ATD-GC-MS method for characterization and quantification of organic compounds associated to gunshot particles

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Numerous studies have shown that military and civil use of lead containing ammunitions is associated to severe environmental and health considerations i.e. high blood levels. This has led to the development of lead-free ammunition however these replacement products have been associated to other health implications such as respiratory irritation, asthma, fever and nausea. Emissions from shooting with small calibre ammunition makes up of a complex mixture of gases and particles. For instance, polycyclic aromatic hydrocarbons (PAHs) that are known to have mutagenic properties have been identified in emissions from small calibre rifles using nitro-based propellants (Moxnes *et al*, 2013). It has further been shown that respirable particles in the size range 0.29-0.57 µm from shooting were associated to higher mutagenic activity as compared to larger particle fractions (Palmer, 1994). The aim of this work was to develop a rapid method for quantitative chemical analysis of mutagenic and toxic organic compounds (PAHs and oxy-PAHs) associated to particles and to apply the method in a study of gunshot particles from lead free ammunition. Two standard reference materials, SRM1649b (urban dust) and SRM 1650b (diesel particulate matter) were used for method validation and comparison.

In a 0.7 m^3 test chamber an assault rifle (AK5C) was mounted and three single shots of lead-free ammunition were fired through remote control. Particles were sampled on glassfiber filters (GFF, Ø25 mm) with a flow of 1.0 l/min for 15 minutes. Particles were also monitored with Electrical Low Pressure Impactor (ELPI) and a medium-volume particle sampler (pre-weighed PTFE-filters) to monitor dynamic properties and accurate mass concentrations, respectively.

Table 1. Measured PAH and oxy-PAH concentrations in SRM 1649b (urban dust) and in gunshot particles.

	1649b Certified (mg/kg)	1649b Measured (mg/kg)	Gunshot Measured (mg/kg)
Pyr	4.78±0.03	4.6±0.6	20±1.6
BaA	2.09±0.05	2.0±0.4	4.0±0.3
BaP	2.47±0.17	2.0±0.2	4.6±0.5
A-9,10-dione	1.9*	1.3±0.2	0.47±0.04
BdeA-7-one	4.1*	5.8±0.4	3.0±0.3
BaA-7,12-dione	5.9*	5.0±0.4	0.44±0.05

*Average of results published by Albinet *et al* (2006) and Layshock (2010)

The GFFs were placed in empty metal sampling tubes and PM-bound organics were analysed using automated thermal desorption coupled with gas chromatography-mass spectrometry (ATD-GC-MS), desorption at 300 °C with a helium flow of 50 ml/min for 5 minutes. Fifteen PAHs and sixteen oxy-PAHs were individually quantified. Furthermore, the particles were analysed for metal content using inductively-coupled plasma mass spectrometry (ICP-MS)

Substantial amounts of particles were emitted (~30 mg/shot) of which the vast majority were smaller than 4 µm. As expected, cupper and zink were the dominating elemental species. Table 1 shows the results for some PAHs and oxy-PAHs in SRM 1649 (urban dust) and in gunshot particles. Generally the PAH content in the gunshot particles were higher than in SRM 1649b while the opposite was seen for oxy-PAHs. Monitoring the particle characteristics with ELPI over time revealed that the size distribution was skewed towards fine and ultrafine particles as demonstrated in figure 1 resembling a typical combustion pattern. We hypothesize that the late appearance of larger particles (>948 nm at ~4 min) is a result of agglomeration and condensation processes.

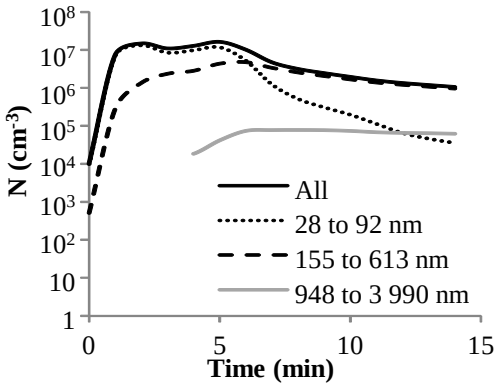

Figure 1. Dynamic properties of small particles emitted from fire arms in the test chamber (ELPI data).

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