Instrumented, unmanned aerial systems (UASs) have been used successfully in eight campaigns since 2010 to determine emission factors from open burning (OB), open detonation (OD), and static firing (SF) demilitarization activities. These systems have sampled directly from the plumes of both test and production activities resulting in emission factors for a range of compounds including CO\textsubscript{2}, CO, particulate matter (PM), metals (e.g., Pb, Cr), polycyclic aromatic hydrocarbons (PAHs), volatile organic carbons (VOCs) including energetics, polychlorinated dibenzodioxin/dibenzo furan (PCDD/PCDF), HCl, and perchlorates (ClO\textsubscript{4}). The sampling system employed in four campaigns included an instrument package lofted by a tethered, helium-filled aerostat. More recent developments have produced a lighter package lofted by a hexacopter UAS (“drone”). Advances in computer miniaturization, sensor development, data telemetry, and methods development have made safe, plume emission characterization possible under real, in-use applications. These methods have been successful, demonstrating excellent repeatability and quality control. Sampling flights have discriminated emissions between munition types, examined the impact of burial depth on OD emissions, recorded particle size distributions, determined metal partitioning to the atmosphere, and sampled for unreacted energetics. These novel, aerial sampling technologies characterize actual, in-plume emissions, providing data useful to addressing environmental considerations.