New Electronic Sniffer by Atmospheric Pressure Glow Discharge Plasma

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Introduction

Plasmas have a long-standing analytical history.

Energetic species in a otherwise non-thermal plasma both dissociates species of interest and excites the elemental constituents.

The atomic emission spectrum serves to identify the compounds and ideally its molecular composition with intensity corresponding to concentration.

Miniaturization permits atmospheric pressure operation and battery scale power requirements, thereby permitting mobile field analysis.

Materials and Methods

- Miniature spectrometers, Ocean Optics Maya2000 Pro, Stellar Net Black Comet and comparison to a ¼ meter (SpectraPro 275) spectrograph from Princeton Instruments.
- Two operational modes for ambient monitoring:
  Continuous and Pulsed for pre-collected solid and aerosol samples.
- Spectra acquired under air and Ar atmospheres.
- Voltages: 500-1500V, Currents: < 12 mA

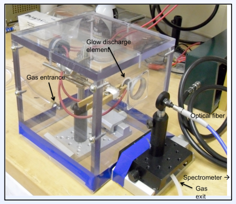
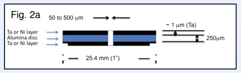


Figure1. Breadboard test system for micro-hollow cathode in glow discharge mode.



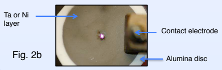


Figure 2. Micro-hollow glow discharge (MHCD) element: (a) schematic (b) photograph of nickel coated alumina disc.

Results

1. Development of Spectral Library

- Identification of compounds depends on associating the plasma emission with a spectral library. This spectral library is comprised of:
  1) Atomic emission spectra based on the NIST Atomic Spectra Database
  2) Diatomic emission spectra based on the LIFBASE database program
  3) MHGD spectra of known analytes.
- Figure 3 shows database spectra in which the transition strength is plotted against wavelength. Such discrete (non-overlapped) transitions enable straightforward identification of elements.

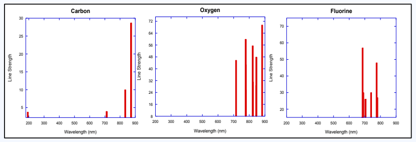


Figure 3. A series of atomic emission spectra showing selected transitions based on NIST Atomic Spectra Database.

- Plasma decomposition of chemical agents can also produce excited electronic emission from molecular fragments. The model diatomic emission spectra plotted in Fig. 4 were generated using a SRI program that includes vibrational-rotational transitions.

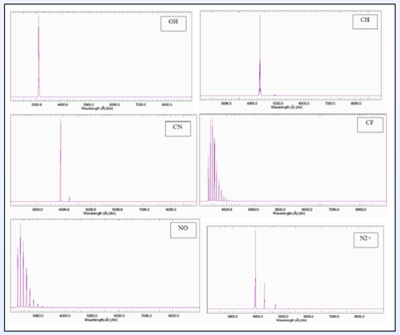


Figure 4. Examples of plasma emission spectra from OH (A-X), CH (A-X), CN (A-X), CF (A-X) and NO (A-X) radicals between 200 – 900 nm.

2. Continuous Flow Mode – Vapor Detection

- Gases were analyzed by exposing them to the MHGD. Survey spectra illustrate the MHGD capability to differentiate various analytes: heptane as a representative aliphatic hydrocarbon, nitrobenzene as a surrogate for TNT based explosives, methanol given its similarity to sugar-peroxide based explosives and chlorobenzene as a representative chlorinated aromatic.

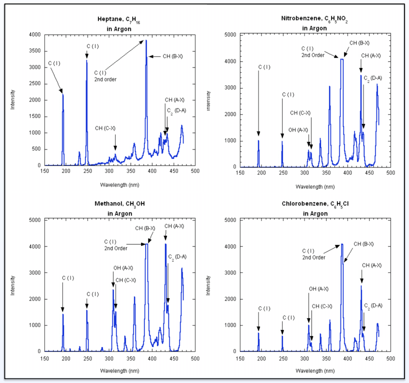


Figure 5. Spectra of model analytes tested in continuous operation

3. Pulsed Operation for Detection of Liquids and Solids.

- Powders and liquids were analyzed in a pulsed operational mode by deposition upon on a conducting (metal) disk that served as a surrogate cathode in the MHGD element. Spectral transitions of target compounds for this operational mode are summarized in Table 1.

Table1. Summary of signature transition(s) and relative intensities observed for compounds tested in pulsed operation.

Molecule	Published Wavelength (nm)	Species/Transition	Relative Intensity
Decane a representative alkane for the aliphatic fraction with diesel fuel	193.3	C (I)	2149
	247.8	C (I)	555
	386.6	C (I) 2nd Order	2423
	389.3	CH (B-X)	1656
	434	C2 (D-A)	1015
Sucrose main ingredient in TATP	193.3	C (I)	231
	247.8	C (I)	376
	386.6	C (I) 2nd Order	354
	434	C2 (D-A)	1201
Potassium Nitrate main ingredient in gun powder	226.2	NO (A-X)	2927
	236.3	NO (A-X)	3509
	247.1	NO (A-X)	2734
	258.7	NO (A-X)	1721
	315.6	N2 (C-B)	3209
	337.0	N2 (C-B)	1615
	356.1	N2 (C-B)	1084
	357.6	N2 (C-B)	1105
Nitrobenzene surrogate for TNT	313.4	N2 (C-B)	2816
	337.0	N2 (C-B)	2286
	356.1	N2 (C-B)	1641
	357.6	N2 (C-B)	1455
	386.6	C (I) 2nd Order	523
	434	C2 (D-A)	536

4. Temperature Measurements

- In non-thermal plasmas, gas temperature may be inferred from the intensity distribution of diatomic emission vibrational-rotational band intensities, as illustrated here by fitting the experimental emission intensity from NO to a numerical simulation using the LIFBASE program.

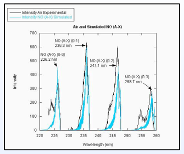


Figure 6. A spectral simulation of NO (A-X) vibrational bands compared to observed MHGD spectrum to infer plasma temperature (~ 1300°C).

Conclusions

- A MHGD unit was successfully developed and applied to the detection of several chemicals related to explosives at trace levels as listed in Table 1. Continuous and pulsed operational modes for analyzing gases, liquids and solids were demonstrated at atmospheric pressure.

Table 2. Detection limit for diverse analytes

Analyte	Heptane	Nitrobenzene	NH3 (aq.)	Chlorobenzene	Benzylamine	Methanol
Estimated Detection Limit (ppm)	2.7	0.01	7.9	0.4	0.03	3.4

- A spectral signature database has been created based on atomic and molecular electronic emission for selected agents within the plasma environment.
- For future alternative plasma configurations will be tested for analytical utility and comparative spectral algorithms will be developed towards compound identification/classification.

Literature Cited

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Acknowledgments

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For Further Information

Please contact rvw12@psu.edu. More information on this and related projects can be obtained at www.eme.psu.edu/faculty/vanderwal.html.