Investigating Guns, Bombs, and Rockets: A New NIST Reference Material for Smokeless Powder Measurements

by William MacCrehan and Mary Bedner

Smokeless powder is the primary propellant used in civilian ammunition and military munitions with applications ranging from handguns to howitzers. Technically, smokeless powder does not explode, but is a rapidly reacting solid and is designated a low explosive. In addition to its main ingredient, nitrocellulose (guncotton), smokeless powder contains several common additives that contribute specific propellant and stabilizing properties to a powder. Nitroglycerin is a common propellant additive, particularly for small arms ammunition. Stabilizer compounds are typically aromatic amines, with diphenylamine and ethyl centralite (*N*, *N*'-diethyl, *N*, *N*'-diphenylurea) being common additives in the United States. Manufacturers control the additive content as well as the size and shape of the powder to achieve the target combustion and safety requirements for each application.

The chemical analysis of smokeless powder provides vital information. Perhaps most importantly, powder manufacturers and military laboratories quantitatively determine the concentrations of available stabilizer(s). Stabilizers react with the nitrogen oxides formed during the aging of the nitrocellulose, preventing a buildup of these destabilizing products. The proportion of the available unreacted stabilizer(s) relative to nitration products provides a good measure of munitions stability.[1] Military munitions dating to WWII are still safely in service, due in part to periodic evaluations of propellant stability by U.S. military laboratories, some of which make over 5000 compositional determinations every year. Evaluation of the remaining residual stabilizer content is crucial to ensure safe transportation of munitions to and from such extreme environments as that around the Persian Gulf.[1]

Evaluation of the composition of smokeless powder and its postcombustion residues is also used in the forensic investigation of explosives and firearms crime. Smokeless powder may be purchased in amounts up to 23 kg (50 lb) without a permit for the reloading of ammunition. Being readily available, it is frequently used as the explosive ingredient in improvised explosives devices (IEDs) such as pipe bombs (*Figure 1*). Following the explosion of an IED, forensic investigators carefully examine the debris from the crime scene to gather evidence about the nature of the device and to identify its fabrication components. Combustion of the low-explosive powder causes

Figure 1 Pipe commonly used in IEDs and "exploded view" fragments of a pipe bomb generated by the FBI laboratory using smokeless powder.

the pipe container to fail, generating the explosive force and shrapnel fragments. However, the burning of the powder is often incomplete, leaving particles that may be recovered and evaluated for their morphology and chemical composition.[2,3] In many cases, data collected on "questioned" residues recovered in evidence are compared to data contained in a database of smokeless powder measurements maintained by such laboratories as the Bureau of Alcohol, Tobacco, Firearms, and Explosives.[2] Although "brand" identification may be complicated by a number of factors,[4,5] it is often possible to categorize a powder sufficiently to provide investigators with a short list of potential powder sources. Of course, if a smokeless powder sample is recovered from a suspect's possession, direct comparisons of chemical composition and morphology can be made. Research has shown that smokeless powder residues may also be recovered by swabbing IED shrapnel for comparison of the composition of the residue and unfired powder.[6]

Another potential application of smokeless powder measurements is in the determination of firearms discharge. When a gun is fired, incompletely combusted particles of smokeless powder are expelled from the breech and muzzle of the weapon. These organic gunshot residue (OGSR)

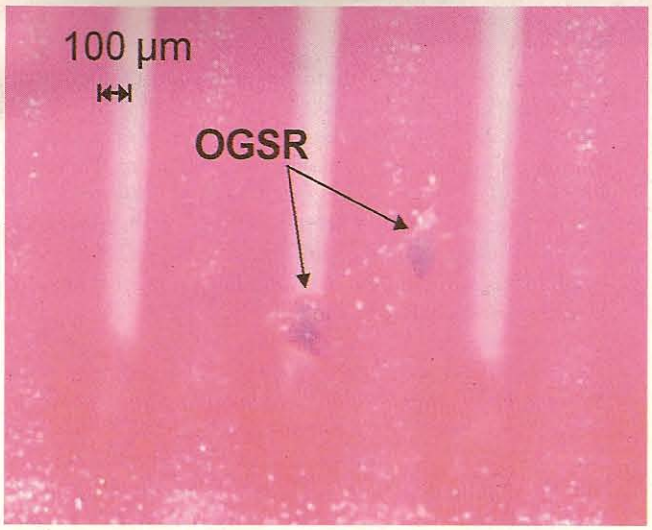

Figure 2 OGSR particles collected from handgun shooter's hair with a fine-toothed comb.

particles may be collected from shooters by such techniques as tape lifting from the hands[7] and fine-toothed combing of the hair (see *Figure 2*).[8] Not only can qualitative detection of the "characteristic" OGSR components confirm the use of firearms, quantitative analysis can often be used to associate the composition of residues and unfired powders.[9,10]

It is clear that the accurate determination of smokeless powder composition has several key forensic and military applications. To determine the state of smokeless powder measurements, NIST (Gaithersburg, MD) conducted an interlaboratory investigation of the determination of the chemical composition of smokeless powder. Two powder samples were characterized by NIST and sent to 19 participant laboratories. Participants included state, local, regional, U.S. national, and international forensic laboratories as well as three U.S. military ordnance laboratories. Examining the qualitative results, all laboratories correctly identified the two powders as "double base," i.e., containing nitroglycerin.[11] Most laboratories also correctly identified the predominant stabilizer, but there were a number of discrepancies between laboratories in the detection of trace stabilizers. When the quantitative measurements were compared, all of the measurements (except for one outlier) of the four key additives (nitroglycerin [NG], N-nitrosodiphenylamine [NnDPA], diphenylamine [DPA], and ethyl centralite [EC]) were in agreement with the consensus mean value within an uncertainty of about 10%.[12] However, when the self-reported uncertainties were considered, the results generally did not encompass the consensus mean.

To help ensure the quality of smokeless powder measurements, NIST is providing RM 8107 Additives in Smokeless Powder (see www.nist.gov/srm) (*Figure 3*). This material was prepared from a single manufactured batch of powder. The additive composition was determined using both micellar capillary electrophoresis and liquid chromatography, with final reference values assigned by LC. *Table 1* presents the reference values and associated uncertainties for the four characteristic additives.

Figure 3 NIST RM 8107 Additives in Smokeless Powder.

Military laboratories making quantitative determination of the stabilizers in propellant powders can use this new reference material (RM) to evaluate the accuracy of their mean value determinations and to evaluate the uncertainty of their measurements. It may also be useful to run the reference material as a periodic "control" to ensure the continued fidelity of the measurements.

On the forensic side of smokeless powder analysis, many laboratories demonstrate the quality of their measurements through voluntary accreditation from the American Society of Crime Laboratory Directors/Laboratory Accreditation Board (ASCLD/LAB). Accreditation is achieved by such activities as analytical method validation, careful record-keeping, proficiency testing, and peer review (see www.ascld-lab.org). Until the release of RM 8107, there were no NIST reference materials that addressed the measurement of explosives. The RM can be used in a number of ways to help forensic laboratories with quality assurance of smokeless powder measurements. Correct identification of the characteristic additives can be used to validate existing and new analytical protocols. The RM may be used as a proficiency test sample to evaluate the performance of laboratory personnel and for the training of new investigators. Since results are often compared between laboratories, the material can be used to confirm the comparability of measurements.

RM 8107 is the first NIST reference material available for explosives-type measurements. NIST is currently developing two additional reference materials for the determination of high-explosive components such as those in plastic and military explosives. One material is focused primarily on the calibration of trace explosives detection equipment, such as the type used in airport security. The other material is aimed at measurements associated with the remediation of the soil at contaminated munitions sites.

continued

Table 1 Assigned additive composition values for RM 8107

	NG	DPA	NnDPA	EC
Mean concentration (mg/g)	129.1	7.80	3.05	36.4
Expanded uncertainty (mg/g)	2.1	0.18	0.09	1.3
Relative expanded uncertainty (%)	1.6	2.3	3.0	3.6

References

1. Stine, G.Y. An investigation into propellant stability. *Anal. Chem.* **1991**, *63*(8), 475A–8A.
2. Selavka, C.M.; Strobel, R.A.; Tontarski, R.E. The systematic identification of smokeless powders: an update. In: Mannheim F.R.G. Proceedings of the International Symposium on Analysis and Detection of Explosives, Jul 10–13, 1989. Fraunhofer-Institut for Chemische Technologie, 1989, 3-1–3-27.
3. Wallace, C.L.; Midkiff, Jr., C.R. Smokeless powder characterization: an investigative tool in pipe bombings. In Yinon, J., ed. Advances in Analysis and Detection of Explosives. Kluwer Academic Publishers: The Netherlands, 1993; pp 29–39.
4. Kelly, R.L.; Mothershead, R.F. Smokeless powder analysis: interpretations and complications. In Cumming, A., ed. Proceedings of the 7th International Symposium on the Analysis and Detection of Explosives, QinetiQ. Edinburgh, Scotland, 2002, 334–46.
5. National Research Council. Black and smokeless powders: technologies for finding bombs and the bomb makers. National Academies Press: Washington, DC, 1999.
6. Smith, K.D.; McCord, B.R.; MacCrehan, W.A.; Mount, K.; Rowe, W.F. Detection of smokeless powder residue on pipe bombs by micellar electrokinetic capillary electrophoresis. *J. Forensic Sci.* **1999**, *44*, 789–94.
7. Northrop, D.M. Gunshot residue analysis by micellar electrokinetic capillary electrophoresis: assessment for application to casework. Part II. *J. Forensic Sci.* **2000**, *46*, 560–72.
8. MacCrehan, W.A.; Layman, M.J.; Secl, J.D. Hair combing to collect organic gunshot residue. *Forensic Sci. Int.* **2003**, *135*, 167–73.
9. Reardon, M.R.; MacCrehan, W.A.; Rowe, W.F. Comparing the additive composition of smokeless powder and its handgun-fired residues. *J. Forensic Sci.* **2000**, *45*, 1232–8.
10. MacCrehan, W.A.; Reardon, M.R.; Duewer, D.L. Associating gunpowder and residues from commercial ammunition using compositional analysis. *J. Forensic Sci.* **2002**, *47*, 260–6.
11. MacCrehan, W.A.; Reardon, M.R. A qualitative comparison of smokeless powder measurements. *J. Forensic Sci.* **2002**, *47*, 996–1001.
12. MacCrehan, W.A.; Reardon, M.R.; Duewer, D.L. A quantitative comparison of smokeless powder measurements. *J. Forensic Sci.* **2002**, *47*, 1283–7.

The authors are with the Analytical Chemistry Division, National Institute of Standards and Technology, Stop 8392, Gaithersburg, MD 20899-8392, U.S.A.; tel.: 301-975-3122; fax: 301-977-0587; e-mail: william.mac.crehan@nist.gov.