Determination of Primary Chemical Constituents of PBX(AF)-108 Warhead Explosive Using microPHAZIR^{TM} Near Infrared (NIR) Handheld Platform

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ABSTRACT

An innovative prognostics and health management (PHM) technique for quantifying and characterizing health status of Plastic Bonded Explosive (PBX) Air force (AF) formula PBX (AF)-108 warhead explosive was developed using Near Infrared (NIR) spectra emitted by microPHAZIR^{TM} NIR, a handheld platform developed by Thermo Fisher Scientific. Benchtop High Performance Liquid Chromatography (HPLC) was used as a reference technique for correlation to microPHAZIR^{TM} NIR measurements.

Near infrared spectra were acquired from twenty freshly manufactured mixes of PBX (AF)-108 explosive formulae, which were used in setting up a D-Optimal full-factorial design of experiment (DOE). Three-hundred and sixty measurements were recorded and analyzed using Partial Least Squares (PLS) regression analysis for model building and method development. Results were correlated to spectra, which were measured using HPLC reference technique. All recorded measurements performed with microPHAZIR^{TM} handheld platform were successfully validated with HPLC measurements. An algorithm was developed for microPHAZIR^{TM} NIR thus qualifying the platform as a real-time nondestructive test (NDT)/ nondestructive evaluation (NDE) tool for quantification of primary chemical constituents of PBX (AF)-108. Primary chemical constituents of PBX(AF)-108 are Polyurethane (PU) binder, Royal Demolition Explosive (RDX) oxidizer/ fuel, Isodecyl Pelargonate (IDP) plasticiser, and E-702 (4, 4'-methylenebis(2,6-di-tert-butyl-phenol) [MBDTBP] anti-oxidant/stabilizer.

This teaming effort between Raytheon Missile Systems (RMS), United Kingdom Ministry of Defence (UK MoD), Alliant Techsystems Launch systems (ATK LS), and Thermo Fisher Scientific demonstrated outstanding ability to utilize miniature cutting edge technology to perform real-time NDT of PBX (AF)-108 warhead explosive without generating chemical waste and/or residue. The new technique will further be adapted for use to measure primary chemical constituents of other warhead explosives and solid rocket propellants. The new technique will significantly reduce costs associated with performing ordnance surveillance and Service Life Extension Program (SLEP) assessment, which is often destructive and requires use of lengthy and expensive test techniques described in North Atlantic Treaty Organization (NATO) Standardization Agreement (STANAG)-4170 and Allied Ordnance Publication (AOP)-7 manuals.

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1. INTRODUCTION

Tactical missiles are often exposed to severe thermal and dynamic stresses associated with long- term exposure to harsh environments, including transportation handling, transportation vibration, diurnal cycling, and much more. These stresses may act individually or synergistically to factor into the aging, deterioration, and eventual decommissioning of some of Department of Defense (DoD) critical warfighting assets. Adverse reliability associated with long-term aging and deterioration of assets significantly affects the total life cycle cost of fielding these weapon systems in a high state of readiness. Reliability evaluation of legacy data has indicated failures in missile structural, energetic and electronic components, all associated with the long-term exposure to static (heat, humidity, salt, etc.), and dynamic (transportation shocks, vibration, etc.) stressors.

Today, most common methods of NDT for evaluating the health of energetic systems are radiographic (X-ray imaging, X-ray computed tomography (CT), etc.), electrical (Eddy-current and electro-magnetic methods), dye penetrant, and acoustic and ultrasonic, or a combination thereof. These methods are used by manufacturers during the production process, mostly for quality control, and are seldom used once the system has been fielded. Moreover, for military energetic systems, it is usually impractical to use these methods in the field. For health monitoring in the field, deployable or portable platforms become valuable as NDT/NDE tools.

A joint effort was carried out between the UK Ministry of Defence (MoD), Raytheon Missile Systems, ATK Launch Systems, and Thermo Fisher Scientific to qualify microPHAZIR^{TM} NIR platform as a portable real-time NDE tool. The effort was successfully executed and will enable RMS, other defense contractors, US DoD and UK MoD to quantify chemical constituents of PBX (AF)-108 warhead explosive, a high energy plastic bonded explosive composition used in the armament subsystem of tactical missiles. The platform will further be adapted for use to measure numerous other explosives, solid and liquid rocket propellants.

The proposed technology is hybrid, in that it does not provide wireless and/or continuous monitoring of the health status of the energetic material (i.e. PHM), yet it is a proactive NDE/NDT technique which replaces the old destructive test methodologies, described in NATO STANAG-4170 and AOP-7 manuals, imposed by Surveillance and Life Extension Programs (SLEP) of past and present day techniques. The proposed technology will define new means for realizing anticipated residual useful life (RUL) of an explosive from a chemical perspective, by quantifying chemical constituents within the explosive matrix, which can shed valuable information about the anticipated mechanical and structural behavior of the explosive matrix. The combination of chemical and mechanical (structural) health of the explosive determines whether a warhead (armament subsystem) would be warranted as “safe and suitable for service (S3)”.

Today RMS and the UK MoD surveillance strategies seek to extend time between periodic evaluations, henceforth reducing tasks associated with subsystem breakdown, test and criticality analysis (BTCA) by as much as 50%. On average, a surveillance program is often recommended once every 4 years on a sample population which represents the fielded and/or stored weapons inventory, and with the introduction of microPHAZIR^{TM} NIR real-time technology it will be feasible to extend the time between surveillance programs and/or reduce the number of assets that undergo surveillance evaluation. When a SLEP plan is established for warhead (armament subsystem) inventory, complex steps must be executed and comprise disassembly, dissection and extensive testing (physical, chemical, and mechanical tests) of the warhead explosive matrix, often referred to as “breakdown, test and criticality analysis (BTCA)”. BTCA coupled with arena testing (static fire) of the warhead as well as other subsystems are challenging tasks, from manpower, cost and schedule perspectives, and therefore the need to exercise cost controls while at the same time maintain absolute confidence in assets health demands that new technologies such as microPHAZIR^{TM} NIR platform and more advanced (exploratory) technologies become integral part of SLEP cost consciousness and technology readiness. Generally, the ultimate goal is to be able to (i) predict subsystems, and henceforth system anomalies proactively and sufficiently in advance to institute corrective actions and/or preventive measures; and (ii) reduce generated chemical waste, logistics footprint, logistics response time, and life-cycle costs, which will ultimately increase systems availability, and enhance customer-supplier business relationship.

The proposed technology will be adopted by RMS and the UK MoD as the principal means for realizing early warnings of unsafe conditions using real-time data, collected with mobile microPHAZIR^{TM} NIR handheld platform and other advanced technologies of Thermo Fisher Scientific. Gaining real-time knowledge about the current health of an explosive matrix will offer effective insight to predicting future SLEP test plans.

Successful application of microPHAZIR^{TM} NIR handheld platform as a NDE/NDT tool is the cornerstone and the spring board for future development of PHM of energetic subsystems: Cartridge Actuated Devices (CADs), Propellant-Actuated Devices (PADs), and electro-explosive devices (EEDs) of tactical and strategic missiles. microPHAZIR^{TM} NIR handheld platform offers enormous potential for applications requiring real-time monitoring of the health status of warheads and solid rocket motors subject to fatigue, chemical and mechanical (structural) degradation.

2. EXPERIMENTAL

All starting raw materials were obtained commercially, in accordance with (IAW) military (MIL) standard MIL-E-8289 specifications and used without further processing.

2.1. Hazards and Safety Protocol

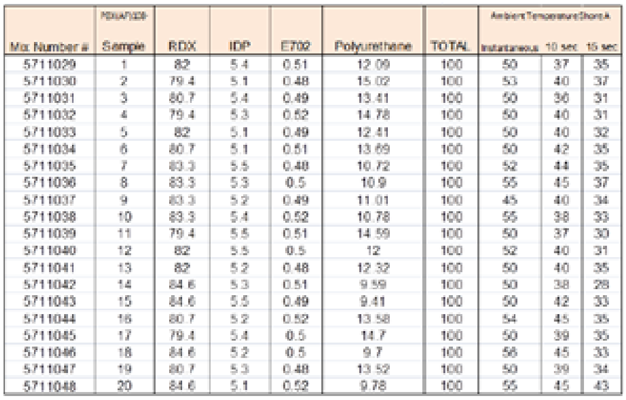
Hazards data comprising impact, friction, electrostatic discharge (ESD), and differential scanning Calorimetry (DSC) were performed on two uncured 10- gram high-speed mixes with the highest and lowest solids DOE iterations (worst and best case scenarios, respectively). Cured 1⁄4-pint (120 gram) mixes of the high solids loaded and low solids loaded PBX (AF)-108 mixes were prepared to identify safety concerns during mixing and preparation of the one-pint (600-gram) mixes and for handling and storage of the cured material. All hazards data were concluded to be low-order and in conformance with actual production mixes. Most importantly, ATK Launch Systems conducted a hazards assessment to evaluate use of the microPHAZIR^{TM} NIR with the PBX (AF)-108 warhead explosive. ATK LS Hazardous Operation Standards (AHOPS) require all portable electrical equipment within 25 feet of explosives or propellants to receive written approval from the Operating Building Electrical Classification Board (OBEC) committee chairman at ATK LS. Hazards analysis was performed for use of microPHAZIR^{TM} NIR with PBX(AF)-108 and assessment of the platform was reviewed and approved by the OBEC, OSCB (Operations Safety Control Board) and PPCB (Plant Process Control Board) committees.

Thermo Fisher Scientific has also conducted numerous tests on various explosives and constituents of the same family, using microPHAZIR^{TM} NIR with the following external group explosives test facilities and DoD depots, to identify RDX explosive:

I. Lew Kansas, Picatinny Arsenal, Dover, NJ.
II. Federal Law Enforcement Training Center.
III. National Forensic Science Technology Center (NFSTC).
IV. Jimmie Oxley, University of Rhode Island.
V. A TF Homemade Explosives Training Course.

A D-Optimal Design of Experiment (DOE) was established, and consisted of manufacture of twenty mix iterations of PBX (AF)-108 with each constituent varied above and below specification limits, to capture high values and low values of each constituent. Twenty 600- gram (1-pint each) mixes of PBX (AF)-108 warhead explosive (Table 1) were prepared using a 1-pint Baker Perkins mixer. Each of the twenty 1-pint mixes was vacuum cast into a teflon-tape -lined cup-like carton. The Teflon tape facilitated carton removal and simulated a production-tooling surface. Each of the twenty cast mixes was cast to produce a rectangular-shaped block of 1-inch by 4-inch by 5-inch geometrical dimension, as depicted in Figure 1. Each of the twenty cast blocks of PBX (AF)-108 mixes was measured in triplicate, at the six sides, depicted in Figure 7, using microPHAZIR^{TM} NIR handheld platform. Afterwards and to validate test results, samples measuring 0.5 to 1.0-gram were removed from the same locations of each rectangular cast block using a stirrup cutter and analyzed in triplicate by benchtop HPLC. The primary measured constituents were:

Table 1. Six-Hundred Gram mix Iterations of PBX(AF)-108



	PBX(AF)108						Ambient Temperature Shore A		
Mix Number #	Sample	RDX	IDP	E702	Polyurethane	TOTAL	Instantaneous	10 sec	15 sec
5711029	1	82	5.4	0.51	12.09	100	50	37	35
5711030	2	79.4	5.1	0.48	15.02	100	53	40	37
5711031	3	80.7	5.4	0.49	13.41	100	50	36	31
5711032	4	79.4	5.3	0.52	14.78	100	50	40	31
5711033	5	82	5.1	0.49	12.41	100	50	40	32
5711034	6	80.7	5.1	0.51	13.69	100	50	42	35
5711035	7	83.3	5.5	0.48	10.72	100	52	44	35
5711036	8	83.3	5.3	0.5	10.9	100	55	45	37
5711037	9	83.3	5.2	0.49	11.01	100	45	40	34
5711038	10	83.3	5.4	0.52	10.78	100	55	38	33
5711039	11	79.4	5.5	0.51	14.59	100	50	37	30
5711040	12	82	5.5	0.5	12	100	52	40	31
5711041	13	82	5.2	0.48	12.32	100	50	40	35
5711042	14	84.6	5.3	0.51	9.59	100	50	38	28
5711043	15	84.6	5.5	0.49	9.41	100	50	42	33
5711044	16	80.7	5.2	0.52	13.58	100	54	45	35
5711045	17	79.4	5.4	0.5	14.7	100	50	39	35
5711046	18	84.6	5.2	0.5	9.7	100	56	45	33
5711047	19	80.7	5.3	0.48	13.52	100	50	39	34
5711048	20	84.6	5.1	0.52	9.78	100	55	45	43

I. E-702 (4, 4’-methylenebis(2,6-di-tert-butyl-phenol) [MBDTBP]) anti-oxidant/stabilizer (Figure 2).
II. HMX/RDX oxidizer/fuel (Figure 3).
III. Isodecyl Pelargonate – IDP plasticizer (Figure 4).
IV. Binder content was determined by difference between the sum of the primary constituents/ingredients in (I), (II), and (III) and 100%].

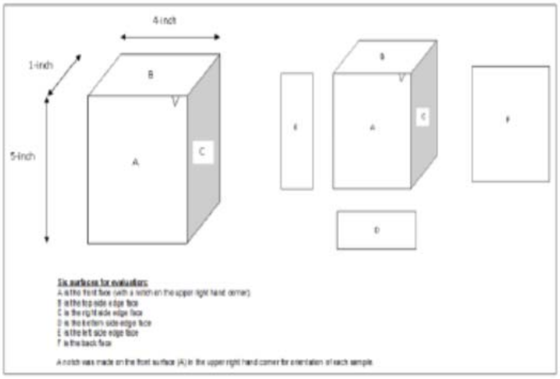


Figure1. Final Dimensions of PBX (AF)-108 Cast Block

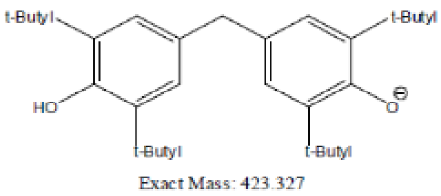


Figure 2. 4,4'-Methylenebis (2,6-Di-Tert-Butyl-Phenol) (MBDTBP)

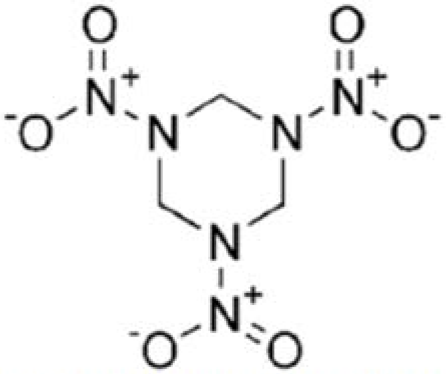


Figure 3. RDX (1,3,5-Trinitro-1,3,5-Triazacyclohexane)

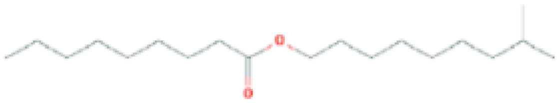


Figure 4. Isodecyl Pelargonate Plasticiser

2.2. Instrumentation

2.2.1. The microPHAZIR^{TM} (NIR) Platform

Near Infra-Red (NIR) spectroscopy is a well-established technique, which has been widely used since the mid-1970s. Only recently has new technology permitted NIR systems to be miniaturized into truly handheld system. One of the most important products is the microPHAZIR^{TM} NIR handheld platform. MicroPHAZIR^{TM} NIR handheld platform is based on near-infrared spectroscopy. The near-infrared region, depicted in Figure 5 is located between the infrared and visible region with wavelengths that range from 800-900 nanometers to 2500 nanometers.

MicroPHAZIR^{TM} NIR handheld platform was developed by Thermo Scientific and is based on vibrational spectroscopy. All molecules perpetually rotate, move, and contort in a complex manner at temperatures above absolute zero. Vibrational spectroscopy probes these contortions (or vibrations) of a sample to determine the chemical functional groups present. A common type of vibrational spectroscopy is infrared (IR) absorption/reflectance. It relies on illumination of the sample with optical radiation to probe the molecular vibrations.

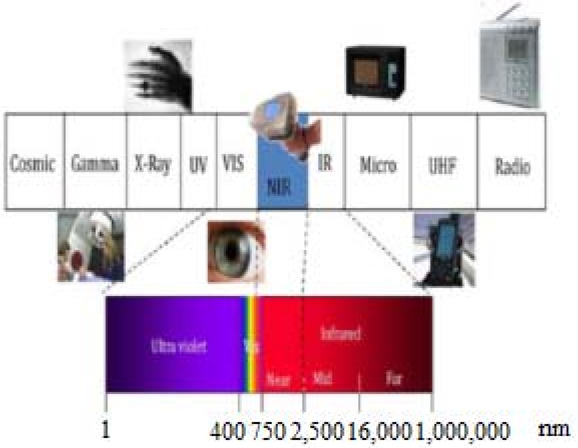


Figure 5. Near Infrared Region of the Light Spectrum

In NIR spectroscopy, the sample is illuminated with a broad spectrum of light in the near- infrared region and the transmission or reflection is recorded as a function of the frequency of the incident light. When the frequency of incident light equals the frequency of a specific molecular vibration, the sample tends to absorb some of the light. A material "fingerprint" results from recording the amount of light absorbed as a function of the wavelength (or frequency). The instrument is depicted in Figure 6. MicroPHAZIR^{TM} NIR is a rugged handheld chemical identification unit designed for point-of-use applications, either in contact or analysis can be conducted through transparent bags and vials. This product allows the identification of chemicals and white powders using the principles of NIR spectroscopy. It is enclosed in a lightweight, rugged, resistant package. The microPHAZIR^{TM} handheld contains a broadband NIR source, a Hadamard interferometer to separate the different wavelengths of light interacting with the sample, and a detector to collect the resulting energy.

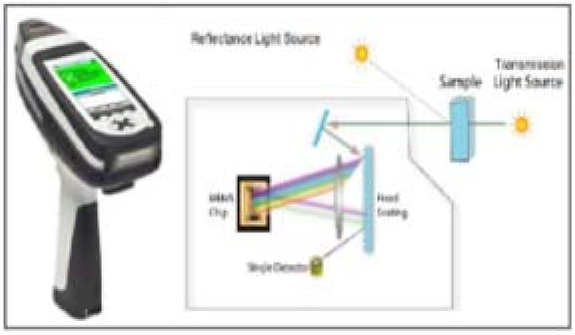


Figure 6. MicroPHAZIR^{TM} NIR and Principle of Operation

2.2.2. Agilent 1100 HPLC Platform

Agilent 1100 Series system with different configurations comprises a vacuum degasser, isocratic pump, high-pressure binary pump, low-pressure quaternary pump, autosampler, thermostatted column compartment, variable wavelength detector and diode array detector. Key measurements are necessary to evaluate the performance of HPLC systems. Some characteristics are influenced by only one part of the system. For example, linearity, spectral resolution and detection limits are influenced mainly by the detector, delay volume and composition accuracy by the pump and carryover by the autosampler. In contrast, other characteristics such as baseline noise and precision of retention times and peak areas are influenced by the complete system. This note describes the following measurements:

I. Detector — baseline noise, drift, wander, linearity, spectral resolution, sensitivity.

II. Pump — composition accuracy, precision, ripple, precision of retention times, delay volume.

III. Column compartment — temperature stability.

IV. Autosampler — precision of peak areas, linearity, carry-over.

2.3. Measurements

Measurements were performed on two platforms: microPHAZIR^{TM} NIR handheld platform and Agilent 1100 High-Performance Liquid Chromatography (HPLC) platform. In the case of microPHAZIR^{TM} NIR handheld platform, measurements were performed and recorded on each of the six faces of each of the twenty blocks (representing twenty mixes), as depicted in Figure 7.

Upon manufacture and vacuum cast of the explosive mix, the energetic surface is binder rich, henceforth prior to performing measurements approximately 1/8” of the binder-rich surface of each cast block is peeled-off and removed from the surface, exposing the homogeneous material. As illustrated in Figure 8.

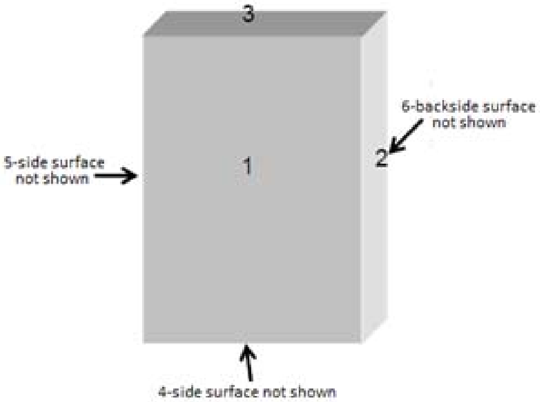


Figure 7. Cast PBX(AF)-108 Blocks Depicting Measured Surfaces

Figure 8. Peeled-Off Binder-Rich Layer

All measurements were recorded in the middle region of the surface of each block, as depicted in Figure 9 (right), in an area that was flat and free of any discoloration. Three independent NIR spectra were collected at each location (six total locations) per 600-gram of PBX(AF)-108 sample block, for a total of 18 readings per block.

In the case of benchtop Agilent 1100 High-Performance Liquid Chromatography (HPLC) platform, samples were prepared for analysis by extracting in triplicate with acetonitrile at a level of 10.0 mg/ml. Extracts were analyzed using an Agilent 1100 High-performance liquid chromatography (HPLC) instrument with an Octadecyl Silane (ODS) column and a diode-array detector. Samples were extracted from each of the six locations of each of the twenty mixes to evaluate the levels of E-702 anti-oxidant (4,4-methylenebis (2,6-di-tert-butyl-phenol)), Royal Demolition explosive (RDX) oxidizer (1,3,5- Trinitro-1,3,5-triazacyclohexane), and Isodecyl Pelargonate (IDP) plasticizer. The pint mixes were formulated with RDX that contained a small percentage of High Melting explosive (HMX). Thus the sum of HMX and RDX percentage by HPLC analysis represented the amount of RDX formulated in PBX (AF)-108 pint mixes.

Figure 9. Measurements Recorded in the Middle and Surrounding Regions of each Face of the Sample Block

2.4. Model Building

2.4.1. Data Collection

Collecting PBX (AF)-108 data using microPHAZIR^{TM} NIR handheld platform followed best practices recommendations of the platform manufacturer, as follows:

I. Obtain representative samples for the library.

A. Obtain realistic sample mixes that will form the library. These sample mixes should be representative of the PBX (AF)-108 material that will be identified. No selectivity is implied for materials until the library is built and validated.

B. Measure samples, as illustrated in Figures 5A and 5B. Perform measurements in triplicate.

C. Label all materials with name (Group ID or Method/Sample), and if appropriate reference value for PLS quantitative analysis.

D. Transfer all names into a ".csv" file, and then use this to populate "GroupID.csv" on the microPHAZIR^{TM} "Config" directory.

II. Obtain reference values.

A. For quantitative analysis, the full range of measurement shall be included in the library. Models only are considered robust over the data range actually referenced.

B. Obtain replicate samples for at least 3 points over the measurement range.

C. For realistic model building, at least 10 reference values over the measurement range shall be obtained. As the size of the range increases, so should the reference values collected. iv. Since samples may change over time, it is appropriate to collect the spectra from the same sample as the reference values are obtained from.

2.4.2. Spectra Generation

I. Pre-spectral collection.

A. Prior to collecting spectra ensure that self-test performance qualification (PQ) has been performed.

B. Ensure that group identifications (groupids) are transferred into GroupID.csv.

C. Also ensure that the GroupID name is the correct name for the material and is present on the Collect screen on the microPHAZIR^{TM}.

II. Spectral collection'

A. The minimum number of spectra collected for any library building is triplicate scans in 3 positions. Position the nose of microPHAZIR^{TM} firmly against the material to be measured, as depicted in Figure 9 (right), and take triplicate scans of the material without moving the sample. This will give information about instrument variability. Repeat twice.

B. Repeat measurements for each side of the block.

C. Repeat steps (A) and (B) for each mix.

2.4.3. Spectral Evaluation

I. Initial spectral evaluation.

A. Load the collected data into Method Generator

B. Ensure that there are no data which show absorbance (y-axis) past 3.

C. Observe if there are any noisy spectra, especially at high absorbance. If so, delete them. These usually arise if the trigger was pressed either without a sample in front or if sample is inadequate.

D. Highlight each group to make sure that all spectra look similar in the same group. Any obvious single outliers may be deleted. The best scenario is when the triplicate scans are right on top of each other, and there is little difference between positional scans. However, as long as the positional replicates appear similar and are close together, this is adequate. If one position is obviously off from the others, keep it, but watch to see if it affects the final results.

E. Delete any spectra where there was awareness of probable mistake in measurement. Do not delete scans just to make everything pretty. Deviations from the norm could be due to actual inherent sample differences and will need to become part of the model.

F. Reference values must be inputted at this time, using the Edit Y-value option.

G. Save the final edited data.

II. Method generation

A. Progress through the standard preprocessing options, and then evaluate the model using Spectral Match.

B. Adequate separation should be observed between samples. There should be a gap between the colors associated with one group and the next closest color of the nearest group.

C. Save the model if the model is acceptable.

D. Load the data files onto the microPHAZIR™ to test the model.

III. Method validation

A. Load a set of spectra into method generator (MG). For true method validation these should be unique spectra, not used in library building.

B. Select Model |Model validation. Browse to locate the application. Press OK

C. A panel will open with the validation results. It will be sorted by sample groups. Therefore it is very important that the GroupID of new spectra be identical to the GroupID of the library spectra. Otherwise a No ID label will be inserted.

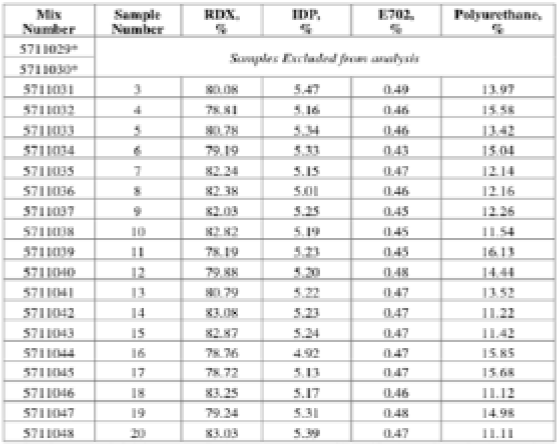
D. The results show number of mismatches, false positives/false negatives, and then the full results of the model validation for each material. It will list the top 3 matches returned and their associated correlation coefficients.

E. The results can be saved as a ".csv" file by selecting File | Save all

3. RESULTS AND DISCUSSION

Test sets collected from all twenty samples were analyzed using microPHAZIR™ NIR handheld platform. Upon reduction and analysis of the data, initial findings indicated near identical readings between those measured using microPHAZIR™ NIR handheld platform and those measured using benchtop HPLC, as listed in Tables 2 and 3 and compared to the initial added quantities of each constituent in Table 1. This finding concluded platform capability to measure oxidizer (RDX), stabilizer (Methylene di-tertiary butyl phenol), and plasticiser (IDP) contents on real-time basis with excellent precision.

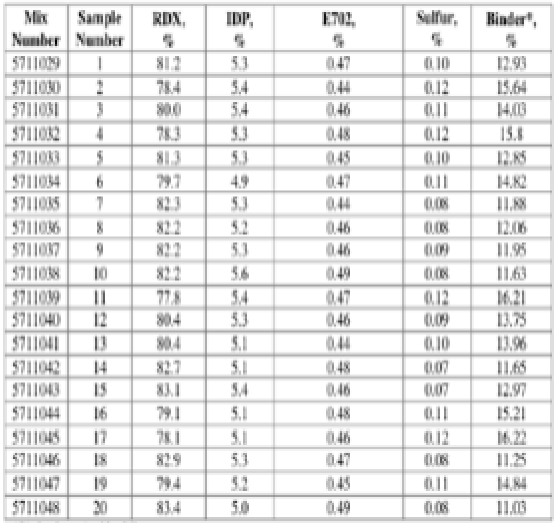
Table 2. MicroPHAZIR™ NIR Results of 20 DOE Mixes



Mix Number	Sample Number	RDX, %	IDP, %	E702, %	Polyurethane, %
5711029*	*Samples Excluded from analysis*				
5711030*					
5711031	3	80.08	5.47	0.49	13.97
5711032	4	78.81	5.16	0.46	15.58
5711033	5	80.78	5.34	0.46	13.42
5711034	6	79.19	5.33	0.43	15.04
5711035	7	82.24	5.15	0.47	12.14
5711036	8	82.38	5.01	0.46	12.16
5711037	9	82.03	5.25	0.45	12.26
5711038	10	82.82	5.19	0.45	11.54
5711039	11	78.19	5.23	0.45	16.13
5711040	12	79.88	5.20	0.48	14.44
5711041	13	80.79	5.22	0.47	13.52
5711042	14	83.08	5.23	0.47	11.22
5711043	15	82.87	5.24	0.47	11.42
5711044	16	78.76	4.92	0.47	15.85
5711045	17	78.72	5.13	0.47	15.68
5711046	18	83.25	5.17	0.46	11.12
5711047	19	79.24	5.31	0.48	14.98
5711048	20	83.03	5.39	0.47	11.11

*Samples excluded due to anomalies in measurements.

Table 3. Average Readings of Benchtop HPLC Results**



Mix Number	Sample Number	RDX, %	IDP, %	E702, %	Sulfur, %	Binder*, %
5711029	1	81.2	5.3	0.47	0.10	12.93
5711030	2	78.4	5.4	0.44	0.12	15.64
5711031	3	80.0	5.4	0.46	0.11	14.03
5711032	4	78.3	5.3	0.48	0.12	15.8
5711033	5	81.3	5.3	0.45	0.10	12.85
5711034	6	79.7	4.9	0.47	0.11	14.82
5711035	7	82.3	5.3	0.44	0.08	11.88
5711036	8	82.2	5.2	0.46	0.08	12.06
5711037	9	82.2	5.3	0.46	0.09	11.95
5711038	10	82.2	5.6	0.49	0.08	11.63
5711039	11	77.8	5.4	0.47	0.12	16.21
5711040	12	80.4	5.3	0.46	0.09	13.75
5711041	13	80.4	5.1	0.44	0.10	13.96
5711042	14	82.7	5.1	0.48	0.07	11.65
5711043	15	83.1	5.4	0.46	0.07	12.97
5711044	16	79.1	5.1	0.48	0.11	15.21
5711045	17	78.1	5.1	0.46	0.12	16.22
5711046	18	82.9	5.3	0.47	0.08	11.25
5711047	19	79.4	5.2	0.45	0.11	14.84
5711048	20	83.4	5.0	0.49	0.08	11.03

*Binder determined by difference.
**For each mix, recorded value is average of 3 readings.

As part of the developed algorithm, binder content would also show a reading, which is calculated based on the difference between the total measured primary constituents and 100 percent. Data produced on the microPHAZIR™ NIR handheld platform were plotted for the primary constituents of PBX (AF)-108. Data are depicted in Figure 10 for IDP plasticizer, Figure 11 for E-702 stabilizer/anti-oxidant, and in Figure 12 for RDX oxidizer, respectively.

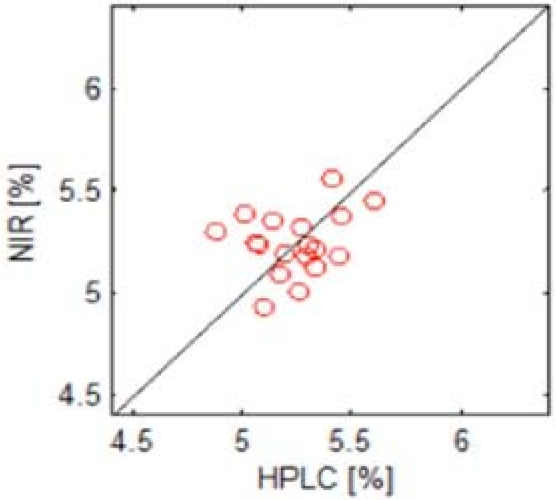


Figure 10. NIR vs. HPLC Concentration for IDP

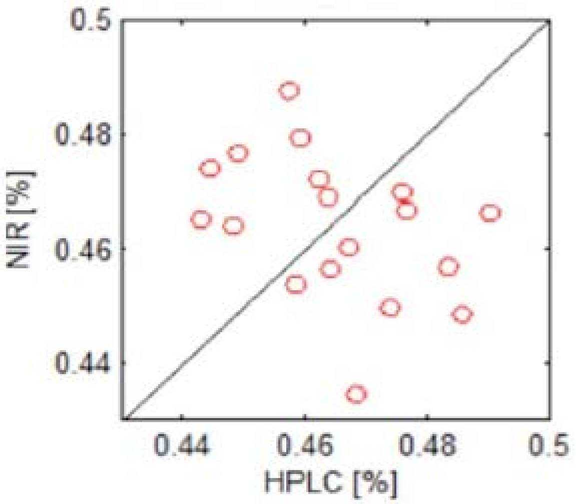


Figure 11. NIR vs. HPLC Concentration for E-702

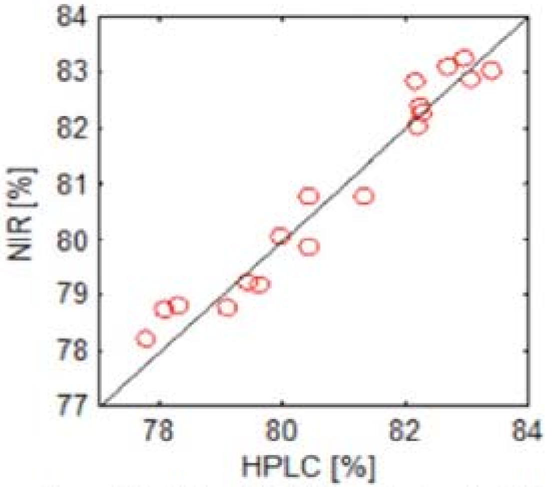


Figure 12. NIR vs. HPLC Concentration for RDX

Results indicate very good agreement for RDX, good agreement for IDP and acceptable agreement for E-702, between both sets of measurements in both handheld platform and benchtop platform, which further confirmed efficacy of using microPHAZIR™ NIR handheld platform as a tool for real-time non-destructive measurements of primary chemical constituents of PBX (AF)-108.

As noted earlier, microPHAZIR™ NIR handheld platform did not directly measure binder content. The algorithm was developed to calculate a value for the binder, which is based on the difference between the sum of the primary ingredients and 100%. Results which were measured using microPHAZIR™ NIR handheld platform are summarized in Table 2 in units of percent by weight.

Results from the HPLC analysis are summarized in Table 3. All measurements indicated close readings between the actual formula of the twenty explosive mixes and HPLC readings, with the exception of readings which were measured for percent Isodecyl Pelargonate (IDP) plasticizer. This is a common trend often observed with plasticizer-containing composite energetics (explosives, boosters, and solid rocket propellants), and was determined to be a result of diffusion (migration) and eventually loss of the plasticizer.

A common limitation with plasticized PBXs is that of plasticizer migration over time and at elevated temperatures during their service and even in the early stages of manufacture, during cure of the explosive charge. Plasticization is one of two mechanisms: internal plasticization, in which plasticizer molecules are attached to the polymer covalently as part of the polymer chain. And external, in which DOA is homogenized and absorbed by the polymer and oxidizer ingredients (as in PBXN-11) and other polymer-based explosives or rocket propellants. In internal plasticization, migration of plasticizers is absent. Plasticizer migration is more a concern when external plasticization occurs.

In almost all plasticizers, loss occurs primarily due to their volatility, which comprises dual transport phenomena. The first is diffusion, which occurs when DOA moves through the explosive matrix from the inner core to the surface, and that is largely influenced by temperature coupled with viscosity and molecular weight of the plasticizer. The second is evaporation, which is greatly influenced by temperature and vapour pressure of the plasticizer.

In the case of PBX (AF)-108 mixes, which were vacuum cast and subjected to high temperature cure, plasticizer migration was present, and could be noticed in coefficient of variation readings, depicted in Figure 13. For each mix, six faces (locations) of the rectangular block (Figure 4) were measured in triplicate, using HPLC bench top instrument. Coefficient of variation was stable (under or around 5%) with the exception of mixes 1, 16, 17, 18, 19, and 20. This variation is more an indication of IDP migration (diffusion) throughout the explosive matrix.

Since coefficient of variation (CV) is a statistical tool generally used to express the standard deviation as a percentage of what is being measured relative to the sample or population mean, this variation is expressed as a percent of the mean. CV is determined by the relationship of "equation (1)":

$$CV = (SD/\bar{X}) \times 100 \qquad (1)$$

Where $\bar{X}$ and SD represent the sample mean and the sample standard deviation, respectively.

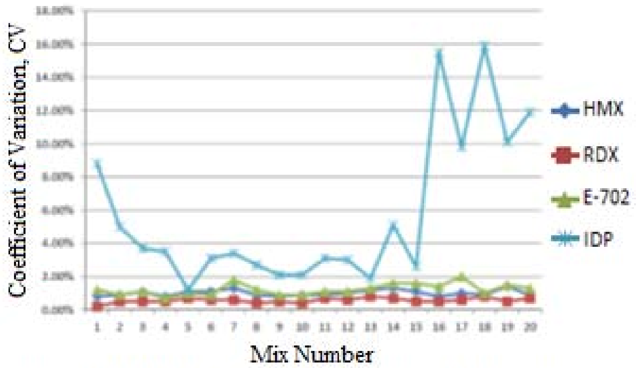


Figure 13. HPLC Coefficient of Variation vs. Mix Number

CV is a reliable reading when standard deviation (SD) rises proportionally with concentration. For example, in a replicate experiment data could indicate a value of 4 for standard deviation at a concentration of 100 units. This value could indicate a reading of 8 for standard deviation but this time at a concentration of 200 units. In both cases, coefficient of variation is the same, i.e. 4.0%. Coefficient of variation in such case is more useful than standard deviation for describing method performance at concentrations in between. In some tests however, standard deviation may be constant over the analytical range. Generally speaking, coefficient of variation CV provides a general "feeling" about the performance of a method. CVs of 5% or less generally give us a feeling of good method performance, whereas CVs of 10% and higher sound bad. However, the mean value becomes important before judging a CV. At very low concentrations, the CV may be high and at high concentrations the CV may be low. For example, a test with an SD of 0.1 mg/dL at a mean value of 0.5 mg/dL has a CV of 20%, whereas an SD of 1.0 mg/dL at a concentration of 20 mg/dL corresponds to a CV of 5.0%.

In Figure 14 the average standard deviation is plotted against the mix number. In the graph, standard deviation for RDX,/HMX, and E-702 is markedly low, and within specifications of +/- 1.7% and 0.01%, respectively (RDX/HMX = 82.0 +/- 1.7%; E-702 = 0.50 +/- 0.01%; IDP = 5.3 +/- 0.10%). In the case of RDX/HMX maximum measured standard deviation value is 0.8%, significantly below the maximum allowable specification and well within acceptable range. Similarly, standard deviation for E-702 is just 0.01 and within its specification limit of +/- 0.01%. In the case of the plasticiser (IDP), standard deviation is relatively higher than would be expected for most composite explosives and propellants with high solids content. This is attributed to (i) migration of the plasticiser within the explosive matrix until steady state is attained (when the explosive is fully annealed); (ii) as depicted in Figure 8, approximately 1/8” of the binder-rich surface of each cast block was peeled-off and removed from the surface of each sample block, henceforth exposing the homogeneous surface of the explosive. In a freshly manufactured mix, this binder-rich layer often contains higher amounts of plasticiser than fully annealed mixes. Because this process was performed by hand, rather than with a precision tool, it would be reasonable to expect higher variability in liquid plasticiser content between mixes, and therefore higher standard deviation. Lessons learned will be instituted in future work by (i) allowing mixes to sit for a period of 6-8 weeks, to allow for the plasticiser component to attain steady state within the matrix; and (ii) a high precision tool will be used in removing the binder-rich layer, so that consistency between all mixes is exercised.

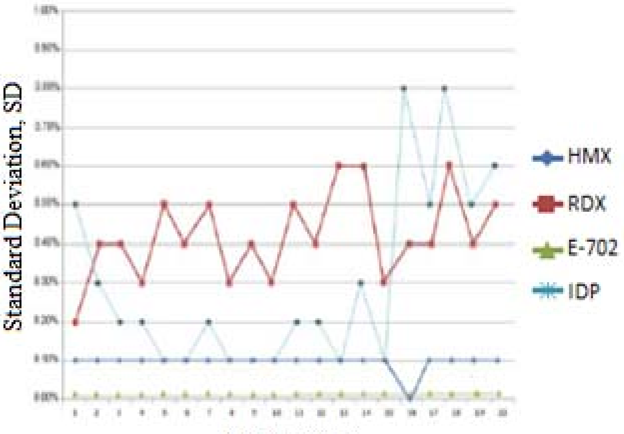


Figure 14. HPLC Standard Deviation vs. Mix Number

In the case of microPHAZIR^{TM}, standard deviation values are higher than HPLC values. This is due to the fact that NIR penetrates as high as 5 mm under the surface, whereas in the case of HPLC, a much larger sample is extracted from several locations and deeper than 5 mm. In both techniques (HPLC vs. microPHAZIR^{TM}) and as summarized in Tables 2 and 3, measured values of primary constituents of each the twenty mixes, correlated quite well.

Generally speaking, it would be reasonable to expect plasticizers in composite polymeric mixes to take longer to reach steady state levels throughout the matrix. These levels however tend to vary from one plasticizer to another, depending on molecular weight, vapour pressure, and viscosity of a plasticizer.

4. CONCLUSION

The D-optimal design of experiment (DOE) was successful in developing an algorithm for microPHAZIR^{TM} NIR handheld platform for use in quantitative determination of primary chemical constituents of PBX (AF)-108. Therefore, use of microPHAZIR^{TM} NIR handheld platform for real-time non-destructive quantification of constituents of plastic bonded explosives was determined to be a valid test method without generating chemical waste and/or residue. Datasets from both microPHAZIR™ NIR handheld platform and Agilent 1100 High-pressure liquid chromatography (HPLC) platform were close to each other and representative of the constituents of PBX (AF)-108 explosive. In the case of the microPHAZIR™ NIR handheld platform, the dataset indicates more stability in variance across the full datasets however observations of measurements collected using Agilent 1100 High-pressure liquid chromatography (HPLC) platform indicates sample inhomogeneity as a result of plasticizer migration. In the case of microPHAZIR™ NIR handheld platform the following observations may be stated:

I. Averaging data improves results.
II. Excellent ability to quantify HMX+RDX concentration 3. Good ability to quantify IDP plasticizer concentration and migration trends
III. Migration trends of IDP plasticizer requires multiple measurement points to improve reliability and confidence levels
IV. Good ability to quantify E-702 stabilizer concentration.
V. Repeat measurements of E-702 stabilizer content will improve reliability and confidence levels

Some drawback associated with microPHAZIR™ NIR handheld platform may be summarized as follows:

I. The platform has not yet been validated to offer reliable measurement of components, which exist in trace concentrations (below 0.1%). More testing will be deemed necessary in future DOEs.
II. The platform periodically undergoes automatic calibration, during measurements, which is a necessary step, but can be frustrating at times.
III. For measuring chemical constituents of other explosives, a new DOE will be required for each explosive formula and an associated algorithm must be developed.
IV. Use of microPHAZIR™ NIR handheld platform for measuring chemical constituents of rocket motor solid rocket propellants will require retrofitting of an optical fiber wand to the machine. The wand will enable the user to measure chemical constituents inside the solid rocket propellant bore.
V. Because microPHAZIR™ NIR handheld platform is a handheld instrument, it requires the use of a rechargeable lithium ion battery, and therefore a spare battery and a battery charger are important components of the platform and are supplied by the manufacturer, Thermo Fisher Scientific.

NOMENCLATURE

AF	Air Force
AOP	Allied Ordnance Publication
ATK	Alliant Techsystems
LS	Launch Systems
BTCA	Breakdown, Test and Criticality Analysis
CAD	Cartridge-Actuated Device
CT	Computed Tomography
CV	Coefficient of Variance
DOA	Dioctyl Adipate
DoD	Department of Defense
DSC	Differential Scanning Calorimetry
DSTO	Defence Science and Technology Organization
E-702	4,4-methylenebis (2,6-di-tert-butyl-phenol)
EED	Electro-Explosive Device
ESD	Electrostatic Discharge
HMX	High Melting eXplosive
HOPS	Hazardous Operation Standards
HPLC	High-Performance Liquid Chromatography
IDP	Isodecyl Pelargonate
MoD	Ministry of Defence
NATO	North Atlantic Treaty Organization
NDE	Non-Destructive Evaluation
NDT	Non-Destructive Testing
NIR	Near-Infrared
OBEC	Operating Building Electrical Classification Board
ODS	Octadecyl Silane
OSCB	Operations Safety Control Board
PAD	Propellant-Actuated Device
PBX	Plastic-Bonded Explosive
PHM	Prognostics and Health Management

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