Effects of Water Absorption on Mercury Contamination in Fiberbank Sediments using X-ray Fluorescence Spectrometer

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Effects of Water Absorption on Mercury Contamination in Fiberbank Sediments using X-ray Fluorescence Spectrometer

Siwen An*, Faisal Zeeshan, Börje Norlin, Göran Thungström
Department of Electronics Design, Mid Sweden University, Holmgatan 10, 85170, Sundsvall, Sweden
*Email: siwen.an@miun.se

Abstract. A large amount of contaminated cellulose and wood fibers were emitted directly onto the seabed by the pulp and paper industry before the year of 1970. This fiber-rich sediment contains concentrations of hazardous substances that cause environmental problems. Mercury (Hg) in the fiber sediment is a worldwide threat because it can bioaccumulate in the aquatic ecosystem and eventually affect human health. X-ray fluorescence (XRF) analysis is an elemental analysis method for earth materials, which is rapid and requires minimal sample preparation. However, for in-situ XRF analyses, constraints in the measurement conditions will strongly affect the measurement sensitivity and accuracy, such as the scattered background and the water content surrounding the sample. In this work, we showed that applying an X-ray beam filter foil, optimized by using the material absorption edge, can improve the sensitivity of the XRF spectrometer system for Hg determination. Furthermore, the influence of water content in XRF measurement for Hg contamination analysis was investigated. The attenuation coefficient in water was determined by simulation of water layer with varying thickness using a Monte Carlo simulation code. The measured intensity for Hg was decreased exponentially as the water thickness increase, as expected. We propose a method to correct the attenuation in water with XRF analysis and we expect that these findings can contribute to an accurate in-situ Hg detection experiment.

1. Introduction
The elevated presence of mercury (Hg) in the environment is a global pollutant that affects human and ecosystem health [1]. Elemental mercury was historically used in the paper and pulp manufacturing process, but the use of Hg in industrial processes is now banned in EU countries. Discharge of untreated paper and pulp industry wastewater during the early-mid 20th century have caused large environmental impact on the sediments along the coasts in Västernorrland, Sweden [2]. Fiber-rich sediments are found close to the industrial factories, which are highly affected by persistent organic pollutant contamination [3,4]. Over time, it gradually built up and created what are known as “fiberbank deposits”. The contaminated fiber materials eventually accumulated on the seabed. In these sediments, Hg can be transformed into methylmercury (MeHg) in anoxic environments, which is the most toxic form of mercury [5]. MeHg in water can be easily bioaccumulated in aquatic food chains, such as fish and shellfish, and eventually consumed by human beings. Furthermore, exposure to high concentrations of MeHg damages the immune system and the nervous system, resulting in acute and chronic human health effects [6]. Thus, understanding the total Hg distribution and the concentration of Hg in sediments is essential for environmental assessment and monitoring.
Atomic absorption spectroscopy (AAS) is a well-established laboratory method used to detect surface Hg contamination, but it takes time for the sample preparation by adding nitric acid [7]. Research showed that portable analyzers for mercury vapor are capable of measuring Hg in air samples [8]. However, a solid sample needs to be pretreated (sample decomposition) in order to obtain the homogenized solution [9]. In addition, X-ray fluorescence (XRF) is widely used in field applications when screening for high concentrations of metal in the analyte [10,11]. The XRF technique offers a non-destructive and cost-effective way for screening of mercury-contaminated areas. Moreover, handheld XRF technology has been proven by the EU Restriction of Hazardous Substances (RoHS) directive to detect mercury. An earlier study showed that the fair detection limit of the XRF method achieved was 7.4 mg/kg Hg for an handheld device with the measurement time of 60 s [12]. However, several parameters, including sample matrix, surface irregularity, particle size and water content, will decrease the quality and the precision of the in-situ XRF analysis [13-15]. For in-situ XRF analysis, the water content of the sediment is critical to the XRF accuracy [16,17]. Essentially, the water surrounding the sediment produces an exponential decrease in X-ray beam intensity and introduces the scattered background noise, which gives rise to a poor limit of detection in the XRF measurement. Thus, it is important to assess the precision and accuracy due to the water influence in an XRF analysis.

In this study, we evaluated the influence of water content on the quantitative analysis of Hg using the XRF method. In order to optimize and facilitate future experimental tasks, an XRF detection system has been modeled by the use of the Monte Carlo method, which can simulate radiation particles transport. Two parameters, including the X-ray filter and the water absorption in the determination of Hg in fiberbank sediment, were evaluated. The study identified the key factors that can be used to improve Hg screening in an in-situ XRF analysis.

2. Materials and Methods
2.1 X-ray Fluorescence Principle
XRF is based on the emission of characteristic X-rays when the material is excited by an external X-rays source. Each emission line corresponds to a transition between two different electron shells. The photon spectrum from X-ray fluorescence contains characteristic lines which can be used to identify materials. Characteristic emission lines from mercury are listed in Table 1 [18]. The strongest line in each shell is assigned to the relative intensity of 100. For underwater measurement, the water absorption will strongly reduce the photon intensity. Thus, the Ka line was chosen to determine Hg due to both the high energy and the high relative intensity. The incident X-ray beam energy should be sufficient to generate a Ka-line fluorescence photon of Hg. Thus, a radioactive metal, Cobalt-57, which mainly emits Gamma and X-ray at 122.06 keV was used as the X-ray source.

| Emission line | Mα₁ | Lα₂ | Lα₁ | Lβ₁ | Lβ₂ | Lγ₁ | Kα₂ | Kα₁ | Kβ₃ | Kβ₁ | Kβ₂ |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Energy (keV)  | 2.20| 9.90| 9.99| 11.82| 11.92| 13.83| 68.90| 70.82| 79.82| 80.25| 82.52|
| Relative intensity | 100 | 11  | 100 | 67  | 24  | 14  | 59  | 100 | 12  | 23  | 8   |

2.2 The MCNP6.2 Code
The Monte Carlo N-Particle code (MCNP) uses the Monte Carlo method to solve problems by statistical simulation of repeated random sampling of stochastic processes. The average of the Monte Carlo results approaches the expected measured value as the number of sampling points becomes large.
The code was developed by Los Alamos during the Manhattan Project in the early 1940s. It can be used to simulate the interaction of both photons and particles with matter [19]. It simulates the physical processes by bombarding a large number of randomly sampled source particles towards the sample surface and scoring the tally results by following every particle of interest. For photon transport, the photon may undergo incoherent scattering, coherent scattering and fluorescent emission after photoelectric absorption depending on the interactions with matter [20]. The version MCNP 6.2 was used in this study. This version can separate the L-lines of the characteristic X-ray emissions with the electron-photon relaxation library (EPRDATA14), which is not available in earlier versions. Modelling of separated L-lines is necessary when simulating environmental XRF measurements for heavy elements, such as Pb and Hg.

2.3 X-ray Filter
Compton scattering and bremsstrahlung radiation normally contribute to the background noise in the XRF measurement, resulting in a poor detection sensitivity. A suitable filter foil placed in front of the primary X-ray source can significantly improve the sensitivity in an XRF analysis [21]. The ideal filter is the combination of material and thickness that results in a minimum reduction of photon flux at useful high energies, but also results in a maximum improvement of the signal-to-noise ratio (SNR) and detection limit for a specific element. The optimum filter material and thickness was simulated by the use of MCNP code, since actual experiments to optimize these parameters are very time-consuming. The performance of six pure metal foils, Ag, Bi, W, Hf, Lu, and Ta were compared. By taking into account the practical measurement condition, a measured X-ray source spectrum from radioactive metal, Cobalt-57, was implemented as the input X-ray source in the simulation. By considering the photoelectric absorption efficiency for different semiconductor materials, a CdTe spectrometer was implemented in the model.

2.4 Simulation of X-ray Absorption in Water
The influence of water content in XRF measurement for Hg contamination analysis was simulated using MCNP6.2. The geometry of the MCNP simulation is shown in Figure 1. The procedure starts with the definition of a filtered X-ray source (defined as a point source here) emitting X-rays towards the center of the top surface of the sample. The sample is a 1 cm$^3$ solution with the Hg concentration at 1000 ppm, which is covered by an additional water layer. In order to study the water influence in the XRF measurement, the CdTe detector was placed 4 cm above the sample surface and the water layer thickness varied from 0 cm to 3.25 cm. The sample was irradiated by the X-ray beam. Subsequently, the fluorescence X-rays coming from the focal spot on the sample are absorbed and recorded by the CdTe detector.

![Figure 1. Geometry model of the XRF setup used for MCNP simulation.](image-url)
2.5 X-ray Attenuation

The attenuation coefficient characterizes how easily X-rays can penetrate a volume of material. Due to that water absorbs X-rays stronger than air, the measured intensity of characteristic X-rays of analytes decreases as the water layer surrounding the sample increases. Assuming that the matrix effect of the sample is constant, the relationship between the reduction in characteristic X-ray intensity of an analyte and the water depth covering sample is based on Lambert-Beer law [17]:

\[ \frac{I_{\text{wet}}}{I_{\text{dry}}} = e^{-\sigma \omega} \]  

(1)

where \( I_{\text{wet}} \) is the measured XRF intensity with water content \( \omega \), while \( I_{\text{dry}} \) is the measured XRF intensity without additional water content, finally, \( \sigma \) is the water absorption attenuation coefficient.

3. Results and Discussions

3.1 Background Suppression with a Primary Beam Filter

The use of X-ray filters can reduce the background of a specific region in an XRF spectrum. The most important consideration in selecting the optimal filter material is that the filter absorbs continuous background radiation by using the absorption edge of that material. Figure 2 illustrates how the X-ray spectrum affected by six primary beam filters, respectively. The interest of regions, which are the fluorescence peaks of Hg, are marked as red lines. For the case of no filter, a high background of scattered radiation is shown in the XRF spectrum. The continues spectrum from low energies to high energies which overlaps with the element of interest peaks, then the intensity of these peaks will be underestimated since these peaks might be hidden in the spectrum. A source peak at 122.06 keV is expected, which is generated from the radioactive material. It should be noted that escape peaks arise when a strong peak is recorded. As a result, the photon can emit a fluorescence X-ray photon from the detector, lost part of its energy and reabsorbed by the detector. In addition to the fluorescence peaks from Cd and Te, four escape peaks at 99.0 keV (Cd, K-α), 96.0 keV (Cd, K-β), 94.7 keV (Te, K-α) and 91.1 keV (Te, K-β) were created (Figure 2, No filter). The filtered spectra were normalized by a factor of 50 to be compared with the original spectrum visually. The inset shows the absorption edge of these metals. The absorption edge of W is at 69.5 keV, which overlaps the Hg Kα2 and it is close to Kα1 peak. Moreover, the characteristic of W Kβ2 at 69.1 keV interferes Hg Kα2. Thus, W filter is not the optimal filter for Hg detection in an XRF measurement. For other materials, the background around 70.82 keV was reduced down to approximately 1.4% by the use of X-ray filter.

Figure 2. XRF primary source spectra of varying X-ray filters.
By applying an X-ray filter, the intensity of the X-ray signal is decreased as the thickness of the filter increase, thus the measuring time is increased accordingly. Hence, a tradeoff between high SNR and short measurement time should be considered when choosing filter material and thickness for a practical XRF setup. The filter’s transmission values \( (I/I_0) \) for six filters at 122.06 keV are listed in Table 2. The filters strongly reduce the intensity of the primary beam. A 3.5 mm Ag filter reserves a good photon flux transmission of 4.49% although the background noise around 80-82 keV is slightly higher than other filters, which was chosen for further test in the water influence measurement.

| Material | Density (g/cm³) | Thickness (mm) | \( I/I_0 \) (%) |
|----------|----------------|----------------|-----------------|
| Ag       | 10.49          | 3.5            | 4.49            |
| Bi       | 9.78           | 4              | ≈0              |
| W        | 19.35          | 1              | 0.66            |
| Hf       | 13.07          | 1              | 4.24            |
| Lu       | 9.81           | 2              | 0.98            |
| Ta       | 16.65          | 1              | 1.52            |

3.2 Water Absorption

In order to investigate the influence of water content on the intensity of the XRF signal, 14 water thicknesses were tested. By considering the water absorption for both the incident radiation and the Hg fluorescence peak, we obtained the final XRF spectra. The self-absorption of the water content in the liquid sample can be considered as a constant, so that we ignored its influence on XRF analysis. The resolved fluorescence peak of Hg Kα₂ is shown in Figure 3. The MCNP code outputs a spectrum normalized to one photon. No normalization of the simulation data is attempted. It should be noted that, in this geometry, the strong peak at 122.06 keV from the radioactive source results in a scattering peak at 82.5 keV when the scattering angle is 180°, which interferes the identification of the Hg Kβ₂ peak. The inset shows that the Hg Kα₁ peak is decreased by increasing the thickness of water, while the background scattering noise is increasing. As a result, the water content surrounding the sample caused a reduction in precision and a lower accuracy for detecting Hg in the XRF system.

![Figure 3. XRF simulations for 1000 ppm Hg liquid sample with various water layers ranging from 0 cm to 3.25 cm.](image)
During the simulations, the Hg characteristic peak is taken as the basic parameter that is directly influenced by the change of water content in the sample. However, light elements comprising water increased the scattered photons from the X-ray source; thus, scattered background must be considered when water content covers the Hg sample. The high scattered background results in higher counts at 70.82 keV when the water thickness is above 1.75 cm. Instead of Hg peak intensity, the peak-to-background ratios (P/B) were calculated, where the background counts were computed by the average of pre-peak and post-peak background. With the water absorber thickness increasing, the P/B of the Hg peak is decreasing exponentially, as shown in Figure 4. We identified that the limit of detection for this system is when the P/B ratio is larger than 3, which means that the characteristic peak of Hg at a concentration is greater above the random variation in the background [22]. Thus, the XRF detection range is the water thickness below 1.5 cm for detecting a 1000 ppm Hg sample.

![Figure 4. Change in P/B ratio of Hg fluorescence peak (Kα1) with various water thicknesses.](image)

### 4. Conclusions
The scattered radiation and the variation of water content in fiberbank sediments are crucial interference factors for in-situ XRF analysis. Tests on filter materials showed that an optimal primary X-ray beam filter can reduce the source noise for a specific energy range, thus, improving the detectability and the precision in an XRF system. The improvement is determined by the X-ray absorption edge of the filter, which is controlled by the filter material and its thickness. For Hg, a 3.5 mm Ag filter is investigated, and it can reduce the background noise and still provide good photon flux transmission. Simulations on a series of water thickness demonstrated that an increase in water content caused a significant decrease in XRF sensitivity due to the absorption of the characteristic X-rays of the analytes and produces a stronger scattering background noise of the primary radiation. This study showed that the detection range in water is 1.5 cm for detecting a 1000 ppm Hg liquid sample. In practical setup mounting, a shorter distance between the primary X-ray beam to the sample surface and the sample surface to the spectrometer is desired.

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