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X-RAY FLUORESCENCE SPECTROSCOPY FOR ANALYSIS OF EXPLOSIVE-RELATED MATERIALS AND UNKNOWN

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14. ABSTRACT: The applicability of X-ray fluorescence spectroscopy (XRF) to analysis of unknowns associated with potential explosives is evaluated. Methods specific to the Primini X-ray fluorescence spectrometer (Rigaku Corporation; Tokyo, Japan) are discussed and applied to known materials to illustrate data quality. Application of the methods to plastic explosives, ammonium nitrate, and calcium ammonium nitrate are reported as examples. Bulk metal samples and a variety of powders and powder mixes are used to illustrate applications to general unknowns. The strengths and limitations of XRF are discussed, and recommendations are provided for the use of XRF in field and forensic laboratories.					
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EXECUTIVE SUMMARY

Recently it has become common for incident response units, ranging from local authorities through National Guard units and traditional military units, to mobilize analytical platforms for rapid on-site evaluation of materials possibly associated with weapons of mass destruction, traditional explosives, and other hazards. In the beginning, the analytical instrumentation associated with these mobile suites was primarily based on target-specific sensors and wet chemical analysis, and it was typically used in conjunction with thoroughly validated target- and matrix-specific analytical methods.

The practice of mobilizing analytical equipment has been expanding to address threats that are not well defined, to use instrumentation that is not amenable to rapid data library search-and-match algorithms, and to evaluate solid materials. A piece of this expansion was the addition of wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) to many mobile suites, with one of the purposes being to aid in the identification of explosives and materials related to explosives. This is in addition to the more general purpose of conducting elemental, rather than molecular, analysis of suspicious materials that are not amenable to examination with traditional methods.

As it is used in many mobile applications, WDXRF is configured in a way that precludes analysis of elements lighter than fluorine; it cannot provide information about the organic or nitrogenous constituents of a sample or provide direct evidence of oxides or lithium, beryllium, or boron in compounds. Additionally, WDXRF is an optical approach to X-ray fluorescence. For its accuracy and precision, WDXRF relies heavily on the assumption of a smooth, flat, homogeneous sample. The processes associated with preparing a smooth and flat sample, such as pressing, melting, grinding, and polishing, are generally precluded in the case of potentially explosive unknowns. Thus, for the purposes of using WDXRF for the intended applications in the field, it is often necessary to operate it using samples that are far from ideal, in terms of whether a sample material is compositionally a good candidate for WDXRF analysis and also whether a specific specimen is prepared in a way that allows for the full benefit of WDXRF.

In this work, the common Primini XRF instrument (Rigaku Corporation; Tokyo, Japan) was used to examine four types of samples from the perspective of WDXRF analysis. The samples included a bulk metal standard, a mixed metal and light element standard, a group of plastic explosive materials, a group of ammonium nitrate materials, and a group of common powders (both neat and mixed). This report illustrates the effects of using WDXRF to analyze samples that are inhomogeneous, samples that are not smooth and flat, and samples that contain only trace components, and common sense approaches are advised for the use of WDXRF in field situations.

To summarize the results, WDXRF is a useful way to readily identify major elemental constituents of most solid samples, albeit with some reservations. The automatic standardless quantitation algorithms are not foolproof and should not be relied on heavily. The assumptions of smooth and homogeneous samples are generally not applicable to field analysis of unknowns and can be expected to result in some inaccuracies. The technique precision is

directly related to how appropriate the sample is to the technique, which is variable in the case of unknowns. In general, samples that are reasonably large, smooth, and homogeneous and that comprise elements heavier than oxygen will yield precise and accurate results, whereas samples that are irregular, small, or primarily elements lighter than oxygen will provide noisy, inaccurate, and imprecise results. The precision and reliability of the results can be evaluated by applying repeated analysis and statistical data analysis.

PREFACE

The work described in this report was authorized under project no. 12P-0282. The work was started in October 2011 and completed in October 2012.

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X-RAY FLUORESCENCE SPECTROSCOPY FOR ANALYSIS OF EXPLOSIVE-RELATED MATERIALS AND UNKNOWN

1. INTRODUCTION

Homemade explosives (HMEs) and improvised explosive devices (IEDs) are significant threats to military and civilian personnel around the world. One aspect of the response to these threats is deployment of mobile laboratories to provide rapid and actionable presumptive identification of field samples. Appropriate suites of analytical instrumentation for these laboratories differ, depending on the primary mission of the organization, the required levels of mobility and hardening, as well as the specific analytical tasks predicted for a given mission. One of the more recent additions to mobile laboratory suites is X-ray fluorescence spectroscopy (XRF). This technique differs from the more traditional field approaches to Chemical, Biological, Radiological, Nuclear, and Explosive analysis in several important ways. XRF is an elemental analysis technique; that is, it provides information only about the elements present and not about the compounds that may comprise those elements, whereas traditional techniques allow for library searching of compounds, either against large preexisting libraries or against libraries of targets that the techniques are intended to identify. Typically, XRF is a solids-analysis technique. Although XRF can be applied to liquids, it is inadvisable to use this technique with unknown liquids. In the analysis of solids, the level of sample homogeneity as well as the sample matrix can have major impacts on the results. When unknown samples are being assessed, these factors cannot be sufficiently well known to provide accurate quantitative analysis. Additionally, XRF generally has a low element cutoff that varies according to instrument configuration (i.e., which crystals and detectors are present in the instrument). Common cutoffs are fluorine, sodium, and titanium. Although it is possible to configure an instrument that can detect down to lithium, beryllium, or boron, those instruments are generally unavailable in the range of equipment that is adaptable to field use. This report addresses the utility of XRF as a complementary technique in field operations, the reality of what it can elucidate about an unknown sample (with possible association to explosive materials), and the limitations of using XRF for these purposes.

2. BACKGROUND

2.1 X-Ray Fluorescence

XRF encompasses several different analytical techniques, each of which is associated with different instrumentation and unique strengths and weaknesses. The commonality among the techniques is the eventual emission and subsequent analysis of X-rays emitted by the sample. The energies, and therefore the wavelengths, of the emitted radiation are characteristic of the electron transitions generating the X-rays, which in turn are characteristic of the atoms in the sample. XRF approaches vary with respect to the means of exciting the sample as well as the methods of analyzing the X-rays that are produced.

Wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) is widely accepted as the gold standard for high-sensitivity and quantitative precision and accuracy in XRF. Typically in these systems, an X-ray source introduces an X-ray beam to the sample. These X-rays are produced at a known energy that is greater than the binding energies of the inner shell electrons in the elements of interest, such that sufficient energy is provided to eject electrons from the inner shells. The atoms in the sample, or more specifically, the electrons in the atoms, are thus excited above their ground states; upon relaxation to ground, X-rays are emitted at energies that correspond to the energy transitions of the relaxing electrons. These energies, like the elemental electron energy levels themselves, are characteristic of the atoms. Thus, $K\alpha$ X-rays emitted from an atom of a given element will have a specific energy that is different from the energy of $K\alpha$ X-rays emitted from any other element. These emitted X-rays impinge on a crystal that diffracts the X-rays toward a detector. The crystals and detectors are moved along a path to control the angle made by the sample–crystal–detector path of the X-rays. When the angle satisfies the Bragg equation, the X-rays enter and are counted by the X-ray detector. In WDXRF, the X-ray detector is typically a scintillation counter or, for lighter elements, a gas flow-proportional counter (F-PC). All X-rays entering the detector are assumed to be of the wavelength selected by the crystal geometry at any given moment, and the entire signal generated at the detector is attributed to that wavelength. The data are collected in the form of measured X-ray intensity as a function of crystal identity and angle, and they are typically presented in the form of intensity as a function of calculated X-ray energy. The different lattice spacings of the various crystals are also taken into account.

Because this technique relies on optical alignment, its precision and accuracy depend on the sample homogeneity and smoothness. Typical sample-preparation techniques used to achieve analytical precision include grinding, pressing, and polishing the sample. Some materials are best prepared by melting and casting. In all cases, the sample thickness must be at least sufficient to prevent the source X-rays from exciting the background material.

In cases where it is impossible, impractical, or unsafe to conduct this type of sample preparation, it is still possible to conduct wavelength dispersive X-ray analysis, but only at the expense of the sensitivity, precision, and accuracy that are the prime advantages of this technique. In these cases, the sample, which is often an irregular object or loose powder, is placed in a sample cup and sealed with a thin, organic film. It is important to note that the elemental composition of the film will be included in the analysis results. Also, if the sample is itself a thin or incomplete layer, the incident X-rays will excite and produce signals from whatever lies behind the sample. Given that the cups and films are generally organic with trace impurities, this limits the analysis of trace elements in organic matrices. Manufacturers of these films and cups typically report lists of the likely trace contaminants in each product, but these reports lack standardization and certification. Analysis of an organic sample that contains trace inorganics would result in ambiguity regarding the source of the trace signals; they could arise from either the sample holder or the sample. Although it may be possible to use standards to devise useful methods for specific materials on an individual basis, it is not possible to do the same for general unknowns.

To enable the source X-rays to successfully irradiate the sample and the emitted X-rays to successfully reach the detector without subsequent absorption by air, WDXRF is ideally carried out in a vacuum or in an atmosphere of light inert gas. Use of a vacuum typically

prevents the analysis of liquids and volatile materials. However, if care is taken, it is possible to analyze liquids by holding them in sample cups covered with thin plastic films that are impervious to the liquid of interest. To attempt this type of analysis, before determining the appropriate film materials to use, it is prudent to understand (as well as possible) the liquid in question. Under these operating conditions, it is important to consider the differential pressures that sealed cups in a vacuum may experience. Additionally, it is important to provide a means of escape for gases trapped in the cup and to remain aware that those gases, which may or may not contain volatile portions of the sample itself, will be removed from the sample and introduced to the pumping system. These considerations affect the accuracy of the results and the safety of instrument maintenance.

2.2 Explosive Materials

From the standpoint of explosives identification, the majority of materials of interest are organic or nitrogenous. Elemental composition of these materials is largely limited to H, C, N, and O. Because these are all lighter than F, they are not visible to the Primini spectrometer used in this work. (The Primini is described in Section 3.) Additionally, WDXRF provides only elemental information and no indication of chemical bonding; thus, compounds of interest cannot be directly identified. However, WDXRF can unambiguously identify the elements it is designed to detect, which makes it an excellent complement to analytical methods that rely on possibly ambiguous identification of compounds. There remain many materials related to explosives that do contain elements detectable by WDXRF, and a table of these materials is provided in Appendix A.

Explosive materials are generally sensitive to heat, friction, pressure, and shock. For these reasons, it is not advisable to prepare suspected explosive samples for ideal WDXRF. Thus, the WDXRF advantages of quantitative precision, sensitivity, and accuracy are compromised by the non-ideal sample preparation methods that are dictated by safety concerns.

3. MATERIALS AND METHODS

3.1 X-Ray Fluorescence Instrument

The X-ray fluorescence instrument used in this project was a Rigaku Primini system (serial number ER09014; Rigaku Industrial Corporation; Tokyo, Japan) with ZSX software, version 3.43. This instrument uses a 50 W X-ray tube with a Pd target and has a sample chamber with a six-sample turret. The maximum sample size is 44 mm in diameter by 33 mm in height. The sample chamber is equipped to allow for optional vacuum operation and sample spin. The chamber geometry is designed such that during analysis, the sample sits above the X-ray source and detectors. This means that if the sample or sample container breaks, the released material will fall into the working parts of the spectrometer. The system is also equipped with the Rigaku data analysis software for standardless, semi-quantitative analysis (SQX).

As configured, there are six possible operation modes for the Primini system, including three operations each in two choices of atmosphere. The simplest operation is called EZ Scan and is intended to allow new users to readily acquire and qualitatively analyze data with

minimal operator input. The operator-controlled method parameters in EZ Scan are extremely limited. EZ Scan measures the full elemental range of F to U with three options for length of scan: the shortest scan is ~6 min; the standard, medium-length scan is ~20 min; and the long scan is ~45 min. The only other operator-selectable parameter in EZ Scan is a choice of metal versus oxide calculation. Selecting oxide predetermines that the elements detected are present as oxides, and the software will report semi-quantitative results based on this assumption. This selection is generally inadvisable when characterizing unknowns because the data produced by the system give the impression that oxides were analytically determined when in fact, the oxide was an assumption made by the analyst. The nature of EZ Scan operation makes it impossible to return to the original data and recalculate.

The second operation is a qualitative analysis that can be subject to a standardless semi-quantitative calculation. As with EZ Scan, this calculation is based on fundamental principles rather than standards. The wavelengths of X-rays resulting from electronic transitions within the elements are well-known theoretically and experimentally. These are coupled with the associated probability of X-ray emission, the expected absorbance of X-rays by the elements present, and the X-ray fluorescence following excitation from other X-rays produced by the sample. Qualitative data collection allows more user selection than is permitted with EZ Scan, but again, many of these options require presupposition regarding the sample nature and identity.

The Primini system used in this work has a scintillation counter and a gas F-PC with three crystals: LiF, pentaerythritol (PET), and a Rigaku proprietary crystal known as RX25. Table 1 summarizes the crystal and detector combinations applicable in this configuration and the range of elements targeted by each.

Table 1. Elements Identified by Crystal and Detector Combinations in the Primini XRF System

Detector	Crystal		
	LiF	PET	RX25
Scintillation counter	Ti–U (continuous scan)	NA	NA
F-PC	NA	Si, P, S, Cl, K, Ca (individual element scans)	F, Na, Mg, Al (individual element scans)

NA, not applicable.

The user-defined methods applied in this study, referred to as applications in the Primini ZSX software, are summarized in Table 2. Preloaded EZ Scan default methods were also used. No options requiring presupposition of sample composition were applied. With the exception of “Forensic 2, no spin”, all methods were run under a vacuum and with sample spin turned on. Primini parameters available for user adjustment are limited to the selection of elements for inclusion or exclusion from the analysis, the size of the scan steps, and time spent counting at each step. Step size and time were independently variable for the heavy-element scan and each of the light-element scans.

Table 2. Parameter Settings Used in Primini Applications for This Study

Parameter	Method					
	Forensic 2 (used as the default standard application)	Forensic 2, No Spin (same as Forensic 2, but with no sample spin)	Forensic 3, Fast (used as the fast method)	Forensic 4 (standard of light elements only)	Forensic 5 (standard of all elements except Al)	Very Long (used as the slow method)
Elements	F–U	F–U	F–U	F–Ca	F–U, except Al	F–U
Analysis time (min)	11	11	6	5	11	50
Step size, heavy elements (deg)	0.02	0.02	0.02	NA	0.02	0.01
Time, heavy elements (s)	0.08	0.08	0.04	NA	0.08	0.2
Scan speed (deg/min)	15	15	30	15	15	3
Step size, light elements (deg)	0.05	0.05	0.05	0.05	0.05	0.01
Time, light elements (s)	0.2	0.2	0.1	0.2	0.2	0.2
Spin	On	Off	On	On	On	On
SQX	Yes	Yes	Yes	Yes	Yes	Yes

NA, not applicable.

3.2 Samples and Materials

Four standards were used to illustrate the operation of the instrument on well-defined samples. As summarized in Table 3, four samples each were used to illustrate the application of XRF to ammonium nitrate materials and plastic explosives, and two samples were used to illustrate accuracy in analysis of mixed materials. With the exception of the Ti and the Al–Cu–F samples, each sample was contained in a Chemplex 1740 sample cup using Chemplex 3024, 12 μm polypropylene film (Chemplex Industries; Palm City, FL).

3.2.1 Standards and Known Materials

The standard and known materials used included a Ti standard that was supplied with the instrument and a known sample that contained Al, Cu, and F. The Ti sample was a solid Ti disk that was machined to fit the Primini sample holder without a plastic sample cup. The Al–Cu–F sample was a similar disk wrapped in Al foil that had a Cu microscope grid attached with an elastomeric fluorocarbon adhesive.

3.2.2 Ammonium Nitrate Materials

The ammonium nitrate family of materials was represented in this study by ammonium nitrate, calcium ammonium nitrate (CAN), and weathered CAN. To compare the results expected from prilled material with those from powders, the weathered CAN was crushed in a glass mortar after analysis, and the same sample was designated “crushed CAN2” and used in the analysis.

3.2.3 Plastic Explosives

The plastic explosive samples used in this study were laboratory samples that had been previously analyzed via gas chromatography, ion chromatography, Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction. These analyses provided an estimate of the trace elements that could be expected to be present in these otherwise purely organic samples. Information about these constituents is provided in Table 3.

3.2.4 Powder Samples

Four different powder samples were used in this study, and Table 3 includes details about the sample compositions. The first, referred to as Powder Mix or Mix 1, was a small (approximately 200 mg) sample made of known weights of Al powder, titanium dioxide powder, and NaCl (table) salt. The second, referred to as Powder Mix 2 or Mix 2, was a larger (approximately 950 mg) sample made of known weights of the three sample powders. Because the Na to Cl ratio found in these samples deviated significantly from the expected 40:60 ratio, a sample of straight table salt (Morton Salt Company; Chicago, IL) and a sample of sodium bicarbonate (generic, locally sourced baking soda) were added for further investigation.

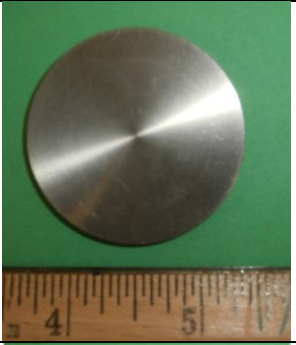
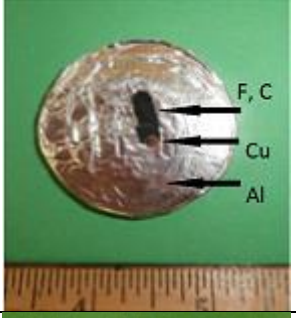
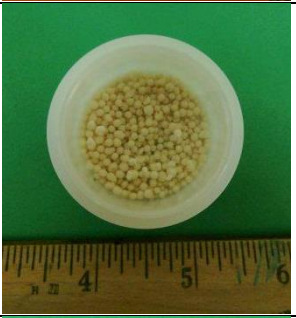
3.2.5 Sample Cups and Film

The samples cups used for this work were Chemplex 1740 vented-cap cups. As reported by the manufacturer, typical impurities are Al, Ca, Ti, Zn, Mg, P, and Si.

All samples except Ti and Al with Cu and F were held in the cups using Chemplex 3024 sample support film, which is a 12 μm polypropylene film. As reported by the manufacturer, typical impurities are Al, Ca, Ti, Zn, Cu, Fe, and Zr.

Replicates were completed without removing the samples between runs. This practice minimizes jostling of particles between runs and minimizes errors associated with introducing the sample into the instrument.

Table 3. Summary of Samples Used in This Study

Sample	Description	Purpose	Image
Ti standard	Rigaku catalog no. 3590T2, 99.7% Ti polished disk	To demonstrate the operation of the instrument on a known ideal sample	
Al with Cu and F	Al foil with a 3 mm, 100 mesh Cu grid, attached with elastomeric fluorocarbon adhesive	To illustrate the averaging of results over gross sample inhomogeneity	
Blank	Empty Chemplex 1740 sample cup with Chemplex 3024, 12 μ m polypropylene film	Method blank	
Ammonium nitrate	Approximately 2.3 g of ammonium nitrate	To provide baseline for comparison of ammonium nitrate materials	
CAN1	Approximately 2.7 g of non-weathered CAN	To demonstrate analytical variations between two samples of the same material	

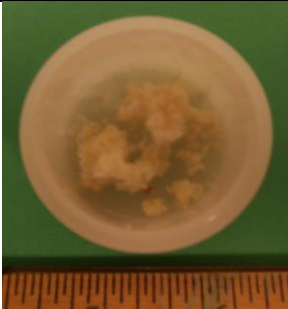
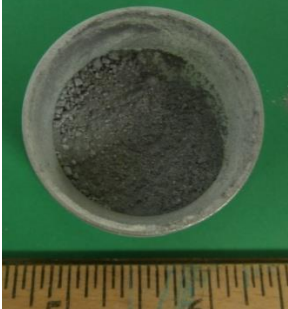
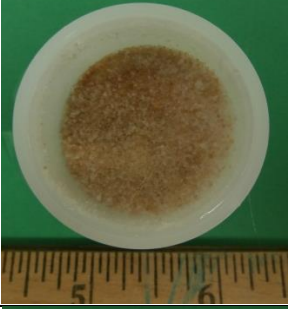
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Table 3. Summary of Samples Used in This Study, Continued

Sample	Description	Purpose	Image
CAN2	Approximately 2.3 g of weathered CAN	To determine whether any effects of weathering could be seen via XRF	
Crushed CAN2	Same sample as CAN2, crushed with glass mortar		
CAN2 Big	Approximately 7.6 g of weathered CAN, enough to fill a sample cup	To investigate possible errors associated with small sample size	
Plastic Explosive 124	Plastic explosive sample previously identified as RDX with PETN (1.26 g)	To illustrate pitfalls of XRF applied to organic materials	
Plastic Explosive 204	Sample previously identified as RDX with HMX (1.02 g)	To illustrate pitfalls of XRF applied to organic materials	
Plastic Explosive 507	Sample previously identified as RDX with HMX and the elements Al, Ca, Fe, Mn, Na, and S present inhomogeneously (0.99 g)	To illustrate pitfalls of XRF applied to organic materials	

(continued)

Table 3. Summary of Samples Used in This Study, Continued

Sample	Description	Purpose	Image
Plastic Explosive 609	Sample previously identified as RDX with HMX and trinitrotoluene and the elements Al, Ca, Cl, Fe, Mg, Na, and Si present inhomogeneously (0.94 g)	To illustrate pitfalls of XRF applied to organic materials	
Powder Mix 1	Sodium chloride, titanium dioxide, and Al mixture, known mass composition: 26% Na, 40% Cl, 8% Al, 16% Ti, and 10% O; total sample weight: 203 mg	To illustrate accuracy in analysis of mixtures; photograph was taken before mixing, so the three separate materials are distinguishable in the image	
Powder Mix 2	Sodium chloride, titanium dioxide, and Al powders; known mass composition: 19% Na, 29% Cl, 9% Al, 26% Ti, and 17% O; total sample weight: 950 mg	To illustrate effects of larger sample by comparison with Powder Mix 1, mixed; photograph was taken after mixing	
Salt	Morton salt, sodium chloride, filling sample cup (6.7 g)	To investigate effects of multiple powder components in the powder mix samples on signals from Na and Cl; photograph was taken after irradiation, which induced the tan coloring	
Sodium bicarbonate	Generic, store-brand baking soda, filling sample cup (7.7 g)	To show effects of atomic numbers of companion elements on results by comparison with salt	

HMX, cyclotetramethylene-tetranitramine.

PETN, pentaerythritol tetranitrate

RDX, cyclotrimethylenenitramine.

4. ANALYTICAL RESULTS

4.1 Standard and Test Sample

The results of analysis of the Ti standard and the created Al, Cu, and F sample are presented in Tables 4 and 5. In Table 4, the standard Forensic 2 method is compared with a faster method (Forensic 3), a very slow method (Very Long), and the manufacturer's EZ Scan method operated at standard speed. The instrument correctly identified Ti as the major component and estimated it as 100% Ti. The possible contaminants together accounted for less than 0.5% of the sample; therefore, they were not reflected in the reported Ti findings because of rounding done by the software. The relative standard deviations (RSDs) were improved by the longer scan times, and the success in identifying very low concentration trace elements was increased with longer scan times. In Table 5, the results from using full scans (application Forensic 2) to analyze the Ti standard are compared with results from analyzing the same sample without analyzing for Ti (application Forensic 4). This was similar to the results that would be expected for analysis of a C- or N-based sample, with impurities present, on the scale of parts per million to parts per thousand, because the C and N are not detected by the instrument. The instrument automatically normalized all detected elements to 100% and ignored the possible presence of undetected elements.

Table 4. WDXRF Results from Analysis of Polished Bulk Ti Standard Sample

Method	Statistic	Element						
		Ti	Cl	K	S	Al	Si	Fe
Forensic 2 (6 runs over 2 days)	Mean (mass %)	100	0.011	0.065	0.002	0.03	0.08	0.00
	RSD (%)	0.00	13.42	14.11	175.0	81.6	8.23	NA
Forensic 3 (6 runs over 2 days)	Mean (mass %)	100	0.003	0.055	0.000	0.016	0.066	0.00
	RSD (%)	0.00	245.0	30.84	NA	113.5	50.30	NA
EZ Scan (3 runs in 1 day)	Mean (mass %)	100	0.010	0.066	0.000	0.024	0.069	0.00
	RSD (%)	0.00	13.08	12.4	NA	8.33	15.16	NA
Very Long (single run)	Mean (mass %)	100	0.097	0.073	0.003	0.048	0.076	0.06

Note: Shaded columns indicate possible contaminants from sample cup (as identified by the cup supplier).
NA, not applicable.

Table 5. Results from EZ Scan and SQX Analyses of Ti Standard Compared with Results with Ti Ignored*

Method	Statistic	Element					
		Ti	Cl	K	S	Al	Si
Forensic 2 (6 runs over 2 days)	Mean (mass %)	100	0.011	0.065	0.002	0.03	0.08
	RSD (%)	0.00	13.42	14.11	175.0	81.6	8.23
Forensic 4 (6 runs over 2 days)	Mean (mass %)	NA	4.40	63.00	4.00	4.83	24.00
	RSD (%)	NA	86.87	12.40	28.40	87.10	4.17

*Simulates analysis of materials composed primarily of light elements.

Note: Shaded columns indicate possible contaminants from cup and film per manufacturer's reporting.

NA, not applicable.

Descriptive statistics were calculated (Table 6) from the data obtained from six successive runs of the Ti standard using the Forensic 2 and the faster Forensic 3 methods. The confidence intervals reflected in Table 6 indicate that the faster runs introduced significantly more uncertainty in the trace elements. However, the identified elements were the same when both methods were used. The identification of Ti as essentially 100% of the standard was not compromised by the faster run.

Table 6. Descriptive Statistics Obtained from Six Runs of Ti Standard Using Forensic 2 Method

Method	Statistic	Element					
		Ti	Cl	K	S	Al	Si
Forensic 2 (6 runs over 2 days)	Mean (mass %)	100.00	0.011	0.065	0.002	0.025	0.078
	95.0% Confidence level (%)	0.00	0.002	0.010	0.004	0.021	0.007
Forensic 3 Fast (6 runs over 2 days)	Mean (mass %)	100.00	0.003	0.055	0.000	0.016	0.066
	95.0% Confidence level (%)	0.00	0.009	0.018	0.000	0.019	0.035

Note: Shaded columns indicate possible contaminants from cup and film per manufacturer's reporting.

In the case of the Al foil sample with a Cu grid attached using F-containing adhesive (Al-Cu-F), shown in Table 7, the instrument reliably identified the Al and Cu regardless of the method used, and the relative standard deviations were reasonable. However, the elements identified as minor constituents were more problematic. The F, which we know was a real constituent of the sample, was not regularly identified as such. The spectra associated with several of these scans are presented in Figures 1–3, and the SQX results specific to these scans are shown in Table 8. In Figures 1–3, the spectral regions associated with each light element are labeled below the respective regions and peaks as identified by the instrument and used in semi-quantitative calculations. Peaks identified in the region but not identified as the respective

element are labeled, to indicate possible peak-overlap issues. It was notable that in the cases of the fast scans (Forensic 3) and standard EZ Scans, the F peak was clearly visible but was not identified or quantified by SQX (indicating a false negative), while the K peak, which was clearly identified as an overlap with the Pd peak arising from the Pd target of the instrument's X-ray source, was included in the semi-quantitative results in all methods (indicating a false positive). With the exception of the Al region, the signal-to-noise ratio (SNR) on these scans was low, and relative peak intensities can be visualized by considering the expansion factors indicated above each spectral region. In general, the faster methods provided poorer peak resolution and a lower SNR, as would be expected. Use of the Forensic 2 method resulted in spectra that appeared slightly cleaner than those produced by a standard EZ Scan and significantly better than those produced by much faster scans.

Table 7. Summary of XRF Results from Analysis of Al Foil Sample with Cu Grid

Method	Statistic	Element									
		Al	F	Cu	S	K	Cl	Si	Ca	Fe	Mg
Forensic 2 (6 runs over 2 days)	Mean (mass %)	82.17	2.77	14.17	0.147	0.069	0.002	0.078	0.004	0.69	0.000
	RSD (%)	1.20	50.64	2.88	161.0	14.76	245	18.82	155.6	3.01	NA
Forensic 3 (6 runs over 2 days)	Mean (mass %)	84.33	0.00	14.67	0.056	0.09	0.000	0.010	0.00	0.71	0.032
	RSD (%)	0.61	NA	3.52	10.28	44.37	NA	244.9	NA	3.65	244.9
EZ Scan Short, 5 min (2 runs in 1 day)	Mean (mass %)	84.67	0.00	14.33	0.00	0.00	0.00	0.00	0.00	0.77	0.00
	RSD (%)	0.68	NA	4.028	NA	NA	0.000	NA	NA	6.38	NA
EZ Scan Standard, 19 min (3 runs in 1 day)	Mean (mass %)	84.67	0.000	14.33	0.05	0.05	0.000	0.07	0.000	0.73	0.00
	RSD (%)	0.682	NA	4.028	12.37	37.28	NA	14.71	NA	4.83	NA
EZ Scan Long, 44 min, (3 runs in 1 day)	Mean (mass %)	84.00	0.000	15.00	0.06	0.06	0.015	0.08	0.000	0.73	0.000
	RSD (%)	0.000	NA	0.00	4.23	10.51	7.873	6.93	NA	1.37	NA
Very Long	Mean (mass %)	85.00	0.000	14.00	0.06	0.04	0.000	0.07	0.000	0.72	0.000
Forensic 5 (3 runs in 1 day)	Mean (mass %)	0.000	7.33	89.67	0.18	0.18	0.034	0.24	0.000	2.13	0.000
	RSD (%)	NA	86.60	7.083	3.27	47.13	141.4	6.28	NA	2.71	NA

Notes:

1. Sample attached using fluorocarbon (Al–Cu–F) adhesive.
 2. Light shading indicates elements known to be in the sample; dark shading indicates elements that may have been present as impurities in the cup and film.
- NA, not applicable.

Table 8. SQX Results Specific to the Data Presented in Figures 1–3

Method	Figure No.	Element (Mass %)							
		Al	F	Cu	S	K	Cl	Si	Fe
Forensic 2	1	82	3	14	0.051	0.062	0	0.085	0.67
Forensic 3	2	84	0	15	0.56	0.024	0	0	0.69
EZ Scan Standard	3	85	0	14	0.54	0.34	0.13	0.64	0.74

Note: Light shading indicates elements known to be in the sample; dark shading indicates elements that may have been present as impurities in the cup and film.

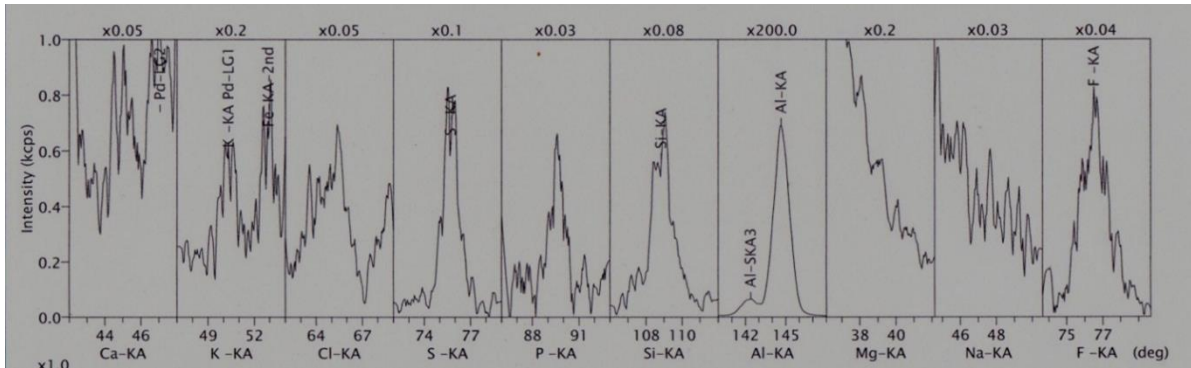


Figure 1. Light element spectra of Al-Cu-F sample obtained using Forensic 2 method.

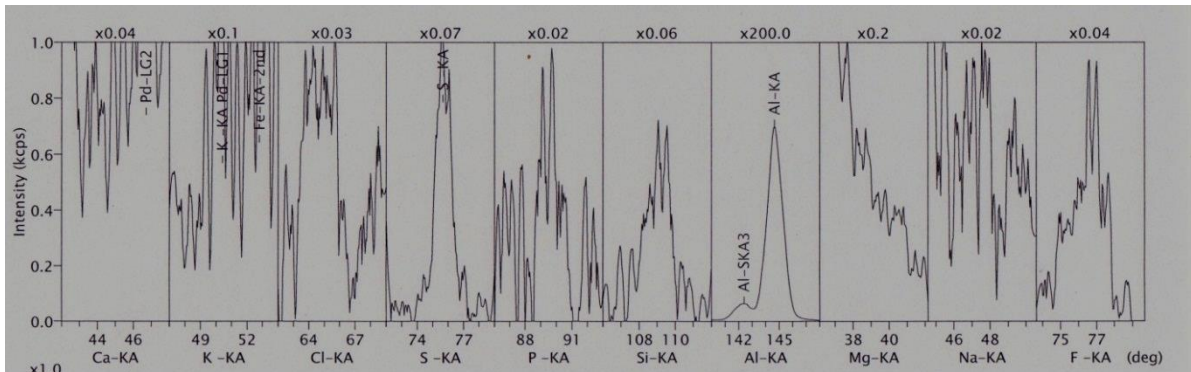


Figure 2. Light element spectra of Al-Cu-F sample obtained using Forensic 3 method.

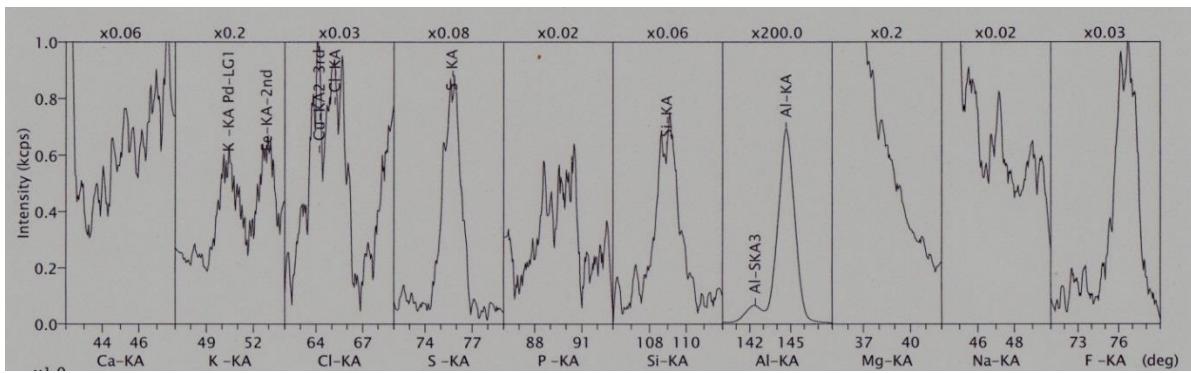


Figure 3. Light element spectra of Al-Cu-F sample obtained using standard EZ Scan method.

Descriptive statistics for the results of the Al–Cu–F sample runs are provided in Table 9. The only method that consistently produced an F peak recognizable to the software was the Forensic 2 method. The faster method and the EZ Scan methods regularly missed this peak.

Table 9. Descriptive Statistics from the Al–Cu–F Sample

Method	Statistic	Element									
		Al	Cu	F	S	K	Fe	Cl	Mg	Si	Ca
EZ Scan Short (3 runs)	Mean (mass %)	84.67	14.33	0.00	0.00	0.00	0.77	0.00	0.00	0.00	0.00
	95% Confidence level (%)	1.43	1.43	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00
EZ Scan Long (3 runs)	Mean (mass %)	84.00	15.00	0.00	0.05	0.06	0.73	0.01	0.00	0.08	0.00
	95% Confidence level (%)	0.00	0.00	0.00	0.01	0.02	0.02	0.00	0.00	0.01	0.00
Forensic 3 (6 runs)	Mean (mass %)	84.33	14.67	0.00	0.06	0.09	0.71	0.00	0.03	0.01	0.00
	95% Confidence level (%)	0.54	0.54	0.00	0.01	0.04	0.03	0.00	0.08	0.03	0.00
Forensic 2 (6 runs)	Mean (mass %)	82.17	14.17	2.77	0.15	0.07	0.69	0.00	0.00	0.08	0.00
	95% Confidence level (%)	1.03	0.43	1.47	0.25	0.01	0.02	0.01	0.00	0.02	0.01

Notes:

1. Sample attached using fluorocarbon (Al–Cu–F) adhesive.
2. Light shading indicates elements known to be in the sample; dark shading indicates elements that may be present as impurities in the cup and film.

4.2 Results from Ammonium Nitrate and CAN

Results are shown for the following combinations of samples and methods: a fresh, unweathered sample of CAN (CAN1) was run 10 times using the Forensic 2 method (Table 10), a weathered sample (CAN2) was run six times using the Forensic 2 method (Table 11), the same CAN2 sample was crushed and run 10 times using the Forensic 2 method (Table 12), and a larger CAN2 sample, which filled the entire sample cup, was run six times (Table 13).

Results are also shown for a blank sample (cup and film) that was run 10 times using the Forensic 2 method (Table 14). The sizes of the confidence levels relative to the mean measurements, which are expressed as relative confidence levels (in terms of percentages of the means), indicated that with the exception of Ag, none of these elements could be considered present in the sample. As discussed in Section 4.3, the Ag might have been an artifact of the Pd target that was used to generate the incident X-rays.

Table 10. CAN1 (Unweathered): Statistics for 10 Successive Runs with Forensic 2 Method

Statistic	Element										
	Mg	P	S	Cl	K	Fe	Al	Si	Ca	Ag	Cd
Mean (mass %)	5.78	0.13	5.90	0.34	1.20	4.41	0.84	2.61	77.20	1.31	0.34
95.0% Confidence level (%)	0.34	0.08	0.24	0.02	0.05	0.31	0.07	0.10	0.81	1.22	0.77
Relative confidence level (%)	5.83	63.63	4.00	6.44	3.97	6.99	8.29	3.97	1.05	92.83	226.22

Note: Shading indicates elements that may be present as trace impurities in the cup and film.

Table 11. CAN2 (Weathered): Statistics for Six Successive Runs with Forensic 2 Method

Statistic	Element								
	Mg	S	Cl	K	Fe	Al	Si	Ca	Ag
Mean (mass %)	5.85	2.82	0.22	1.25	5.10	0.74	2.05	80.50	1.47
95.0% Confidence level (%)	0.79	0.18	0.02	0.20	0.27	0.11	0.17	1.96	2.39
Relative confidence level (%)	13.56	6.42	10.12	15.71	5.37	15.25	8.41	2.44	163.14

Note: Shading indicates elements that may be present as trace impurities in the cup and film.

Table 12. CAN2, Crushed: Statistics for 10 Successive Runs with Forensic 2 Method

Statistic	Element									
	Mg	P	S	Cl	K	Fe	Al	Si	Ca	Ag
Mean (mass %)	5.550	0.017	1.610	0.212	1.041	5.340	0.650	1.780	83.300	0.630
95.0% Confidence level (%)	0.514	0.038	0.079	0.016	0.113	0.315	0.056	0.088	0.483	0.951
Relative confidence level (%)	9.26	226.22	4.89	7.43	10.86	5.90	8.68	4.94	0.58	151.02

Note: Shading indicates elements that may be present as trace impurities in the cup and film.

Table 13. CAN2: Statistics for Six Successive Runs of Large Sample* with Forensic 2 Method

Statistic	Element							
	Mg	S	Cl	K	Fe	Al	Si	Ca
Mean (mass %)	5.18	2.73	0.34	1.20	5.33	0.76	2.23	82.00
95.0% Confidence level (%)	0.70	0.09	0.04	0.15	0.54	0.13	0.18	0.94
Relative confidence level (%)	13.46	3.13	12.77	12.37	10.08	16.74	8.23	1.14

*Sample weight: 7.6 g; filled cup.

Note: Shading indicates elements that may be present as trace impurities in the cup and film.

Table 14. Blank:* Statistics for 10 Successive Runs with Forensic 2 Method

Statistic	Element										
	Rb	Ag	Zr	Nb	Th	U	Pu	Y	Br	Mo	Sr
Mean (mass %)	2.94	59.80	1.40	3.84	3.33	4.18	4.01	6.13	0.09	8.30	6.20
95.0% Confidence level (%)	2.38	27.66	1.50	4.98	4.39	4.68	4.69	10.56	0.21	14.47	11.94
Relative confidence level (%)	81	46	107	130	132	112	117	172	226	174	193

*Cup and film only.

Using the EZ Scan method at the three available speeds and performing each run six times successively on sample CAN1 resulted in the data shown in Table 15. Comparing the short, medium, and long versions of EZ Scan provided a convenient way to illustrate the effects of scan rate on data. It was clear from these data that the relative error, as indicated by the relative size of the 95% confidence level, decreased significantly with scan length. It was also clear that the short EZ Scan method failed to identify the Mg and Fe, which were known (from previous testing) to be components of these samples.

The CAN1 sample was used for this comparison, and six runs of each method were performed for statistical evaluation. The numerical results are shown in Table 15, and the corresponding spectra are shown in Figures 4–6. Although the short EZ Scan method only identified Ca and S in the numerical data, the spectrum indicates that K, Cl, Si, Al, Mg, and Fe may have also been present. The medium EZ Scan method automatically picked up these elements and provided a strong indication for the presence of P. The long EZ method identified the P along with all of the other elements. From the spectra, it is clear that these elements were all present to some degree. With the exception of the Ca numbers that resulted from the short EZ Scan method, the precision of all measurements also increased with the scan length.

Table 15. CAN1 (Unweathered): Comparison of Short, Standard, and Long EZ Scans

Method	Statistic	Element								
		Ca	S	Mg	Al	Si	Cl	K	Fe	P
EZ Scan, Short (6 min)	Mean (mass %)	93.83	6.13							
	95.0% Confidence level (%)	0.43	0.31							
	Confidence level (%)	0.46	5.04							
EZ Scan, Standard (19 min)	Mean (mass %)	79.17	5.97	5.12	0.88	2.68	0.33	1.23	4.77	
	95.0% Confidence level (%)	2.52	0.11	2.64	0.09	0.12	0.02	0.11	0.32	
	Confidence level (%)	3.18	1.82	51.52	9.84	4.57	6.50	8.79	6.63	
EZ Scan, Long (44 min)	Mean (mass %)	78.17	5.97	5.97	0.90	2.62	0.32	1.23	4.82	0.15
	95.0% Confidence level (%)	0.43	0.09	0.18	0.06	0.08	0.02	0.09	0.15	0.08
	Confidence level (%)	0.55	1.44	3.08	6.67	3.02	5.08	6.95	3.21	52.90

Note: Shading indicates the element was not detected.

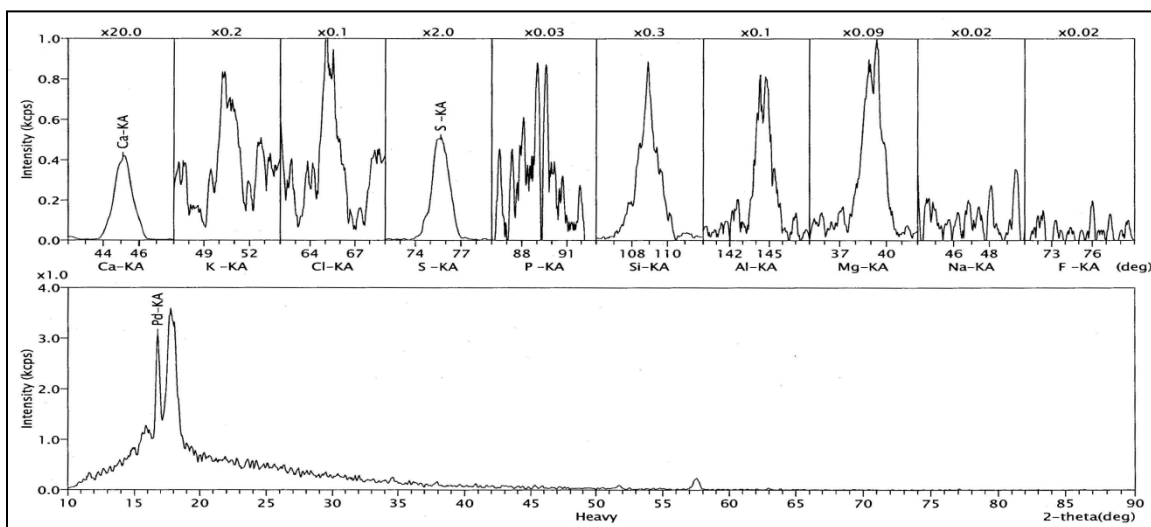


Figure 4. WDXRF spectra of CAN1 obtained using short EZ Scan method.

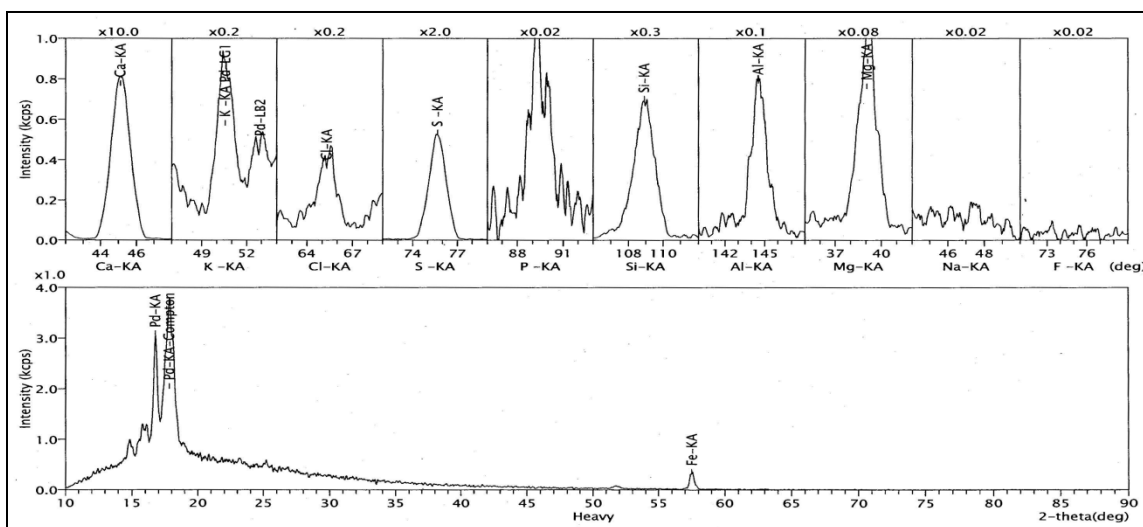


Figure 5. WDXRF spectra of CAN1 obtained using medium EZ Scan method.

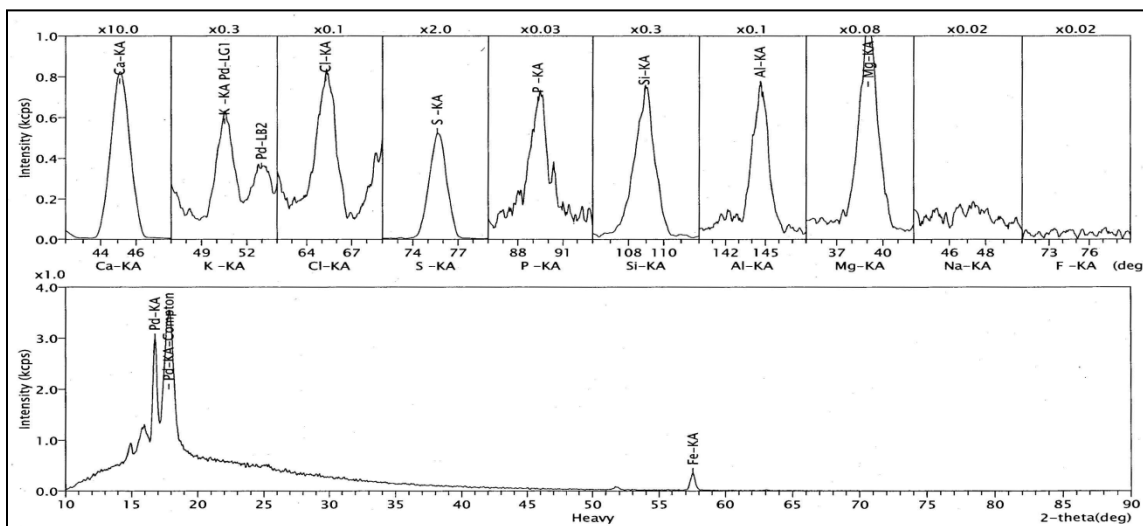


Figure 6. WDXRF spectra of CAN1 obtained using long EZ Scan method.

In the case of ammonium nitrate that has not been altered by the addition of Ca and Mg, the expected composition is N, O, and H, none of which are detectable using this configuration of WDXRF. The results are therefore completely attributable to contaminants and artifacts. Representative results from this analysis are shown in Table 16. As there is no way to determine what percentage of the sample comprises the reported elements, these reported percentages have to be treated as ratios rather than absolute values. An example of this is the Mg reported for CAN1 and for ammonium nitrate. In the case of CAN1, it is a known significant additive, whereas in the ammonium nitrate, it is a minor contaminant. However, the amount of Mg in the ammonium nitrate relative to the amount of the other elements reported is higher than the amount of Mg in CAN relative to the amount of other elements reported.

Table 16. Ammonium Nitrate: Statistics for Six Successive Runs Using Forensic 2 Method

Statistic	Element							
	S	Mg	Fe	K	Ca	Al	Si	Ag
Mean (mass %)	6.35	16.90	3.34	3.32	1.93	0.39	59.10	8.48
95.0% Confidence level (%)	0.61	0.71	0.39	0.41	0.33	0.30	2.71	3.55
Relative confidence level (%)	10	4	12	12	17	77	5	42

Note: Shading indicates elements that may be present as impurities in the cup and film.

4.3 Results from Plastic Explosives

The plastic explosive samples studied were C4-type compositions, primarily RDX and HMX, which would not be expected to provide any WDXRF information other than possible trace contaminants. The samples were designated with numbers and are referred to as Plastic Explosive 124, 204, 507, and 609. In previous analyses, Samples 124 and 204 showed no inorganic constituents. Sample 507 was previously identified to contain trace amounts of Al, Ca, Fe, Mn, Na, and S, distributed inhomogeneously, and sample 609 was previously identified to contain traces of Al, Ca, Cl, Fe, Mg, Na, and Si, also distributed inhomogeneously.

The Forensic 2 method, which includes a sample spin option, was used for the first set of runs. The purpose of this option is to homogenize signal differences that are due to uneven sample surface and composition. Results are presented in Table 17. From these results, it was clear that the instrument was identifying elements that were highly unlikely to be present in the samples, based on the lack of evidence in previous analyses as well as the rarity of many of the identified elements. The spectra from these, an example of which is shown in Figure 7, suggest that the erroneous identifications arose from excessive noise in the heavy-element spectrum. It was hypothesized that this noise could have resulted from mechanical shifting of the irregular samples during rotation, which would have caused changes in the distance to the sample. To eliminate these peaks, Samples 124 and 204 were run again using the Forensic 2 method with no spin, which was identical to the Forensic 2 method but with the sample spin turned off. This was effective in removing most of the misidentified peaks. Additionally, Sample 204 was gently flattened to remove some of the irregularity of the sample surface. It was then run six more times. The spectra resulting from these corrections are shown in Figure 8. It is clear from Table 18 and Figures 7 and 8 that both the removal of sample spin and the flattening of the sample helped in eliminating the spurious peaks from the analysis results for Sample 204.

Table 17. WDXRF Forensic 2 Method Results from Four Examples of Plastic Explosives

Element	124 Spin			204 Spin			507 Spin			609 Spin		
	Mean (Mass %)	Confidence Level (95.0%)	RSD (%)	Mean (Mass %)	Confidence Level (95.0%)	RSD (%)	Mean (Mass %)	Confidence Level (95.0%)	RSD (%)	Mean (Mass %)	Confidence Level (95.0%)	RSD (%)
Al				0.78	0.45	57	0.41	0.69	169			
S	2.73	5.81	213	0.19	0.31	162	0.22	0.42	195	4.86	6.83	141
Cl	0.05	0.13	257	0.04	0.11	245				0.20	0.51	257
K	13.42	28.61	213	1.48	1.94	131	3.08	2.65	86	43.82	44.53	102
Ca	3.43	7.06	206	1.19	2.43	204	1.20	1.37	11	6.68	13.85	207
Fe	1.03	2.66	257				0.20	0.51	25			
Ag	76.50	39.61	52	37.00	21.85	59	44.00	41.82	95	44.50	51.21	115
Mo	0.53	1.37	257	23.31	14.92	64	14.80	26.19	177			
Tc	1.22	1.98	163	13.47	11.52	85	0.92	2.36	257			
Zr	0.52	1.33	257	0.51	0.39	76	4.57	7.73	169			
Nb	0.55	1.41	257	0.36	0.40	111	0.45	0.85	190			
Y				0.40	0.41	103	3.28	4.48	137			
Cd				8.14	9.50	117						
Sb				4.71	11.54	245	6.83	17.57	257			
Sr				0.08	0.20	245	2.73	4.37	160			
Cs				8.29	20.27	245						
Br							0.27	0.69	257			
Rb							0.43	1.11	257			
Ru							6.67	17.14	257			
Th							0.48	1.24	257			
U							4.92	9.12	185			
Pu							4.55	9.08	200			

Note: Shading indicates the element was not detected.

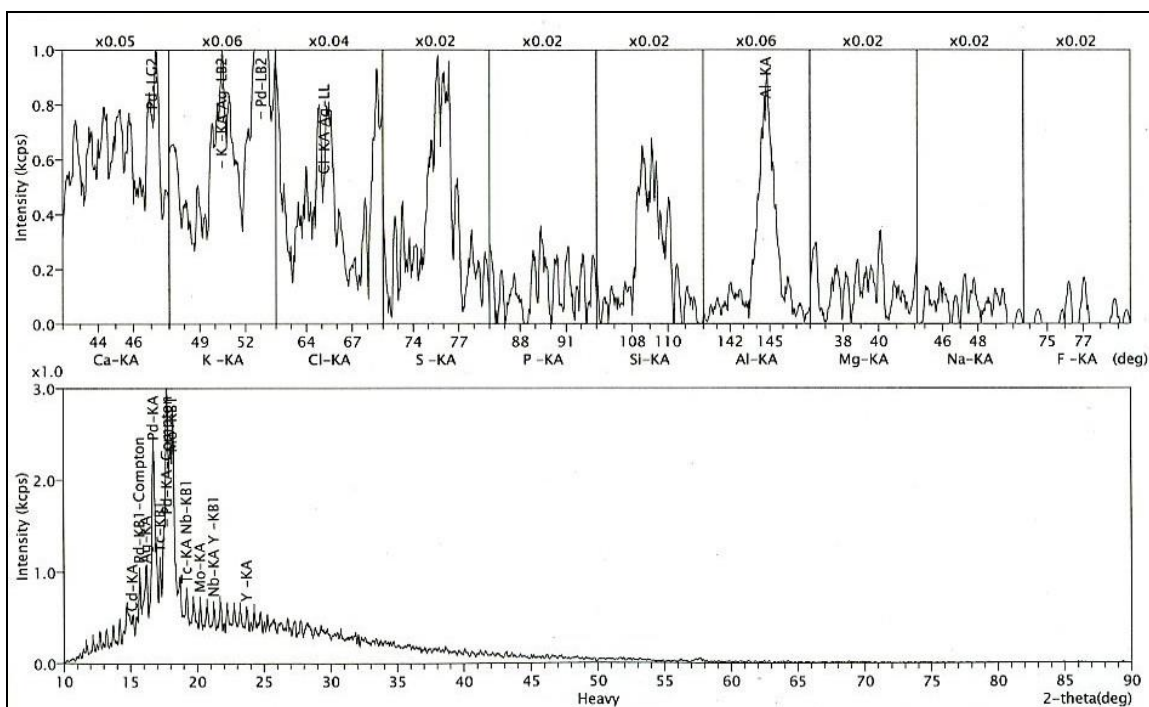


Figure 7. Individual light-element (top) and continuous heavy-element (bottom) WDXRF scans of Sample 204 obtained using Forensic 2 method.

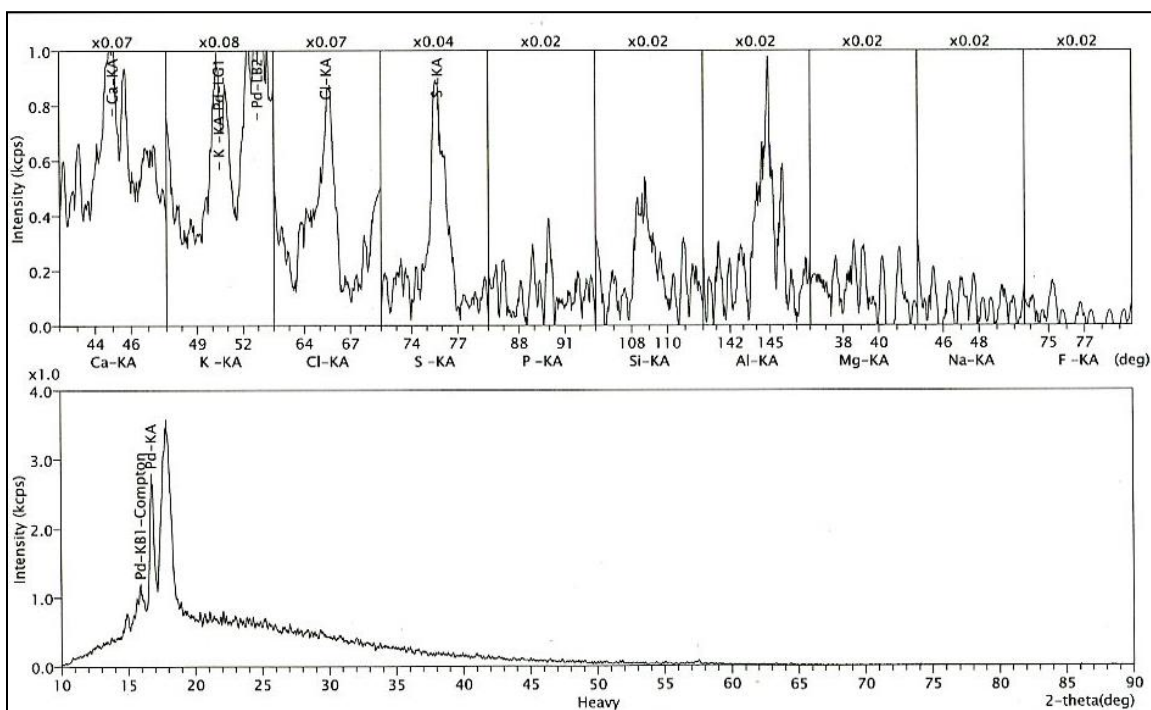


Figure 8. Individual light-element (top) and continuous heavy-element (bottom) WDXRF scans of Sample 204 obtained using Forensic 2, no-spin method.

Table 18. WDXRF Results for Plastic Explosive 204: Forensic 2 Method; Forensic 2, No-Spin Method; and Forensic 2, No-Spin Method on a Flattened Sample

Element	Sample 204: Spin			Sample 204: No Spin			Sample 204: No Spin, Flattened		
	Mean (Mass %)	95.0% Confidence Level (%)	RSD (%)	Mean (Mass %)	95.0% Confidence Level (%)	RSD (%)	Mean (Mass %)	95.0% Confidence Level (%)	RSD (%)
Al	0.78	0.45	57.16	20.13	12.48	61.98			
S	0.19	0.31	162.34	3.47	3.86	111.45	4.02	3.92	97.51
Cl	0.04	0.11	244.69	4.38	7.82	178.39	9.95	3.86	38.80
K	1.48	1.94	130.61	23.52	16.77	71.33	29.17	3.60	12.34
Si				1.83	4.71	257.06			
Ca	1.19	2.43	203.89	17.17	13.74	80.03	57.00	7.96	13.97
Ag	37.00	21.85	59.05	28.33	37.33	131.74			
Mo	23.31	14.92	63.98						
Tc	13.47	11.52	85.49						
Zr	0.51	0.39	75.57						
Nb	0.36	0.40	111.24						
Y	0.40	0.41	102.66						
Cd	8.14	9.50	116.65						
Sb	4.71	11.54	244.69						
Sr	0.08	0.20	244.69						
Cs	8.29	20.27	244.69						

Note: Shading indicates the element was not detected.

Sample 124 was the second plastic explosive that was used to examine the effect of spin on results. Data from this comparison are shown in Table 19. Most of the spurious peaks were effectively removed by keeping the sample stationary during analysis. With the exception of the Ag peak, all of the peaks had confidence intervals that were larger than the measurements; therefore, they cannot be considered reliable.

Table 19. WDXRF Results for Plastic Explosive 124: Forensic 2 Method and Forensic 2, No-Spin Method

Element	Sample 124: Spin			Sample 124: No Spin		
	Mean (Mass %)	95.0% Confidence Level (%)	RSD (%)	Mean (Mass %)	95.0% Confidence Level (%)	RSD (%)
S	2.73	5.81	212.80	3.00	5.22	174.09
Cl	0.05	0.13	257.06			
K	13.42	28.61	213.23	34.03	48.53	142.61
Ca	3.43	7.06	205.76			
Fe	1.03	2.66	257.06	1.83	4.71	257.06
Ag	76.50	39.61	51.77	61.17	49.90	81.59
Mo	0.53	1.37	257.06			
Tc	1.22	1.98	162.78			
Zr	0.52	1.33	257.06			
Nb	0.55	1.41	257.06			

Note: Shading indicates the element was not detected.

Regarding the Ag peak, in samples of organic materials with little or no presence of elements analyzed by the instrument, it is common for results to indicate the unexpected presence of K or Ag, and statistics often support the claim. This is because the incident X-rays arise from a Pd target; therefore, the Pd signal is always present in the results. With very low SNRs, this minor Pd peak is often identified as either Ag or K, which are misleading results. Because the peak is real, and it is only the identification that is erroneous, the precision appears to be acceptable. It is the accuracy that suffers. Examples of these overlaps are shown in Figure 9.

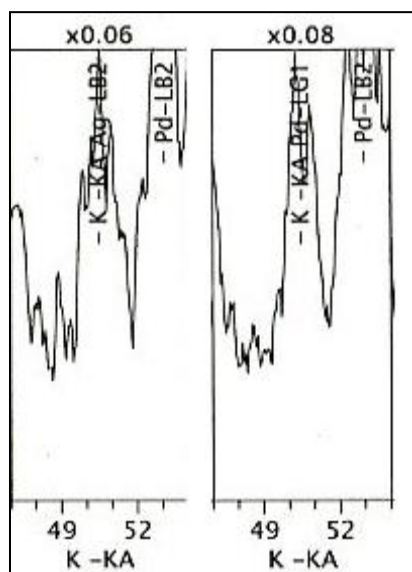


Figure 9. Examples of Pd $L\gamma_1$ line overlapping with Ag $L\beta_2$ (left) and K $K\alpha$ (right).

These issues of spurious and misidentified peaks are particularly problematic in cases of unknown samples that are primarily organic or nitrogenous. The software is presented with a spectrum that has a very low SNR and few to no peaks of identifiable elements, and it is tasked with determining a total 100% mass composition. Seeing only small peaks of possible trace contaminants, perhaps from the sample holder rather than the sample, the software normalizes them to 100%. There is no consideration of major elements that are present but not visible to the spectrometer.

4.4 Results from Mixed Powders and Sodium Compounds

The powder mixes were mixtures of Al powder, table salt, and titanium dioxide in known compositions. The samples were commercial products rather than chemical standards; although some level of impurity was expected, exact levels were unknown. The expected values, which were based on the mass of each material in the mix, are included with the results shown in Table 20. The differences between the two mixes were (1) Mix 1 had a smaller total weight than Mix 2, approximately 200 mg versus approximately 900 mg, respectively; and (2) the compositions were not identical. It is immediately apparent from Table 20 that there was a problem with the NaCl. Because Al and Na readings are obtained from the same detector/crystal combination and the Al was readily seen, this problem cannot be attributed to instrument issues

(for example, a corrupted or misaligned crystal). Possible explanations are that the lower-energy Na K α X-rays were absorbed by the surrounding material and did not reach the detector, or that within the mixture, the flake Al material and the nanoparticle aggregate of titanium dioxide coated the salt crystals, which are on the order of 100 μm , and effectively obscured them from the detector. With just the results of the WDXRF analysis, it is not possible to determine whether either of these scenarios occurred. In Mix 1, Ag, As, and Y traces were reported, including good statistics on the Ag; however, it is highly unlikely these elements were present. Mix 2 of the same materials does not show the presence of As or Y. The Ag exhibited poor statistics, as did the Zr and P (reported in Mix 2 but not in Mix 1). In this case, the use of multiple analyses and descriptive statistics helped to exclude most of the spurious identifications, but it should be noted that a single analysis would not have allowed these peaks to be eliminated. The other trace materials identified in the samples, Si, S, K, Ca, and Fe, are common elements, and their presence was not surprising.

Table 20. Results from Powder Mixes

Mix 1												
Value	Na	Cl	Al	Ti	Si	S	K	Ca	Fe	Ag	As	Y
Expected (mass %)	29	44	9	17	0	0	0	0	0	0	0	0
Mean (mass %)	0.00	8.25	46.5	43.5	0.25	0.04	0.19	0.02	0.59	0.57	0.02	0.02
95.0% Confidence level (%)	0.00	0.53	1.59	1.29	0.04	0.03	0.02	0.03	0.13	0.08	0.05	0.05
RSD (%)	0.00	6.4	3.4	3.0	15.3	67.3	12.4	116	22.2	14.2	257	257
Mix 2												
Value	Na	Cl	Al	Ti	Si	S	K	Ca	Fe	Zr	P	Ag
Expected (mass %)	23	35	11	32	0	0	0	0	0	0	0	0
Mean (mass %)	0.00	1.25	26.0	72.0	0.22	0.02	0.08	0.02	0.50	0.01	0.00	0.06
95.0% Confidence level (%)	0.00	0.34	1.15	1.15	0.04	0.01	0.03	0.02	0.10	0.03	0.01	0.15
RSD (%)	0.00	27.5	4.4	1.6	16.2	26.4	40.8	117	19.4	257	257	257

To understand the observations of NaCl in the mixes, the salt was run independently of the other two powders. To separate any possible interference of the Cl with the Na, a sample of sodium bicarbonate was also run. Again, to provide statistics, these samples were run a total of six times each. Other than impurities, the sodium bicarbonate was expected to show only Na. Results of these analyses are provided in Table 21. Even with the elimination of most of the potentially interfering elements, the Na-to-Cl ratio measured for the salt was far from the expected value. This is an effective illustration of the severe loss of sensitivity that this instrument exhibits at low atomic numbers. Only by providing the instrument with a sample that was purely Na (for these purposes) could we expect the Primini system to come close to an accurate Na determination.

Table 21. Results from Na Compounds

NaCl								
Value	Na	Cl	Al	Si	S	K	Ca	Br
Expected (mass %)	40	60	0	0	0	0	0	0
Mean (mass %)	6.23	89.00	0.01	2.67	0.31	0.60	0.99	0.05
95.0% Confidence level (%)	0.31	0.66	0.02	0.05	0.03	0.14	0.11	0.06
RSD (%)	4.96	0.75	257.06	2.03	9.35	23.12	11.51	115.65
Sodium Bicarbonate								
Value	Na	K	Ca	Cl	Ag			
Expected (mass %)	100	0	0	0	0			
Mean (mass %)	89.17	6.88	0.38	0.13	3.67			
95.0% Confidence level (%)	7.84	2.05	0.99	0.34	9.43			
RSD (%)	8.79	29.84	257.06	257.06	257.06			

Note: Shading indicates the element was not detected.

The spectra from Powder Mix 2 and salt (Figures 10 and 11, respectively), revealed that the Ca, S, and Si identified in the salt results were real, and the Al and Br reported in the salt results were from misidentification, as was indicated by the relative confidence levels. Also, the K had a Pd overlap that may be significant.

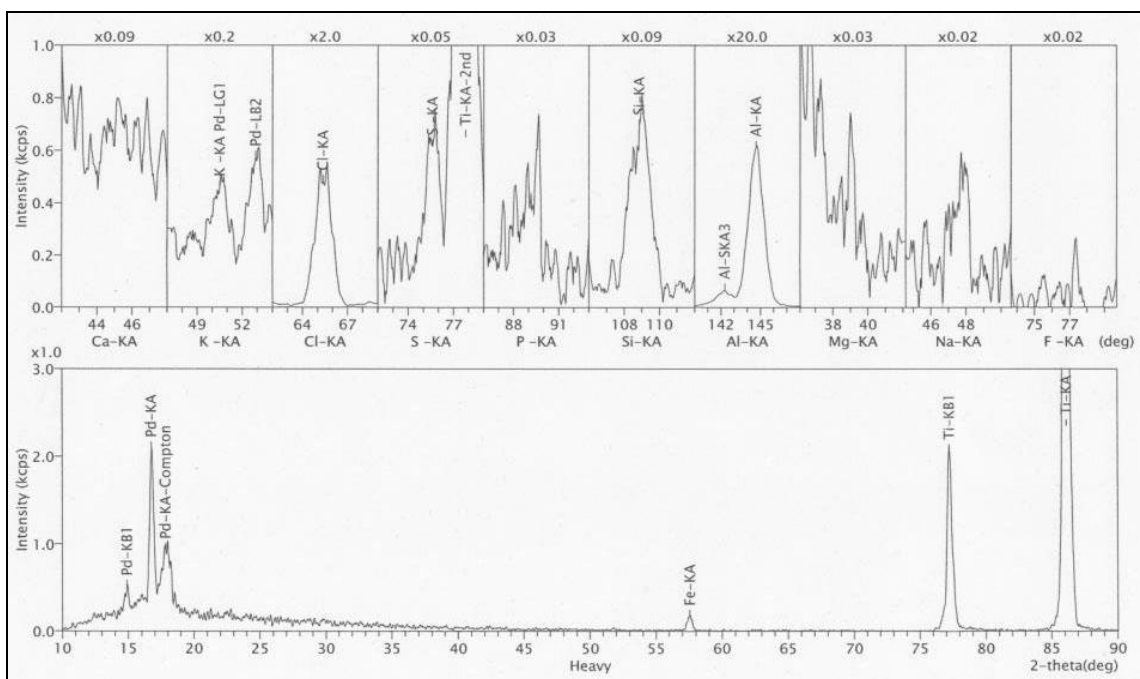


Figure 10. WDXRF spectra of Powder Mix 2 (salt, Al, and titanium dioxide).

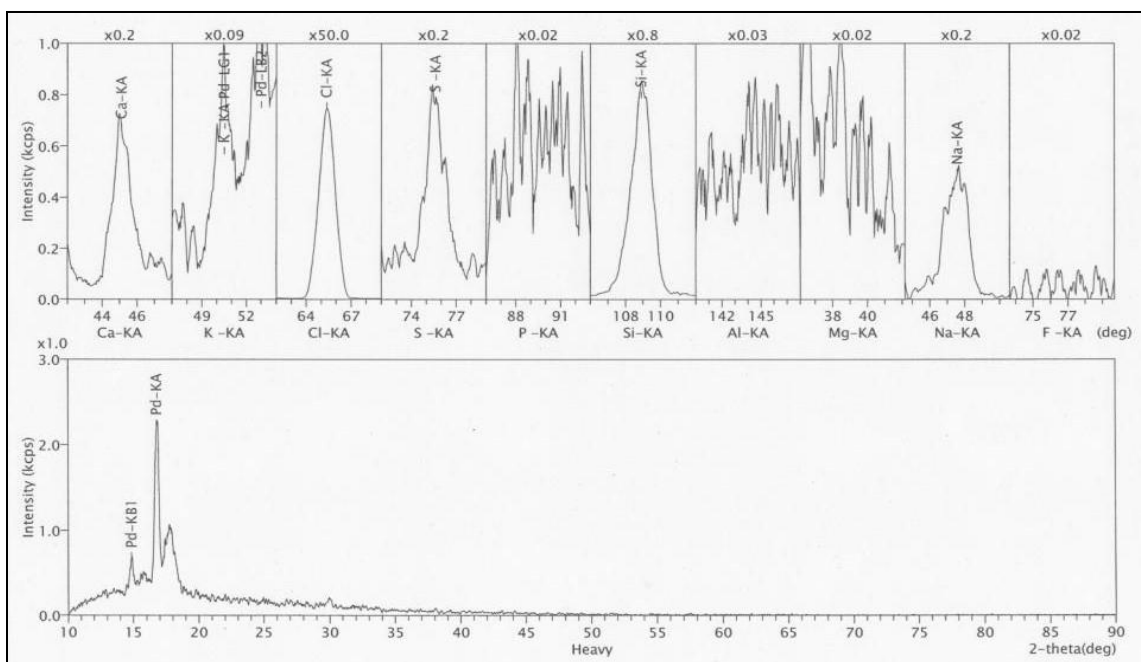


Figure 11. WDXRF spectra of salt alone.

5. CONCLUSIONS

XRF has strengths and weaknesses for application to explosive materials, and more specifically, to unknowns that are potentially explosive-related. Two significant strengths of most X-ray techniques are that the analytical techniques themselves, independent of any requisite sample preparation, are generally noninvasive and minimally energetic. In the case of unknown materials that are potentially related to explosives, this means that the possibility of detonation due solely to the analysis is minimal, and that beyond any required sample handling, the technique is generally nondestructive. However, in most situations, results are subject to the severe limitation of analyzing only for elements that are heavier than oxygen (as was the case for the Primini system used in this work). Any quantification provided under these conditions is normalized to 100%, and the absence of all lighter elements is assumed. Thus, the results provided are relative at best. For samples related to explosive materials or chemical and biological defense materials, the samples are largely volatile, organic, or nitrogenous, and the utility of elemental analyses that cannot see these elements is limited. For materials that do contain the identifiable elements, and for which identification is relevant to the mission, XRF can be a useful tool for identifying the elements present to support compound identifications using complementary techniques. For these purposes, it is advantageous that XRF techniques identify elements using methods that are based on fundamental physics, and results are generally unambiguous. In all cases, it is important to approach WDXRF analyses with common sense and avoid relying entirely on the mass percent compositions provided by the instrument. If the interest is only to determine major elemental constituents of a sample, it is adequate to run a quick scan. However, if there is any interest in determining minor constituents, it is prudent to use the longest scan that time will allow. WDXRF approaches that are generally associated with best practices, such as using a sample that fills the sample cup; using a smooth, flat sample; and using homogeneous samples, will provide more accurate results, but they are not always

practical for analyzing field samples of potentially hazardous materials. Additional strategies for maximizing the effectiveness of WDXRF include the following:

- Using longer scan times improves SNR and increases the chance of finding trace elements.
- Using flat samples improves reproducibility of the results.
- Including sample spin is useful for averaging the effects of inhomogeneities, but it introduces significant noise in highly irregular samples.
- Using larger samples will reduce the relative effects of trace impurities in the sample cup and film.
- Visual inspection of spectra should accompany evaluation of SQX results.
- Consider suspect any quantitative results involving light elements and qualitative results indicating the absence of light elements. These results should be verified by inspecting the spectra. However, qualitative results indicating the presence of these elements are generally reliable, especially when verified by inspection of the spectrum.
- It is essential to remain aware of the elements that the instrument does not “see”, as samples containing large amounts of these can provide very misleading results. Also keep in mind that the relative contributions of experimental uncertainty, such as trace constituents of the sample holders, are magnified when the bulk of the sample comprises elements not recognized by the instrument.
- Whenever practical, but particularly in cases that involve noisy spectra or unusual trace elements, much can be gained by running several successive replicates of the analysis and using statistical measures to determine the reliability of the data.

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ACRONYMS AND ABBREVIATIONS

CAN	calcium ammonium nitrate
F-PC	flow-proportional counter
HME	homemade explosive
HMX	cyclotetramethylene-tetranitramine
IED	improvised explosive device
PET	pentaerythritol
PETN	pentaerythritol tetranitrate
RDX,	cyclotrimethylenenitramine
RSD	relative standard deviation
SNR	signal-to-noise ratio
SQX	standardless, semi-quantitative analysis
WDXRF	wavelength dispersive X-ray fluorescence spectroscopy
XRF	X-ray fluorescence spectroscopy

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APPENDIX A

ELEMENTS EXPECTED FROM X-RAY SPECTROSCOPY OF EXPLOSIVE-RELATED COMPOUNDS

Table A-1. Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WDXRF)-Identifiable
Elements Present in Explosive-Related Compounds

Element	Possible Explosive Components	Other Expected Elements
Ag	Silver acetylide	–
	Silver azide	–
	Silver fulminate	–
	Silver perchlorate	Cl
Al	Aluminum perchlorate	Cl
	Aluminum	–
	Aluminum and iodine	I
Ba	Barium perchlorate	Cl
Bi	Triphenyl bismuth	–
Ca	Calcium perchlorate	Cl
Cd	Cadmium perchlorate	Cl
Cl	Potassium perchlorate	K
	Aluminum perchlorate	Al
	Barium perchlorate	Ba
	Cadmium perchlorate	Cd
	Calcium perchlorate	Ca
	Cobalt perchlorate	Co
	Iron perchlorate	Fe
	Lead perchlorate	Pb
	Magnesium perchlorate	Mg
	Manganese perchlorate	Mn
	Mercury perchlorate	Hg
	Nickel perchlorate	Ni
	Silver perchlorate	Ag
	Sodium perchlorate	Na
	Strontium perchlorate	Sr
	Uranium perchlorate	U
	Zinc perchlorate	Zn
	Titanium perchlorate	Ti
	Muriatic acid	–
	<i>m</i> -Picrylpicryl chloride	–
	Nitrogen trichloride	–
	<i>N</i> -Perchlorylpiperidine	–
	Picryl chloride	–
	Potassium chlorate	K
	Potassium perchlorate	K
	Tetraamminecopper(II) chlorate	Cu
	Trichlorotrinitrobenzene	–

(continued)

Table A-1. WDXRF-Identifiable Elements Present in Explosive-Related Compounds (Continued)

Element	Possible Explosive Components	Other Expected Elements
Co	Cobalt perchlorate	Cl
Cu	TACC	Cl
F	Picryl fluoride	–
	Tris[1,2-bis(difluoroamino)ethyl] isocyanate	–
Fe	Iron perchlorate	Cl
	Potassium ferricyanide	K
	Potassium ferrocyanide	K
	Sodium ferricyanide	Na
	Sodium ferrocyanide	Na
Hg	Mercurous nitratophosphite	P
	Mercury fulminate	–
	Mercury oxalate	–
	Mercury tartrate	–
	Mercury perchlorate	Cl
I	Nitrogen triiodide	–
	Aluminum and iodine	Al
K	Potassium chlorate	Cl
	Potassium ferricyanide	Fe
	Potassium ferrocyanide	Fe
	Potassium nitrate	–
	Potassium nitroaminotetrazole	–
	Potassium perchlorate	Cl
	Potassium picrate	–
	Potassium salicylate	–
	Potassium permanganate	Mn
Mg	Magnesium	–
	Magnesium	Al
	Magnesium perchlorate	Cl
Mn	Manganese perchlorate	Cl
	Potassium permanganate	K
Na	Sodium azide	–
	Sodium salicylate	–
	Sodium nitrate	–
	Sodium ferricyanide	Fe
	Sodium ferrocyanide	Fe
	Sodium picramate	–
	Sodium perchlorate	Cl
	Sodium chlorate	Cl
Ni	Nickel perchlorate	Cl
P	Phosphorus	–
	Mercurous nitratophosphite	Hg
	Lead nitratophosphite	Pb

(continued)

Table A-1. WDXRF Identifiable Elements Present in Explosive-Related Compounds (Continued)

Element	Possible Explosive Components	Other Expected Elements
Pb	Lead mononitroresorcinate	—
	Lead nitratophosphite	P
	Lead picrate	—
	Lead styphnate	—
	Lead perchlorate	Cl
Pt	Platinum fulminate	—
S	Sulfur	—
	Nitrogen sulfide	—
	Sulfuric acid	—
Si	Glass microspheres	—
Sr	Strontium perchlorate	Cl
Ti	Titanium perchlorate	Cl
	Titanium	—
U	Uranium perchlorate	Cl
Zn	Zinc perchlorate	Cl
	Zinc	—
Zr	Zirconium	—

—, none.

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APPENDIX B

SAMPLE HANDLING

Ideally, X-ray fluorescence spectroscopy (XRF) samples are manufactured disks with smooth, polished, or pressed surfaces of appropriate size to fit into the sample holders of the instrument. When this is not possible, the samples are liquids, loose powders, or bulk objects held in plastic sample cups with thin-film windows that allow the X-rays to penetrate. Cutting, polishing, milling, or pressing samples for close-to-ideal presentation to the Primini system is not advisable for unknowns, particularly if they are suspected explosives. Thus, sample preparation is limited to placing samples in appropriate cups using appropriate films.

Several thin films are available for this purpose, and the choice is dependent on the sample properties. One should use only thin films that are resistant to known components of the sample. Table B-1 indicates the degradation resistance of common thin-film materials.

Table B-1. Compatibility of Support Films for Wavelength Dispersive XRF Samples

Sample Component	Etnom	Polypropylene	Polyimide (Kapton)	Prolene	Ultrapolyester
Dilute or weak acids	G	E	N	G	G
Concentrated acids	G	E	N	E	G
Aliphatic alcohols	G	E	G	E	N
Aldehydes	F	E	E	E	N
Concentrated alkalis	G	E	E	E	N
Esters	F	G	G	G	N
Ethers	F	N	N	N	F
Aliphatic hydrocarbons	G	G	G	G	G
Aromatic hydrocarbons	G	F	F	F	F
Halogenated hydrocarbons	F	N	F	N	F
Ketones	G	G	G	G	N
Oxidizers	F	F	N	F	F

Key: E, excellent (green); G, good (green); F, fair (yellow); N, not recommended (red).

In addition to the susceptibility of film materials to sample properties, the film materials also absorb some X-rays. This reduces the intensity of XRF peaks, thereby reducing the sensitivity of the technique and the detectability of trace elements. This effect is more significant for lower-energy X-rays and will thus have a larger effect on the detectability of lighter elements. Figure B-1 shows the X-ray transmittance of common support films and the effects of film thickness on X-ray transmittance.

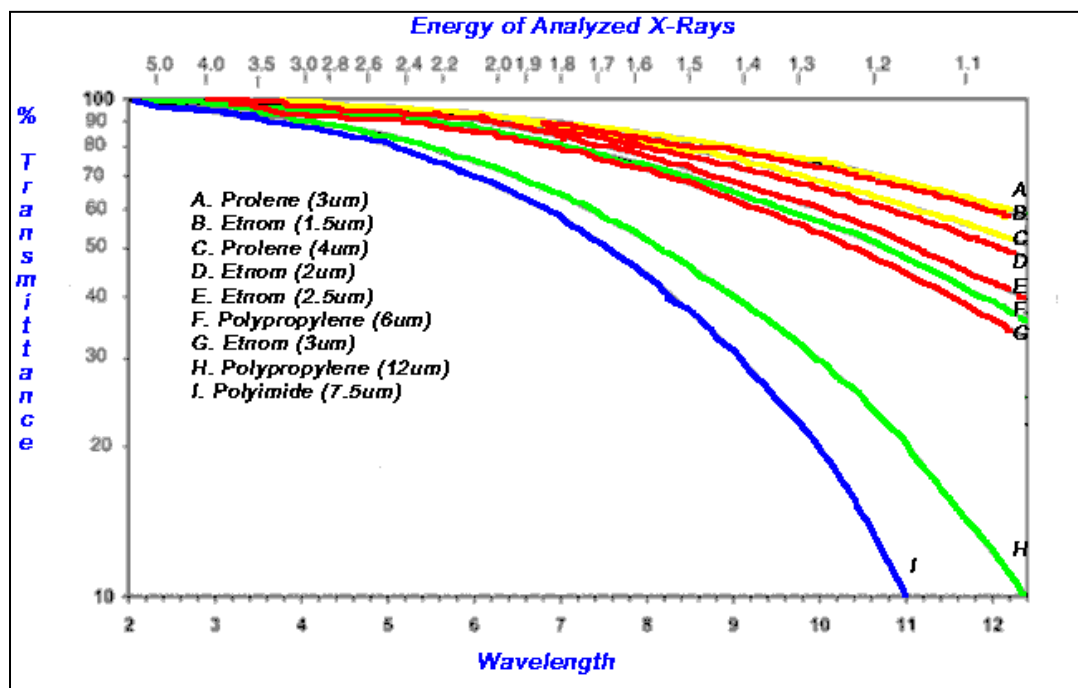


Figure B-1. X-ray transmittance of support films for use with XRF samples.

There are several cautions to keep in mind when preparing a sample for XRF analysis:

- When using a vacuum atmosphere, make sure that the sample holder does not trap air. Use either a venting sample cap or a microporous film over the top. If the sample is sandwiched between two films, ensure that the bottom film is nonporous, and the top film is porous.
- When using a vacuum atmosphere, be cognizant of the vacuum exhaust. Volatile components of the sample are carried by this exhaust. If the exhaust is into the laboratory enclosure, personnel present are breathing these volatile components.
- Remember that the spectrometer sits below the sample when the sample is in place for analysis. The bottom surface of the sample is the analyzed surface. If the support film under the sample fractures, the sample will fall into the working parts of the spectrometer.
- Never reuse sample support films. Contamination can occur even with solid bulk samples, and the films themselves can be embrittled by irradiation as well as by the samples.

When analyzing a small sample of powder, either as-received or the filtrate or dried residue of a liquid, follow one of these two procedures, in accordance with the handling properties of the material and the available quantity:

- **Loose-powder method.** Affix the selected thin-film support to the bottom of the sample cup using an appropriate collar. Pour the powder into the cup. Backfill the cup about halfway with crumpled support material or any dry solid that is known to not contain elements of interest, or cover it with microporous film held in place by a collar, or use a vented lid. Be careful not to let any material extend above the top of the cup.
- **Film-sandwich method.** Place the sample on a thin-film support sitting on top of the sample cup collar. Cover it with microporous film. Attach the sample cup. Backfill the cup about halfway with crumpled support material or any dry solid that is known to not contain elements of interest, or cover it with microporous film held in place by a collar, or use a vented lid. Be careful not to let any material extend above the top of the cup.

LIQUID SAMPLE PREPARATION FOR XRF

It is possible to analyze liquid samples using the Primini system, but this is not recommended, for the following reasons:

- The geometry of the instrument is such that a damaged film support would drop the sample onto the optics.
- Without experimentation, it is impossible to predict the resistance of a thin-film support material to an unknown liquid.
- The surface sensitivity of the technique means that suspended particulate matter is unlikely to be detected, and if it is detected, it will be indistinguishable from dissolved solids or elemental constituents of the liquid.

Follow these procedures for liquid sample preparation:

1. Based on available information, select an appropriate thin-film material.
2. Attach the thin film to the sample cup using a matching collar.
3. Pipette a small amount of liquid into the sample cup.
4. Attach a microporous membrane in the top collar.

Note: DO NOT run liquids under vacuum.

POWDER/SOIL SAMPLE PREPARATION FOR XRF

This procedure may also be used for solid samples.

1. Based on available information, select an appropriate thin-film material.
2. Place the film material over an inverted sample cup collar.
3. Insert the sample cup into the collar.
4. Place the sample in the cup (film is now the bottom of the cup and should be flat and smooth).
5. Place a sheet of microporous film over the top opening of the cup, and secure it with a collar.

SMALL/LIMITED SAMPLE POWDER/SOIL PREPARATION FOR XRF

In this procedure, a sandwich of powder is made between one sheet of nonporous film and one sheet of porous film, with the nonporous film at the bottom surface.

1. Based on available information, select an appropriate thin-film material.
2. Place the film material over an inverted sample cup collar.
3. Place the powder on top of the film.
4. Place a sheet of microporous film over the powder.
5. Insert the sample cup into the collar.

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