A LASER-BASED SENSOR FOR AMBIENT DETECTION OF RDX AND TNT

Stephen D. Roberson* and Rosario C. Sausa
U.S. Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ABSTRACT

We detect trace residues of RDX and TNT by surface photofragmentation - fragment detection in real time at ambient conditions. An infrared or visible laser generates signature, NO molecular fragments, and a second, low energy, ultraviolet laser facilitates their detection by resonance enhanced multiphoton ionization. We present the effects of pump laser wavelength, laser energy, delay timing between the pump and probe beams, and analyte concentration on signal intensity. Sensitivity analyses yield RDX and TNT detection limits in the low ng/cm^2.

1. INTRODUCTION

The detection of energetic materials is a serious concern in the war on terror, either on the war front or in our homeland. With the widespread use of improvised explosive devices and the increased potential for homeland attack, a sensor that detects energetic materials that is robust, accurate, and easy to deploy would undoubtedly reduce the risk to warfighters and civilians. As a result, there has been much interest in developing such a sensor.

The vapor pressures of energetic materials hexahydro-1,3,5-hexanitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) are very low at ambient conditions. The following Clausius–Clapeyron equations express their concentration as a function of temperature:

$$\log P(RDX[ppt]) = \frac{-6473}{T[K]} + 22.50 \tag{1}$$

$$\log P(TNT[ppb]) = \frac{-5481}{T[K]} + 19.37 , \tag{2}$$

where P is the pressure and T is the temperature (Dionne et al., 1986). At 298 K, the vapor pressure for RDX is 6 ppt and that for TNT is 9 ppb. The low number of airborne energetic particles created naturally under ambient conditions challenges the sensor's sensitivity requirement.

Humans teamed with canines or other animals can detect energetic materials by means of the animal's sensitive, olfactory receptors. Unfortunately, the teams require training, and fatigue from either team member, false positives, or low sensitivity for some compounds hinders their effectiveness for trace energetic material detection. Lasers are gaining widespread use outside the laboratory for their ability to accurately detect spectroscopically low concentrations of energetic materials in real time at ambient conditions. Two laser techniques are laser induced breakdown spectroscopy (LIBS) and laser photofragmentation (PF) - fragment detection (FD).

LIBS uses high-powered, focused lasers to create a plasma at the site where the laser interacts with the material, completely breaking down a complex energetic material into its constituent elements (Munson et al., 2005, 2007, and references therein). Commonly, LIBS employs a Nd-YAG laser with a primary output wavelength of 1064 nm. Sometimes, the Nd-YAG output is frequency doubled, tripled, and even quadrupled because of the lower amount of laser pulse power needed to create a plasma at shorter wavelengths. The material is identified by examining the elemental spectra looking for intensity ratios of two elements, elevation of certain elements above ambient conditions, the presence of strange elements, etc. (Munson et al., 2005). This method of identification can be a problem for a large number of energetic materials due to the common elements found in their composition; namely carbon, nitrogen, and oxygen.

PF/FD techniques use one or multiple lasers to identify the energetic materials (Lemire et al,., 1993; Simeonsson and Sausa, 1998; Heflinger et al., 2002; Cabalo and Sausa, 2005, and references therein). One laser tuned to a specific wavelength both photofragments the target molecule and facilitates the detection of characteristic fragments by resonance enhanced multiphoton ionization (REMPI), laser induced fluorescence (LIF), or both. Alternatively, in a two-laser setup, one laser photofragments the target molecule and a second laser, time-delayed from the first laser, probes the photofragment. As opposed to LIBS, photofragmentation causes the complex molecule to break down into larger fragments or signature molecular groups. These molecular groups would not commonly be found in large quantities under ambient conditions, indicating the presence of the energetic material.

****Presenter; ARL/NRC Postdoctoral Research Associate***

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **01 DEC 2008**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE
A Laser-Based Sensor For Ambient Detection Of RDX AND TNT

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**5**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

In this paper, we present our results on the detection of trace RDX and TNT at ambient conditions using a surface PF/FD technique. An infrared or visible laser generates characteristic NO fragments from the target material and an ultraviolet laser tuned to near 226 nm facilities their detection by REMPI. We report the effects of analyte concentration, laser energy, and time-delay between lasers on signal intensity, and determine detection limits for both RDX and TNT.

2. APPROACH

Figure 1 illustrates the PF/FD technique for energetic materials. Many energetic molecules have NO_2 groups, as shown in figure 2 for RDX and TNT, that are weakly bonded to their skeletal structure. Infrared, visible, or ultraviolet laser radiation ruptures these bonds to form excited or ground state NO_2 molecules. Oftentimes, the excited, displaced NO_2 molecules predissociate and NO molecules are readily created:

$$R - NO_2 \xrightarrow{n_1 h\nu_1} R + NO(X\,^2\Pi) + O \qquad (3)$$

NO is then detected by its prompt emission if formed electronically excited, or by LIF, REMPI, or both, if formed in its ground electronic state. The LIF and REMPI processes are represented by the following equations:

$$NO(X\,^2\Pi) \xrightarrow{n_2 h\upsilon_2} NO(A^2\Sigma^+) \rightarrow NO(X\,^2\Pi) + h\nu_3 \qquad (4)$$

$$NO(X\,^2\Pi) \xrightarrow{n_2 h\nu_2} NO(A^2\Sigma^+) \xrightarrow{n_2 h\nu_2} NO^+(X\,^1\Sigma^+) + e^- \qquad (5)$$

The phtofragmentation and detection processes depicted in the above expressions are extremely fast, typically in the fsec to msec- timescale.

LIF is widely used to detect airborne NO because of its ease of setup and sensitivity. LIF also offers the ability to make measurements in real time that allow for calculations of quantities like temperature and concentration (Andresen, 2001). It has been widely used to detect NO in a number of places including exhaled human air (Mitscherling et al., 2007), high altitude (Sandholm et al., 1997), and flames (Venizelos and Sausa, 1998).

One significant challenge when trying to use LIF to detect energetic materials under ambient conditions is collisional quenching. Collisional quenching at atmospheric pressure reduces the radiative lifetime of

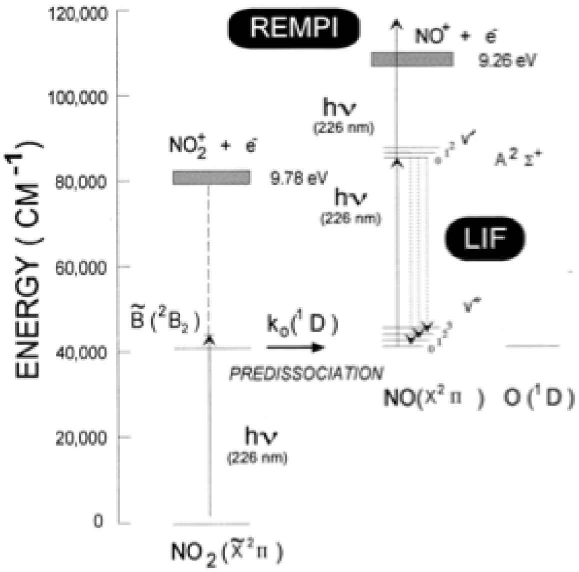

Figure 1 –- An energy diagram of PF / FD for NO detection from an NO_2 fragment. The energies required for both REMPI and LIF are shown.

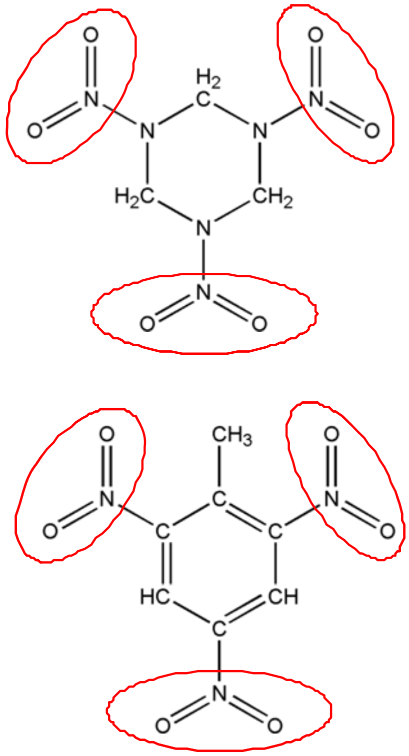

Figure 2- Structural Diagram of RDX (top) and TNT (bottom). The circled NO_2 groups are the signature molecular fragments to be detected using PF/FD.

NO making it more difficult to detect. An excited NO fragment is more likely to transfer its energy to a neighboring molecule without emitting a photon at atmospheric pressure as opposed emitting one at lower pressures. REMPI mitigates this problem to a large extent because the ionization process is much faster that the collision quenching process.

In the REMPI technique, a laser selectively creates ions of interest in an electric field between two plates. The plates capture almost all of the charged particles, making for a more effective detection of small amounts of NO than LIF. REMPI has been used to detect NO in a number of experiments. It was used to detect concentrations of NO in a NO/NO_2 gas mixture (Pastel and Sausa, 2000). Most importantly for this research, previous work shows that we can detect TNT easily using REMPI at atmospheric pressure (Swayambunathan et al., 1999).

3. EXPERIMENTAL SETUP

We use a two-laser, pump-probe system to detect energetic materials on quartz substrates. A schematic of the experimental setup is seen in Figure 3. A continuous, infrared laser (CO_2 Synrad Series 48-2-28 (W)) or visible laser (Continuum Sunlite EX OPO pumped by a Continuum Powerlite® Precision II Nd:YAG laser) generates airborn energetic molecules or the characteristic NO fragments, and an ultraviolet laser (frequency doubled, Lumonics Hyperdye 300 laser, pumped by a Continuum Surelite II Nd:YAG laser) facilitates their detection by REMPI. The laser wavelengths are approximately 9.6 to 11.6 μm, 455, 470, 500, and 550 nm, and ~ 227 nm, and their respective energy is up to 2 J, up to 35 mJ, and ~ 50 μJ.

The probe laser beam passes through either a germanium lens with a focal length of about 38 mm or quartz lens with a focal length of 75, 200, or 300 mm that focuses the beam near the substrate's surface containing the energetic material. The surface is near the focal length of the lens but not at the focal point; 0.6 mm for the infrared lens and 60, 163, and 261 mm for the 75, 200, and 300-mm quartz lenses, respectively. If the surface is too close to the focal point, the pump laser beam will either etch the surface or create a plasma, thus producing false REMPI signals. Our infrared laser fluence is ~ 0.4 Jcm^2 and our visible laser fluence ranges from 0.6 to 1.4 J/cm^2.

The REMPI probe is fabricated in-house. It contains two metals plates about 1.3 cm by 2 cm in size with two, 3.2-mm holes in the center that allow the pump beam to pass through and strike the surface. The plates are 4 mm apart from each other, and the lower plate is 1 mm from the substrate's surface. The average electric field is 250 V/mm for a 1000-V bias between the plates. A current amplifier (Keithley 427, gain 10^6-10^7 V/A, time constant 0.01 ms) amplifies the signal, whose output is fed to a 125-MHz oscilloscope (LeCroy 9400) for display. A personal computer records the signals from a boxcar averager (Stanford Research Systems, SR250). We use a digital delay generator (Stanford Research Systems, DG535) to control the pulse length of the infrared lasers, as well as the time delay between the pump and probe lasers.

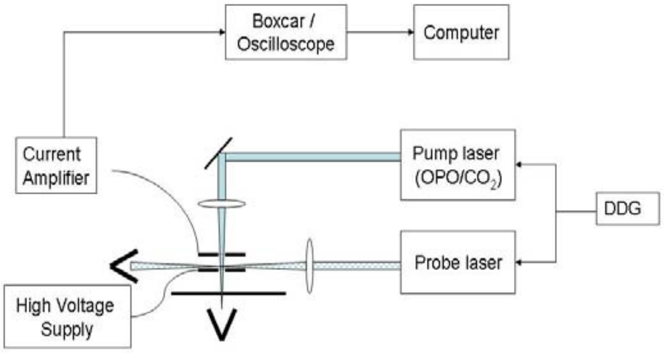

Figure 3 – Diagram of the experimental setup.

We prepare thin films of TNT and RDX by coating circular quartz plates with 1 ml of dilute solutions of the target compound in methanol and then evaporating the solvent with a hotplate. We mount the substrate on a computer-controlled, XYZ stage and record the ionization signal with the pump beam on, while we simultaneously move the substrate at a rate of ~7 mm/sec and scan the probe laser at a rate of 0.0025 nm/s over the region of 226.75 to 227.25 nm. We determine the technique's sensitivity by recording the REMPI response of TNT and RDX films prepared from serial dilution of ~ 0.17 g/ml of TNT/methanol or RDX/methanol stock solution. The REMPI response for a given sample concentration is the integral of the area underneath the curve for each spectrum.

4. RESULTS AND DISCUSSION

Figure 4 shows REMPI spectra of NO from TNT and NO. We employ infrared, laser radiation or 450-nm radiation to vaporize/photolyze the target material and ultraviolet laser radiation to selectively excite the characteristic NO fragment. The infrared laser power is 200 mW, whereas the visible and ultraviolet laser energy is about 18 mJ and 50 μJ, respectively. We also show a spectrum of NO in a gas cell at ambient conditions for comparison purposes. The prominent spectral features of the energetic material are similar to those of NO, and are attributed to NO rotational lines of the A$^2\Sigma^+$ - X$^2\Pi$ (0,0)

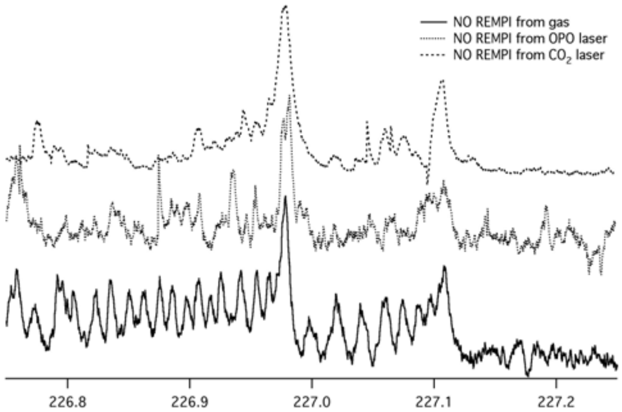

Figure 4 – REMPI signal from NO from a gas cell, from the sample using an infrared laser, and from the sample using a visible laser.

band. The visible laser spectrum is easily reproduced compared to the infrared laser spectrum, which was more difficult to obtain. Pump laser wavelengths of 470, 500, and 550 nm yield similar spectra that show the main NO features.

Figure 5 shows the NO signal dependence on infrared laser power for TNT and RDX. The pulse duration is 500 microseconds. The signal strength increases linearly with laser power for both compounds, but RDX's response is almost a factor of 10 more than TNT's response at 1 W. Also, an increase in laser fluence per unit time increases the signal intensity, as expected. We obtain similar results with 455-nm laser radiation up to about 20 mJ. Under our experimental conditions, our laser power densities are insufficient to either etch the quartz or generate a plasma at the quartz's surface.

Figure 6 shows the NO signal dependence on TNT and RDX concentration using the infrared pump laser (top) and visible laser (bottom). The time delay between the pump and probe laser is 1 ms. We find that the signal intensity does not change when we vary the pump-probe delay between 1 and 10 ms. As shown in figure 3, the RDX and TNT signals are linear over a wide range of concentrations. Also, the response signals of RDX are greater than those of TNT. Cabalo and Sausa report a similar trend using a similar setup, but with a 248-nm pump laser (Cabalo and Sausa, 2005). They attribute RDX's higher sensitivity compared to that of TNT to the fact that the nitrogen-nitrogen bond found in RDX is weaker than the carbon-nitrogen bond found in TNT. More energy from the laser is needed to overcome this bond in the TNT molecule, resulting in a lower level of detection for TNT than RDX. They also point out that TNT has several alternative decomposition pathways that compete with R—NO_2 bond scission such as CH_3 oxidation to form anthranil, nitro–nitrite isomerization, and catalysis. These pathways also decrease the initial production of NO_2 and contribute to TNT's lower sensitivity relative to RDX. A sensitivity analysis of our data that utilizes knowledge of effected area of the energetic material yields RDX and TNT detection limits in the order of ng/cm^2.

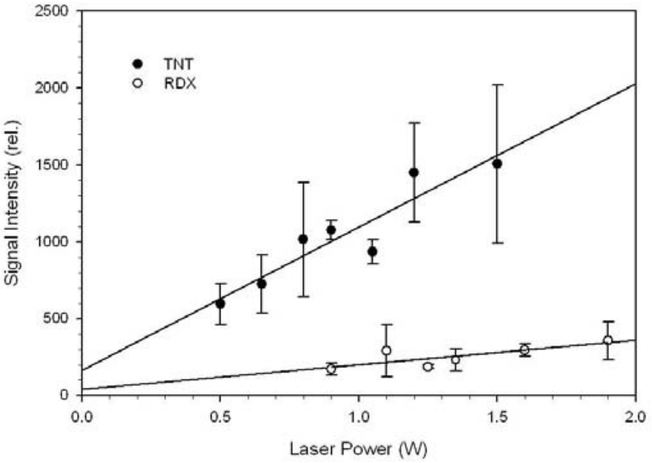

Figure 5 - Signal strength vs. laser power. As the laser energy increases, the signal strength from the REMPI probes increases, indicating better detection

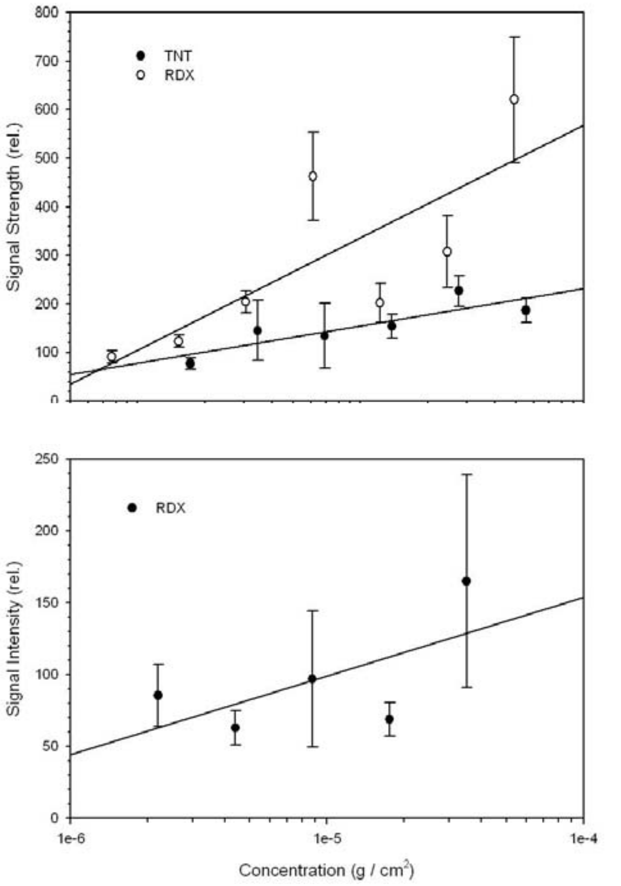

Figure 6 – Concentration analysis graph for the CO_2 laser (top) and the OPO laser (bottom).

CONCLUSION

The surface PF/FD technique exhibits great potential for detecting residues of RDX and TNT at ambient conditions in real time because of its high sensitivity and selectivity. The probe laser generates copious, signature NO fragments, which are detected by REMPI using a probe laser. This technique is not restricted to TNT and RDX, and has the potential to be extended to other energetic materials.

ACKNOWLEDGEMENTS

We thank Dr. Rose Pesce-Rodriguez of the Army Research Laboratory (ARL) for providing us with the TNT and RDX samples, and Dr. Barrie Holman of ARL for the use of his CO_2 laser. We also thank Drs. Chiung-Chu Chen and Michael Grams, both from ARL, for their invaluable assistance. Support from the National Research Council Postdoctoral Research Associateship Program is greatly appreciated.

REFERENCES

Andresen, P., 2001: Laser induced Fluorescence. *Optical Measurements: Techniques and Applications (Heat and Mass Transfer),* O. Feldmann and F. Mayinger, Eds., 2nd ed. Springer, 195-226.

Bradshaw, J. D., M. O. Rodgers, and D. D. Davis, 1982: Single photon laser-induced fluorescence detection of NO and SO_2 for atmospheric conditions of composition and pressure. *Appl.Opt.,* **21**, 2493-2500.

Cabalo, J., R. Sausa, 2005: Trace detection of explosives with low vapor emissions by laser surface photofragmentation-fragment detection spectroscopy with an improved ionization probe. *Appl.Opt.,* **44**, 1084-1091.

Dionne, B. C., D. P. Rounbehler, E. K. Achter, J. R. Hobbs, and D. H. Fine, 1986: Vapor pressure of explosives. *Journal of Energetic Materials,* **4**, 447.

Heflinger, D., T. Arusi-Parpar, Y. Ron, and R. Lavi, 2002: Application of a unique scheme for remote detection of explosives. *Opt.Commun.,* **204**, 327-331.

Lemire, G. W., J. B. Simeonsson, and R. C. Sausa, 1993: Monitoring of vapor-phase nitro compounds using 226-nm radiation: fragmentation with subsequent NO resonance-enhanced multiphoton ionization detection. *Anal.Chem.,* **65**, 529-533.

Mitscherling, C., J. Lauenstein, C. Maul, A. A. Veselov, O. S. Vasyutinskii, and K. Gericke, 2007: Non-invasive and isotope-selective laser-induced fluorescence spectroscopy of nitric oxide in exhaled air. *Journal of Breath Research,* **1**, 026003.

Munson, C. A., De Lucia, Jr., Frank C., T. Piehler, K. L. McNesby, and A. W. Miziolek, 2005: Investigation of statistics strategies for improving the discriminating power of laser-induced breakdown spectroscopy for chemical and biological warfare agent simulants. *Spectrochimica Acta Part B: Atomic Spectroscopy*, **60**, 1217-1224.

Munson, C. A., J. L. Gottfried, De Lucia, Jr., Frank C., K. L. McNesby, and A. W. Miziolek, 2007: Laser-based Detection Methods of Explosives. *Counterterrorist Detection Techniques of Explosives,* J. Yinon, Ed., Elsevier B.V., 279-321.

Pastel, R. L., R. C. Sausa, 2000: Spectral Differentiation of Trace Concentrations of NO_2 from NO by Laser Photofragmentation with Fragment Ionization at 226 and 452 nm: Quantitative Analysis of NO-NO_2 Mixtures. *Appl.Opt.,* **39**, 2487-2495.

Sandholm, S., S. Smyth, R. Bai, and J. Bradshaw, 1997: Recent and Future Improvements in two-photon laser-induced fluorescence NO measurement capabilities. *J. Geophys. Res.,* **102**, 28,651-28,661.

Simeonsson, J. B., R. C. Sausa, 1996: A Critical Review of Laser Photofragmentation/Fragment Detection Techniques for Gas-Phase Chemical Analysis. *Applied Spectroscopy Reviews,* **31**, 1-72.

--1998: Laser photofragmentation/fragment detection techniques for chemical analysis of the gas phase. *TrAC Trends in Analytical Chemistry*, **17**, 542-550.

Swayambunathan, V., R. C. Sausa, and G. Singh, 2000: Investigations into Trace Detection of Nitrocompounds by One- and Two-Color Laser Photofragmentation/Fragment Detection Spectrometry. *Appl. Spectrosc.,* **54**, 651-658.

Swayambunathan, V., G. Singh, and R. C. Sausa, 1999: Laser Photofragmentation-Fragment Detection and Pyrolysis: Laser-Induced Fluorescence Studies on Energetic Materials. *Appl.Opt.,* **38**, 6447-6454.

Venizelos, D. T., R. C. Sausa, 1998: Laser-induced fluorescence, mass spectrometric, and modeling studies of neat and NH_3-doped $H_2/N_2O/Ar$ flames. *Combustion and Flame,* **115**, 313-326.