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Application of X-ray Fluorescence Spectroscopy to Material Analysis of Threaded Fasteners

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INTRODUCTION

To maintain the integrity of assembled components of spacecraft, all fasteners used in space flight assemblies are subjected to quality control standards not typically imposed on non-flight fasteners. Concern over the flight worthiness of fasteners has increased in recent years due to the existence of counterfeit bolts. Fasteners purchased for flight use must have adequate documentation describing material composition, strength and lot homogeneity.

Under certain circumstances fasteners can be converted from non-flight to flight by meeting the requirements for the flight bolts, i.e., strength testing and elemental analysis. Typically elemental analysis is performed by optical emission spectroscopy (OES) using an inductively coupled plasma (ICP) technique. As the ICP/OES technique is both destructive and time consuming, the number of fasteners analyzed is typically not statistically significant.

The effort of this research program was to determine if a portable X-ray fluorescence (XRF) analyzer could be adapted to perform elemental analysis of small threaded fasteners in the 10-32 and 1/4-28 range. The attributes of the XRF analysis are that it is non-destructive and can be performed in a fraction of the time required for ICP/OES analysis. These attributes enable the interrogation of larger sample sizes which in turn provides greater confidence in the lot integrity.

BACKGROUND

X-ray Fluorescence Spectrometry is a non-destructive analysis technique used to qualitatively determine the presence of elements in a sample and quantitatively determine element concentrations. The excitation of atoms in a sample by high energy photons and subsequent de-excitation of those atoms by the emission of high energy photons serve as the basis for the technique. A sample is exposed to x-rays from a radioactive source. The inner shell electrons of atoms in the sample absorb x-rays from the source and are ejected from the atom. Electrons from higher energy shells then fall to the lower, more stable energy shell vacancies by the emission of high energy photons in the form of x-rays. The x-rays emitted by atoms in the sample can be detected and displayed as a plot of intensity (number of photons detected per second) vs. photon energy. Because the electrons of each element can assume a limited number of discrete energy states there is a unique set of spectral lines (i.e. photon energies) associated with each element. Qualitative analysis, then, consists of examining the detected spectrum for peaks, finding the energy at which the peaks occur, and matching those peak energies with the known energies associated with elements in the detection range. (See figure 1.)

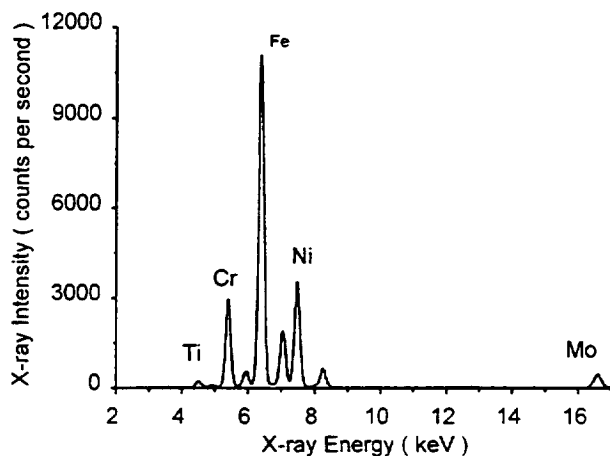


Figure 1. X-ray emission spectrum of A-286 high temperature corrosion resistant steel.

Quantitative analysis relies on the use of standards of approximately the same composition as the material to be measured and for which the elemental composition is known. The relative intensities of the peaks seen for different elements cannot be taken to be indicative of relative concentrations. The shape of the sample to be measured, placement with respect to the x-ray source and detector, and matrix composition affect the measured intensities of spectral lines. The amount of sample material that fluoresces also affects the intensities of the detected x-rays. The amount of sample material seen by the detector is related to the exposed area, the distance from the radioactive source, the distance from the detector, and the maximum depth from which emitted x-rays can escape the sample. This depth is on the order of 0.1 - 1 mm for metals and is strongly dependent on material composition. With a flat sample specimen the distance from the radioactive source and the detector is controlled entirely by a polypropylene film over the instrument's measurement aperture. Irregularly shaped specimens may have portions of their surface elevated above the polypropylene film, thus reducing measured intensities.

TEST EQUIPMENT

The portable x-ray fluorescence spectrometry system used is Metorex Inc.'s X-MET 920¹. The system is composed of a cadmium¹⁰⁹ source, a silicon (drifted with lithium) semiconductor detector, a 2048 channel multi-channel analyzer card, and a software controller package running under MS-DOS² on a portable, IBM³ compatible computer. (See figure 2.) The portable computer requires

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² MS-DOS is a registered trademark of Microsoft Corporation.

³ IBM is a registered trademark of International Business Machines, Inc.

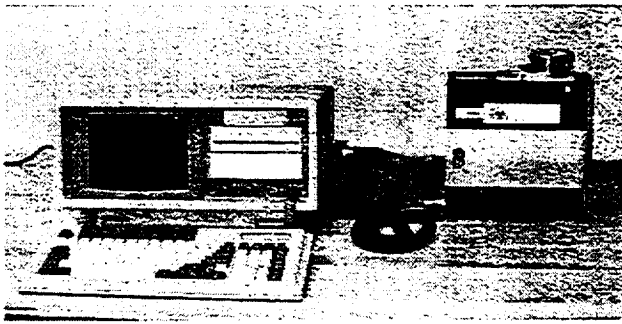


Figure 2. Portable computer and XRF probe consisting of radioactive source and x-ray detector.

a grounded electrical outlet. Liquid nitrogen is required to cool the detector and to provide gas pressure to move the radioactive source into position for measurements. A full charge of liquid nitrogen will last for several hours of moderate use.

The Si(Li) detector is an energy dispersive detector. The detector converts x-rays emitted from and scattered by a sample into electrical pulses. The amplitude of each pulse is proportional to the energy of the absorbed x-ray. The pulses are pre-amplified, sent to the multi-channel analyzer, and discretized into 2048 channels of 12.7 eV width. The detection method introduces a gaussian distribution to the lines detected. It is therefore necessary for the controller software to establish measurement "windows" for each element of interest. An element window defines the upper and lower bounds of measured x-ray energies that will be considered to represent that element's spectral line. Pure standards are measured for each analyzed element, and the full width of the distribution at half of the maximum measured intensity is used as the measurement window. (See figure 3.)

The Cd^{109} source will excite the elements having atomic numbers 20 through 44 (calcium through ruthenium) and 56 through 92 (barium through uranium). This range includes the important alloying elements in corrosion resistant and stainless steels, but excludes Mg, Al, Si, S, P, and C. Most steel alloys have specified limits on silicon, sulfur, phosphorus, and carbon content and therefore cannot be conclusively verified to meet all specified requirements by the use of the XRF system.

An ARL 3520 AES, an optical emission spectrometer using inductively coupled plasma excitation, is used to determine the composition of the bolts to be used as calibration standards for the XRF system.

In order to present the same sample surface area and geometry to the detector an aluminum disk 6.35 mm thick

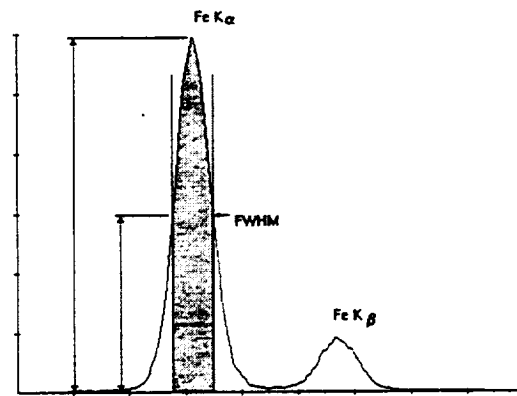


Figure 3 Element Measurement Window. Width is set equal to the full width of the distribution at one half of the maximum measured intensity.

(.250 in.) with a threaded hole through the center is used as a sample holder and mask. Aluminum is used as the mask material because it is not detected when using the Cd^{109} source.

TESTING PROCEDURE

Several concerns were addressed in attempting to use a portable XRF system for elemental analysis of small bolts. The primary concern was that the XRF analysis is sensitive to the size, shape, and placement of the sample in the XRF window. The XRF analyzer determines element concentrations by measuring the intensity of a spectral line for each element and applying a calibration curve previously determined using standards. The intensities of x-rays emitted by the sample are affected by a number of factors. Two samples with the exact same elemental composition will be reported to have different elemental compositions by the XRF system if the amount of material fluorescing is substantially different. XRF analysis is best performed on samples that have a flat surface, that cover the entire measurement aperture, and that are thicker than the maximum penetration depth of the source x-rays. With such samples the only factor influencing the intensity of x-rays detected is the material composition.

Because small bolts do not cover the entire aperture, the consistent placement of samples on the XRF window is problematic. Also, bolts vary tremendously in size and shape. (See figure 4.) Bolts of a designated size/thread series (e.g. 10-32) may vary in length and head shape, but the tip of the threaded end is substantially consistent. With a mask to hold the bolts in place and to prevent detection of material other than the first 1 to 2 mm, the detector sees the same amount of material for each specimen. (See figure 5.)

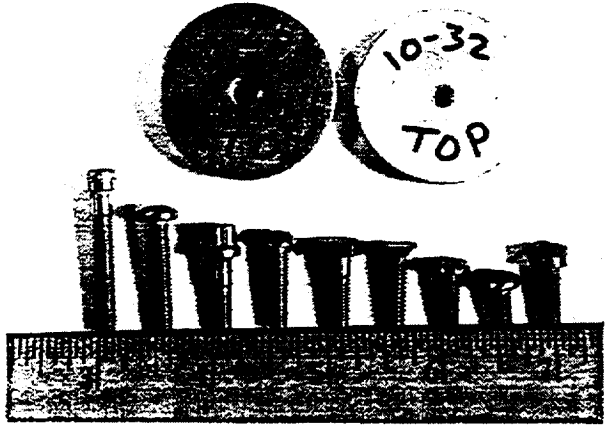


Figure 4. Aluminum Masks and an Assortment of Threaded Fasteners.

Variations in the surface roughness and differences in chamfer at the threaded ends of different fasteners will still cause some measurement variation.

The second concern is that standards for which the material compositions are accurately known are needed to calibrate the system. Standard Reference Materials⁴ typically come in the form of thick disks or loose chips. Neither shape is consistent with the geometry of the bolts to be measured. Preliminary work on this research program showed that Standard Reference Materials disks used with a mask do not provide an adequate calibration. One solution is to use ICP/OES to determine the elemental composition of several bolts, making several measurements of each bolt to obtain the mean values. The bolts are then used as calibration standards. The accuracy of the OES is a limiting factor to the accuracy of the XRF calibration. Another possible solution, not explored here, is to obtain certified reference materials in rod form and machine the rods to the desired thread series.

The third concern is that the excitation x-rays are provided by a radioactive source rather than an x-ray tube. The decay of the radioactive source causes the intensity of x-ray emissions to decrease over time. The Cd^{109} source has a half-life of 1.3 years, so the decrease in emitted x-ray intensity is significant. The X-MET 920 system automatically performs an internal check to adjust calibrated analysis routines for the drop in detected x-ray intensities. The use of a radioactive excitation source also limits the range of elements that can be made to fluoresce, as mentioned previously.

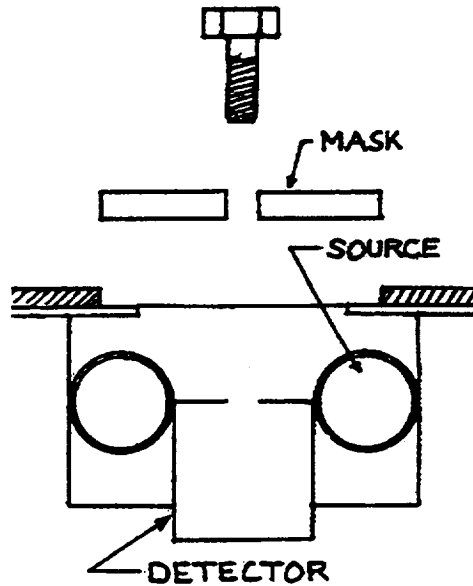


Figure 5. Schematic Representation of XRF Probe Arrangement. Fastener threads into mask which fit snugly in the aperture of the probe.

The bolts used to calibrate the XRF system were analyzed by inductively coupled plasma optical emission spectrometry. Because threaded fasteners used in space flight applications are typically 300-series stainless steels or A-286 corrosion resistant steel the elements of interest are Ti, Cr, Fe, Mn, Ni, Cu, and Mo. Although in most stainless steel alloys titanium is not a major alloying element, it is an important component of alloy A-286 corrosion resistant steel. The ICP/OES is calibrated using NIST-traceable standards. Elemental composition analysis is performed several times on material taken from the bolt heads. The mean values of the element compositions are then taken to be the known element compositions for the purpose of calibrating the XRF system. These compositions, together with element line intensities measured by the XRF system are used to generate multivariable linear least-squares fit calibration curves for each element. The X-MET 920 calibration software allows the analyst to choose which element line intensities to include as terms in the regression equation. The analyst can also view the calibration curve, set of residuals for each calibration standard, and correlation coefficient for each set of regression terms.

For verification of bolt material composition ideally one would have several analytical routines, each calibrated in a narrow range about the specified material limits of a common bolt material (e.g. A-286, 302HQ). If a more general assay is needed, for example, to determine the composition of a fastener of which the material composition is unknown, a wider calibration range should

⁴ Standard Reference Materials is a registered trademark of the National Institute of Standards and Technology, and of the Federal Government.

be used. After a general assay is done to suggest an alloy or family of alloys, another assay using a method specifically calibrated for the appropriate element concentration ranges can be performed.

The calibration bolts are threaded into the aluminum mask until the end is flush with the surface of the mask. The mask completely covers the aperture of the XRF detector. Although the aluminum disk does not completely block source x-rays, the 6.35 mm thickness is sufficient to stop x-rays emitted from material above the disk from reaching the detector. The amount of a bolt specimen seen by the detector is approximately the first 1 mm of the threaded end, which is the same for any bolt of a given nominal diameter and thread series. The mask also serves to position the bolts in the same position relative to the x-ray source and the detector.

The duration of measurement is set during calibration but may be changed during analysis. Measurement time is typically 120 seconds. Longer measurement times are expected to give more accurate results as the effects of count rate variations become less significant. For testing large lots of fasteners the shortest measurement time that gives reasonable accuracy is desired.

RESULTS

Two analytical routines were calibrated on the XRF system, one for 10-32 threads and one for 1/4-28 threads. Tables 1 and 2 show the material types of the bolts used as calibration standards. A calibration blank consisting of a plain aluminum mask was also used in the calibration of the analysis routine for 10-32 bolts. Figure 5 shows the calibration curve for each element. The multiple least squares fit linear regression used by the XRF system to compute calibration curves assumes that errors in the independent variable are negligible. The independent variables in this case are the compositions of elements in a calibration standard determined by ICP/OES. If errors in the ICP/OES measurements are purely random then a large set of calibration standards should mitigate the effects of variation in the independent variable on the XRF calibration curves. If, however, the errors in ICP/OES measurements are biased then the XRF calibration curves will be adversely affected.

Table 1. Compositions of 10-32 bolts used as standards, given in weight percent.
(Determined by ICP/OES)

	Ti	Cr	Mn	Ni	Cu	Mo	
Bolt 1	1.9	14.0	1.12	23	0.150	1.21	A-286
Bolt 2	2.2	14.8	0.38	26	0.21	1.28	A-286
Bolt 3	2.20	14.71	0.93	24.4	0.169	1.308	A-286
Bolt 4	2.1	14.9	1.56	25	0.160	1.34	A-286
Bolt 5	—*	18.4	0.697	9.1	3.32	0.268	302HQ
Bolt 6	—	18.5	0.66	9.7	3.31	0.296	302HQ
Bolt 7	—	18.5	1.56	8.71	4.09	0.609	302HQ
Bolt 8	—	17.6	1.67	7.7	0.41	0.55	303

Table 2. Compositions of 1/4-28 bolts used as standards given in weight percent.
(Determined by ICP/OES)

	Ti	Cr	Mn	Ni	Cu	Mo	
Bolt 1	—	19.0	1.95	8.8	0.332	0.51	303
Bolt 2	—	19.1	1.6	8.6	—	0.45	302HQ
Bolt 3	—	19.3	1.5	9.7	0.067	0.095	304
Bolt 4	2.17	14.9	1.2	26.4	0.100	1.307	A-286
Bolt 5	2.20	15.4	0.30	25.5	0.317	1.149	A-286
Bolt 6	2.25	15.5	0.27	26.3	0.058	1.19	A-286
Bolt 7	2.26	15.6	0.30	26	0.304	1.17	A-286

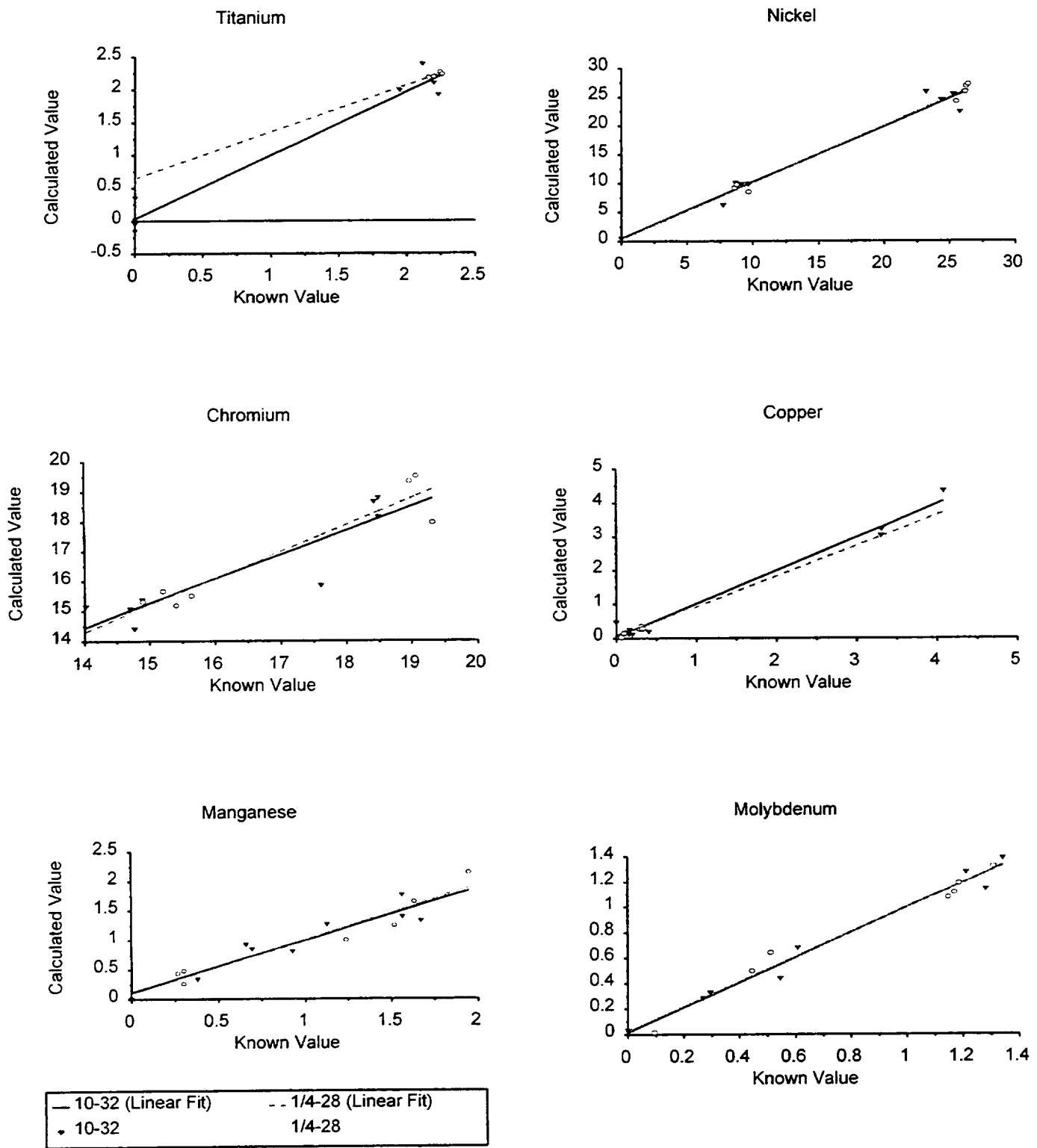


Figure 5. Calibration Curves for 10-32 and 1/4-28 Fasteners

In order to determine the most effective measurement duration a single bolt was chosen and measured 10 times at each of three different measurement durations. No copper was detected in the sample chosen, so there is no data for that element. It was felt that measurement times above 180 seconds are too long to be useful when dealing with large lots. The change in precision as measurement duration shortens is different for each element. The determination of a shortest acceptable measurement time therefore depends on the elements being assayed.

Table 3. Relative Standard Deviation of Set of Ten Measurements

	180 seconds	120 seconds	60 seconds
Ti	5.53	8.41	9.06
Cr	.63	0.93	0.95
Mn	4.22	6.58	11.9
Ni	2.02	0.52	1.59
Cu	N/A	N/A	N/A
Mo	1.35	1.42	1.47

Five bolts of 10-32 size and unknown material composition were analyzed with the XRF system to evaluate the system's material identification capabilities. Portions of the bolts were subsequently analyzed by ICP/OES. Table 4 below lists the element compositions determined by both methods and the material type suggested. In the ICP/OES results a dash in lieu of a number indicates that the instrument warned that the measurement lay outside of the calibrated range. The XRF system used in this test program does not have such a warning feature. Problems may arise as in the case of unknown #5. The reported chromium concentration, 9.32 wt%, is gravely in error. The linear calibration curve for chromium is fit only in the region of 14 to 18.5 wt%. The calibration curve is heavily skewed

outside of this range to the extent that an XRF analysis of the plain aluminum mask reports the chromium content as about 9 wt%. When using the XRF system an operator should take advantage of the ability to view the entire detected x-ray spectrum. In the case of unknown #5 it is immediately apparent that no peak exists above background intensity in the region of the chromium line. (See figure 6.)

One fastener, a 10-32 bolt composed of A-286, was analyzed repeatedly over the course of two weeks to monitor possible drift in the calibration. If the XRF system did not correct for the decay of the radioactive source, an exponential drop in measured element concentrations would be expected. For each analysis the material composition of the bolt was measured eight times. The mean and standard deviation of the measurement sets were recorded. Both linear and exponential least squares fits were tried on the data for each element. In all cases the correlation coefficients (R^2 values) were below 0.22 and were generally quite less. It is possible that due to the X-MET's internal correction neither a linear model nor an exponential model is appropriate to describe drift that may occur in the calibration. There may be no drift in the calibration. Or the magnitude of random error may completely obscure a systematic trend in calibration error over the observed period. In any of the cases above the reliability of a calibrated method does not diminish within a reasonable period after initial calibration.

Thirteen bolts randomly chosen without replacement from one lot of 10-32 bolts were analyzed. No bolt was observed to differ significantly from the rest with respect to material composition. Table 5 compares the mean and standard deviations of element composition measurements for the first eight of the thirteen bolts to the corresponding statistics for a single bolt from the lot measured eight times.

Table 4. Comparison of XRF measured values (Regular typeface), and ICP/OES measured values (*Italic typeface*).

	Ti	Cr	Mn	Ni	Cu	Mo	
Unknown 1	0.21	16.78	1.00	18.3	0.04	0.12	384
	—	<i>15.72</i>	<i>0.84</i>	<i>18.4</i>	<i>0.02</i>	<i>0.11</i>	
Unknown 2	0.11	18.13	0.98	10.5	3.25	0.17	302HQ
	—	<i>17.58</i>	<i>0.75</i>	<i>8.28</i>	<i>3.28</i>	<i>0.27</i>	
Unknown 3	0.21	17.33	1.50	12.2	0.01	0.15	305
	—	<i>18.15</i>	<i>1.32</i>	<i>12.0</i>	<i>0.04</i>	<i>0.14</i>	
Unknown 4	0.06	18.51	1.27	10.8	3.30	0.36	302HQ
	—	<i>17.80</i>	<i>1.06</i>	<i>8.97</i>	<i>3.40</i>	<i>0.27</i>	
Unknown 5	0.72	9.32	0.68	1.96	0.05	0.37	(Low Alloy)
	—	—	<i>0.86</i>	—	<i>0.08</i>	<i>0.31</i>	

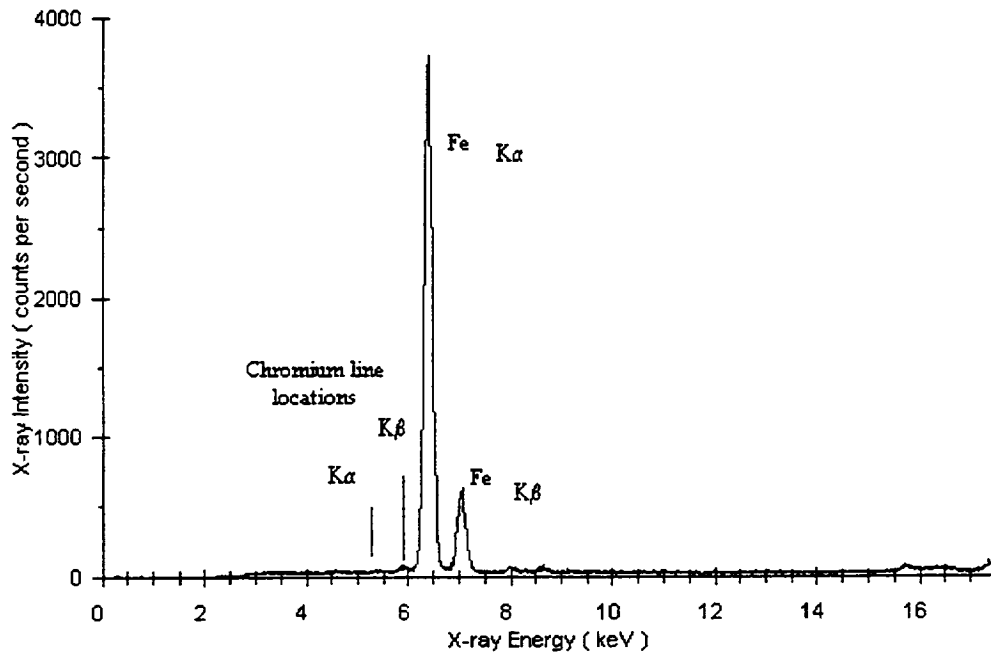


Figure 6. Size 10-32 cap screw, unknown #5.

Table 5. Comparison of measurement distribution for lot analysis and replicate analysis.

	<u>8 Bolts Randomly Drawn from Lot 04</u>		<u>Single Bolt from Lot 04, 8 Measurements</u>	
	Mean	Sample Standard Deviation	Mean	Sample Standard Deviation
Titanium	1.96	0.16	2.00	0.08
Chromium	14.46	0.17	14.57	0.11
Manganese	0.43	0.10	0.38	0.13
Nickel	21.96	0.55	21.90	0.43
Copper	0.21	0.14	0.24	0.13
Molybdenum	1.20	0.03	1.22	0.02

Nineteen bolts from what was thought to be a single lot were analyzed. The head markings on all of the bolts are identical. The bulk of the lot was found to be type 305 stainless steel. However, three bolts were found to have different material composition than the others. (See figure 7.) The manganese, nickel, copper, and molybdenum content of the three nonconforming fasteners differ from the other bolts by significantly more than measurement error. The high copper content, at about 2% by weight, in an 18-8 stainless steel immediately suggests type 302HQ stainless steel. Subsequent visual inspection revealed that the three nonconforming bolts have threads 1/8th inch

longer than the others, though total bolt length is the same. In this case the two alloy types in the batch of fasteners are sufficiently different to be differentiated by the XRF system. The mixing of a batch of type 302 and type 303 stainless steels might not be detected by the portable XRF system used in this research program. Type 303 stainless steel differs from type 302 in the allowed limits on phosphorus, sulfur, and copper content. The phosphorus content and sulfur content are not measured, and if the copper content conforms to the maximum limit of 0.50 % for type 303 stainless steel then it also conforms to the limit for type 302 stainless steel (0.75 %).

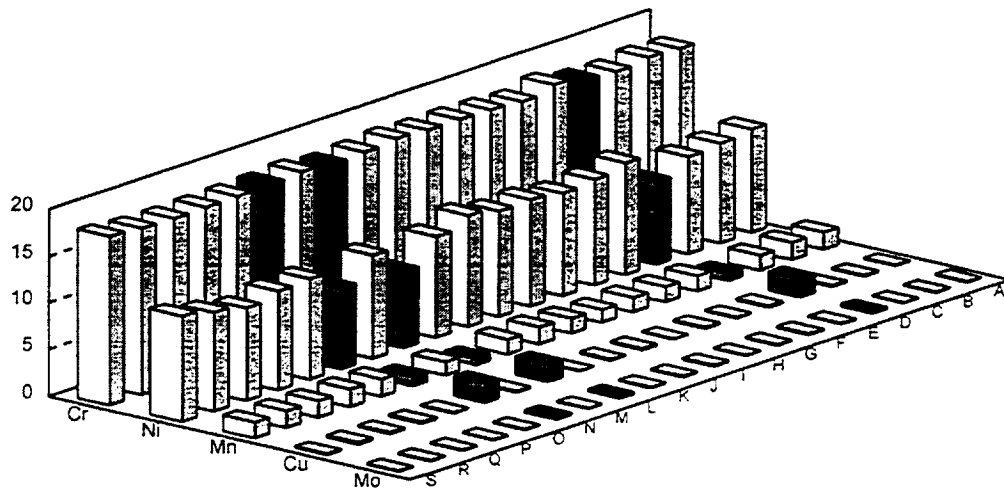


Figure 7. Elemental compositions of test batch of thirteen bolts

CONCLUSIONS

If a mask is used to insure consistent placement of fasteners to be measured, a portable XRF system can be calibrated to perform quantitative measurement of threaded fasteners. The accuracy of the calibration curves is sufficient to determine the alloy type of fasteners provided that the alloy can be distinguished from other alloys based on the concentrations of elements in the measurement range of the XRF system. With that proviso, the portable XRF system is sufficiently precise to verify the homogeneity of a batch of fasteners. The XRF technique is well suited to testing large lots of fasteners because it is non-destructive. In addition, the XRF analysis time is much shorter than the sample preparation and analysis time required for other methods of elemental analysis.

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