security checkpoints, but the results from applying these techniques are only used for flagging specific objects for additional testing, not for direct identification of opioids and explosives. The expectation is that a multi-energy radiography (based on the use of radiographic images taken with more than 2 energies) will improve detectability of opioids and explosives when compared to dual-energy radiography. Comparison to the dual-energy approach and hyperspectral image processing are also presented. Although the presented application is not exactly an industrial NDT technique, the same approach of multi-energy x-ray radiography can be used for identification and testing of organic components in an industrial environment.

2. Equipment

All radiographic images were taken with a micro focus x-ray tube (YXLON-Y.FXE-225.48, maximum power of 300 W) with x-ray tube voltage varying from 20 to 220 kV and x-ray tube current varying from 0.1 to 3 mA. A flat-panel digital detector (THALES FlashScan-35) was used for recording of the X-ray radiography images with the following specifications:

- Active Area: 12” x 16” (305 x 406 mm, 2240 x 3200 pixels),
- Pixel size: 127 μm x 127 μm,
- Scintillator: Gd2O2S:Tb, thickness 130 mg/cm²,
- Analogue-to-digital converter (ADC) resolution: 14 bit,
- Readout time (minimum exposure time): 1.4 seconds,
- Window Material: carbon-fiber, and
- Energy range: 20 to 220 keV without shielding.
3. Samples

The aim of the testing was to evaluate the ability of different radiographic techniques and image processing methods to discriminate between different organic materials. For these purposes, twelve dual-component (a mixture of two pure components) simulated opioid samples were prepared. The samples were based on a mixture of Caffeine (C₈H₁₀N₄O₂, molar mass of 194.208 [g/mol], density of 1.298 [g/cm³]) and Quinine (C₂₀H₂₄N₂O₂, molar mass of 324.432 [g/mol], density of 1.20 [g/cm³]). Caffeine was used as a surrogate for opioids, while Quinine is a known cutting agent. Samples were mixed in 50 mL centrifuge tubes using a VORTEXER centrifugal mixer to maximise homogeneity. Sample nomenclature and corresponding concentrations of Quinine in the samples is presented in Table 1. The final packaging of each sample saw 5 grams of powder placed in a plastic polyethylene bag.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Concentration of Quinine [weight %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D01</td>
<td>0.00</td>
</tr>
<tr>
<td>D02</td>
<td>33.47</td>
</tr>
<tr>
<td>D03</td>
<td>49.54</td>
</tr>
<tr>
<td>D04</td>
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<td>D11</td>
<td>49.83</td>
</tr>
<tr>
<td>D12</td>
<td>49.64</td>
</tr>
</tbody>
</table>

4. Measurements

All measurements were performed inside an x-ray exposure cabinet. Only 8 samples could be radiographed simultaneously, so two (2) sets of measurements were performed, with 8 samples included in each set. The two setups are presented in Figure 1 and Figure 2, along with the integration areas for the samples and for the background. For each set of measurements, several filters were used in combination with different voltages for the x-ray tube. The filters used were:

- No Filter
- 100 µm Al
- 500 µm Al
- 1000 µm Al
- 60 µm Fe
- 80 µm Cu
- 127 µm Pb
- 254 µm Pb
For each filter, radiographic images were collected using a set of different x-ray tube voltages in the range from 20 to 220 kV, with the x-ray tube current and exposure time adjusted to ensure reasonable image intensity without saturation. A total of 537 x-ray radiographic images were recorded using different x-ray tube voltages, x-ray tube currents, and filters. Results from different ways of processing the radiographic images are presented in the following sections. All image processing was carried out using macros made in-house for the ImageJ software application, capable of processing 16-bit radiographic images.

5. Image processing based on averaged intensity over area

The first radiographic image processing was based on calculating average signal intensity over pre-selected regions (see Figure 1 and Figure 2 for the area definitions) for each sample and for the background next to the samples. The calculated signal and the background areas were normalised to units [counts/sec/mA] for each radiographic image. Results from the evaluation of the first 8 samples are presented here, i.e., only images recorded using Setup #1 as defined in Figure 1 were used.
5.1 Dual-energy radiography techniques based on filters

In this case, we use the averaged signals ($S$) and the averaged backgrounds ($B$), however we used two images recorded using the same voltage setting for the x-ray tube, but with different filters. The final calculated parameter is $\left[ \frac{\ln(B_1/S_1)}{\ln(B_2/S_2)} \right]$, where $B_1$ and $S_1$ are for filter #1, and $B_2$ and $S_2$ are for filter #2. More than 600 combinations, using different filters at the same voltage setting for the x-ray tube, were evaluated. The dependence of the achieved correlation coefficient $R^2$ as a function of x-ray tube voltage is presented in Figure 3 for different filter combinations. As can be seen, only two combinations of filters render $R^2$ above 0.6 in the energy range from 125 kV to 185 kV:

- $(60 \, \mu m \, Fe) / (80 \, \mu m \, Cu)$ in the x-ray tube voltage range from 135 kV to 185 kV, and
- $(80 \, \mu m \, Cu) / (127 \, \mu m \, Pb)$ in the x-ray tube voltage range from 125 kV to 170 kV.

The best linear fits from both combinations of filters are presented in Figure 4. The overall conclusion is that a dual-energy radiography technique based on filters can be used for discrimination between the different mixtures of Caffeine and Quinine, and potentially for detecting opioids, but the sensitivity will not be high (maximum correlation coefficient $R^2$ was 0.847).

![Figure 3: Correlation coefficients for classical dual-energy radiography technique.](image-url)
5.2 Extended dual-energy radiography techniques based on filters

Not only it is possible to combine radiographic images taken with different filters at one and the same x-ray tube voltage, but one can also combine radiographic images taken with different filters at different x-ray tube voltages. This approach is outside the classical way of implementing the dual-energy radiography technique. Two different parameters were used for this version of the dual-energy radiography technique, and correlation coefficients $R^2$ were calculated for them versus the concentration of Quinine:

- $\frac{\ln(S_1(F_1, E_1))/\ln(B_1(F_1, E_1))}{\ln(S_2(F_2, E_2))/\ln(B_2(F_2, E_2))}$
- $\ln\left[\frac{B_1(F_1, E_1)}{S_1(F_1, E_1)}\right]/\ln\left[\frac{B_2(F_2, E_2)}{S_2(F_2, E_2)}\right]$  

Here $F_1$ and $E_1$ represent the filter and the energy (i.e., x-ray tube voltage) for the first measurement (radiographic image), and $F_2$ and $E_2$ represent the filter and the energy for the second measurement. For the first parameter, $\frac{\ln(S_1(F_1, E_1))/\ln(B_1(F_1, E_1))}{\ln(S_2(F_2, E_2))/\ln(B_2(F_2, E_2))}$, based on all possible combinations of measurements performed (more than 60,000 combinations for the first 8 samples of setup #1), there were more than 70 combinations with $R^2 > 0.9$, with maximum $R^2 = 0.972$. Practically all of the combinations with $R^2 > 0.9$ were different combinations of voltages for 60 \(\mu\)m Fe and 80 \(\mu\)m Cu filters, with only one combination of voltages for 80 \(\mu\)m Cu and 127 \(\mu\)m Pb filters. Some of the best fits for the first parameter are presented in Figure 5. For the second parameter, $\ln\left[\frac{B_1(F_1, E_1)}{S_1(F_1, E_1)}\right]/\ln\left[\frac{B_2(F_2, E_2)}{S_2(F_2, E_2)}\right]$, based on all possible combinations of performed measurements (more than 60,000 combinations for the first 8 samples of setup #1), the maximum $R^2$ was 0.898, but the sensitivity coefficients are about two orders of magnitude higher in comparison to the sensitivity coefficients for the first parameter.
6. Pixel-by-pixel multi-energy radiography without normalisation

The next image processing methods implemented multi-energy radiography techniques, i.e., more than two radiographic images were used to obtain the results. The radiographic images were not normalised, i.e., they were not converted to units [counts/sec/mA], but rescaling factors were used inside the applied processing equations. The purpose of this image processing was to evaluate the importance of normalisation, and to verify that processing without normalisation and without collection of background (blank) radiographic images can produce acceptable results. Only results for radiographic images taken in Setup #1 as per Figure 1 are presented here.

6.1 Multi-energy radiography Equation #1

This method is based on using four (4) raw radiographic images. The following pixel-by-pixel calculation was used to obtain the final image, i.e. the signal for each pixel \((i, j)\) was calculated as per Equation 1:

\[
\text{FinalSignal}(i,j) = \frac{LN\left[ \frac{C_2 S_{i,j}(F_1, E_1)}{C_3 S_{i,j}(F_2, E_2)} \right]}{LN\left[ \frac{C_4 S_{i,j}(F_3, E_3)}{C_6 S_{i,j}(F_4, E_4)} \right]} \quad \text{Eq. (1)}
\]

where \(C_1, C_2, C_3, C_4, C_5, \text{ and } C_6\) are rescaling coefficients, and \(S_{i,j}(F, E)\) is the raw signal for pixel \((i, j)\) for filter \(F\) and energy \(E\). Coefficients \(C_1\) and \(C_4\) were usually set to be equal to 1000, while coefficients \(C_2, C_3, C_5, \text{ and } C_6\) were usually set in the range from 1 to 10. The
final parameter was calculated using averaging over pre-selected regions, as shown in Figure 1. These parameters were correlated to the concentration of Quinine by linear fit. The total number of combinations of x-ray tube voltages was 6561. 10 different combinations of filters were tested, and for each combination of four filters, the optimization for all 6561 combinations of x-ray tube voltages was performed. The best correlation coefficient obtained was $R^2 = 0.818$, (F1: Al 500 μm at 50 kV; F2: No Filter at 60 kV; F3: Cu 80 μm at 70 kV; F4: Pb 127 μm at 80 kV).

### 6.2 Multi-energy radiography Equation #2

The second image processing method for multi-energy radiography was again based on the use of four (4) radiographic images, but the final image was obtained using the pixel-by-pixel formula:

$$FinalSignal(i,j) = \frac{\ln[C_1 S_{i,j}(F_1,E_1)]/\ln[C_2 S_{i,j}(F_2,E_2)]}{\ln[C_3 S_{i,j}(F_3,E_3)]/\ln[C_4 S_{i,j}(F_4,E_4)]}$$  Eq. (2)

with rescaling coefficients $C_1, C_2, C_3$ and $C_4$ set to 3. Again, after the pixel-by-pixel processing, the final averaged signal was calculated over pre-selected regions, as shown in Figure 1. For each combination of four filters, a total of 6561 combinations of x-ray tube voltages were used to calculate $R^2$ between the calculated parameter and the concentration of Quinine. The best combination for multi-energy radiography equation #2 had $R^2 = 0.819$, (F1: Cu 80 μm at 70 kV; F2: No Filter at 80 kV; F3: Fe 60 μm at 40 kV; F4: Pb 127 μm at 50 kV).

### 7. Pixel-by-pixel multi-energy radiography with normalisation

The image processing methods described in this section are the same as those described in Section 6, except that the images were normalized to units [counts/sec/mA] before processing. The intent was to compare the multi-energy image processing methods with and without normalisation. Rescaling factors were also used inside the applied processing equations. Results only for radiographic images taken within Setup #1 as per Figure 1 are presented here. The image processing was based on pixel-by-pixel calculation using four (4) normalized images, and, after obtaining the final processed image, an averaged signal was calculated over pre-selected regions as per areas defined in Figure 1.

#### 7.1 Multi-energy radiography Equation #3

The third image processing method for multi-energy radiography uses the same equation as the one described in Section 6.1, but is based on normalised pixel intensities.

$$FinalSignal(i,j) = \frac{\ln[C_2 S_{i,j}(F_3,E_3)]/\ln[C_4 S_{i,j}(F_4,E_4)]}{\ln[C_5 S_{i,j}(F_5,E_5)]/\ln[C_6 S_{i,j}(F_6,E_6)]}$$  Eq. (3)

where $C_1, C_2, C_3, C_4, C_5$, and $C_6$ are rescaling coefficients, and $S_{i,j}(F, E)$ is the raw signal for pixel $(i, j)$ for filter $F$ and energy $E$. Coefficients $C_1$ and $C_4$ were set to 1000, while coefficients $C_2$, $C_3$, $C_5$ and $C_6$ were set to $\{1 / (0.3 \cdot [mA] \cdot [sec])\}$. The final parameter was calculated using averaging over pre-selected regions, as shown in Figure 1, and was correlated to the concentration of Quinine by linear fit. The best correlation coefficient obtained was $R^2 = 0.835$, (F1: Cu 80 μm at 80 kV; F2: Al 500 μm at 40 kV; F3: Pb 127 μm at 80 kV; F4: No Filter at 50 kV).
7.2 Multi-energy radiography Equation #4

The fourth image processing method for multi-energy radiography uses the same equation as the one described in Section 6.2, but is based on normalised pixel intensities.

\[
\text{FinalSignal}(i,j) = \frac{\text{Ln}[C_1 \cdot S_{i,j}(F_1,E_1)]}{\text{Ln}[C_3 \cdot S_{i,j}(F_3,E_3)]} \frac{\text{Ln}[C_2 \cdot S_{i,j}(F_2,E_2)]}{\text{Ln}[C_4 \cdot S_{i,j}(F_4,E_4)]}
\]

with rescaling coefficients \(C_1, C_2, C_3,\) and \(C_4\) set to \(\{1 / (0.3 \cdot I[\text{mA}] \cdot t[\text{sec}]\}\}). Again, after the pixel-by-pixel processing, the final averaged signal was calculated over pre-selected regions, as shown in Figure 1, and was used to calculate \(R^2\) between the calculated parameter and the concentration of Quinine. The best combination for multi-energy radiography Equation #4 had \(R^2 = 0.756\), (F1: Al 500 \(\mu\)m at 50 kV; F2: No Filter at 70 kV; F3: Cu 80 \(\mu\)m at 80 kV; F4: Pb 127 \(\mu\)m at 100 kV).

8. Chemometric spectroscopic processing

The next step was to apply chemometric processing to multi-energy radiography of opioids. The aim was to use multiple combinations of filters and voltages for the x-ray tube, and to try to correlate the calculated set of parameters to the concentration of Quinine, using Principal Component Analysis (PCA) and the Partial Least-Square (PLS) method. Commercially available UNSCRAMBLER software by Camo Analytics Inc., was used (https://www.camo.com/unscrambler/). Two sets of already processed data were selected:

- Four groups of results were selected from the data used in Section 6.1:
  - Group 1 included 81 combinations with \(R^2 > 0.60\);
  - Group 2 included 40 combinations with \(R^2 > 0.65\);
  - Group 3 included 25 combinations with \(R^2 > 0.70\);

- Six groups of results were selected from the data used in Section 7.1:
  - Group 5 included 90 combinations with \(R^2 > 0.60\);
  - Group 6 included 61 combinations with \(R^2 > 0.65\);
  - Group 7 included 30 combinations with \(R^2 > 0.70\);
  - Group 8 included only the 13 best combinations with \(R^2 > 0.74\);
  - Group 9 included only the 4 best combinations with \(R^2 > 0.78\);
  - Group 10 included only the 3 best combinations with \(R^2 > 0.80\).

An example of PCA analysis from UNSCRAMBLER software for Group 7 with \(R^2 > 0.7\) is presented in Figure 6. The analysis was performed using 8 samples, 30 variables, and 4 principal components. Principal component PC-1 explains 95\% of the variance of the data, while PC-2 explains additionally only 2\% of the variance of the data. There is no clear separation or grouping of the samples related to the concentration of Quinine in the principal components space.

The next step was to perform the PLS analysis and to evaluate how well the UNSCRAMBLER software can be used for predicting concentration of Quinine. An example of PLS analysis from UNSCRAMBLER software for Group 10 with \(R^2 > 0.8\) is presented in Figure 7, together with the predicted concentrations of Quinine with error-boxes. The analysis was performed using 8 samples, 3 variables, and 3 factors. Factor #1 explains 97\% of the variance of the data.
Figure 6: Screen-captures from UNSCRAMBLER software of PCA analysis of Group 7.

Figure 7: Screen-captures from UNSCRAMBLER software of PLS analysis of Group 10.
9. Hyperspectral chemometric processing

There is a special version of the UNSCRAMBLER software that is specifically designed for processing images from hyperspectral cameras (UNSCRAMBLER HSI, https://www.camo.com/unscramblerhsi/). Since multi-energy radiography is essentially the same as hyperspectral imaging (HSI) or multi-spectral imaging, it was decided to test whether this software can be applied for processing multi-energy radiographic images of opioids. A demonstration version of the UNSCRAMBLER HSI was used for processing the images. A set of 44 images, 9 images based on 9 kV setting of the x-ray tube, using filters: "No Filter", Al, Fe, and Cu, and 8 images based on 8 kV setting of the x-ray tube for Pb filter, were used for this evaluation. No preliminary processing of the images was done; the raw radiographic images, as recorded during exposures, were used. In order to improve the performance of the UNSCRAMBLER HSI software, the 44 images were converted into a TIFF stack, and the region containing samples D2, D3, D4, D6, D7 and D8 was cropped from the whole stack. The size of the images was rescaled to 300x340 pixels, and the TIFF stack was saved as an ENVI file (specialised hyperspectral imaging format) using ImageJ. The current version of the UNSCRAMBLER HSI software can only be used with ENVI files and does not accept 16-bit TIFF stacks. Samples D2, D3, D4, D6, D7 and D8 were selected because they have different concentration of Quinine.

9.1 PCA analysis

All 44 images were used for performing PCA. Six areas corresponding to the six samples were defined as shown in Figure 8, where the blue set is used for analysis as the training (or calibration) set and the red set is used as a testing set for validation and prediction. Results for the training (calibration set) from the PCA are presented in Figure 9, where the coloured training set demonstrates that the samples can be separated. In Figure 10, PC-1 explains 98% of the variance of the data, whereas PC-2 explains additionally only 1% of the variance of the data. As can be seen from the figure, all six samples are well separated and grouped in the principal component space. Another important observation is that there are also two separate groups corresponding to the samples in the first and the second row. This is due to the fact that the x-ray beam created non-uniformity and a variable background in the two rows of samples. No pre-processing, such as normalisation, subtraction, or ratio, was performed on the background. These results are very promising and suggest that PCA analysis can be applied to spectroscopic x-ray radiography imaging.

Figure 8: Definition of the areas of interest for the six samples.
9.2 PCA analysis with background region and range normalisation

Again, two sets of regions were defined: a training (calibration) set, and a testing (validation) set, as per Figure 8, however, for each set there were now 7 regions defined: six areas corresponding to the six samples, and a separate area corresponding to the background. All 44 images were used for performing PCA. The images were pre-processed using "range
normalisation"; each image was divided by (Range Maximum Value – Range Minimum Value). PCA results for both the training and testing sets are presented in Figure 11. The correspondence of colours, which represent results for the different samples with different Quinine concentrations, can be seen between the training (left image) and testing sets (right image). PC 1 explaining 97% of the variance of the data, while PC-2 explains 3% of the variance of the data. A plot of PC-1 versus PC-2 seen in Figure 12 shows good grouping and separation of the samples related to the quinine concentration, as well as the background in the principal components space. Although there is not a complete overlap between the training and testing sets in the principal components space, due to the x-ray beam non-uniformity that could not be fully corrected with the pre-processing, the classification of the samples is still possible, and the identification of the samples based on their different concentration of Quinine is achieved.
10. Conclusions and Recommendations

- Dual-energy x-ray radiography can be used for detection of opioids, but the low sensitivity and low selectivity, which will lead to a significant number of false positives.
- Dual-energy x-ray radiography can be improved by using two different settings for the x-ray tube voltage in combination with two different filters, but this will require changes to installed software and hardware. This option will be studied further, because it provided high correlation coefficient of $R^2 = 0.97$.
- Multi-energy x-ray radiography (based on 3 or 4 different settings for the x-ray tube voltage in combination with different filters) will improve the sensitivity and selectivity in detection of opioids. This approach requires further studies using real samples.
- For both, the dual-energy x-ray radiography and the multi-energy x-ray radiography, the recording and use of background (blank) images is mandatory in order to achieve the best possible sensitivity and selectivity for detection of opioids. Although measurements without blank images are very attractive from an operational point of view (no need of daily background measurements), the tests performed without the use of background (blank) radiographic images clearly demonstrate that this step cannot be omitted.
- For both, the dual-energy and the multi-energy x-ray radiography, more reliable results can be obtained if the images are normalised to units of [counts/sec/mA].
- The chemometrics approach, based on the use of spectroscopic PCA and PLS analysis software (i.e., UNSCRAMBLER) does not provide sufficient improvement to the standard 4-image multi-energy x-ray radiography. The best 4-image multi-energy x-ray radiography gave (correlation coefficient) $R^2 = 0.835$ for a single set of 4-images, whereas the best PLS model for the same sample set, but based on 3 sets of measurements (i.e., 3 sets of 4 radiographic images) gave $R^2 = 0.845$.
- The use of “UNSCRAMBLER HSI” chemometrics software for hyperspectral imaging for processing images for multi-energy x-ray radiography seems promising. Furthermore, the initial testing was performed with raw images. It would therefore be beneficial to test the hyperspectral chemometrics software using processed images.
- It is recommended that further testing is performed with this software on images from real samples. This software will also be useful for experimenting with spectroscopic x-ray radiography images.
- Separate testing should be performed to evaluate the usefulness of calibration objects embedded inside the image (such as known opioids or compositions). This is equivalent to the use of penetrameters (also known as image quality indicators) in traditional industrial radiography. This will improve reliability of dual-energy radiography, and could be a more cost-efficient option for development of multi-energy radiography, since it will require only limited hardware changes.
- Dual-energy radiography and spectroscopic x-ray radiography are single-exposure methods. The multi-energy radiography results presented here are based on multiple exposures. Additional work and analysis are necessary to evaluate how one can minimize the hardware changes when transitioning from dual-energy radiography to multi-energy radiography.

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