The use of x-ray fluorescence as a rapid, onsite screening tool in the assessment of cadmium surface contamination

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1.   Abstract

Portable x-ray fluorescence (XRF) has successfully been used in the past to quickly and nondestructively evaluate occupational exposure to airborne and surface metal contaminants. Traditional methods of evaluating metal surface contamination involve the costly and time-consuming collection and laboratory analysis of wipe samples, thereby making XRF an attractive method to screen worksites and reduce delays in risk assessment decision making. Existing research into this use of XRF has primarily been centered on the analysis of airborne and surface lead contamination and there is very little literature which examines the use of XRF with other metals. The present study evaluated the use of XRF in the screening of cadmium surface contamination. Wipe samples were collected and screened with XRF prior to being sent to the laboratory for analysis to assess the correlation between XRF semi-quantitative readings in percent mass with laboratory quantitative results in μg/ft2. XRF readings were strongly linearly correlated with laboratory results, as indicated by the R^2 value of 0.9929. This linearity of the results demonstrates that with a more sensitive instrument and greater sample size, this is a fruitful avenue for research. The methodology described could be practically used as a screening tool of wipe samples for clearance.

2.   Introduction

I.   Regulatory Background

Following the establishment of cadmium as a material known to be carcinogenic, the Occupational Safety and Health Administration (OSHA) promulgated a substance specific standard with the intent of reducing the risk of adverse health outcomes in workers routinely exposed to cadmium (Occupational Safety and Health Administration [OSHA], 2020). One of the aspects of these substance specific standards are the permissible exposure limits (PEL) of these materials. For cadmium, OSHA established a PEL of 5 μg/m^3 over an 8-hour time weighted average (TWA) (OSHA, 2020). These PELs, however, only consider the inhalable exposures of these two materials. Dermal exposure has been shown to be a significant contributor to worker exposure for these two substances. Significant dermal exposure limits the usefulness of only monitoring airborne exposures (American Conference of Governmental Industrial Hygienists [ACGIH], 2019; Dost, 1995). The guidance OSHA presents regarding dermal exposure monitoring is limited. The cadmium standard states that surfaces must be kept, "as free as practicable" of accumulations of the materials on workplace surfaces (OSHA, 2020). Several options are available for employers to demonstrate compliance with the surface decontamination requirement, including decontamination and confirmatory wipe sampling.

II.   Sampling Methods and Significance

Traditionally, assessment of surface contamination involves the collection of wipe samples. Wipe samples are collected according to NIOSH 9100 methodology or similar. These wipe samples are then sent to a laboratory and analyzed with a laboratory technique applicable to the analyte under study (National Institute for Occupational Safety and Health [NIOSH], 1996).

However, these wipe sampling methods and laboratory analytical methods can become very costly if a large quantity of samples is necessary. For example, the cost of analyzing an arsenic wipe sample is about $41 per sample (SGS Galson, 2020). Additionally, the lead time between when the sample is sent to the lab and results are received can be weeks at a time. Since the purpose of these results is to ensure worker protection and evaluate risk at a worksite, this lead time can be problematic. Therefore, access to a timelier alternative is important to ensure that measures can be taken to reduce workplace exposure as soon as possible.

Portable x-ray fluorescence (XRF) presents a potential avenue to achieve this rapid, onsite risk assessment that is not available in laboratory analysis due to the potentially long lead time. XRF functions by irradiating the sample surface with x-rays. These x-rays cause the atoms within the sample to become excited and emit x-rays. These emitted x-rays are known as fluorescent x-rays, and the spectra emitted are characteristic of the materials which they originate from. The fluorescent x-rays generate signals within the XRF instrument which indicate the amount of material present in the XRF window area (Pesce & Grodzins, 2012). This process is illustrated in Figure 1.
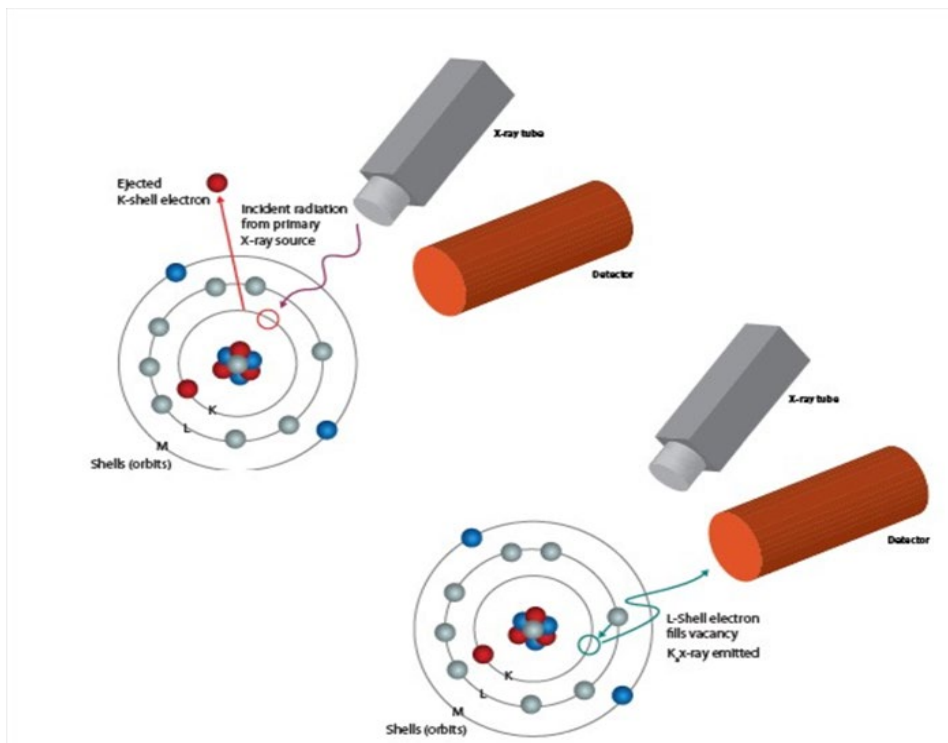
Figure 1. Demonstration of how x-ray fluorescence (XRF) irradiates and excites the analyte for elemental analysis. From Blondel, 2020.

An important limitation of XRF in the occupational setting is that XRF can only be used semi-quantitatively with most materials aside from lead. Accurate XRF quantification of data relies on a homogeneous sample of sufficient thickness that the sample under study can be assumed "infinitely thick." Infinitely thick means that all incident x-rays are absorbed. Where a sample is not infinitely thick, a material-specific calibration is required which relates the intensity of the x-ray to the thickness of the sample. Such calibrations have been created for lead, but are not currently present for other materials (Seyfarth, n.d.). In an occupational setting, this principle of infinitely thick cannot be assumed due to irregularity of sample deposits.

III.   Literature Review

In spite of these limitations, portable XRF has successfully been used in the evaluation of airborne and surface lead contamination in the workplace. This is illustrative of the potential of occupational application of the technology. The potential of XRF application in the occupational setting presents an important opportunity for worksites to increase efficiency of their risk assessment decision making. This increased efficiency is a result of accurate, timely data which translates to improved long-term worker health outcomes. Early investigations into the applications of XRF technology evaluated the capability of the instrument to correctly identify materials under study, ascertain detection limits, and determine accuracy to approved sampling and analytical methods. These investigations are key considerations in determining the validity of XRF use in occupational applications.

In the assessment of XRF capabilities of airborne filter analysis, XRF was able to successfully identify materials under study and obtain results similar to approved analytical methods. Detection limits for XRF in the assessment of a thin film application were found to be less than occupational exposure limits under study. Additionally, XRF had narrower error ranges than the laboratory method XRF was compared to. This reemphasizes the potential usefulness of XRF in occupational exposure assessment and introduces the possibility that XRF may be less variable than destructive analytical methods (Bernick & Campagna, 1995).

In another airborne filter application, the accuracy of XRF readings compared to laboratory results varied based on the material under study. XRF consistently read lower results for iron, nickel, manganese, and copper. Conversely, XRF results were consistently higher for lead than laboratory analysis. These differences may be attributable to either the use of pure oxides in lieu of calibration standards or particle size and inter-element interference effects

affecting analytical performance. Portable XRF in this use also displayed lower limits of detection less than 1/10th the occupational exposure limit (OEL) for most materials under analysis aside from lead and cadmium. Generally speaking, the lower limits of detection for portable XRF were found to be an order of magnitude higher than the lower limits of detection of laboratory-based XRF. Lower limits of detection are required to be 1/10th the OEL to ensure there is 95% confidence that the instrument used can detect the material under analysis at the levels indicated (Dost, 1996).

XRF was also able to successfully detect and identify the removeable and total surface contamination of the materials under study and obtain similar results to accepted sampling and analytical methods, which were wipe samples followed by laboratory analysis. XRF consistently read higher than the laboratory analysis of the wipe samples. This difference between wipe samples and XRF can be attributable to inefficiencies in wipe sampling, which were reduced when repeated wipe samples were taken. Additionally, XRF provided insight into applications where wipe sampling may not be possible. Wipe sampling does not effectively recover materials under analysis in areas where the surface is rough or porous. XRF sampled carpeted areas and was able to detect the materials under study in high-level contamination areas, such as process areas, and low-level contamination areas, such as office spaces. The significance of this difference in XRF and wipe sampling results is difficult to evaluate due to the lack of quantitative limits for dermal exposure. The use of XRF in this manner introduces the potential merit of evaluating XRF use in areas where wipe sampling may not be feasible, but still have contamination present in levels which may contribute significantly to worker exposure (Dost, 1996). The outcome of this use of XRF is also further indication of the capacity of XRF to accurately assess surface contamination, in addition to airborne filter analysis.

With the establishment of the capability of XRF to successfully identify and detect materials under analysis, the focus of XRF application turned to focus more on the precision of the instrument and how the accuracy of XRF compared to analytical methods changed with differing air samplers. In contrast to earlier applications, later uses of XRF were primarily concerned with lead, rather than the range of materials seen in earlier uses. This examination of XRF in lead exposure analysis may have been due to the renewed focus on occupational lead exposure due to the regulatory review of the construction lead standard in 2007. Or, this focus on lead may have been the result of the prevalence of lead exposures in the workplace (OSHA, 2007). This assessment of precision and accuracy of XRF lead analysis was still centered around these principles in occupational applications of airborne filter and surface contamination analysis.

Regarding surface lead contamination, the precision of the XRF instrument remained high when multiple measures were taken, even with the potential confounding factor of paint chips in some of these samples. This precision increased with increasing lead concentration. These results are significant because onsite analysis of surface lead could potentially reduce lead abatement clearance delays, which in turn reduces overall worker exposure to lead (Sterling et al., 2000). Interestingly enough, unlike earlier research, there was no indication that wipe sampling underestimated XRF results. Another benefit noted was that XRF is a nondestructive analytical method. This means that even where there is uncertainty in XRF results, it can be used as a screening tool to inform risk assessment decisions immediately while more accurate results from the lab are pending (Gorce & Roff, 2016). The use of XRF in this capacity strengthens the notion of the use of the instrument as a risk assessment screening tool in the workplace.

The results of XRF in the analysis of airborne lead filters were more variable in their findings. Good overall correlation between XRF and inductively coupled plasma mass spectrometry (ICP-MS) were found utilizing NIOSH 7702, Airborne Lead by XRF, methodology and then NIOSH 7300 laboratory analysis, Elements by ICP-MS. The samples which were tested spanned 12 different lead-producing workplaces in Korea. This correlation remained good near the Korean PEL of 50 μg/m3. This correlation also remained favorable when sample groups were separated by specific type of lead-producing industry (Kim et al., 2007). The high correlation between portable XRF and ICP-MS near the PEL of the worksites under study is further indicative of the validity of XRF use in the occupational setting.

The NIOSH accuracy requirement of plus or minus 25% is an instrument bias consideration, not so much a true accuracy consideration (Barley et al., 2007). From this consideration, a 35% accuracy criterion was proposed and multiple samplers were tested with the use of XRF in Millipore air filter analysis. The results found the IOM and Button samplers to be inadequate under these parameters due to bias in the Button sampler and the inability to have homogeneous samples for the IOM sampler. The validity of the use of the other samplers under study was not well defined. The most recent research into the use of XRF in the analysis of Millipore filters for airborne metals showed that XRF correlated well to laboratory analysis. However, the use of the IOM sampler in this study prevented air filter analysis from being more than semi-quantitative. This is due to the inability to account for sample deposits on the filter window (Gorce & Roff, 2016). This application of XRF is important because it highlights the importance of considering the type of air sampler used when assessing XRF use. The type of sampler used impacts factors which affect XRF performance such as homogeneity of samples and bias of the sampler itself.

Although early research into the use of portable XRF contained the analysis of many different metal types, the most recent research was primarily centered on lead. There is a lack of in-depth studies into the effectiveness of XRF in the analysis of other metals beyond the identification and detection capacity of XRF. Additionally, previous studies have not addressed what sampling mode they are using their XRFs in these in-situ evaluations. XRF instruments have multiple different sampling modes based on the application. Some of these modes include soil mode and dust wipe mode. In soil mode, there is an assumption of an "infinitely thick," sample, meaning that the sample thickness is great enough that the incident x-rays are totally absorbed. If the sample is not infinitely thick, then not all x-rays are absorbed and some sort of calibration must exist which relates the sample thickness to the intensity of the x-ray along a curve which is unique to the material under analysis (Seyfarth, n.d.). The application under use is important to understand in sampling, for the materials under analysis to understand what underlying assumptions there are about the sampling and analysis processes. These assumptions in turn inform the limitations of the results of the studies. These considerations determine whether the results of analysis are quantitative or qualitative in nature. Therefore, with a well-thought out sampling strategy, XRF may be used as a fast and reliable screening tool in the analysis of occupational cadmium and arsenic exposure. The proposed screening measures have the potential to allow for fast, accurate risk assessment measures to be taken pending more detailed wipe sampling analysis results.

3.   Methods

I.   Overview

For the purposes of this study, XRF was utilized to analyze wipe samples prior to laboratory analysis to determine if a screening value/calibration curve could be obtained which would subsequently improve clearance at the wipe sampling regimes of the worksites under study. Wipe samples were collected in accordance with Brookhaven National Laboratory standard operating procedure IH75190, which is a field procedure for wipe sampling surface metals based on NIOSH 9100, Lead in Surface Wipe Samples, methodology (Brookhaven National Laboratory [BNL], 2017). Background readings of surrounding light element materials were taken with the Olympus DELTA Family Handheld XRF Analyzer prior to reading the wipe samples to ensure there was no metal background. These wipe samples were then analyzed with an Olympus DELTA Family Handheld XRF Analyzer for presence of cadmium and then sent to a laboratory for quantitative analysis. Wipe samples were collected from an aircraft parts manufacturing facility utilizing cadmium in its brush plating process. Worksites where collection took place were characterized from interviews with facility personnel. During the pilot test portion of data collection, both 4-inch by 4-inch and 12-inch by 12-inch sample areas were wiped with pre-moistened LeadWipes. The two different sample areas were used in order to ensure that the limit of detection of the instrument was met. In subsequent sample collection, only the 12-inch by 12-inch area was utilized. Wipe samples were screened with XRF analysis prior to laboratory analysis to evaluate if XRF screening improved clearance. Laboratory analysis was conducted in accordance with NIOSH 9102 methodology utilizing inductively coupled plasma, atomic emission spectroscopy (ICP-AES) (SGS Galson, 2020).

Samples were collected at one worksite. Cadmium surface samples were collected from various stations at a cadmium plating process at an aircraft part manufacturing facility. Stations where samples were collected from included a drip tray, the floor next to a brush plating station, a quality control station, and the floor by the quality control station. The primary goal of this study was to determine if XRF can be used as a rapid, nondestructive, onsite screening tool to improve clearance times of cadmium and arsenic surface contamination over wipe sampling alone. Data recorded for the purposes of this study was obtained from XRF readings taken on the collected wipe samples and also the results obtained from quantitative laboratory analysis. Statistical analysis was then performed on the data to determine if there was a statistically significant correlation between sample site clearance and XRF validation. The present study expands on existing research because the focus is on surface cadmium contamination, rather than lead which has been more typical in the literature. The significance of this goal is the improvement in the timeliness of risk assessment decision making.

II. *Materials and Instrumentation*

For surface sample collection, gloves appropriate to the material were worn during the wipe sample collection process. Gloves were selected based on what BNL IH75190 specified as appropriate to cadmium sample collection. Appropriate gloves for cadmium are natural latex rubber, nitrile, PVC, or polyethylene gloves. Wipe samples were collected with LeadWipes™. Wipe samples were taken within a template area. In the pilot test phase of data collection, half the samples taken in the first phase of sample collection were taken in a 4-inch by 4-inch template area, half were taken in a 12-inch by 12-inch template area. Samples in the subsequent two phases of sample collection were only taken in the 12-inch by 12-inch template area due to low quantities of cadmium present. XRF readings of the wipe samples were taken with an

Olympus DELTA Family Handheld XRF Analyzer. Wipe samples collected were then transferred to a vial for laboratory analysis, as specified by the laboratory (BNL, 2017).

III. Data Collection

For data collection, there were two phases of sample collection and laboratory analysis. The purpose of the first phase of sample was to conduct a pilot test to determine if there was a detectable amount of cadmium by the portable XRF prior to proceeding with the subsequent phase of the study. In the second phase, further cadmium wipe samples were collected to obtain a better distribution of data from the pilot test. These samples were then analyzed with XRF to determine if a screening value or ad-hoc calibration curve could be established and related to the results of quantitative laboratory analysis.

In the first phase of the study, the pilot test, 10 cadmium wipe samples were collected from an aircraft parts manufacturing facility and then analyzed with XRF. The cadmium wipe samples from the aircraft parts manufacturer were collected from a cadmium plating operation. Areas for sample collection included the drip tray of a cart used for drying parts, the floor next to the brush plating station, the quality control work bench, and the floor near the quality control work bench. 6 of the 10 wipe samples from each set were obtained using a 4-inch by 4-inch template. The other 4 were obtained using a 12-inch by 12-inch template. The purpose of utilizing two different template areas was to increase the likelihood that the XRF would obtain readings above its detection limit.

First, wipe samples were taken in accordance with BNL IH75190 methodology, which a standard operating procedure for surface wipe sampling of metals that is based on NIOSH 9100 – "Lead in Surface Wipe Samples," (BNL, 2017). LeadWipes were utilized for this portion of

data collection. Next, a template was placed over the sampling area. The template size was 4-inch by 4-inch for six of the wipe samples, 12-inch by 12-inch for the other four samples. After the template was placed, the surface was wiped with vertical "S" strokes which cover the entire template area. The exposed side of the wipe was folded inward after the first pass was completed. After the wipe was folded once, another "S" shaped pass which was horizontal (90° to the initial pass) was taken. The exposed side of the wipe was folded after this. Next, a third "S" pass was made over the template area in the same direction as the first pass. The exposed side of the wipe was folded inward for a third time following this pass. This process for wipe collection is illustrated in Figure 2 below.

Figure A: NIOSH Surface Wipe Method
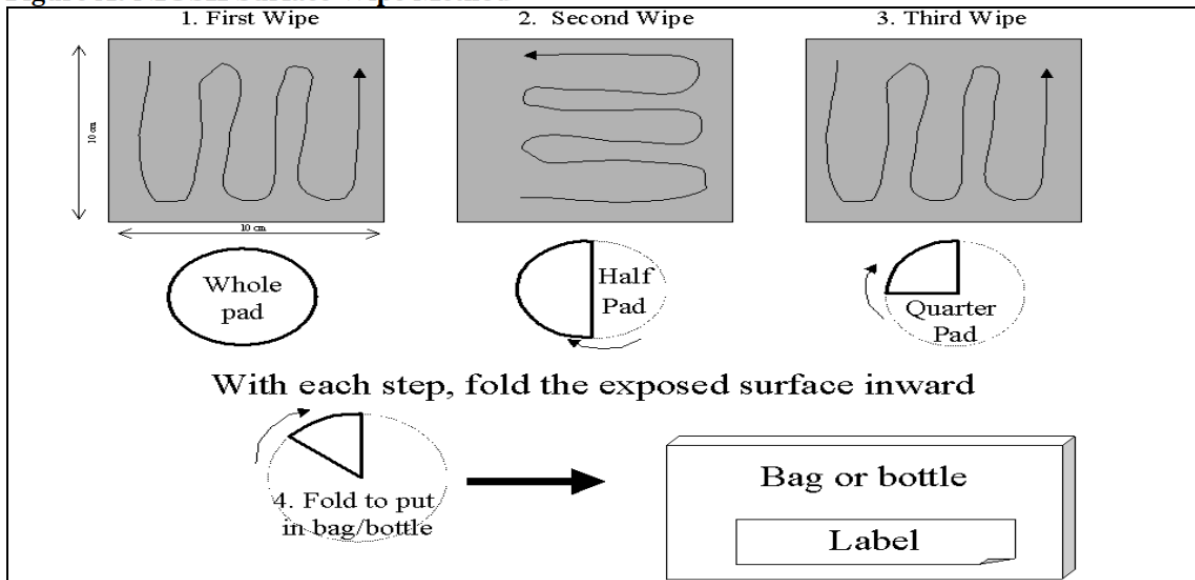
Figure 2: Wipe sampling pattern within template area and how wipes were folded between passes of template area. From BNL, 2017.

Next, the portable XRF was utilized to determine if detectable cadmium was present on the wipe, the percentage of which was then recorded. In order to do this, the wipe sample was placed on the cardboard box as shown in Figure 3.

Figure 3: XRF Analysis Setup

The cardboard box was utilized in order to create enough distance between the XRF and surfaces below to attenuate interfering reflections from those surfaces. Prior to taking the XRF readings, background readings of surrounding light element material was done to ensure there was no metal background readings. Three XRF shots were then taken from the top, middle, and bottom sections of the sample, which appear as left to right in Figure 3. Figure 4 (see below) shows the NIOSH 7702 method of collecting XRF shots. Lastly, folded samples were transferred to vials for laboratory analysis.
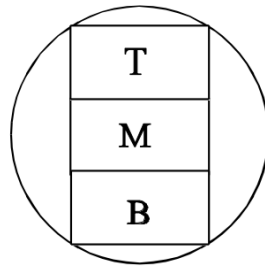
Figure 4. NIOSH 7702 XRF sample locations on a 37-mm filter, demonstrating the principle behind wipe sample analysis. From NIOSH, 1998.

       The preliminary results from this pilot test yielded some quantities of cadmium which were very high due to collection from the drip tray, and a lot of non-detect results from other areas. In spite of the disparity between values displayed, a high R^2 was seen in both a linear and second order relationship between XRF and laboratory results. However, because there were limited results in between these two extremes, this relationship between the two data groups is not plausibly applicable. Therefore, for phase two of sample collection, the methodology was revised to improve cadmium recovery and the range of XRF detection recorded.

       The second phase of the project involved the collection of 10 more cadmium samples from similar locations to the pilot test at the aircraft parts manufacturing facility. These samples were then analyzed with XRF and then sent to the laboratory for analytical analysis using NIOSH 9102 – (ICP-AES). Wipe samples were collected and analyzed as indicated from the pilot test with a few slight changes due to the nature of the preliminary results. Due to the prevalence of left censored data, the 12-inch by 12-inch template area became standard for data collection. Finally, in order to attempt to improve XRF detection with the cadmium levels under

study, after the wipe sample was collected and folded three times as indicated above, the wipe was then folded in thirds and then in half again such that the wipe sample approximated the size of the XRF analyzer window.

The results of XRF analysis for each sample were summed and reported in percent mass. These samples were then sent to the laboratory and analyzed utilizing NIOSH 9102, Elements on Wipes, ICP-AES technology. Laboratory analysis results were reported in $\mu g/ft^2$. The XRF data and laboratory data were then analyzed for a linear correlation between the two data sets utilizing a simple regression analysis. From a linear correlation, an ad-hoc calibration correlation was developed by reporting which percent area results related to which results in $\mu g/ft^2$.

IV. Data Analysis

Laboratory analysis was conducted in accordance with NIOSH 9102, Elements on Wipes methodology. Wipe samples in vials were solubilized via mixture with nitric acid and subsequent heating. After wipe samples were solubilized, they were analyzed with inductively coupled argon plasma, atomic emission spectroscopy (ICP-AES) and concentration of cadmium on wipe samples was quantified.

Once laboratory analysis results were obtained, a regression line was plotted and a regression equation and coefficient of determination was then determined. Based on the linearity of the regression line and the value of the coefficient of determination, the linearity (or lack thereof) of the relationship between XRF screening and laboratory analysis was determined.

VII. Limitations

Portable XRF analysis has some notable limitations. These limitations are a result of sample composition and analysis. In order to accurately quantify samples, XRF requires a

sample which is homogeneous and sufficiently thick to assume an "infinitely thick" sample. Where this assumption cannot be made, as is the case in occupational sample sites, the data collected from XRF cannot be treated as quantitative. In this scenario, a material-specific calibration is required which relates the thickness of the sample to the intensity of the x-rays. Current XRF technology only has such calibrations for lead. Therefore, the data obtained for cadmium can only be used semi-quantitatively, as was conducted in the present study with the ad-hoc calibration curve developed from comparison of XRF readings to laboratory results (Seyfarth, n.d.).

4.   Results

I.   Overview

Samples were collected from one worksite for the present study. Cadmium samples were collected from an aircraft parts manufacturing facility. Sample locations in the aircraft parts manufacturing facility were work tables for a quality control station, the floor near the quality control work tables, the floor near drip trays, the floor near the aisle by the cadmium brush plating station, and the floor on the non-aisle side of the cadmium brush plating station.

Sample collection was done in two phases. The first phase of sample collection was a pilot test to determine what levels of cadmium were present in the aircraft parts manufacturing facility, the sensitivity of the XRF, and determine a standard sampling area based on the sensitivity of the data. Wipe samples were collecting in accordance with BNL standard operating procedure IH75190. Cadmium samples were then analyzed with the XRF according to NIOSH 7702 methodology. Following the results of the pilot test, 12-inch by 12-inch became the standard template area for sample collection at the aircraft parts manufacturing facility. Folding

the wipes into thirds and then in half again to approximate the sample window size also became

standard after the pilot test. Wipe samples were then analyzed in the lab according to NIOSH

9102 methodology. The primary goal of this study was to determine if XRF can be used as a

rapid, nondestructive, onsite screening tool to improve clearance from wipe sampling alone. This

timeliness is important in order to facilitate faster risk assessment decision-making regarding

worker exposure to these materials.

II.   *Results*

According to the method indicated above, 10 samples were collected in the second phase

of data collection. The results of this data collection are indicated in Table 1. Any left censored

data was corrected by dividing the estimated detection limit of the instrument, 0.013% mass, by a

censor of 2 in order to obtain numerical results for all samples collected. Following the receipt of

data and data organization, a scatter plot of the data was plotted. The XRF results in % mass

were plotted on the x-axis, the laboratory results in $\mu g/ft^2$ were plotted on the y-axis. A

regression line and R^2 value were then calculated. This graph is shown in Figures 7 and 8.

Sample Number	Sampling Area	Type of Surface	XRF Reading (% mass)	XRF Reading Error	Adjusted XRF Reading (value/sqrt(2))	Laboratory Results (ug/ft^2)
1	Quality Assurance Operation	Work table	0.135	0.0027	N/A	5800
2	Quality Assurance Operation	Work table adjacent to sample #1 work table	0.5603	0.0104	N/A	36000
3	Quality Assurance Operation	Facedown side of work mat on sample #2 work table	0.9829	0.0137	N/A	64000
4	Quality Assurance Operation	Floor near work tables	0.0749	0.0021	N/A	6400
5	Quality Assurance Operation	Floor near work tables (same sample location as sample #4)	ND		0.0065	320
6	Brush Plating Operation	Floor near drip trays	0.0664	0.002	N/A	3800
7	Brush Plating Operation	Floor on aisle side of workstation	ND		0.0065	850
8	Brush Plating Operation	Floor on aisle side of workstation, noticeable cleaner than spot for sample #7	ND		0.0065	240
9	Brush Plating Operation	Floor mat on non-aisle side of workstation	0.2457	0.004	N/A	20000
10	Brush Plating Operation	Floor on non-aisle side of workstation	0.0374	0.0018	N/A	2900

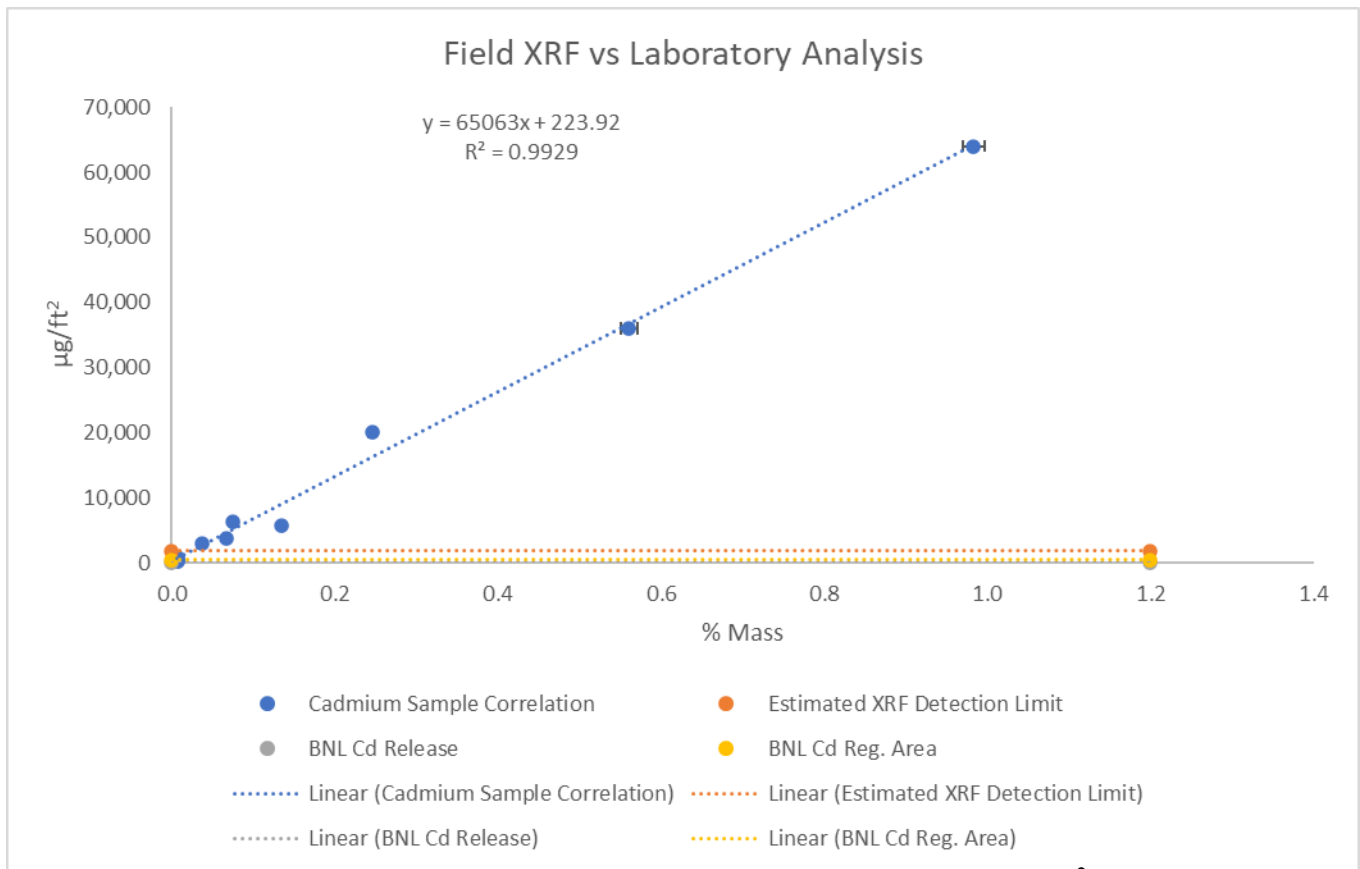*Table 1*: XRF and laboratory results for phase II cadmium sample collection

Figure 7: XRF results in percent mass plotted against laboratory results in μg/ft^2 with a regression line and R^2 value indicated.

In the absence of a regulatory limit for surface contamination, the Brookhaven National Laboratory recommended surface wipe criteria were utilized to compare results to. There are two limits for cadmium that BNL has listed. The first is for a cadmium regulated area, which is an area where there are levels of cadmium present expected to be above the PEL (BNL, 2017). The second, is for a non-operational area, which is where these levels are not expected. In Figure 7 and Figure 8, these levels are indicated by horizontal lines named "BNL Cd Reg. Area," and "BNL Cd Release," respectively. These limits, which results of data collection were compared to, are 465 μg/ft^2 for a regulated area and 31 μg/ft^2 for a non-operational area. An estimated detection limit of the XRF was also calculated and plotted on the graph. The detection limit was estimated by averaging the highest left censored result, 850 μg/ft^2, with the lowest detectable result, 2900 μg/ft^2, for an estimated detection limit of 1875 μg/ft^2. The results obtained ranged from 240 μg/ft^2 to 64000 μg/ft^2 over 10 samples collected, from 8 different locations within the worksite.

5.   *Discussion and Conclusion*

The present study exhibited a strong linearity between XRF onsite analysis and laboratory analysis of cadmium surface wipe samples. This was seen by the R^2 value of 0.9929 and a positive linear regression line exhibited when these two data sets were plotted. XRF was considerably less sensitive than laboratory methods, however. Laboratory methods were capable of quantifying results for all ten samples collected, whereas XRF analysis was only able to quantify, albeit semi-quantitatively, samples which were above about 1875 μg/ft^2.

These results show that laboratory analysis could be estimated using the results of XRF analysis. This means that prior to investing the resources to send wipe samples to the laboratory for analysis, they can effectively be screened onsite to determine if the relative levels of surface

cadmium in the workplace. Based on the relative levels indicated, a decision can be made about whether or not further cleaning is necessary prior to obtaining quantitative measures of onsite cadmium from a laboratory. Since the portable XRF used in the present study displays results in relative percentages, the strong linearity exhibited could possibly be attributable to changing relative percentages of the whole quantity of materials analyzed for by the instrument.
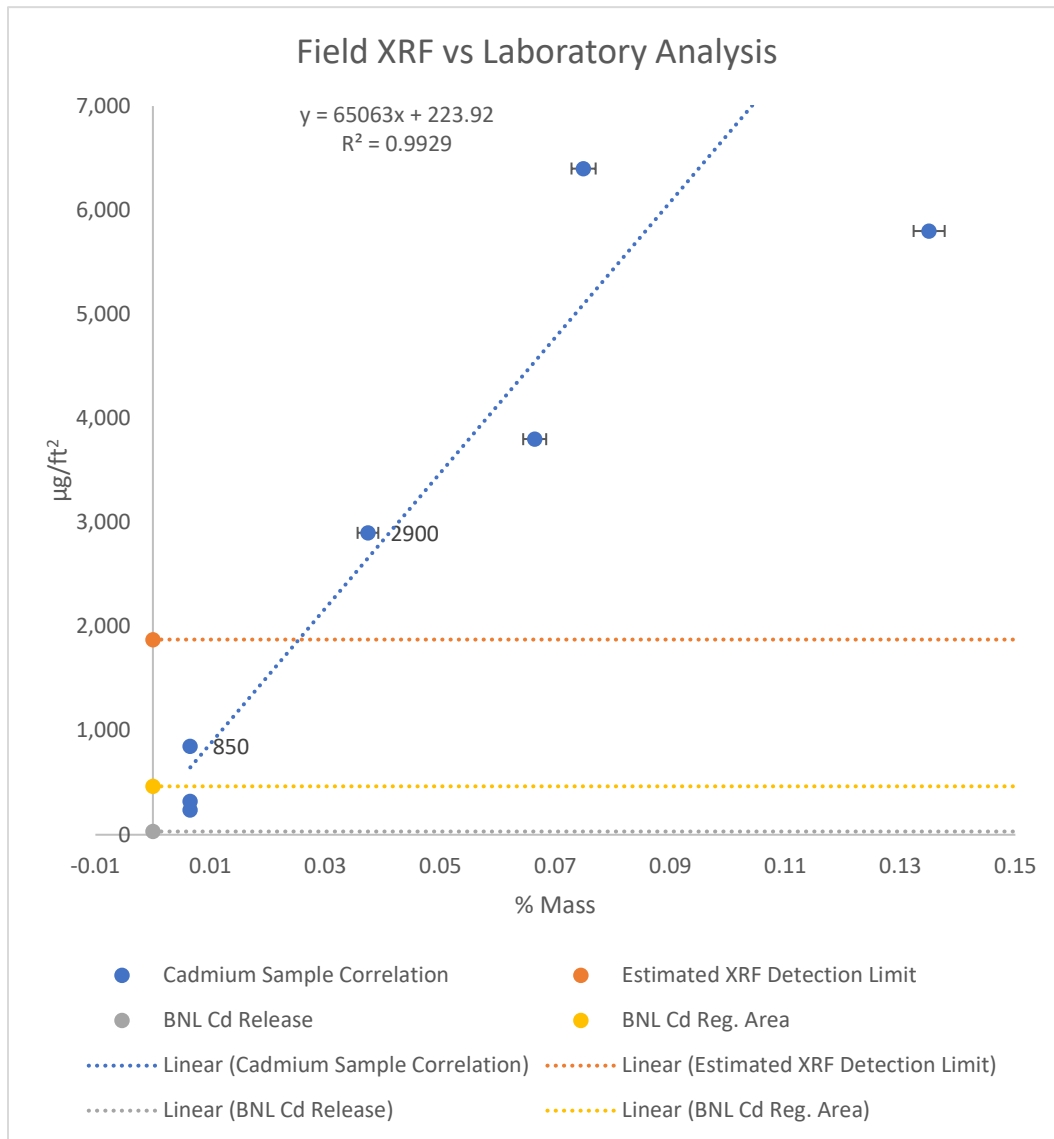

Figure 8: Closer perspective on left cluster of Figure 7 results

Additionally, the sample size for the present study was relatively small, so the linearity of the results may not remain consistent at larger sample sizes. Therefore, the possibility remains that the linearity of the instrument is not as strong as what was shown in the displayed results.

Previous studies have also displayed strong linearity between XRF and laboratory analysis. This was seen in the high R values between XRF and laboratory analysis in the study of leaded paint, as well as the high R^2 value exhibited in the comparison of lead surface wipe samples and portable XRF readings of the template area (Sterling et al., 2000; Gorce & Roff, 2016). These strong, positive correlations differ from the present study slightly because they refer to direct surface monitoring with the portable XRF, whereas the present study screened the surface wipes directly. Additionally, the portable XRF for the present study did not have the capability to monitor and quantify surfaces directly, only obtain semi-quantitative, relative percentages of a whole sample area. However, the strong correlation between portable XRF analysis and laboratory methods in the present study and previous studies remains consistent.

Although the correlation between the XRF results and the laboratory results was high, the sample size was relatively small. Because of this, the statistical strength of the paper is weaker than past studies. Additionally, because the material under study is cadmium and not lead, there was not an instrument capability of quantifying the data, as that requires a correlation relating the intensity of the x-ray beam to the depth of the sample. This type of correlation was not available for the present study and therefore the results obtained were only relative percentages of the materials visible in the XRF window. Therefore, this specific instrument cannot be used solely to characterize and quantify exposure to surface cadmium. However, the use of XRF in this manner remains useful. If there is detection on the present instrument, then it can be presumed that the

area under study does not meet clearance, based on the BNL limits and therefore merits further cleaning before quantifying wipe samples in the laboratory.

The present study aimed to determine if portable XRF could successfully be utilized as a screening tool of wipe samples in order to improve worksite clearance of wipe samples. Although the present instrument was not sensitive enough to work alone, it did provide useful information in the assessment of the worksite under study. Areas which were detectable with XRF merited further cleaning and analysis in order to be protective of workers. Therefore, portable XRF can potentially be used effectively to screen wipe samples to inform decisions regarding existing controls and also to reduce costs associated with traditional wipe sampling. Further analysis of worksites with a more sensitive instrument and greater sample sizes is necessary to determine whether the indicated method is truly valid and practical for worksite applications. However, the results indicated are a promising step in that direction.

6.   References

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