

Glow Discharge Mass Spectrometry Analysis of LX-17 and PBX-9502 High Explosive Samples

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December 16, 2002

U.S. Department of Energy

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This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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Glow discharge mass spectrometry analysis of LX-17 and PBX-9502 high explosive samples

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Abstract. We present the analysis of several LX-17 and PBX-9502 samples using the glow discharge mass spectrometer to measure both the main constituents of the high explosive as well as any trace materials that may be present.

Introduction

As part of the Campaign 4 effort in A Division we have done an analysis of several high explosives that are used in the current nuclear stockpile. In particular we have looked at samples of LX-17 and PBX-9502. The analysis was done using the glow discharge mass spectrometer that is currently located in B132N and operated by Mark Lane of the Chemistry and Material Science (CMS) Directorate. George Overturf from CMS obtained small samples of high explosive for the measurements. From the analysis we wanted to verify the actual atomic composition of the high explosive, see how that compared with the nominal composition, and understand whether any significant impurities existed in the samples.

Glow Discharge Mass Spectrometry

The Glow Discharge Mass Spectrometry (GDMS) is an extremely powerful technique for analyzing all the trace elemental constituents of many materials. GDMS can also be used for elemental depth profile analysis, providing elemental data in micron divisions by sputtering into the surface. This is useful in determining coating thickness and if a contaminant is surface related or a homogenous problem. The instrument used for this analysis is a VG9000, manufactured by VG Elemental, United Kingdom. Ref. 1 has a nice description of the GDMS technique.

One advantage of the GDMS is that the samples are analyzed in solid form and so do not require the dissolution methods used with other techniques such as Inductively Coupled Plasma-

Mass Spectrometry. GDMS does not suffer from the extreme matrix dependence of most other elemental analysis techniques, minimizing the need for matrix matching standards.

The principle of the GDMS technique is to atomize the solid sample by sputtering in a low-pressure DC plasma. The sputtered atoms are then ionized in the plasma and extracted into the mass analyzer for separation and detection.

The plasma, or glow discharge, used for sampling is contained in a discharge cell made from pure tantalum with ultra high purity argon (99.9999%) used as the discharge gas. The pressure within the cell is approximately 1 torr. A potential of 1 kV is applied between the cell body, which serves as the anode, and the sample, which serves as the cathode, in order to establish a glow discharge. Typical currents are 1 milliamp. Positive argon ions formed in the glow discharge are accelerated toward the sample. After impacting the surface of the sample, neutral particles and positive ions are released. The positive ions are attracted back to the sample surface and redeposit there. The sputtered neutral particles diffuse across the plasma "dark space" surrounding the cathode towards the anode region of the plasma and are then ionized through interaction with the meta-stable argon atoms of the plasma, primarily forming singly charged ions.

Penning ionization is the primary mechanism responsible for the ionization of the sputtered neutral sample atoms. Meta-stable argon atoms collide with sample atoms, transferring their energy to the sample atoms. Meta-stable argon atoms possess energies of 11.55 and 11.72 eV, sufficient energy to ionize the bulk of the elements in the Periodic Table, without ionizing the atmospheric impurities in the discharge gas. Electron impact ionization will ionize some of the sample materials with higher ionization potential such as O, F, and Cl.

An important feature of the DC ion source in the GDMS is that the processes of atomizing and ionizing the sample are separated. Therefore, ion yields are mostly based upon the ionization potentials of the elements and the plasma conditions and not on the sample matrix. This insensitivity to the matrix results in the range of sensitivity factors for most elements being less than one order of magnitude over a wide variety of matrices. Other methods such as thermal ionization mass spectrometry (TIMS) and laser ion-desorption mass spectrometry (LIMS) have the atomization and ionization processes occurring concurrently. This results in severe matrix effects, because the condition of atom ionization is directly tied to the nature of the matrix that surrounds the atom at the time of ionization.

After being formed, the ions are extracted out of the plasma cell by a combination of gas flow and electrical potential and are accelerated through a series of electronic optics into the mass analyzer. The extraction-acceleration voltage is about 8 kV. The ions are separated by their mass to charge ratio in the high-resolution mass analyzer, which is a double focusing unit of reverse Nier-Johnson geometry. The working mass resolution was 10,000 with 95% transmission of the beam. This is defined as the mass of interest divided by the change in mass that can be resolved. This enables one to resolve different isotopic species at ultra-trace levels that are separated by only 0.001 amu at 10 amu and 0.01 amu at 100 amu. This is vital for providing meaningful analyses at or below the 10 to 50 parts per million (ppm) by weight level. The result is that the GDMS can detect any element in the periodic table with masses between 1 and 260 AMU and at concentrations down to the 0.1 ppm.

The detection system for the GDMS is comprised of two detectors, a Faraday Cup and a Daly system with photo-multiplier. The Faraday Cup is used to detect ion signals from 0.1 picoamps up to 1 milliamp. This covers the major element constituents as well as those down to around 1000 ppm. The Daly detector can measure signals up to a million times weaker. The Daly detector uses a pulse counting system that can detect ion currents lower than one ion per second. The Daly detector is used to measure ion currents between 0.2 picoamps and 10^{-7} picoamps. With matrix currents in the range of 1 nanoamp, the detection system has a dynamic range from the matrix level to below the ppb level.

Ideally the samples to be analyzed by the GDMS should be electrically conductive. However, non-conductive samples can be analyzed through the use of "binder" materials. The non-conductive sample is combined with an appropriate conductive material in such a way that the resulting sample provides enough conductivity to establish the glow discharge yet still obtain the maximum signal from the sample itself. Since the high explosive used in these experiments is non-conductive, the 10 mg sample of high explosive was wrapped in an ultra high purity indium binder to make the conductive target. The indium used is from a 99.9999% pure, polycrystalline ingot, purchased from Alfa Aesar, Ward Hill, MA. The stock number is 10618, lot A19I30, and has a certificate of analysis. The indium impurities are measured by the GDMS and the atom counts are subtracted during the HE sample impurity calculations. No significant impurities were measured in the In binder.

Calibration

In GDMS the calibration curves are linear over a wide range of concentrations, removing the need for different sets of standards for low and high-alloy materials. To calculate the calibration factors for the elements, the instrument data (counts or ion beam ratio) is plotted against the known concentration values on an X, Y plot. From the gradient of the line, the calibration factor, or more accurately the relative sensitivity factor (RSF) for each element is obtained. The instrument data is multiplied by these factors to give calibrated results. The VG9000 GDMS at LLNL has been calibrated with NIST standards from mostly steel alloy standards. Some elemental RSF's have been cross-referenced and verified from glass matrixes (NIF), molybdenum matrixes (NAI), and uranium matrixes (AVLIS). Additionally the carbon, nitrogen and oxygen RSF's, have been verified against the reported values from LECO standards in steel and uranium matrixes.

In the absence of standards with the same major element matrix as the unknown sample, semi-quantitative data is quite reliable because of the minimal matrix effects from ionization. This is done by transferring known calibrated RSF's from matrix to matrix. Since the majority of certified metal standards contain iron and iron is the most abundant element in the periodic table, most calibration experiments set iron at an RSF of one. All other elemental RSF's are first calculated from the iron matrix and establish an RSF ratio relative to iron. For example, to transfer calibrated RSF's from a steel matrix to a copper matrix, with copper having an RSF of three, the copper is set to an RSF of one and all other elemental RSF's are divided by three. Reported studies show the stability of this technique to be 10% RSD.

Typically we expect the GDMS quantitative accuracy to be 20% on average at ppb levels, 5 to 10% on average at ppm levels, and 0.5 to 3% on average at the percent levels.

High Explosive Samples

For this analysis we obtained several samples of LX-17 and PBX-9502 that are used in the nuclear stockpile. The actual samples consisted of 10 milligram samples of molding powder from actual batches used in the stockpile.

The nominal LX-17 composition is 92.5% TATB by weight combined with 7.5% Kel-F 800 binder. TATB is $C_6H_6N_6O_6$ -1,3,5,-trinitrobenzene. The Kel-F 800 is poly (chloro-trifluoro-ethylene/vinylidene fluoride) and is a co-polymer used as a binder in some insensitive high explosives. The nominal composition of Kel-F 800 is $(C_2F_3Cl)_3 (C_2H_2F_2)$. The nominal LX-17

density is 1.9 grams per cm³. The nominal atomic fractions for the LX-17 are 0.241969 H, 0.254016 C, 0.237953 N, 0.237953 O, 0.022086 F, and 0.006023 Cl. Samples were taken from batches G146 851-005 and G146 851-008. These batches were made using the wet amination process. The wet process reduces the amount of chlorine by-product that can become occluded into the TATB.

For PBX-9502, the nominal composition is 95% TATB by weight combined with 5% Kel-F 800 binder. The nominal atomic fraction for the PBX-9502 is 0.244697 H, 0.252651 C, 0.242046 N, 0.242046 O, 0.014583 F, and 0.003977 Cl. Samples were taken from batch C-382 891-007. This batch was produced by blending reclaimed PBX-9502 with new production. The PBX-9502 uses the dry amination process.

One concern with using small samples from the molding powder is that they do not contain contamination that could happen in the process of actually molding the final parts. Also any local contamination that occurred in producing the molding powder would be missed.

Measurements

As mentioned above the high explosive samples were wrapped in a high purity indium binder that was conductive to create the actual sample that was ionized. Tables 1 – 4 present the analysis of the samples. Table 5 shows the 66 isotopes from Li7 to U238 that the GDMS tried to measure but did not observe any signal at the 0.1 ppm by weight level. Looking at Table 1 for the LX-17 sample we show the fractional weight in ppm, the standard error in each measurement, and the % standard error. The weight fractions are converted into atomic mole fractions and then compared with the nominal atomic fraction composition that is expected for the sample. The last column gives the percentage difference between the measured and nominal atomic fraction. There are small differences, generally less than 4%, between the nominal and measured composition for the normal constituents of the LX-17. While some of these differences are greater than the standard error they probably reflect small differences in the amount of Kel-F 800 binder used or the uniformity of the mixing process for the TATB and binder. The largest impurity is Fe, which is less than 1 ppm.

The analysis of the second LX-17 sample, shown in Table 2, is very similar to that of Table 1. The differences between nominal and measured constituents are less than 4%. The Fe impurity is larger, but still only 3 ppm.

Turning to PBX-9502, Tables 3 and 4 show the analysis of two samples from the same batch. Looking at the normal constituents of the high explosive, the F content is measured to be 11% larger than expected and is larger than the measurement errors. Since the F and Cl are only in the binder, it suggests that the percentage of binder used may be larger than nominal. Given that the F is 11% high while the Cl is only 3% high suggests that the relative ratio of chlorotrifluoro-ethylene to vinylidene fluoride in the binder may be different than nominal. Keep in mind that the measurement errors were large in Table 3 for the F and Cl but significantly reduced in the second measurement shown in Table 4. The biggest surprise is the large amount of Fe impurity, 185 ppm, observed in the first PBX-9502 sample, shown in Table 3. The second sample from the same batch observes only 3 ppm of Fe. There is always the potential for contaminating the sample in the preparation process. In spite of the large Fe impurities in Table 3, the Cr and Ni impurities are less than 1 ppm, which suggests that any stainless instruments used in the preparation would not likely be the source of Fe since stainless typically contains more than 10% Cr and half as much Ni.

Conclusions

Using the GDMS we have measured the composition of two high explosive samples each of LX-17 and PBX-9502 taken from batches of molding powder used to make parts in the nuclear stockpile. The analysis of the high explosives shows compositions generally within 4% of nominal values. For the PBX samples, the F content is about 11% high. The impurity levels are very low, with Fe being the only significant impurity above 1 ppm. In one sample of LX-17 and one of PBX-9502 the Fe is measured at 3 ppm. However the other sample of PBX-9502 has the Fe impurity measured at 185 ppm.

Acknowledgements

This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

References

[1] See web page from Shiva Technologies at <http://www.shivatec.com/new/gdmsdesc.php4> for a good description of GDMS technique.

Table 1. Elemental analysis of LX-17 sample from batch G146 851-005

Element	Weight (ppm)	Std Error (ppm)	% Std error	Atomic mole fraction measured	Nominal atomic fraction	Difference from nominal (%)
H 1	21,679	1,237	5.7	0.238950	0.241969	-1.2
C 12	278,298	9,374	3.4	0.257420	0.254016	+1.3
N 14	297,873	313	0.1	0.236269	0.237953	-0.7
O 16	343,229	8,952	2.6	0.238337	0.237953	+0.2
F 19	38,900	788	2.0	0.022748	0.022086	+3.0
Cl 35	20,017	1,393	7.0	0.006273	0.006023	+4.2
Cr 52	0.0913	0.0474	52	1.95e-8		
Fe 56	0.8502	0.3555	42	1.69e-7		
Ni 60	0.1868	0.1104	59	3.54e-8		
Cu 63	0.2027	0.1451	72	3.54e-8		
Mo 98	0.0900	0.0314	35	1.04e-8		

Table 2. Elemental analysis of LX-17 sample from batch C146 851-008

Element	Weight (ppm)	Std Error (ppm)	% Std error	Atomic mole fraction measured	Nominal atomic fraction	Difference from nominal (%)
H 1	23,083	636	2.8	0.251188	0.241969	+3.8
C 12	267,780	1,789	0.7	0.244532	0.254016	-3.7
N 14	305,499	767	0.3	0.239227	0.237953	+0.5
O 16	345,193	881	0.3	0.236644	0.237953	-0.6
F 19	38,545	101	0.3	0.022253	0.022086	+0.8
Cl 35	19,897	112	0.6	0.006156	0.006023	+2.2
Cr 52	0.1934	0.0061	3.2	4.08e-8		
Fe 56	3.1810	0.0292	0.9	6.25e-7		
Ni 60	0.1718	0.0024	1.4	3.21e-8		
Cu 63						
Mo 98						

Table 3. Elemental analysis of PBX-9502 sample from batch C-382 891-007.

Element	Weight (ppm)	Std Error (ppm)	% Std error	Atomic mole fraction measured	Nominal atomic fraction	Difference from nominal (%)
H 1	22,675	2,021	8.9	0.246031	0.244697	+0.5
C 12	283,501	7,417	2.6	0.258139	0.252651	+2.2
N 14	305,166	2,069	0.7	0.238275	0.242046	-1.6
O 16	346,979	4,304	1.2	0.237180	0.242046	-2.0
F 19	28,189	2,089	7.4	0.016227	0.014583	+11.1
Cl 35	13,297	1,117	8.4	0.004102	0.003977	+3.1
Cr 52	0.2081	0.0464	22.3	4.38e-8		
Fe 56	185.32	5.289	2.9	3.63e-5		
Ni 60	0.3814	0.0848	22.2	7.11e-8		
Cu 63	0.7229	0.1328	18.4	1.24e-7		
Mo 98	0.7573	0.1293	17.1	8.63e-8		

Table 4. Elemental analysis of PBX-9502 sample from batch C-382 891-007. This is second sample from same batch as Table 3.

Element	Weight (ppm)	Std Error (ppm)	% Std error	Atomic mole fraction measured	Nominal atomic fraction	Difference from nominal (%)
H 1	22,721	1,088	4.8	0.246359	0.244697	+0.7
C 12	283,599	5,278	1.9	0.258052	0.252651	+2.1
N 14	306,444	9,019	2.9	0.239110	0.242046	-1.2
O 16	345,593	4,400	1.3	0.236071	0.242046	-2.5
F 19	28,253	1,165	4.1	0.016253	0.014583	+11.1
Cl 35	13,364	240	1.8	0.004120	0.003977	+3.6
Cr 52						
Fe 56	3.25	0.05	1.6	6.36e-7		
Ni 60						
Cu 63						
Mo 98						

Table 5. The analysis looked for the following elements and detected no observable signal at the 0.1 ppm level for any of these isotopes in any of the four samples tested. The symbol and atomic mass associated with each element is given below.

Li 7	Be 9	B 11	Na 23	Mg 24	Al 27	Si 28
P 31	S 32	K 39	Ca 44	Sc 45	Ti 47	V 51
Mn 55	Co 59	Zn 66	Ga 69	Ge 73	As 75	Se 77
Br 79	Rb 87	Sr 88	Y 89	Zr 91	Nb 93	Ru 102
Rh 103	Pd 105	Ag 109	Cd 111	Sn 119	Sb 121	I 127
Te 128	Cs 133	Ba 138	La 139	Ce 140	Pr 141	Nd 146
Sm 147	Eu 151	Gd 156	Tb 159	Dy 163	Ho 165	Er 167
Tm 169	Yb 172	Lu 175	Hf 177	Ta 181	W 183	Re 185
Os 188	Ir 191	Au 197	Pt 198	Hg 202	Tl 205	Pb 207
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