

U.S. Army Environmental Center's Development of AP-42 Emission Factors for Munitions Use

Mr. James C. Bach

U.S. Army Aberdeen Test Center, CSTE-DT-ATC-SL-E, Aberdeen Proving Ground, MD 21005-5059
james.bach@us.army.mil

Ms. Brooke E. Conway

U.S. Army Environmental Center/Booz Allen Hamilton, 5179 Hoadley Road, ATTN: SFIM-AEC-ATT,
Aberdeen Proving Ground, MD 21010-5401
brooke.conway@us.army.mil

Mr. Sean B. Mulligan

MACTEC Federal Programs, Inc., PO Box 12077, Research Triangle Park, NC 27709-2077
sbmulligan@mactec.com

Ms. Kimberly A. Watts

U.S. Army Environmental Center, 5179 Hoadley Road, ATTN: SFIM-AEC-ATT, Aberdeen Proving
Ground, MD 21010-5401
kimberly.watts@us.army.mil

ABSTRACT

The need to effectively quantify emissions resulting from munitions use, and to assess the potential health and environmental impact of these emissions, has become a critical issue for the U.S. Army. The U.S. Army Environmental Center (USAEC) initiated effort to generate the quantitative data necessary to address this issue and reduce the Army's significant liability in this arena. In order to generate the required data, USAEC developed a comprehensive program to quantify emissions resulting from the tactical use of munitions on training ranges. Data gathered from this program will provide information on the concentration, transport, dispersion, and fate of the air emission products.

USAEC has worked with the U.S. Environmental Protection Agency (USEPA) during the development and implementation of the munitions test programs. As a result, the program produces scientifically defensible emission factor data that USEPA has accepted for publication in their Compilation of Air Pollutant Emission Factors, better known as AP-42. To date, over 180 munition items have been tested and 57 items are available on the USEPA's AP-42 website: (<http://www.epa.gov/ttn/chief/ap42/index.html>).

This paper describes the munitions test facilities, identifies the constituents for which sampling analysis has been conducted, and explains the quality assurance program that has been implemented. In addition, this paper contains a discussion of the test data analysis and the assignment of test data ratings, a description of the calculations used to develop AP-42 emission factors for each constituent measured, and a description of the methodology used to rate the emission factors.

INTRODUCTION

The need to effectively quantify the emissions resulting from munitions use, and to assess the potential health and environmental impact of these emissions, has become a critical issue for the U.S. Army. The need for such data was first identified as a result of occurrences at the Massachusetts Military Reservation (MMR). Since that time, other requirements, such as reporting under the

Emergency Planning and Community Right to Know Act - Toxic Release Inventory (EPCRA-TRI) have also been identified.

In September 1997, the Director of the Army Staff directed the Assistant Chief of Staff for Installation Management (ACSIM) to establish a General Officer Steering Committee (GOSC) to address the implications of MMR, National Environmental Policy Act (NEPA), Clean Air Act (CAA), and Health Hazard Assessments (HHAs) for the U.S. Army. The ACSIM directed and funded the U.S. Army Environmental Center (USAEC) to gather emissions data. From this directive, USAEC initiated the effort to generate the quantitative data necessary to address these issues and reduce the Army's significant liability in this arena.

In order to generate the required data, USAEC developed a comprehensive program to identify the emissions resulting from range operations that involve weapons firing, smoke and pyrotechnic devices, and exploding ordnance, and to assess the environmental and health hazard impacts resulting from their use. The data being gathered from this program will provide information on the concentration, transport, dispersion, and fate of the emission products.

These data will support Army responses to regulatory questions and public concerns raised at many training and testing issues. Uses for these data include HHAs, Environmental Impact Statements, Environmental Assessments, Resource Conservation Recovery Act (RCRA) Subpart X Permits, EPCRA input, and Health Risk Assessments (HRAs) for surrounding communities. These data may also be used to support, define, and possibly modify, future Army training and testing practices.

USAEC has funded the following organizations as an integrated core team for the review, comment, direction, and conduct of these test projects to develop the Munitions Emission Characterization Study to identify and quantify the emissions resulting from the use of munitions currently fielded by the U.S. Army:

- U.S. Army Aberdeen Test Center (ATC), Aberdeen Proving Ground (APG), Maryland.
- U.S. Army West Desert Test Center (WDTC), Dugway Proving Ground (DPG), Utah.
- U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM), APG, Maryland.
- U.S. Environmental Protection Agency (EPA), Research Triangle Park (RTP), North Carolina.

The program developed by USAEC consists of several projects which are examining munition emissions. These projects include the following:

- Firing Point Emission Study - The purpose of this study is to obtain the data necessary to quantify the emissions generated by representative U.S. Army munition classes at the weapon firing position. Phase I of this study investigated existing data, predictive emission and air dispersion models, and test methodologies. Phase II of this study involves the firing of test munitions to generate the required emissions data.
- Smoke and Pyrotechnic Emission Study - The purpose of this project is to obtain the data necessary to quantify the emissions generated from the use of smoke grenades, flares, and related pyrotechnics.
- Exploding Ordnance Emission Study - The purpose of this project is to obtain the data necessary to quantify the emissions generated from the down range functioning of munitions containing explosives or other energetic fills (e.g., flash compound).

Follow-on efforts will use the gathered data to assess the dispersion, fate, and transport of the emissions and to validate/calibrate existing and next generation models.

The following sections describe the munitions test facilities, identify the constituents for which analysis has been conducted, and explain the quality assurance program that has been implemented. Prior to submitting the ordnance emission factors to USEPA for incorporation into AP-42, the test data, analytical data, and resulting emission factors are subjected to an independent third party review for overall data quality control and quality assurance. Additional sections contain discussions of the steps performed during this review: test data analysis and the assignment of test data ratings, recalculation/validation of the emission factors, and assignment of emission factor ratings.

BODY

Emissions Characterization Test Facilities

Descriptions of the facilities where the tests are conducted are given below. An overview, where possible, of approximate dimensions, construction, instrumentation and measurement, video capability, mixing fans, and sampling is given for each test facility.

Emissions Characterization Chamber (ECC)

The ECC, a test chamber developed at ATC, is used in the conduct of some of the firing point emission tests. Physically, the ECC is a steel cylinder with parabolic caps welded to each end (Figure 1). The chamber is made of mild steel and is approximately 7 feet in diameter, 15 feet long, and is 3/8 inch thick. A high-solids epoxy coating has been applied on all interior and exterior surfaces. A personnel access door and remotely operated firing port door are integrated into the rear and front parabolic caps, respectively. A series of 12 ports, each 18 inches in diameter, are located along the sides and top of the chamber. Steel covers, modified to accommodate blast over-pressure, thermal, combustion product, and other instrumentation as required are placed as appropriate. For ports where photographic coverage is required, lexan port covers are used. The remaining ports are capped with solid port covers (lexan or steel) to provide an airtight seal. Mixing fans are located throughout the interior of the ECC.

Figure 1. Exterior view of the ECC.



A removable interior partition, located between the second and third instrumentation ports, allows the test volume of the ECC to be selected at approximately 219, 240, or 520 cubic feet depending on the physical size of the item to be tested and the expected quantity of emissions to be generated. Munition items that have small quantities of energetic material are tested in the ECC. This allows for higher, more measurable concentrations of emission gases due to the smaller chamber volume. Example items that are tested inside the ECC include small arms (0.22 caliber up to 81 mm), mortars, initiators, blasting caps, and small pyrotechnic devices.

Large Octagon Test Chamber (LOTC)

The LOTC, a chamber developed at ATC, is used in the conduct of some of the exploding ordnance emissions tests. The LOTC is an eight-sided structure with flat ends made from 1 inch thick mild steel plates and is designed to withstand the pressures and stress generated by detonation of ordnance mounted internally (Figure 2). The eight sides, hence octagon, are increased to sixteen sides internally with the addition of plates welded over each seam. These plates serve to strengthen the LOTC and remove sharp interior corners that would inhibit gaseous mixing during testing. Additional plates are added to the upper and lower internal corners to create more parabolic ends. This structure provides an interior volume of approximately 2400 ft³ arranged to maximize gaseous mixing of ordnance emissions for accurate measurement. The interior wall to wall dimension of the LOTC is 14.5 feet. The interior floor to ceiling dimension is 14 feet. There is a measurement assembly and an instrumentation enclosure mounted on top of the chamber, which are not included in the floor to ceiling dimension. The measurement assembly is situated in the center of the chamber ceiling and is lowered into the chamber through the center of the ceiling.

Figure 2. Exterior view of the LOTC.



The LOTC has two flanged viewing ports for video recording of testing and two ports with hinged internal doors through which mixing fans are inserted into the LOTC. These fans are deployed post-detonation and mix the gaseous detonation products after the shock wave has dissipated. In addition, there is a sampling assembly that is mounted on rollers in vertical tracks. This assembly is lowered into the detonation volume by an electric hoist before sampling begins.

The measurement assembly is constructed such that when it is fully raised, the measurement media and sampling lines are shielded from the detonation blast. After detonation this measurement assembly is lowered into the octagon's internal volume. A metal cover on the top of the assembly seals the interior preventing detonation products from escaping. This cover also has a flange through which the sampling lines are passed to the lower assembly. The measurement media and sampling points are mounted within the assembly that is lowered into the detonation volume. Once this assembly is fully lowered test sampling can begin.

The electric hoist is capable of safely lowering the measurement assembly in approximately 60 seconds. When the measurement assembly is lowered into chamber several safeguards are taken to prevent detonation gases from escaping. The measurement assembly is fully surrounded with an instrumentation enclosure. This instrumentation enclosure has a door through which personnel may replace media and service sampling lines. The door will remain closed and mixing fans will be turned off while the measurement assembly is lowered into the chamber.

An exterior stairway circles the LOTC to a platform that is mounted even with the top of the chamber. This is for operator access to the sampling media and measurement lines pre-detonation and post-detonation and facilitates instrumentation for testing. The LOTC is also mounted on large castors that permit its movement and storage when not in use. The dimensions of the LOTC were made based on tests of demolition blocks in free and open space. The size of the resulting fireballs from several different weights of demolition blocks served to provide the necessary dimensions for the LOTC. The fireball from a 2-1/2 pound demolition block produced a 12 foot diameter fireball. While the LOTC is designed to withstand a 5 pound TNT charge, the 14 foot diameter chamber limits the charge weight to 2-1/2 pounds for emissions testing.

Blast Sphere

The Blast Sphere, a chamber developed at ATC, is used in the conduct of some of the exploding ordnance emission tests. Physically, the Blast Sphere is a spherical structure with walls made from 2-3/4 inch thick mild steel sections welded together and is designed to withstand the pressures and stress generated by detonation of ordnance mounted internally (Figure 3). The suitability of the Blast Sphere to conduct this test was made based on tests of demolition blocks in free and open space. The size of the resulting fireballs from several different weights of demolition blocks served to provide the necessary dimensions for the suitability of the Blast Sphere to be able to conduct this test. The fireball from a 40-pound demolition block produces a 28 foot diameter fireball. While the Blast Sphere was engineered to withstand a 75-pound TNT charge, the 30 foot diameter chamber limits the charge weight to 40 pounds for emissions testing. The walls were then reinforced with 1-inch thick armor plating with blank welds throughout the interior of the Blast Sphere. These plates serve to strengthen the Blast Sphere and remove sharp interior corners that would inhibit gaseous mixing during testing. This structure provides an interior volume of approximately 14,100 ft³ arranged to maximize gaseous mixing of ordnance emissions for accurate measurement. The interior wall diameter of the Blast Sphere is 30 feet. There is a 5 foot wide equatorial walkway located along the interior wall. The Blast Sphere has two flanged viewing ports for video recording of testing and five ports with hinged internal doors through which mixing fans and a sampling rack are inserted into the chamber. The fans are deployed post-detonation and mix the detonation products after the shock wave has dissipated. For ports where photographic coverage is required, lexan port covers will be used. Additionally, there are several ports

in the sphere that are available for future applications. The remaining ports are capped with solid port covers made of mild steel.

Figure 3. Exterior view of the Blast Sphere test complex.



The Flight Tunnel is connected to the side of the sphere which contains the sampling rack and an instrumentation enclosure adjacent to it. The sampling rack will be transferred into the blast sphere after the test event via an air winch. The sampling rack is situated in the center of the Flight Tunnel and is mounted on rollers in horizontal tracks. The sampling rack is pneumatically deployed into the chamber through an access port on the side of the wall of the Blast Sphere.

The sampling rack is constructed such that when it is fully contained in the Flight Tunnel, the measurement media and sampling lines are shielded from the detonation blast. After detonation, the sampling rack is transferred into the sphere's internal volume. A metal cover at the back of the sampling rack seals the interior of the sphere, preventing detonation products from escaping. This cover also has a flange through which the sampling lines are passed to the instrumentation enclosure. The measurement media and sampling points are mounted within the assembly that is transferred into the detonation volume. Once this assembly is fully inside the sphere, test sampling can begin.

An exterior stairway with a landing is attached to a personnel access door on the front of the Blast Sphere and another is attached at the entrance to the flight tunnel. This is for operator access to the sampling media and measurement lines pre-detonation and post-detonation and facilitates inspection and modification of the instrumentation for testing. The Blast Sphere is partially underground, permitting no movement of the facility.

Barricade 2 (B2)

Another facility used by ATC for firing point emissions testing is B2. Physically, B2 is a reinforced concrete structure that is 74 feet wide by 70 feet deep by 36 feet high (Figure 4). The opening of the facility is closed with a set of polymer strip curtains. A steel blast shield, equipped with an internal door and remotely operated external door, is located immediately in front of the strip-door. Together the shield and curtain absorb the blast from the weapons firings while maintaining the required seal for emissions characterization. The interior volume of B2 is approximately 186,000 ft³.

Figure 4. Exterior view of B2.



For the handling of weapons and munitions the barricade is equipped with a 10 ton capacity overhead crane, weapons mount, and three temperature conditioned ammunition bunkers. Electric power, compressed air, and lighting are available in and around the barricade. Eight high-volume fans located around the interior perimeter of B2 ensure even distribution of the weapon emission products.

A separate instrumentation and test control building is part of the facility. For specialized test instrumentation vans, electrical power drops are available next to the test control building. Instrumentation and firing of the weapon are controlled via an automated countdown procedure. Example items that are tested inside B2 are large caliber cannons from 90 mm up to 155 mm.

BANGBOX

The BANGBOX Smoke Characterization Test Chambers (Figures 5 and 6) are chambers developed by WDTC and are used in conduct of some of the smoke and pyrotechnic emission tests. One, a modified mobile freezer unit, is referred to as the smoke chamber. Physically, the smoke chamber is approximately 7 feet wide, 20.2 feet long, and 6.3 feet tall for two-thirds of its length and 4.7 feet tall for the remainder. The walls provide 6 inches of insulation and the ceiling provides 10 inches of insulation. The interior volume of the smoke chamber is approximately 791 ft³.

The smoke chamber has been equipped with its own interior power for circulation fans as well as for lighting and heating. A 3.0-m (10-ft) long, 25-cm (10-in) diameter, stainless steel stack has been installed, along with a blower assembly for evacuation of excess sample material. The stack and blower assemblies are equipped with shutters to prevent venting of material during testing. Six 1.3-cm (0.5-in) vent lines provide for fresh air makeup and mixing during sampling.

The other chamber is referred to as the BANGBOX test facility. Physically, it is a 50 foot diameter hemisphere constructed of coated fabric anchored onto a concrete pad with an interior volume of approximately 32,700 ft³. A small blower provides filtered air to keep the chamber inflated. The resiliency of the structure allows for detonation of up to 0.5 pounds of trinitrotoluene (TNT) equivalent or burning of up to 5 pounds of energetic material without damage to the structure. A shrapnel shield located in the center of the facility protects the outer fabric walls. It is equipped with an overpressure hatch to protect the structure from stress rupture.

Figure 5. Exterior view of the BANGBOX test complex.



Figure 6. Interior view of the BANGBOX smoke chamber.



A Command Post (CP) is maintained 550 m from the BANGBOX chambers and contains the data acquisition system (DAS) file server, remote DAS monitors, the detonation/ignition firing system firing station, and a small computer workstation for conducting test support. Individuals in the CP have an unobstructed view of the majority of the BANGBOX facilities and can remotely observe the test chamber interior via a television monitor. The firing circuit for the smoke chamber terminates in a locked box in the CP (accessible only to authorized individuals).

Constituents for Which Analyses Have Been Conducted

Ambient, source, or a combination thereof, and industrial hygiene sampling and analysis methods are employed for the test. Over 280 constituents are sampled and analyzed during testing. All methodology employed in the conduct of these tests are approved by the USEPA prior to the start of the test. Examples of potential emissions of interest and the associated sampling methodologies are:

- Oxides of nitrogen (NO_x) - source

Real-time concentrations of NO_x are collected via a Continuous Emission Monitoring (CEM) system. A Thermo Environmental Instruments Inc., model 42C-HL, chemiluminescence analyzer is used to detect and quantify oxides of NO_x in accordance with EPA 40 CFR 60, Appendix A, Method 7E.

- Carbon monoxide (CO) - source

Extractive Fourier Transform Infrared (FTIR) spectroscopy is used to measure real-time concentration of the SF₆ tracer gas and ammonia as well as to qualitatively identify other permanent gas species using a methodology based on EPA 40 CFR 63, Method 320, Appendix A.

- Sulfur dioxide (SO₂) - source

Real-time concentrations of SO₂ are collected via a CEM system. A Thermo Environmental Instruments Inc., model 43H, pulsed fluorescence analyzer is used to detect and quantify oxides of SO₂ in accordance with EPA 40 CFR 60, Appendix A, Method 6C.

- Acid gases - industrial hygiene

Sampling for acid gases is accomplished by drawing air samples through silica gel sorbent tubes (ORBO-53) with the aid of a sampling pump. The sampling and analysis for acid gases is performed in accordance with National Institute for Occupational Safety and Health (NIOSH) Method 7903. The sorbent tubes are desorbed with deionized water and the extract is subsequently analyzed by ion chromatography.

- Hydrogen cyanide (HCN) - modified industrial hygiene

The sampling and analysis of HCN is performed using NIOSH Method 7904. Sampling is accomplished with a 1-micron Teflon filter and a 0.1-N potassium hydroxide (KOH) impinger. The impinger solution and extracted filter are analyzed by ion chromatography.

- Total suspended particulates (TSP) - ambient/source

TSP is sampled using an Air Metrics TSP ambient air-sampling module. The TSP module is equipped with a quartz fiber particulate filter. TSP is sampled using EPA 40 CFR 60, Appendix A. The calculated volume of air drawn through the filter is divided into the weight difference between the initial and final filter weights to determine the TSP concentration.

- Particulate matter less than 10 microns (PM₁₀) and less than 2.5 microns (PM_{2.5})- ambient/source

PM₁₀ and PM_{2.5} are sampled using separate Air Metrics PM₁₀ and PM_{2.5} ambient air sampling modules. The modules are equipped with a polytetrafluoroethylene (PTFE) particulate filter equipped with a polymethylpentene support ring. PM₁₀ and PM_{2.5} are sampled using EPA 40 CFR 60, Appendix A. The calculated volume of air drawn through the filter is divided into

the weight difference between the initial and final filter weights to determine the PM₁₀ and PM_{2.5} concentrations.

- Total carbon - ambient/source

The sampling and analysis of carbon is performed using NIOSH Method 5040. The particulate sample is collected using a 37-mm heat-treated quartz fiber filter. The filter is analyzed using a thermo-optical analyzer to differentiate between the forms of carbon present on the filter.

- Toxic metals - ambient

The TSP filter is also analyzed for metal composition. The quartz fiber filter is digested with acid and analyzed by inductively coupled plasma (ICP) spectroscopy. Metals sampling and analysis of the filter media is carried out in accordance with method EPA 40 CFR 60, Appendix A.

- Hexavalent chromium (Cr^{VI}) - ambient/source

The sampling and analysis of Cr^{VI} is performed using SOP No. CAD 70.1. The only modification made to the method is the use of a 0.8- μ m pore size PVC filter in lieu of a 5- μ m PVC filter. The filter media is extracted and analyzed by ion chromatography with post-column derivatization and detection with an ultraviolet-visible (UV-Vis) detector.

- Carbonyls/aldehydes - ambient

The sampling of aldehydes and carbonyl compounds use EPA Compendium Method TO-11A as a guideline. Dinitrophenylhydrazine (DNPH) laden cartridge tubes are used as a direct probe to trap and derivatize aldehydes and carbonyl compounds. The DNPH tubes are extracted and analyzed by high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

- Volatile organic compounds (VOCs) - ambient

The sampling and analysis procedure for VOCs use EPA Compendium Method TO-14A as a guideline. A XonTech, Inc. pressurized canister sampler and a silicon-lined canister are used to sample for VOCs. The canister is analyzed using gas chromatography/mass spectrometry/scan mode (GC/MS/SCAN).

- Semi-volatile organic compounds (SVOCs) and Polyaromatic Hydrocarbons (PAHs) - ambient/source

SVOCs and PAHs are sampled using a Tisch Environmental, Inc., model No. TE-1002, ambient air sampling module equipped with a quartz fiber particulate filter and a XAD-2 resin packed cartridge using EPA Compendium Method TO-13A. The initial sample analysis is performed using a GC/MS operating in selected ion mode, which allows for enhanced instrument sensitivity. The extracts are also reanalyzed with the mass spectrometer operating in scan mode.

- Dioxins/furans - ambient/source

Dioxins/furans are sampled using a Tisch Environmental, Inc., model No. TE-1002, ambient air sampling module equipped with a quartz fiber particulate filter and polyurethane foam (PUF) packed cartridge. The sampling module meets requirements established in the compendium method for dioxins/furans as specified in EPA Compendium Method TO-9A, Modified via EPA Method 1613B. The PUF cartridge and filter are extracted and analyzed by GC/High Resolution Mass Spectroscopy (HRMS).

- Residual energetic materials/propellant ingredients - ambient/source

Energetic compounds are sampled using a Tisch Environmental, Inc., model No. TE-1002, ambient air sampling module equipped with a quartz fiber particulate filter and XAD-2 resin packed cartridge. The sampling module meets the requirements established in the compendium method for PAHs as specified in EPA Compendium Method TO-13A. The energetic compounds are extracted from the XAD-2 resin using isoamyl acetate and analyzed by gas chromatography with electron capture detection/mass selective detector (GC/ECD/MSD).

- Perchlorate (ClO_4^-) - ambient/source

The sampling of particulate salts of ClO_4^- is performed using a 50-mm Teflon open-face filter cassette with 2-micron pore size Teflon filters using NIOSH Method 7904 (Sampling Train). A backup Teflon midget impinger containing deionized water is used as a trap for any perchloric acid vapor. The filter extract and impinger solution are analyzed by ion chromatography with conductivity detection.

In order to obtain a mass balance, carbon dioxide (CO_2) and light hydrocarbons (C1-C4) are also measured. Gas leakage from the test chamber is measured by sulfur hexafluoride (SF_6) recovery. Efforts are taken to determine tentatively identified compounds (TICs) not found on some of the methods analyte lists. In particular, an expanded compound target list is measured by gas chromatography/mass spectrometry (GC/MS) on VOC and SVOC analysis. Additionally, attempts are made to detect other permanent gases by FTIR spectroscopy.

Efforts are also made to obtain measurement of the detonation plume, fireball, or pyrotechnic flash. This data is used as additional inputs to the air dispersion models to help improve the accuracy of the model calculations.

Quality Assurance/Quality Control (QA/QC)

A QA/QC plan has been developed for each test chamber and test event and generally consists of the following criteria:

- Precision. Precision measures the reproducibility of repetitive measurement and is strictly defined as the agreement among independent measurements produced by applying the same process under similar conditions. Precision is evaluated by the relative percent difference (RPD) between duplicate sample analyses or relative standard deviation (RSD) among probable analytical determinations.
- Accuracy. Accuracy is defined as the closeness of agreement between the measured value and the true value. Sources of error are the sampling process, field contamination, handling, sample matrix, sample preparation, and analysis techniques. A measurement is accurate when the reported value does not differ unacceptably from the true value or known concentration of a spike or standard. Accuracy is measured by determining the percent recovery of known concentrations of target analytes spiked into a field or laboratory sample. The spiking material can be either the native analyte (matrix spike) or an isotopically labeled compound (surrogate spike). Accuracy is presented as percent recovery.
- Representativeness. Representativeness expresses the degree to which data accurately and precisely represent a characteristic of population, parameter variations at a sampling point, a process condition, or an environmental condition.

- **Comparability.** Comparability expresses the confidence with which data sets can be compared. It is a measure of the similarity of data collection operations and is based on the use of identical, or nearly identical, methods and procedures.
- **Completeness.** Completeness measures the amount of valid data obtained from a measurement system compared to the amount of data that will be expected to be obtained under correct normal conditions.

Additionally, the QA/QC plan addresses holding times for chemical samples, chain of custody procedures to verify integrity of samples, and sample documentation. Many target chemicals occur in the ambient air as contaminants or produced by other activities near the test chambers. Therefore, background measurements are made in the test chamber prior to the initiation of the munition being tested. The same methodologies and sampling periods being employed during testing are used for performing the background measurements. Results of the background measurements are subtracted from the test firing measurements to generate adjusted emission factors. All values are detailed in the final report, i.e., the measured concentration from the actual test firings, the background measurements, and the adjusted emission factor.

Test Data Analysis and Ratings

EPA Guidance Regarding Test Data Quality Ratings

Prior to inclusion of emission factors in AP-42, the reliability of the underlying emission test data were appraised in accordance with the rating system specified in Reference 4. Under this rating system, test data are assigned a rating from A to D, where an “A” rating is assigned to the highest quality data. The criteria used to assign a specific data quality rating are summarized below.

- A** Tests are performed by using an EPA reference test method, or when not applicable, a sound methodology. Tests are reported in enough detail for adequate validation and raw data are provided that can be used to duplicate the emission results presented in the report.
- B** Tests are performed by a generally sound methodology, but lacking enough detail for adequate validation. Data are insufficient to completely duplicate the emission result presented in the report.
- C** Tests are based on an unproven or new methodology, or are lacking a significant amount of background information.
- D** Tests are based on a generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

Four specific criteria are identified in Reference 4 for consideration to assist in the assignment of a test data quality rating. These four criteria are:

- **Source operation.** If the manner in which the source was operated is well documented in the report and the source was operating within typical parameters during the test, an “A” rating should be assigned. If the report stated parameters that were typical, but lacked detailed information, a “B” rating should be assigned. If there is reason to believe the operation was not typical, a “C” or “D” rating should be assigned.
- **Test methods and sampling procedures.** In developing the ratings, the estimated accuracy and precision of the test method as well as the adequacy of the documentation should be considered.

In general, if a current EPA reference test method, appropriate for the source, was followed, the rating should be higher (“A” or “B”). If other methods were used, an assessment should be made of their validity. If it is judged that the method was likely to be inaccurate or biased, a lower rating (“C” or “D”) should be given. A complete report should indicate whether any procedures deviated from standard methods and explain any deviations. If deviations were reported, an evaluation should be made of whether these were likely to influence the test results.

- Process information. During testing, many variations in the process can occur without warning and sometimes without being noticed. Such variations can induce wide deviations in sampling results. If a large variation between test run results cannot be explained by information contained in the site final test report or from test reports of other sources, the data are suspect and should be given a lower rating or excluded. However, it should be recognized that a process may have highly variable emissions and a lower rating may not be appropriate solely on the basis of wide deviations in sampling results.
- Analysis and calculations. Ideally, final test reports should contain original raw data sheets and other documentation such as gas parameters (dry cubic feet per minute, oxygen percentage), calculation sheets, or example calculations describing how the calculated emission results were obtained. If there are data sheets, the nomenclature and equations used should be compared to those specified by EPA to establish equivalency. The depth of review of the calculations should be dictated by the reviewers’ confidence in the ability and conscientiousness of the tester, based on such factors as consistency of results and completeness of other areas of the final test report. Reports may indicate that raw data sheets were available, but were not included. If the final test report is of high quality based on the other criteria, the quality rating should not be lowered due to a lack of data sheets. Overall test data quality rating were assigned based upon the ratings assigned for each of the four criteria.

Analysis of Test Data

Data included in the final test report, the detailed test plan, and in the analytical data supporting the test report were rated in accordance with the rating system described above. Typical results for each of the four criteria described above are presented in the following sections.

Source Operations. The manner in which the ordnance were deployed (i.e., used) was documented in the final test report associated with each test series. With the exception of adaptations that were made to facilitate test firing the ordnance (e.g., adding a blasting cap to initiate some exploding ordnance), each ordnance that was tested was deployed in a manner similar to that which would occur in the field. The tests appear to have replicated typical ordnance operating parameters; consequently, the test data were assigned an “A” rating based on this criterion.

Test Methods and Sampling Procedures. The test methods and sampling procedures were evaluated as being appropriate and consistent with EPA test methods or sound methodology. Unless issues were identified with the test methods or sampling procedures used to measure specific compounds, the test data were assigned an “A” rating based on this criterion. Three issues that were typically identified with the test methods and sampling procedures are discussed below.

CEM Measured Data. CEM raw data were provided for all of the tests, but were not always provided for the pre- and post-test quality control (QC) activities. It was not always clear that CEM QC measures specified under 40 CFR 60, Appendix A, EPA Methods 3A, 7E, and 6C were followed. Furthermore, calibration gas certifications were not always supplied. It should be noted that there was no evidence of bias in the data. However, when the issues noted above were identified, the test data for

the CEM-measured compounds (i.e., CO, CO₂, NO_x, and SO₂) were assigned a “B” rating based on this criterion.

Compounds Sampled or Analyzed Using More than One Test Method or Analytical Method. Depending upon the test series, between 20 and 35 compounds were either sampled or analyzed using two different methods. For each of these compounds, emission factors were calculated based upon the data measured using the more appropriate test or analytical method; data obtained using the less appropriate method were ignored. The more appropriate method was identified by reviewing the methods and the target compound lists associated with each method. If a specific compound appeared on the target compound list for one method but not the other, the method targeting the compound was selected. If a specific compound appeared on the target compound lists for both methods, the method judged to provide the most accurate data was selected. Three examples are provided below.

- If a compound was analyzed using both the SW8270M (SVOC) and TO-14A (VOC) methods, the TO-14A method analysis was judged to be more accurate and was therefore selected.
- For compounds analyzed using both the SW8270M (SVOC) and TO-13A (PAH) methods, the TO-13A value was selected because TO-13A allowed quantification of compounds at lower levels than SW8270M.
- If a compound analyzed using both the TO-11A (aldehydes) and TO-14A (VOC) methods, the TO-11A method analysis was judged to be more accurate and was therefore selected.

Tentatively Identified Compounds. During the analysis conducted for most test series, the highest VOC and SVOC nontarget “peaks” were tentatively identified using computerized mass spectral matching techniques. Emission factors were developed for these tentatively identified compounds (TICs) if all of the following criteria were met.

- The TIC corresponded to a unique compound (e.g., ethylbenzene). Emission factors were not developed if the TIC corresponded to a class of compounds (e.g., unknown alcohol).
- The TIC was not identified using another analysis method that provided higher confidence data. Emission factors were developed based upon the higher confidence analysis method if such data were available.
- The TIC was not present in the method blank. Emission factors were not developed if the TIC was found in the corresponding method blank.

Because of the uncertainty in the true identity of the TICs, the test data were assigned a “C” rating.

Process Information. Ordnance are manufactured to tight tolerances and are expected to deploy in a very repeatable fashion. Consequently, the test data were assigned an “A” rating based upon this criterion. However, large relative percent differences (i.e., greater than 100 percent) between test runs were occasionally noted for specific compounds. The equation below illustrates calculation of relative percent difference:

$$\text{relative percent difference} = \frac{\text{test 1 concentration} - \text{test 2 concentration}}{\text{average of test 1 and test 2 concentrations}} \times 100\%$$

When a relative percent differences greater than 100 percent was identified between test runs, the test data were assigned a “C” rating. The remainder of the data were assigned an “A” rating based on this criterion.

Analysis and Calculations. For each test series, the test report, detailed test plan, and analytical data supporting the test report were reviewed to determine whether they contained all of the original raw data, other documentation, and example calculations. Although the test reports did not typically contain raw field data, the data were made available upon request. While the test reports usually lacked certain calibration data, the missing information was judged insufficient to result in a downgrade of the test data quality rating.

The raw data and sample calculations presented in the final test report, detailed test plan, and analytical data supporting the test report were reviewed to determine if the emission factors presented in the report could be duplicated. Where differences were found between the emission factors calculated using Excel spreadsheets and those presented in the test report, an examination was made to determine the reason for the differences.

Several minor errors were noted in the calculation of the emission factors within many of the test reports, particularly with respect to correcting sample volumes to standard conditions and the incorporation of analytical detection limits into the emission factors. The emission factors submitted to EPA for presentation in AP-42 are based upon the corrected spreadsheets. Based upon the raw data, other documentation, and the spreadsheet calculations, the test data were assigned an “A” rating with the exception of the two instances documented below.

First, emission factors developed for compounds present in the method blank at levels of 20 percent to 50 percent of test values were assumed to be biased high. For these compounds, the test data were assigned a “B” rating. When compounds were found in the method blank at levels greater than 50 percent of both test values, the data were assumed to be suspect and no emission factors were developed.

Second, the test reports occasionally indicated that the recommended holding times to extraction and subsequent analysis were exceeded for specific compounds. If the recommended holding times were deemed to have been exceeded by an excessive amount of time, these test data were assigned a “C” rating based upon this criterion.

Test Data Quality Ratings

Upon completing the analysis described in the preceding section of this document, the test data quality ratings assigned as a result of the four criteria were reviewed. Data that received an “A” rating for all four of the criteria were assigned an “A” rating. Data that received anything less than an “A” rating for any of the four criteria were downgraded to the lowest rating received (i.e., either a “B” rating or a “C” rating).

Emission Factor Calculations

As previously mentioned, an third party contractor independently calculated emission factors using the test data supplied by USAEC. This exercise was completed to determine whether the emission factors presented in the final test reports^{1,2,3} could be duplicated and, if not, to determine the reasons for any differences noted. The methodologies and procedures that were used to develop emission factors from the test data are described in this section. A similar approach was typically used to calculate emission factors for TSP, PM-10, PM-2.5, metals, SVOC, PAH, and energetic materials. The calculation steps that were performed for each sample and each configuration are summarized below.

- 1) The sample volumes associated with the background and test runs were corrected to the EPA Stationary Source Program standard temperature and pressure (i.e., 68°F and 29.92 inches of mercury).
- 2) For compounds for which more than one test sample was obtained, analytical detection limits were incorporated into the test data.
- 3) The background compound concentration was calculated by dividing the mass of compound detected during the background run by the background run sample volume corrected to standard conditions.
- 4) The test compound concentration was calculated by dividing the mass of compound detected during the test run by the test run sample volume corrected to standard conditions.
- 5) A background-corrected concentration was calculated by subtracting the background concentration from the test concentration.
- 6) A dilution-corrected concentration was calculated by dividing the background-corrected concentration by the test dilution correction factor.
- 7) The mass of compound released during the test run was calculated by multiplying the dilution-corrected concentration by the volume of the test chamber.
- 8) Emission factors for each sample and test run were calculated by dividing the mass of compound released by the number of ordnance detonated during the test run or by the Net Explosive Weight (NEW) detonated during the test run, as appropriate.
- 9) Average emission factors were calculated for each compound.

Because concentration data (i.e., milligrams per cubic meter [mg/m^3], parts per million by volume [ppmv], or parts per billion by volume [ppbv]) were recorded for VOC, hydrocarbons, FTIR-measured compounds, and CEM-measured compounds, it was not necessary to calculate a corrected sample volume as described in step 1 or to calculate background and test concentrations as described in steps 3 and 4. Detection limits were applied directly to test compound concentrations of VOC, hydrocarbons, FTIR-measured compounds, and CEM-measured compounds, as described in step 2. Where present, ppmv and ppbv values were converted to mg/m^3 . Emission factors for VOC and hydrocarbons were then estimated in accordance with steps 5 through 9 described above. FTIR- and CEM-measured compound emission factors were estimated in accordance with steps 5 through 9 described above, except that step 6, the dilution correction, was not required. FTIR- and CEM-measured concentrations were determined from initial steady-state points that occurred prior to significant dilution.

If measured during a test series, test and background concentrations of acid gases, hydrogen cyanide, aldehydes, dioxin/furan, total carbon, and hexavalent chromium were provided by the laboratory. The laboratory calculated the concentrations based upon the sample volumes as measured at actual conditions. Concentration data received from the laboratory were corrected for volume at Stationary Source Program standard conditions and analytical detection limits were incorporated as described in step 2. Emission factors for these compounds were then estimated in accordance with steps 5 through 9 described above. The following sections describe each of the nine emission factor calculation steps listed above in more detail.

Correction of Sample Volume to Standard Conditions

Because sample volumes were typically reported in the test reports at actual conditions, calculations to correct the sample volumes to the EPA Stationary Source Program standard temperature of 68°F and pressure of 29.92 inches of Hg (20°C and 760 mm Hg) were performed. To obtain the sample volume at EPA Stationary Source Program standard conditions (V_{stat}), the sample volume at actual conditions (V_{act}) was multiplied by the ratio of pressure at actual conditions (P_{act}) to temperature at actual conditions (T_{act}) and by the ratio of temperature at Stationary Source Program standard conditions (T_{stat}) to pressure at Stationary Source Program standard conditions (P_{stat}). This calculation is illustrated by the following equation:

$$V_{stat} = V_{act} \times \frac{P_{act}}{T_{act}} \times \frac{T_{stat}}{P_{stat}}$$

Incorporation of Analytical Detection Limits to the Test Data

In most cases, more than one test sample was obtained for a specific compound (i.e., more than one test run was conducted). When multiple samples were obtained for the same compound, a comparison was made of all the sample data collected. Based upon the results of the comparison, the following adjustments were made to the test data:

- If all of the samples indicated that a compound was “not detected,” the sample data were not adjusted.
- If all of the samples indicated that a compound was detected, the sample data were not adjusted.
- If one or more of the samples indicated that a compound was detected and one or more of the samples indicated that a compound was not detected, the “not detected” values were replaced with a value equal to one half of the compound’s analytical detection limit. The assumption inherent to this adjustment was that the measured presence of a compound in one or more samples was indicative of the compound’s presence in all samples. The analytical detection limits for each sample were obtained from the analytical data supporting the test report.

Determination of Background Concentration

For TSP, PM-10, PM-2.5, metals, SVOC, and PAH, the background compound concentration (BC) was calculated by dividing the mass of compound detected during the background run (Bkgd mass) by the background run sample volume corrected to EPA Stationary Source Program standard conditions (Bkgd V_{stat}). The background concentration calculation is illustrated by the following equation:

$$BC = \frac{Bkgd\ mass}{Bkgd\ V_{stat}}$$

When measured, the background compound concentrations of acid gases, hydrogen cyanide, aldehydes, dioxin/furan compounds, total carbon, and hexavalent chromium provided by the lab were calculated using the sample volume at actual conditions (Bkgd V_{act}). In order to correct the concentrations to EPA Stationary Source Program standard conditions (Bkgd V_{stat}), the uncorrected concentrations (Bkgd UC) were multiplied by the ratio of volume at actual conditions to volume at standard conditions. This calculation is illustrated by the following equation:

$$BC = Bkgd UC \times \frac{Bkgd V_{act}}{Bkgd V_{stat}}$$

FTIR- and CEM-measured compounds were not sampled for during the background runs. However, background data were recorded for each test run between the time the FTIR and CEM began sampling and the time of detonation. The only FTIR- or CEM-measured compound for which significant background concentrations were recorded was CO₂. The CO₂ background concentration was assumed to equal a representative value over the sampling period. Background concentrations for the other FTIR- and CEM-measured compounds were assumed to be zero.

Determination of Test Compound Concentration

For TSP, PM-10, PM-2.5, metals, SVOC, PAH, and energetic materials, the test compound concentration (TC) was calculated by dividing the mass of compound detected during the test run (Test mass) by the test run sample volume corrected to EPA Stationary Source Program standard conditions (Test V_{stat}). This test compound calculation is illustrated by the following equation:

$$TC = \frac{Test\ mass}{Test\ V_{stat}}$$

Where measured, test compound concentrations of acid gases, hydrogen cyanide, aldehydes, dioxin/furan compounds, total carbon, and hexavalent chromium provided by the lab were calculated using the sample volume at actual conditions. In order to correct the concentrations to EPA Stationary Source Program standard conditions, the uncorrected concentrations (Test UC) were multiplied by the ratio of the volume at actual conditions (Test V_{act}) to the volume at EPA Stationary Source Program standard conditions (Test V_{stat}). This calculation is illustrated by the following equation:

$$TC = Test\ UC \times \frac{Test\ V_{act}}{Test\ V_{stat}}$$

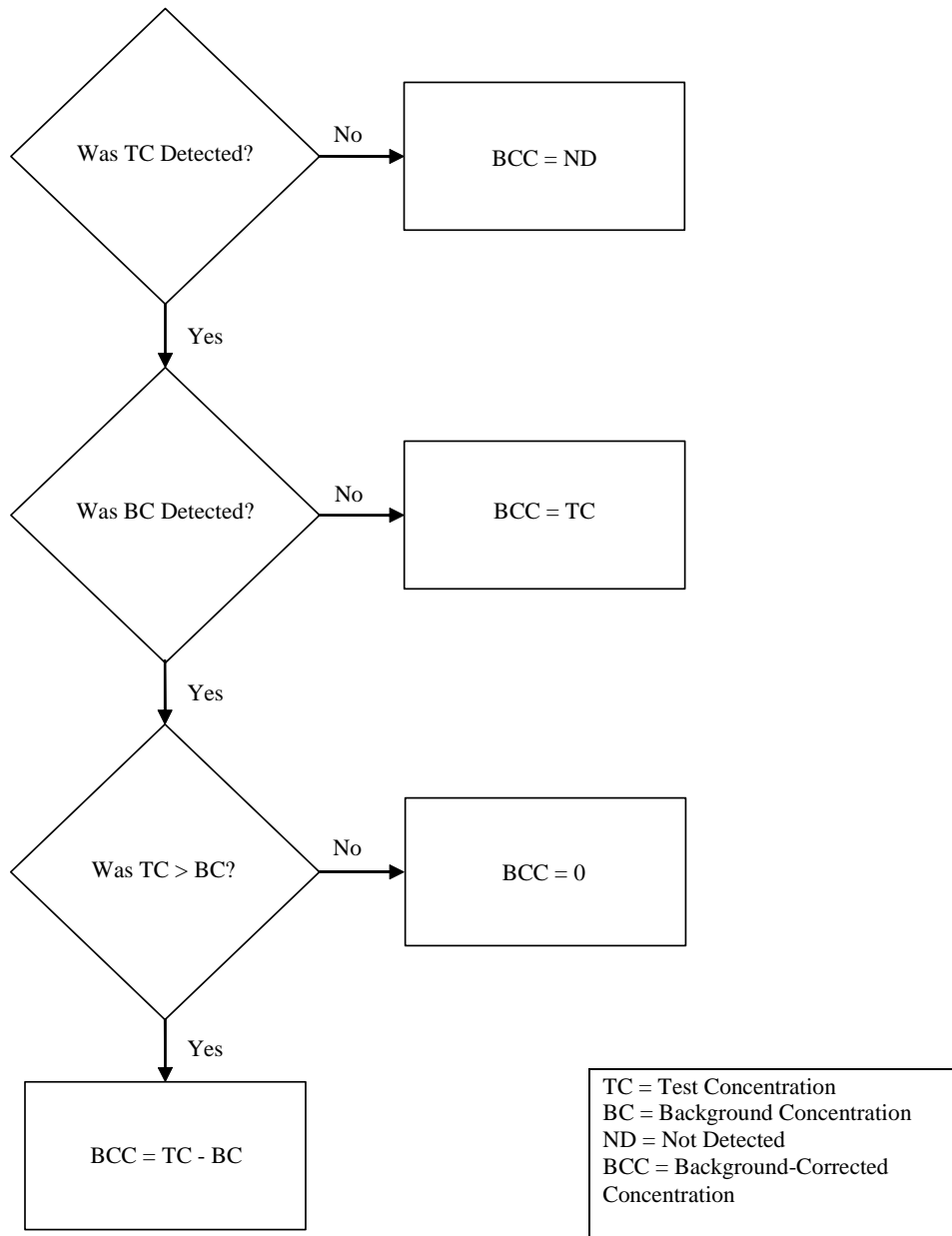
For VOC, hydrocarbons, FTIR-measured compounds, and CEM-measured compounds, sample volume correction was not required. VOC and hydrocarbon test concentration values were used directly. Test concentrations of CEM- and FTIR-measured compounds were determined based upon the initial steady-state values reached after detonation. The time at which a compound's concentration reached an initial steady state was determined by visually inspecting plots of the concentration data versus time. The initial steady state corresponds to the time at which a compound was well mixed within the test chamber, but before the compound's concentration began to decrease at a steady rate due to dilution.

Determination of Background-Corrected Concentration

For all compounds, the calculation of the background-corrected concentration (BCC) was dependent on whether the background (BC) and test concentrations (TC) were detected and whether they were less than, equal to, or greater than one another. The procedures used to calculate the background-corrected concentration for each sampling train and compound are described below and are displayed graphically in Figure 7.

- If the test concentration was not detected (ND), the background-corrected concentration equaled ND.

Figure 7. Calculation of background-corrected concentration.



- If the test concentration was detected and the background concentration was not detected, the background-corrected concentration equaled the test concentration.
- If the test and background concentrations were detected and the test concentration was less than or equal to the background concentration, the background-corrected concentration equaled 0.
- If the test and background concentrations were detected and the background concentration was less than the test concentration, the background concentration was subtracted from the test concentration. This calculation is illustrated by the following equation:

$$BCC = TC - BC$$

In most cases, when a detonator, blasting cap, or similar device was used to initiate the detonation of a weapon but is not used when the weapon is tactically detonated, the detonator was also

used during the background run. This allowed the emissions associated with the detonator to be quantified and subsequently subtracted from the resulting emission factors. As a result, it was necessary to correct these background concentrations for dilution. This was accomplished by multiplying the background concentration by the ratio of test dilution correction factor (DCF_{test}) to background dilution correction factor ($DCF_{background}$) prior to completing either step 3 or step 4 as described above. The calculation of the background-corrected concentration for those weapons that were tested with a detonator or similar device is illustrated by the following equation:

$$BCC = TC - BC \times \frac{DCF_{test}}{DCF_{background}}$$

Determination of Dilution-Corrected Concentration

The dilution-corrected concentration (DCC) was calculated by dividing the background-corrected concentration by the applicable test dilution correction factor. This calculation is illustrated by the following equation:

$$DCC = \frac{BCC}{DCF_{test}}$$

With the exception of CEM- and FTIR-measured compounds, dilution correction factors were obtained from the final test reports or from supplemental data provided upon request. Because the test concentrations of CEM- and FTIR-measured compounds were obtained prior to dilution, it was not necessary to calculate a dilution corrected concentration for these compounds.

Determination of Mass of Compound Released

The mass of compound released was calculated by multiplying the dilution-corrected concentration by the volume of the test chamber. This calculation is illustrated by the following equation:

$$\text{Mass compound released} = DCC \times \text{Test chamber volume}$$

Determination of Emission Factors

Once the mass of compound released was calculated, two emission factors were developed for each sample and for each test run: the mass of compound released per item (i.e., per single ordnance) and the mass of compound released per pound NEW. The NEW for all ordnance were determined from data included in the final test reports.

Determination of Average Emission Factors

Steps 1 through 8, as described above, are applicable to individual samples within individual test runs. The final step in the emission factor calculation process was to calculate average emission factors for each compound in terms of mass released per item and mass released per pound NEW. The average emission factors for each compound were calculated as the arithmetic mean of the individual samples associated with the compound. If all samples indicated that the compound was not detected (ND), then the average emission factor was assigned a value of ND.

Emission Factor Ratings

The final step in the emission factor development process is to appraise the emission factors in accordance with the rating system specified in Reference 4. Under this rating system, emission factors are assigned a rating from A to E, where an “A” rating is assigned to the highest quality factors. The criteria used to assign a specific emission factor rating are summarized below.

- A** Excellent. The emission factor was developed primarily from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population was sufficiently specific to minimize variability.
- B** Above average. The emission factor was developed primarily from A- or B-rated test data from a moderate number of facilities. Although no specific bias was evident, it was not clear if the facilities tested represented a random sample of the industry. As with the “A” rating, the source category population was sufficiently specific to minimize variability.
- C** Average. The emission factor was developed primarily from A-, B-, and/or C-rated test data from a reasonable number of facilities. Although no specific bias was evident, it was not clear if the facilities tested represented a random sample of the industry. As with the “A” rating, the source category population was sufficiently specific to minimize variability.
- D** Below average. The emission factor was developed primarily from A-, B-, and C-rated test data from a small number of facilities, and there may have been reason to suspect that these facilities did not represent a random sample of the industry. There also may have been evidence of variability within the source category population.
- E** Poor. The emission factor was developed from C- and D-rated test data from a very limited number of facilities, and there may have been reason to suspect that the facilities tested did not represent a random sample of the industry. There also may have been evidence of variability within the source category population.

Although the ordnance emission factors were developed primarily using A- and B-rated test data, only two tests were conducted per ordnance. Consequently, emission factor ratings of A and B were considered inappropriate.

Conversely, ordnance are manufactured to very tight tolerance levels so there is little variability among items, and there was no evidence that suggested the tested items within each type of ordnance were specially selected. These considerations ruled out assigning the emission factors an E rating. Although the number of items tested within each ordnance was very limited, the other considerations lead to the judgment that a C rating was a better fit than a D rating for all of the emission factors except those based upon C-rated test data. The emission factors for compounds with C-rated test data were assigned a D rating.

The primary reason that the ordnance emission factors have not received higher emission factor ratings is the limited number of test runs associated with each ordnance type. It was decided early in the program that the greater benefit would be to test many types of munitions a few number of times, rather than the same munition multiple times. However, USAEC is currently analyzing the test data obtained to date to identify similarities between test data obtained from different test series. It has been noted that the same pollutants are often emitted from similar types of ordnance (e.g., small caliber bullets) and that the magnitude of the corresponding emission factors are often similar. Therefore, it may be possible to increase the emission factor ratings that are assigned by taking a comprehensive view of the ordnance

emission factors that have been developed rather than by focusing on the test data associated with individual types of ordnance.

CONCLUSIONS

USAEC initiated efforts to generate the quantitative data necessary to effectively quantify emissions resulting from the use of munitions, and to assess the potential health and environmental impact of these emissions. A comprehensive test program has been conducted and has produced scientifically defensible emission factor data for the tactical use of military munitions on U.S. Army training ranges. Data gathered from this program are providing information on the concentration, transport, dispersion, and fate of the air emission products.

USAEC has worked with the USEPA during the development and implementation of the munitions test programs. As a result, USEPA has accepted the resulting emission factors for publication in the *Compilation of Air Pollutant Emission Factors*, better known as AP-42. To date, over 180 munition items have been tested and 57 items are available on the USEPA's AP-42 website: (<http://www.epa.gov/ttn/chief/ap42/index.html>).

REFERENCES

- 1) *Sampling Results for AEC Phase I Training Ordnance Emission Characterization*, Radian International LLC, Oak Ridge, TN, March 1999.
- 2) *Report No. 1 for the Firing Point Emission Study Phase II*, Military Environmental Technology Demonstration Center, U.S. Army Aberdeen Test Center, Aberdeen Proving Ground, MD, March 2001.
- 3) *Report No. 1 for the Exploding Ordnance Emission Study Phase II*, Military Environmental Technology Demonstration Center, U.S. Army Aberdeen Test Center, Aberdeen Proving Ground, MD, August 2002.
- 4) *Procedures for Preparing Emission Factor Documents*, EPA-454/R-95-015, U.S. Environmental Protection Agency, Research Triangle Park, NC, November 1997.

KEY WORDS

Emission factors
Munitions
Ordnance
U.S. Army Environmental Center
U.S. Army
AP-42