

Comparison of Atmospheric Pressure Chemical Ionization and Atmospheric Sampling Glow Discharge Ionization Combined with Tandem Mass Spectrometry for Explosives Vapor Detection

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Although vapor detection is not appropriate for all explosives detection scenarios, it can be a key component in an overall strategy for minimizing the threat of terrorism. Because the number of gas-phase explosives molecules available for analysis is indirectly related to the amount of condensed-phase material, reaching ever lower levels of explosives detection minimizes the system's "false negative" rate. At the same time, the capability of discriminating against all irrelevant compounds in the sample matrix minimizes the "false positive" rate. The detection system must therefore combine high sensitivity with high specificity. Our strategy for meeting these challenging requirements is based on the combination of negative ion formation with tandem mass spectrometry (MS/MS).

Tandem mass spectrometry can enhance the specificity of analysis over that provided by single-stage mass spectrometry. An established application of MS/MS is targeted analysis, explosives vapor detection being a prime example. Selective ionization also facilitates parts-per-trillion level analysis in a complex sample matrix. Thus, negative ion formation is used in this problem because, unlike most compounds in nature, explosives readily form anions. A widely used method for negative ion formation is atmospheric pressure chemical ionization (APCI) in which reagent ions are generated by an atmospheric pressure corona discharge. Efficient negative ion production via electron capture is also effected by atmospheric sampling glow discharge ionization (ASGDI) due to the high number density of thermal electrons in its reduced pressure discharge.

Because the ASGDI source conditions are significantly different from those used in APCI, the performances of the devices differ. Therefore, ORNL, SCIEX, and MSA are currently undertaking a joint effort to investigate the use of ASGDI on a SCIEX triple quadrupole mass spectrometer. The standard APCI interface of the instrument has been modified to allow for either APCI or ASGDI operation. Each ionization source, in combination with the triple quadrupole mass spectrometer, has been demonstrated to be viable for detection and identification of vapors from compounds such as NG, DNT, TNT, PETN, RDX, and HMX. Figures 1 and 2 show calibration data for TNT and RDX, respectively, using the multiple reaction monitoring parameters shown in Table 1. The sample concentrations indicated are in solvent, which was introduced via 20 μ L flow injection.

TABLE 1	Precursor Ion	Product Ion(s)
TNT		
APCI	227 M ⁻	210 (M-OH) ⁻ , 197 (M-NO) ⁻
ASGDI	227 M ⁻	210 (M-OH) ⁻ , 197 (M-NO) ⁻
RDX		
APCI	257 (M+ ³⁵ Cl) ⁻ , 259 (M+ ³⁷ Cl) ⁻	46 NO ₂ ⁻
ASGDI	176 (M-NO ₂) ⁻	102 (M-NO ₂ -CH ₂ N ₂ O ₂) ⁻ , 46 NO ₂

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TNT

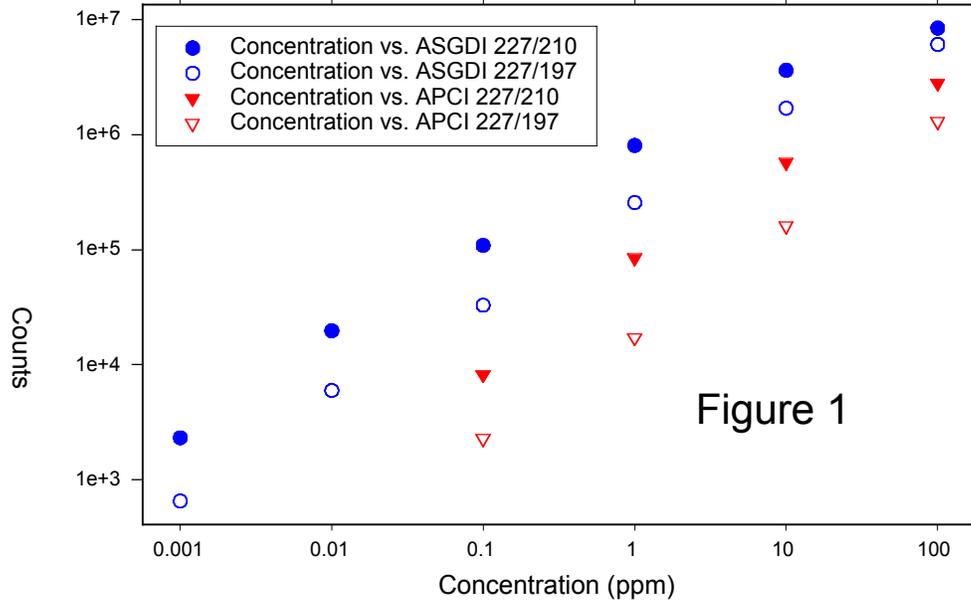


Figure 1

RDX

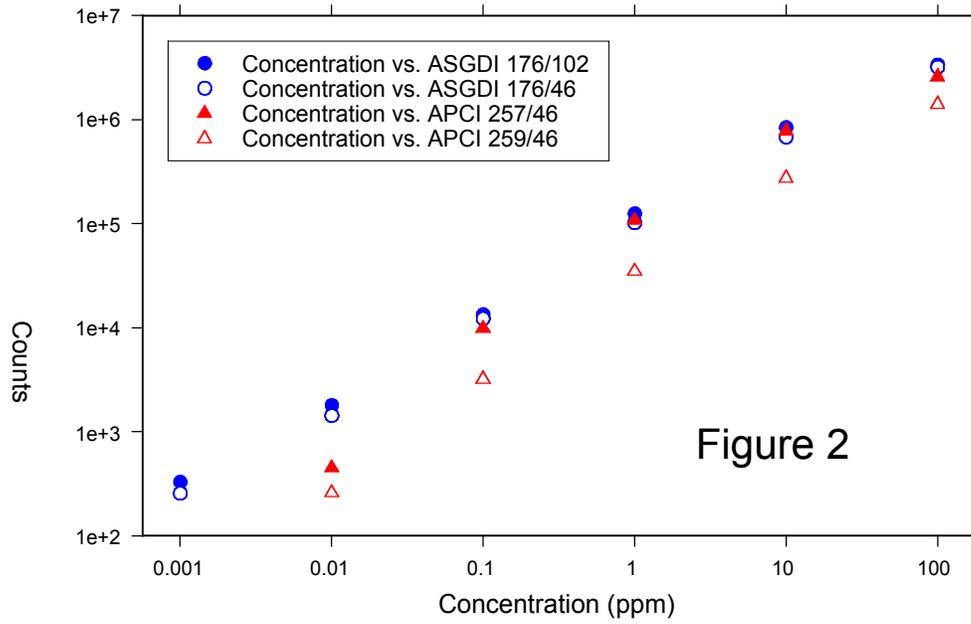


Figure 2