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EFFECTS OF SAMPLE FORMULATION ON THE ANALYSIS OF HEAVY METALS BY X-RAY FLUORESCENCE

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RESEARCH AND TECHNOLOGY DIRECTORATE

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A key area of research in environmental studies is the identification and analysis of metals in soil. Methods of testing soil samples have, in the past, involved much time in the laboratory setting. This report describes the use of an x-ray fluorescence spectrometer (X-MET 840) that can be used in the field, and a method of creating standard samples for its calibration. The method was developed to decrease the time factor involved in calibrating the X-MET 840 and testing soil samples for heavy metal contaminants. Analysis by x-ray fluorescence has many advantages because of the ease of operation and portability of instrumentation. This report describes the effect of pelletizing samples upon reproducibility of analysis.

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PREFACE

The work described in this report was authorized under Contract No. DAAL03-91-C-0034, Task No. 93116, and Delivery Order No. 639 from the U.S. Army Research Office in support of the U.S. Army High School Science and Mathematics Faculty Program. Sandra J. Steele is a science teacher at Pikesville High School, Baltimore, MD. This work was started in July 1993 and completed in August 1993.

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CONTENTS

LIST OF TABLES

EFFECTS OF SAMPLE FORMULATION ON THE ANALYSIS OF HEAVY METALS BY X-RAY FLUORESCENCE

1. INTRODUCTION

Monitoring and assessing soil samples for heavy metal contamination is an important method of maintaining and evaluating environmental integrity. During the last 18 years, x-ray fluorescence has become a valuable method for analysis of metals. The simplicity of the instrumentation coupled with improved microprocessors has led to the development of portable battery operated instruments that can be readily used in the field as well as in the laboratory.[1,2] Because sample preparation is minimal, the total time for analysis is considerably shorter than that for atomic spectroscopy methods like atomic absorption and flow emission spectroscopy.

Reproducibility is one of the limitations of the technique. Results from multiple runs on the same sample in the same orientation usually vary to less than a tenth of a per cent. In contrast, analyses of different portions of the same sample or different orientation (when the sample is a single item) may vary by a few per cent. Our hypothesis was that the analysis was limited to the surface region. If the surface could be made more uniform and reproducible, then the precision of measurement would be increased.

2. INSTRUMENTATION[3]

The method for qualitative and quantitative analysis of metals by x-ray fluorescence involves excitation of atoms by x-rays and subsequent analysis of energy and intensity of emitted radiation. The X-MET utilizes radioactive isotopes to generate characteristic x-rays. The following isotopes are available from the manufacturer: Cd-109, Cm-244, Fe-55 and Am-241. Source selection depends on the mass of elements to be analysed. An Americium - 241 source was selected with peak emission in the range of 59 kev. This source is best suited for measuring the presence and concentrations of elements with atomic numbers (Z) between 22 and 92 (Titanium and Uranium respectively).

The spectrum of x-ray emission from a sample is accumulated, stored, and displayed by digitising the characteristic energy into a grid that is 256 by 256 channels. The vertical scale represents the number of x-ray events per second, while the horizontal scale represents the characteristic energy of each x-ray. Photons produced by x-ray events are detected at a rate of 1000 to 5000 photons per second in a sequential manner. As a result, the output of the X-MET is a histogram of x-ray intensity in electrical pulses vs. x-ray energy in 256 channels correlating to kev's.

The detection process produces a Gaussian shaped curve around the peak x-ray energy level. Resolution of the X-MET is a function of the width of the curve created by x-ray intensity and the peak energy emission from the sample being measured. The width of the curve created by x-ray emission is measured at half maximum of the peak (fwhm) and compared to the x-ray energy in kev. As an element's peak emission energy approaches that of the americium source, the resolution decreases slightly.

The X-MET contains eight model channels that can be calibrated to identify elements in a sample, measure concentrations of elements in a sample, or merely display raw count rates for a sample. The operator controls the measurement time (between 1 and 32767 seconds) and function to be used.

Instrument calibration is carried out by first selecting one of 8 models and a measurement time to use. A measurement time of 100-300 seconds is suggested as a good range for most cases (manual p. 5-5). Elements for calibration are selected dependant on the samples you will be studying. All elements that may exist in the group to be tested for identification purposes or all elements that may have spectral lines similar to those of interest are used in the instrument calibration process.

Pure samples, supplied by CSI, are used for initial calibration of the instrument. A backscatter sample is also included and must be measured during the instrument calibration. The microprocessor in the X-MET uses the pure sample and backscatter spectra to "set" the channels used for subsequent analysis. When calibrating the instrument, all elements present (both analysed and unanalysed) must be included.

After completion of instrument calibration, raw count rates can be measured and displayed for samples. If selecting the identification or quantitative functions, standard calibration samples must be prepared or purchased and measured. These functions will be discussed later.

Test Plan

As mentioned previously, one of our primary areas of interest was to develop a method of preparing standard calibration samples for use in identification and quantitative analysis. Samples used for calibration must generate reliable and reproducible data. Many variables can affect measured x-ray fluorescence from a given sample. Measurement consistency of standard samples is imperative to the calibration of the X-MET for use in these functions.

3. EXPERIMENTATION

3.1 Sample Preparation

Two powders were selected as the medium for preparing the pellets. Arizona Road Dust is a well characterized red powder that is available in several size ranges and frequently used for testing aerosol penetration. This (0 to 5 microns) material was obtained from Majac Corporation in Tulsa, OK. Arizona Road Dust has the colloquial name of AC dust due to its extensive use by General Motors. The graphite, Asbury 260, was obtained from Asbury Feast in Atlanta, GA. This material consists of thin flakes with a mean molecular diameter of about 4 microns.

A standardized method of producing a stable, pelletized sample was developed. AC dust and graphite were selected as medium materials. X-ray fluorescence spectra produced by the X-MET for these mediums indicated that their presence would not interfere with emission energies produced by metals of interest. Transition metals used for experimentation were Iron, Copper, Mercury, and Nickel. Figures 1-8, display each metal X-ray fluorescence spectrum overlayed with the mediums used. The only interference of a medium with a metal of interest may be AC dust which contains trace amounts of Iron[4] (see figure 8). Graphite, composed of planer carbon, contains none of the metals of interest.

The sample compartment for the Heavy Element Probe System (HEPS) consists of a circular well 0.3 inch deep and in diameter 1.3 inch with a window 0.75 inch in diameter. For maximal intensity and optimal reproducibility, samples need to be between .8 and 1.1 inches in diameter. A die was designed by us and fabricated by the Precision Machine Branch of Research & Engineering Support Directorate. The die was essentially a larger version of the apparatus marketed by Perkin Elmer[5] for preparing KBr pellets of solid samples for infrared spectroscopy. The die consisted of a hardened steel cylinder, 2 inch in diameter and 3 inch long, a sole plate, a circular disk 1 inch in diameter and 3/8 inch long, and a 1 inch piston that was machined to fit snugly but not tightly into a hole drilled lengthwise through the cylinder. The pellet was prepared by inserting the disk into the cylinder (polished side up) placing the cylinder on the sole plate, adding powder into the hole, inserting the piston, and pressing. A die was prepared by ERDEC laboratory (after the Perkin-Elmer evacuable KBr die; 1986[5]) to press soil samples into pellet form. A diameter of 25mm was selected to cover the entire exposure shutter in the X-MET probe. A sample of the salt to be analyzed was added to the medium, ground with a mortar of pestle to ensure uniformity and placed in the die. A Carver Lab Press (model C) was used at 15,000 lbs of pressure for 2 mins. to compress the samples into pellet form. Through a series of trials, it was determine that 2g samples of AC Dust and 1g of samples of graphite produced stable pellet standards. This method of preparation was used throughout the following experiments.

3.2 Optimum Sample Thickness

The first variable studied was the limit of x-ray excitation in a sample. We were concerned with the optimum thickness for data reproducibility.

Two experiments were developed to determine penetration limits. The first involved preparing samples of increasing mass and thickness. The mass of salt containing a measurable metal ion would be held constant while the mass of a soil medium would be increased with each sample. If x-ray fluorescence was measured throughout a sample, the count rates should remain constant. If excitation is measured only at the surface, the net count rates should diminish with each increase in the mass of the medium.

$FeSO_4$ and AC dust were selected to prepare samples for this experiment. Pressed pellets were used so thickness of each sample could be easily measured with calipers, and surface density would remain constant. Pellets were prepared in consistency with the standard sample model. The first pellet contained 0.2g of $FeSO_4$ and 0.8 g of AC dust. Each pellet thereafter increased in mass by 0.25 to 0.5 grams, the extra mass being AC dust. The maximum mass used to prepare pellets for this experiment was 3.0 grams. The thickness of the pellets ranged from 1.29mm to 3.70 mm, and mass thickness varied between 0.77 g/mm and 0.85 g/mm.

The X-MET was calibrated for this experiment with iron and backscatter (BS) pure samples, supplied by CSI. Raw counts were recorded for each sample in the region of the iron spectra; peak channel = 53 with a FWHM of 8 channels.

The X-MET produces raw count data of 3 types. The first, TCR, is the total count rate in all 256 channels. The second, PUL (pulse channel frequency), is the total count rate in all channels which correspond to the element of interest; in this case the 8 channels in the spectrum of iron. The third, INT, displays the net count rate in corresponding channels after background and overlap are subtracted by the X-MET. These 3 count rates can be displayed after the measurement of any sample.

For this experiment, measurement time was set at 100 seconds. PUL, INT, and TCR were recorded for each sample. The road dust used to prepare each sample is known to contain from 2-4% iron[4], so increasing the dust component could elevate x-ray emission in the iron range. But the concentration of salt decreased from 20% to 7% so the probability of iron occurrence at the surface decreased with each test pellet.

The gross count rate (PUL) for signature channels of iron remained nearly constant; 1.0 g pellet mean PUL = 204.3, 3.0 g pellet mean PUL = 202.1. This difference (2 counts) is insignificant according to the operators manual[3] (p 5-50). Because of counting statistics associated with the random nature of radiation emission, the standard deviation of count rates measured by the X-MET is +,- 2 counts. The net count rate (INT) for the 8 iron channels measured decreased by 38%, from 1.0 g pellet mean = 141.7 to 3.0 g pellet mean = 87.8.

The data suggests that the americium-241 source excites and measures x-ray emission only at the surface. The constant PUL count would indicate no change in materials within the FWHM of iron. But the decrease in INT which is a net count for spectral identification of iron, indicated a definite decrease in the x-ray intensity. Since the actual mass of iron did not vary, the lower INT appears to be indicative of the infiltration of AC dust at the surface of the pellet. The conclusion would be that the X-MET measures x-ray emission from ions only at the surface of a sample.

The TCR for samples prepared in this experiment increased from 1.0 g mean = 1772.5 to a 3.0 g mean of 2611. This would suggest that the increase of AC dust at the surface increased the amount of interfering x-ray emissions being measured by the X-MET.

The second experiment was developed to validate the findings in experiment 1. A 15 g sample was prepared containing 10% $FeSO_4$ and 90% AC dust. The sample was mixed and ground in a mortar and pestle, and samples of the powder ranging in mass from 1.0 g - 2.5 g were pressed into pellet form in consistency with the previous experiment. The thickness of the pellets ranged from 1.19mm (1 g sample) to 3.01mm (2.5g sample). Mass thickness varied slightly; .83 g/mm to .88 g/mm.

In this experiment, the PUL increased from 178.04 for the 1.0g sample to 211.03 for the 2.5 g sample. The TCR also increased from 1.0 g mean of 1774 to the 2.5 g sample mean of 2480. But the INT varied only slightly around the mean net count rate of 109.12 with a standard deviation of 2.13. The variation in count rate for actual measurement of iron ions falls within the acceptable limits suggested by the manual.

It appears that the conclusion from experiment 1 was verified by experiment 2. Although PUL and TCR increased with increasing mass and thickness of a pelletized sample, the INT remained constant. The increasing PUL and TCR counts can be attributed to an increasing sample mass producing excessive backscatter and overlap which are not subtracted. But with the elimination of background and overlap in the INT count, the concentration of iron appears to remain constant with increasing thickness and mass.

In conclusion, the X-MET measures element concentrations only at the surface of a sample.

3.3 The Effects of Surface Area, and Medium Type on the Reproducibility of Measurement

The second variable affecting reproducibility of measurement that was tested was the effect of surface area. Would a larger and more variable surface area intensify characteristic x-ray detection or diminish it due to absorption. Also investigated was the effect of varying surface area on the fluctuation of characteristic x-ray intensity. Three salts, ($CuSO_4.5H_20$, $Hg(CH_3CO_2)_2$, and $NiCl_2.6H_20$), were tested in a series of six experiments. Each salt was prepared in pellet and powder form in two different mediums; AC dust and graphite.

In the first two experiments, 10%, 20%, and 30% concentrations of $CuSO_4.5H_20$ were prepared in 1 gram samples using graphite as a medium in the first and AC dust in the second. Samples prepared with AC Dust were increased to a total mass of 2 g. We felt it was imperative to measure x-ray emission from pellets produced by the exact powder sample that was measured. This procedure was replicated for the other salts tested. Measurement time was set at 100 sec. Table 1 lists peak channels and FWHM for graphite, AC dust, mercury, copper, and nickel.

$CuSO_4.5H_20$ and graphite were first prepared in powder form using a mortar and pestle for grinding. PUL, INT, and TCR were measured 5 times. The powder was stirred each time to observe any variation in measurement. Sample standard deviations were calculated for INT values. Pellets were then prepared from the powder samples using the standard sample model. PUL, INT, and TCR were again measured 5 times. The orientation of the pellet sample was changed for each measurement; i.e., side changed and pellet turned. Sample standard deviations for INT were calculated. Table 2 delineates the fluorescence intensity and standard deviation for the powder & pellet formulations hexahydrate ($CuS0_4.5H_20$ FW = 249.7) mixed with graphite and Arizona Road Dust (AC). Table 3 describes similar measurements with mercuric acetate ($Hg(CH_3C0_2)_2$ FW = 318.7). Table 4 contains analogous results for nickel chloride ($NiCl.6H_20$ FW = 237.7). Figures 9-14 depicts the recalculated data that graphically illustrates the intensity of fluorescence as a function of metal ion concentration alone. The difference in the resulting intensity with the two media (i.e. graphite and AC) demonstrate the importance of having consistent formulations for standards and samples.

Table 1: Peak Emission of Sample Preparation Materials

Pure Sample	Peak Channel	FWHM
Graphite	103	11
AC dust	54	14
Copper	66	10
Mercury	82	11
Nickel	61	9

4. CONCLUSIONS AND RECOMMENDATIONS

Reproducibility was enhanced by pelletization. In 12 of the 18 samples tested, the standard deviations were lower for the pelletized samples. One can also conclude that AC dust is a better suited medium for preparation of standard calibration samples. In 13 of the 18 samples measured, standard deviations were lower when samples were prepared with AC dust.

Mixtures prepared with graphite exhibited much higher INT's than samples prepared with dust. The intensity of x-ray emission from the metal ions would appear to be elevated because of the presence of graphite. The value of INT's for graphite and copper samples is, in some cases, 4 times greater than those prepared with AC dust. A comparison of powder vs pellet samples prepared with graphite also indicates an unusual pattern. When comparing these samples, the INT values increase by 300 to over 400 counts. The XINT for pellet and powder samples produced with AC dust increased a maximum of 50 counts. The 10% AC dust preparation increased by only 7 counts. This general trend, an elevated intensity of x-ray emission in graphite prepared samples, continues with the other metal ions tested.

It would appear that standard samples for calibration of the X-MET should be prepared using AC dust as a medium in a pellet form. The effects of graphite on x-ray fluorescence should be more thoroughly tested before it is used for standard sample preparation.

The greater fluorescence intensity in the graphite samples does not appear to be due principally to absorption of incident radiation by Arizona Road Dust nor by fluorescence of the graphite itself. Further work is needed to determine the cause of this phenomenon.

Table 2: Analysis of Copper ($CuSO_4 . 5H_2O$ FW 249.7)

Concentration of Salt	Medium	Intensity (Standard Deviation)	
		Powder	Pellet
0	Graphite	5.8 (1.3)	16.8 (1.7)
	Arizona Road Dust	5.2 (1.0)	5.2 (0.8)
10%	Graphite	296.0 (37.7)	592.1 (11.4)
	Arizona Road Dust	103.0 (6.9)	120.0 (3.6)
20%	Graphite	494.5 (25.6)	859.4 (7.0)
	Arizona Road Dust	214.5 (17.2)	275.6 (16.2)
30%	Graphite	852.6 (18.3)	1293.2 (17.0)
	Arizona Road Dust	342.0 (21.0)	390.1 (14.3)

Table 3: Analysis of Mercury Acetate (Hg0Ac FW 318.7)

Concentration of Salt	Medium	Intensity (Standard Deviation)	
		Powder	Pellet
0	Graphite	5.8 (1.3)	16.8 (1.7)
	Arizona Road Dust	5.2 (1.0)	5.2 (0.8)
10%	Graphite	670.4 (24.0)	955.1 (13.0)
	Arizona Road Dust	262.1 (3.3)	296.7 (14.8)
20%	Graphite	956.0 (8.2)	1217.1 (5.6)
	Arizona Road Dust	493.8 (1.3)	526.9 (19.4)
30%	Graphite	1052.5 (20.7)	1290.8 (5.9)
	Arizona Road Dust	696.8 (2.8)	708.7 (23.3)

Table 4: Analysis of Nickel ($NiCl_2.6H_2O$ FW 237.7)

Concentration of Salt	Medium	Intensity (Standard Deviation)	
		Powder	Pellet
0	Graphite	5.8 (1.3)	16.8 (1.7)
	Arizona Road Dust	5.2 (1.0)	5.2 (0.8)
10%	Graphite	238.6 (6.8)	418.2 (27.6)
	Arizona Road Dust	85.5 (1.6)	97.0 (2.2)
20%	Graphite	383.2 (8.9)	460.0 (8.8)
	Arizona Road Dust	115.4 (6.8)	155.2 (5.6)
30%	Graphite	513.6 (3.6)	641.9 (5.9)
	Arizona Road Dust	162.3 (2.2)	220.0 (1.8)

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APPENDIX A

TABULAR DATA AND HISTOGRAMS

Figure 1: Comparison of X-ray Fluorescence Spectrums for Pure Samples of Graphite and Copper

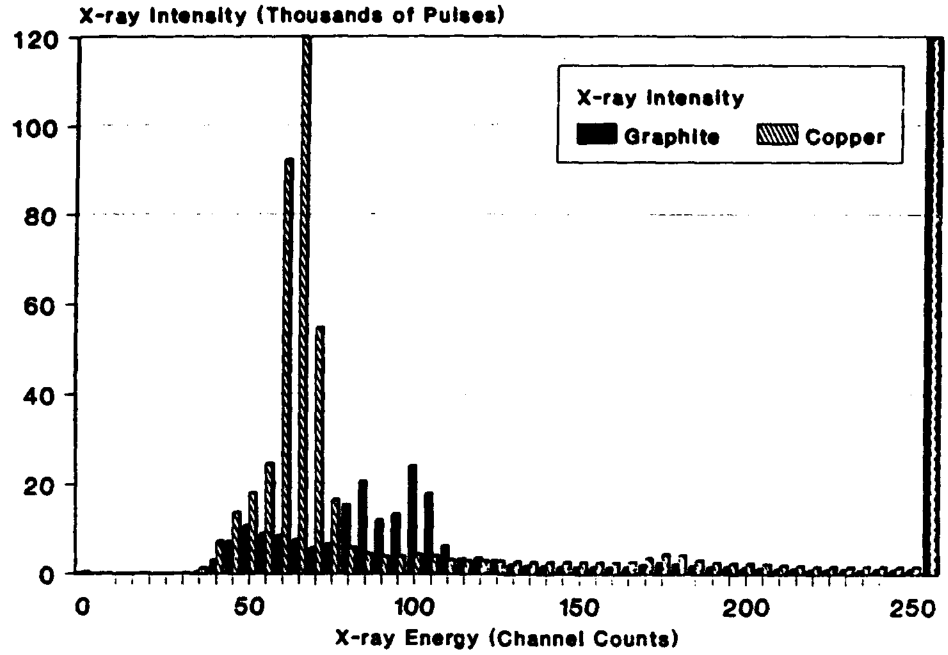


Figure 2: Comparison of X-ray Fluorescence Spectrums for Pure Samples of AC Dust and Copper

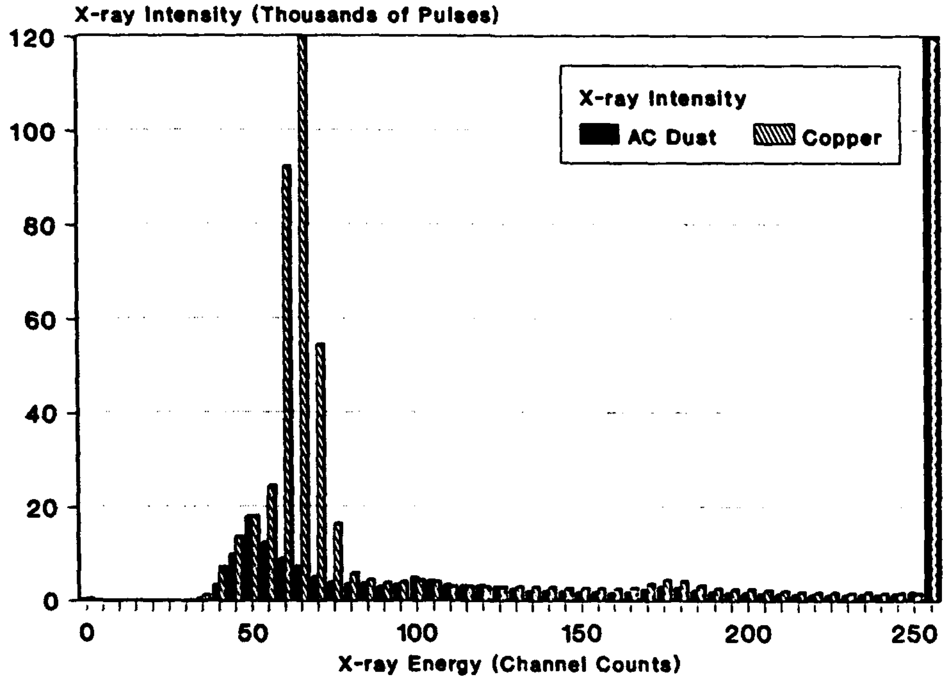


Figure 3: Comparison of X-ray Fluorescence Spectrums for Pure Samples of Graphite and Mercury

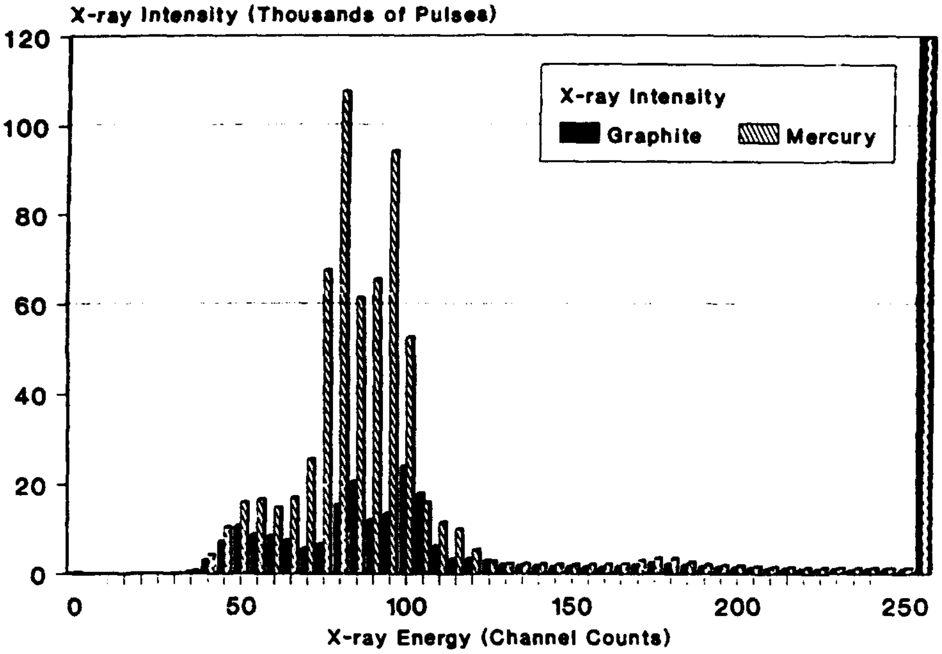


Figure 4: Comparison of X-ray Fluorescence Spectrums for Pure Samples of AC Dust and Mercury

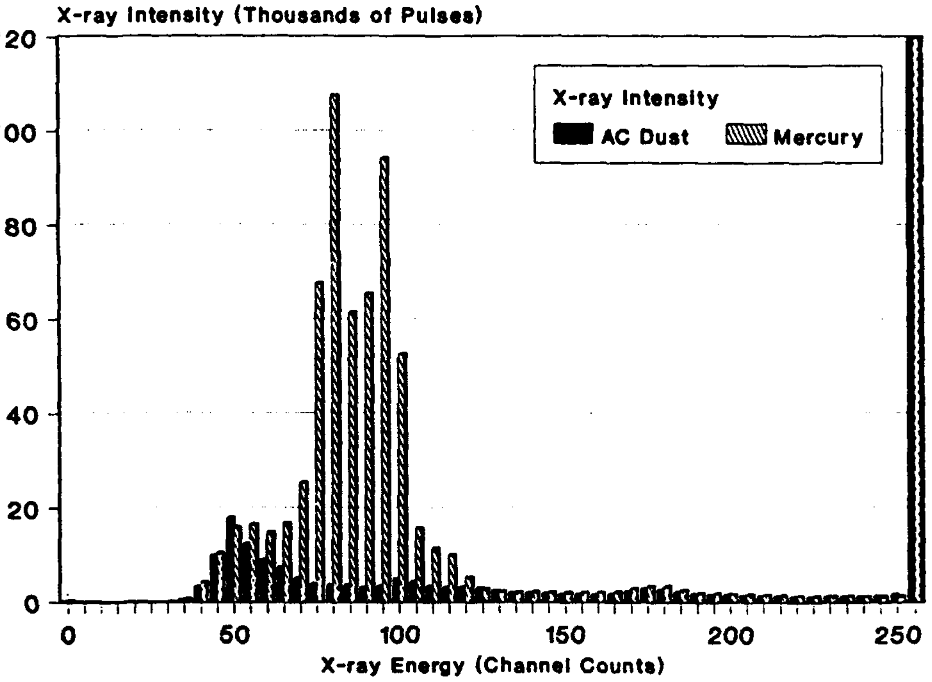


Figure 5: Comparison of X-ray Fluorescence Spectrums for Pure Samples of Graphite and Nickel

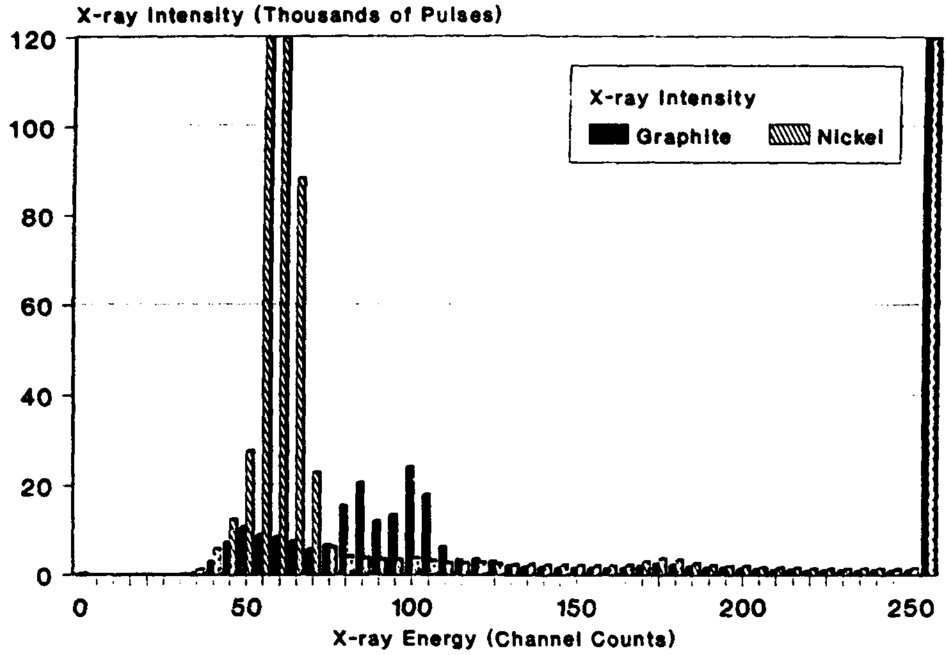


Figure 6: Comparison of X-ray Fluorescence Spectrums for Pure Samples of AC Dust and Nickel

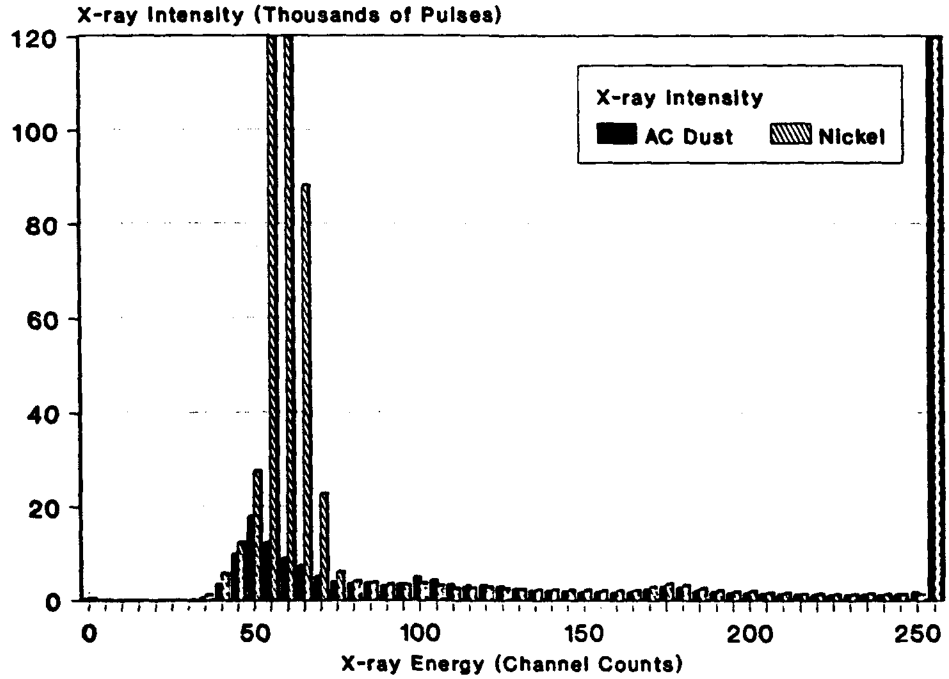


Figure 7: Comparison of X-ray Fluorescence Spectrums for Pure Samples of Graphite and Iron

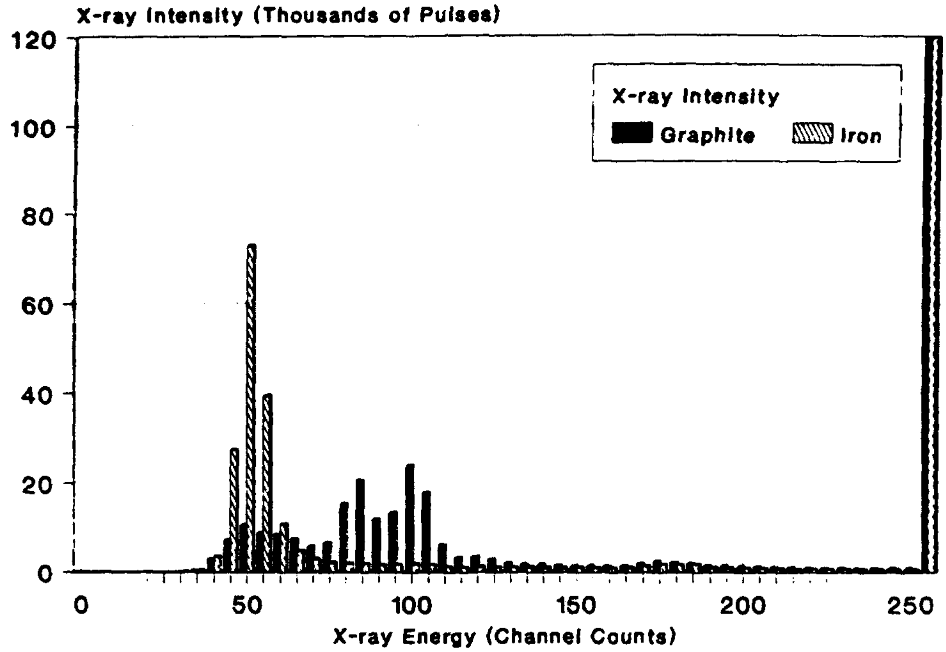


Figure 8: Comparison of X-ray Fluorescence Spectrums for Pure Samples of AC Dust and Iron

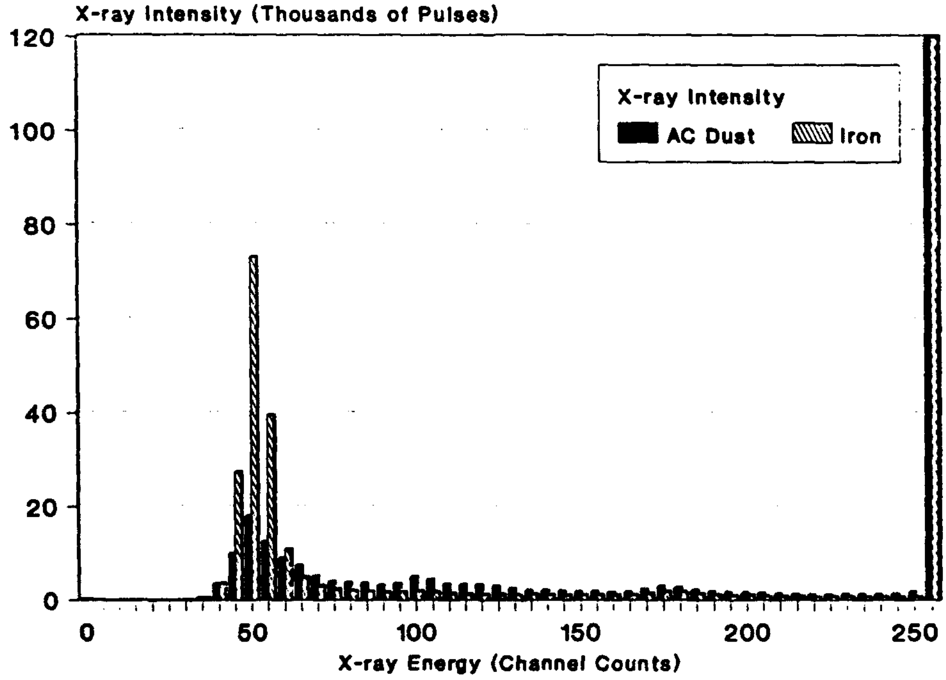


Figure 9: Mean X-ray Fluorescence Intensity of Copper Samples Prepared with Graphite

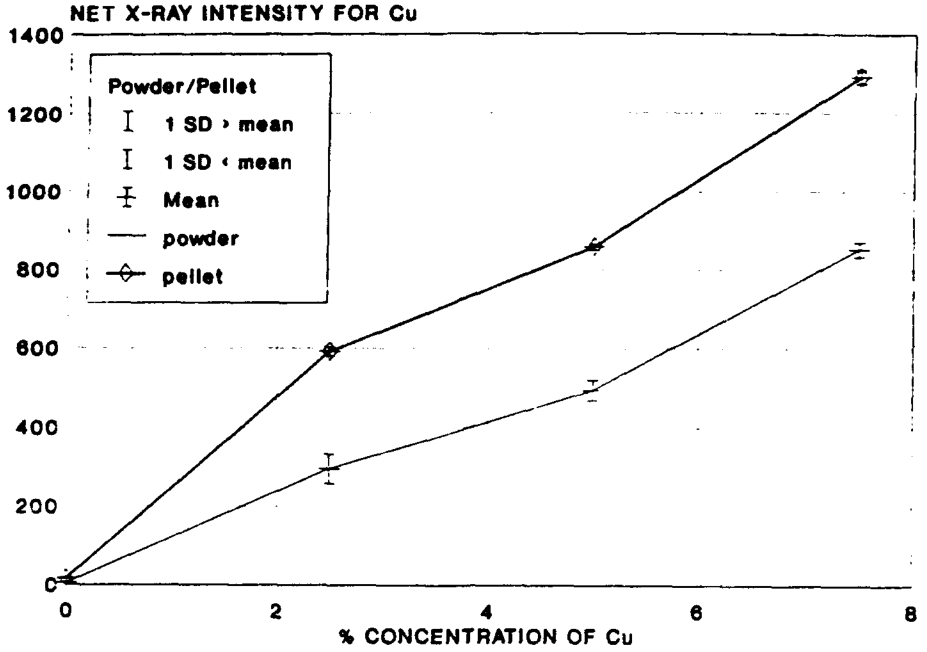


Figure 10: Mean X-ray Fluorescence Intensity of Copper Samples Prepared with AC Dust

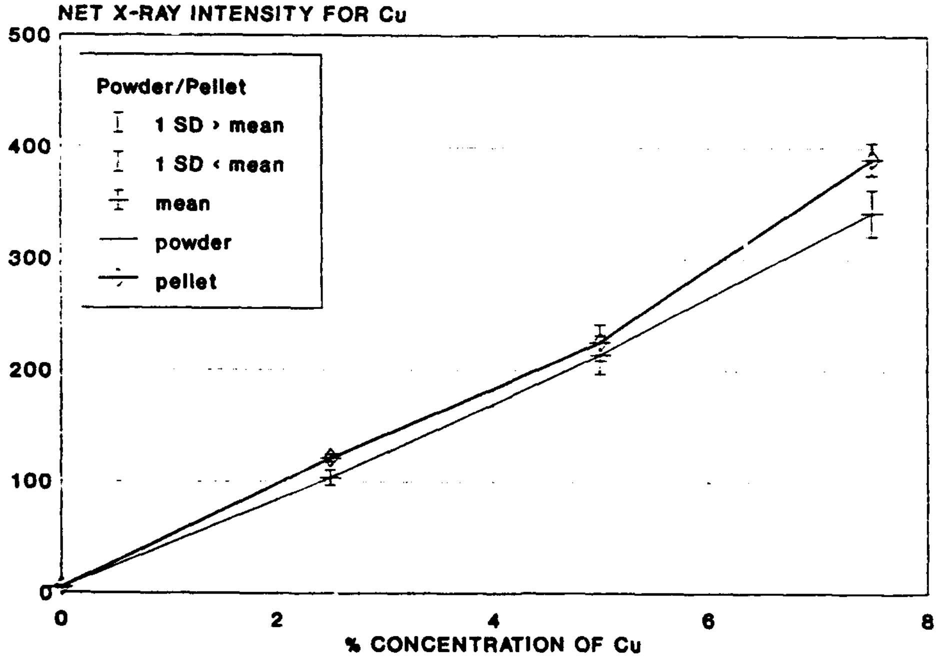
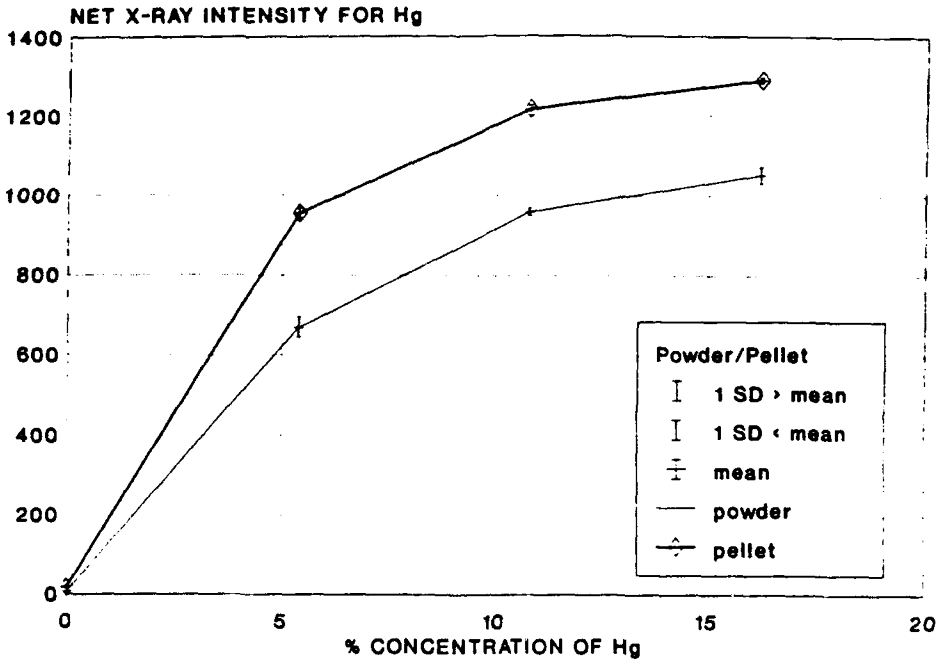


Figure 11: Mean X-ray Fluorescence Intensity of Mercury Samples Prepared with Graphite



Figrue 12: Mean X-ray Fluorescence Intensity of Mercury Samples Prepared with SC Dust

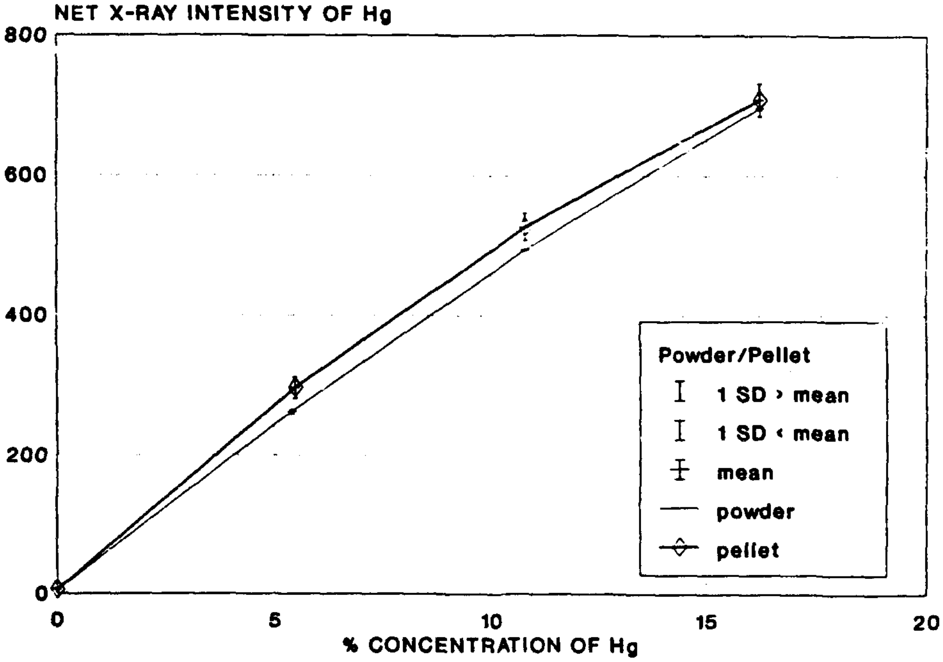


Figure 13: Mean X-ray Fluorescence Intensity for Nickel Samples Prepared with Graphite

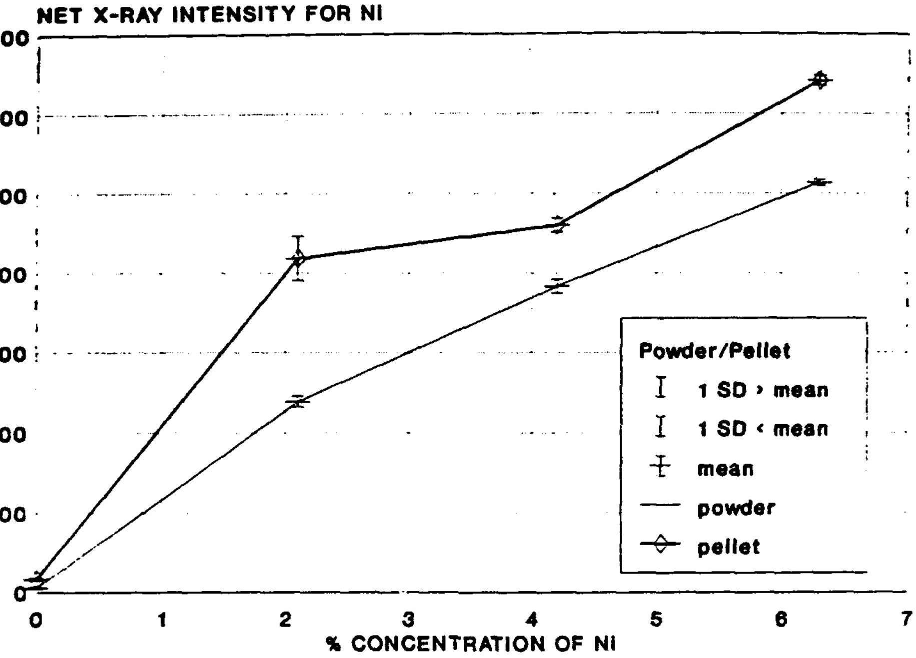


Figure 14: Mean X-ray Fluorescence Intensity of Nickel Samples Prepared with AC Dust