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13. ABSTRACT (Maximum 200 words)

The sensitivity and detection capability of a deep-UV laser-induced-fluorescence system for detection of trace species in water was investigated and studied. Dissolved Organic Compounds (DOCs) and other related trace species were measured for the first time in drinking water and in Reverse Osmosis Processed water. The portable LIF system was used to analyze in real time the input water and the output water from a laboratory Reverse Osmosis water unit. The input water (obtained from surface wells and used for irrigation purposes) had a large spectral signature near 450 nm due to DOCs in the water. The RO output water has a much reduced level of DOCs and was an effective monitor of the filter membrane condition. It was found that the fluorescence spectrum is different for 266 nm excitation than for 355 nm excitation, with 266 nm appearing to produce greater DOC fluorescence. Preliminary LIF spectra of the weak vinegar (0.01M) acid wash water used to clean a ROWPU were obtained. We also studied similar spectra for other trace and toxic chemical species related to the RO process and eventually related to toxic and chemical agent contamination. We studied and demonstrated the first use of deep-uv LEDs for LIF type detection of DOCs and trace species in water. The initial results were very promising, and the LIF type signal was found to be on the same order of magnitude as that using the UV laser source. We plan to extend these results and develop a compact LED based LIF system for water monitoring in real-time.

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Real-Time Detection of Trace Contaminants and Bio/Chemical Agents in ROWPU Processed Drinking Water using Reagentless UV Laser-Induced-Fluorescence

Final Progress Report

Period: 1 May 2005 - 30 November 2006

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Abstract:

The sensitivity and detection capability of a deep-UV laser-induced-fluorescence system for detection of trace species in water was investigated and studied. Dissolved Organic Compounds (DOCs) and other related trace species were measured for the first time in drinking water and in Reverse Osmosis Processed water. The portable LIF system was used to analyze in real time the input water and the output water from a laboratory Reverse Osmosis water unit. The input water (obtained from surface wells and used for irrigation purposes) had a large spectral signature near 450 nm due to DOCs in the water. The RO output water has a much reduced level of DOCs and was an effective monitor of the filter membrane condition. It was found that the fluorescence spectrum is different for 266 nm excitation than for 355 nm excitation, with 266 nm appearing to produce greater DOC fluorescence. Preliminary LIF spectra of the weak vinegar (0.01M) acid wash water used to clean a ROWPU were obtained. We also studied similar spectra for other trace and toxic chemical species related to the RO process and eventually related to toxic and chemical agent contamination. We studied and demonstrated the first use of deep-uv LEDs for LIF type detection of DOCs and trace species in water. The initial results were very promising, and the LIF type signal was found to be on the same order of magnitude as that using the UV laser source. We plan to extend these results and develop a compact LED based LIF system for water monitoring in real-time.

1. Introduction and Background

ARO and RDECOM Needs for monitoring of ROWPU purified Drinking Water

ARO and RDECOM/Edgewood Chemical Biological Center have a need for real-time, sensitive detection and monitoring of trace and toxic contaminants in drinking water sources for the Army. In particular, it is important to be able to detect the level of DOCs, toxic chemicals, and trace species for water that has been purified by the micro-filter and Reverse Osmosis water purification system (ie., Reverse Osmosis Water Purification Unit: ROWPU). Currently, monitoring is conducted by taking water samples that are then sent out for wet-chemical laboratory analysis. These standard analysis techniques (Mass spectroscopy, liquid chromatography, etc.) serve as the "gold standard" for the quality and efficacy of the ROWPU but are not conducted in real-time and often require adding reagents to the water samples. It would be advantageous to add another level of analysis aimed at real-time detection of some of the trace species that could be present in the ROWPU outflow. It would be advantageous if the analysis did not require reagents so as to reduce storage requirements and chemical life-time issues.

In addition, ARO also has a primary need to be able to detect chemical agents and biological related agents in water.

Technical Background of Laser Induced Fluorescence System

Previously, our research group developed a portable UV Laser-induced-fluorescence (LIF) that had been shown to provide sensitive detection of trace organic species in both seawater and bottled drinking water.[1-5] The system was shown to detect trace DOCs (Dissolved Organic Compounds) in water with a sensitivity approaching two to three orders of magnitude better than previous commercial spectrofluorometers and an absolute sensitivity approaching parts-per-trillion in terms of the fluorescence standard Quinine Sulfate. The system detects the natural fluorescing compounds in the water and does not require regents or outside chemicals for operation.

A photo of the portable LIF system is given in the Fig. 1a and a schematic is given in Fig. 1b. The LIF system uses two lasers (266 nm, 355 nm; 8 kHz pulsed laser) and 23 channel emission PMT detection system. The LIF system is portable and has been able to plot in real-time the relative concentration of DOCs and dissolved or leached plasticizer compounds in the water sample.[1-5] For example, Figures 2 and 3 show the detected LIF spectrum of different water samples showing the high level of DOCs (related to the fluorescence emission seen near 450 nm) from tap water, and the lower levels measured for different bottled purified water samples. As can be seen, the LIF system is a very sensitive detection system of levels of DOCs in water and may have application to a wider range of toxic chemicals that may be present in water such as chemical agents.

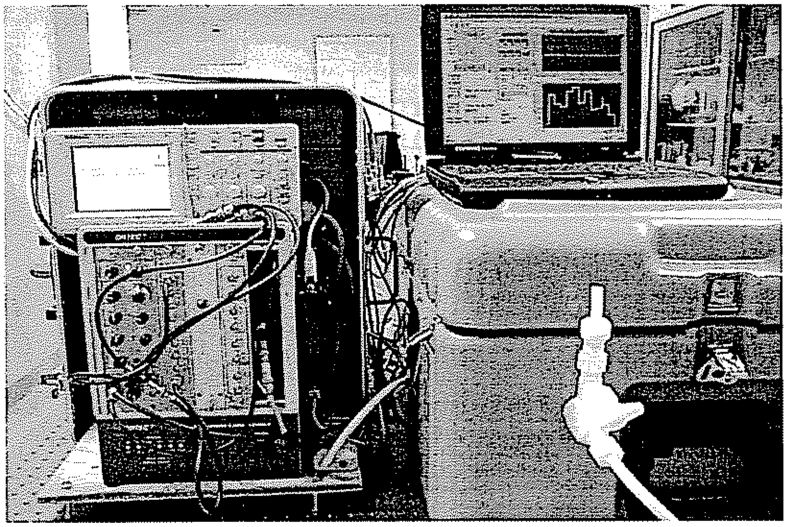

Fig.1a. Photo of portable Laser-Induced-Fluorescence (LIF) system used to detect dissolved organic compounds (DOCs) and toxic trace species in water

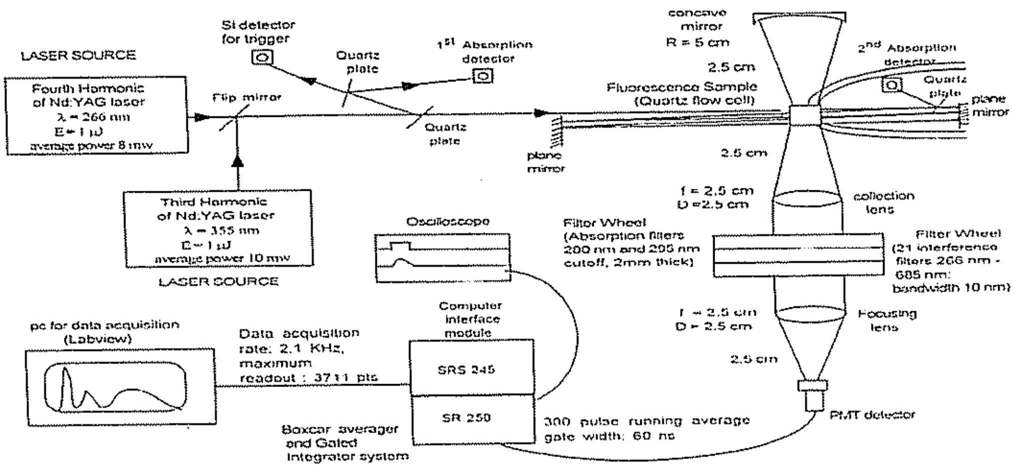

Figure 5.1 Schematic of the experimental setup of the portable Laser Induced Fluorescence (LIF) system.

Fig. 1b. Schematic of Deep-UV LIF system

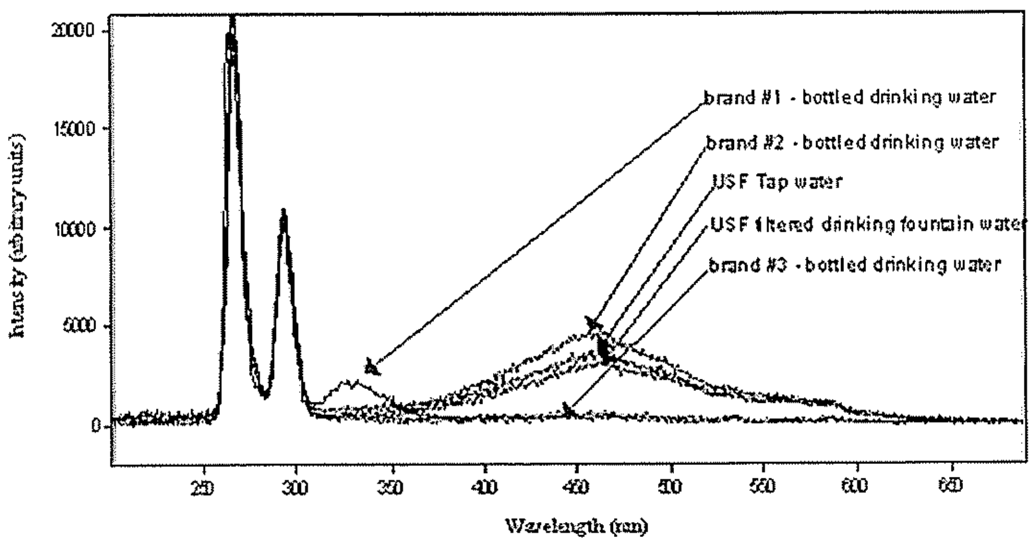

Figure 2: LIF signal from several different commercial bottled water samples showing different levels of fluorescing DOCs and leached plastic compounds.

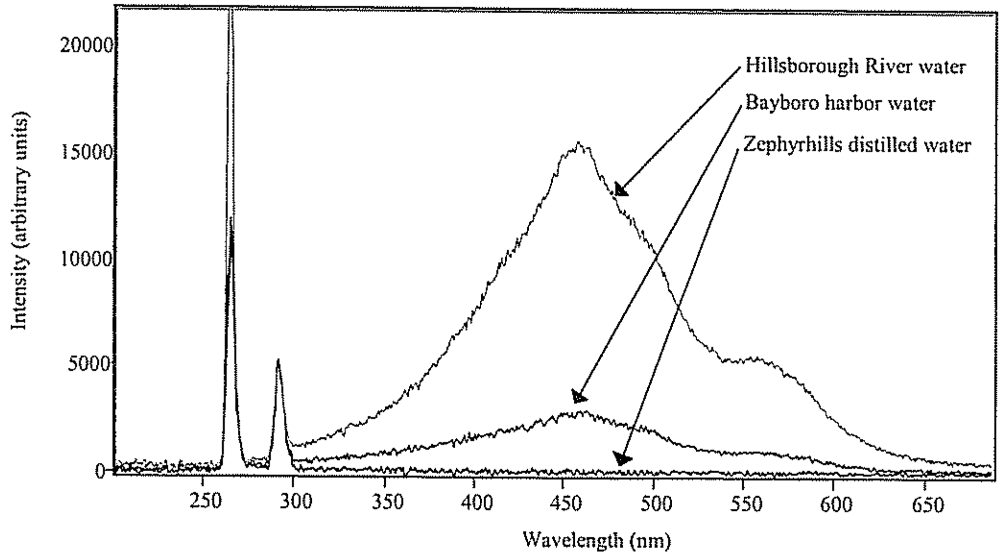

Figure 3: LIF spectrum of ground water samples and distilled water samples showing high levels of DOCs in ground water

2. Statement of Problem Studied

We studied the sensitivity and detection capability of a deep-UV laser-induced-fluorescence system for detection of trace species in water. Dissolved Organic Compounds and other related trace species were measured for the first time in drinking water and in Reverse Osmosis Processed water.

3. Summary of Results and Progress Made During Research Period (1 May 2005 – 30 November 2006)

We modified and used the LIF system toward monitoring of the water processed by the ROWPU, establish its sensitivity and utility toward different species, and applied the system for the initial detection of chemical agents and associated toxic species.[6-8]

Task 1: Initial application of existing LIF system for ROWPU water analysis:
The portable LIF system has been used to analyze the input water and the output water from a laboratory Reverse Osmosis water unit for the first time. Water samples from the RO unit were obtained and used in the quartz flow cell of the LIF system. The measured spectrum of the water is shown in Figs. 4 and 5. As can be seen, the input water (obtained from surface wells and used for irrigation purposes) has a large spectral signature near 450 nm due to DOCs in the water. The RO output water has a much reduced level of DOCs.

It was found that the fluorescence spectrum is different for 266 nm excitation than for 355 nm excitation, with 266 nm appearing to produce greater DOC fluorescence.

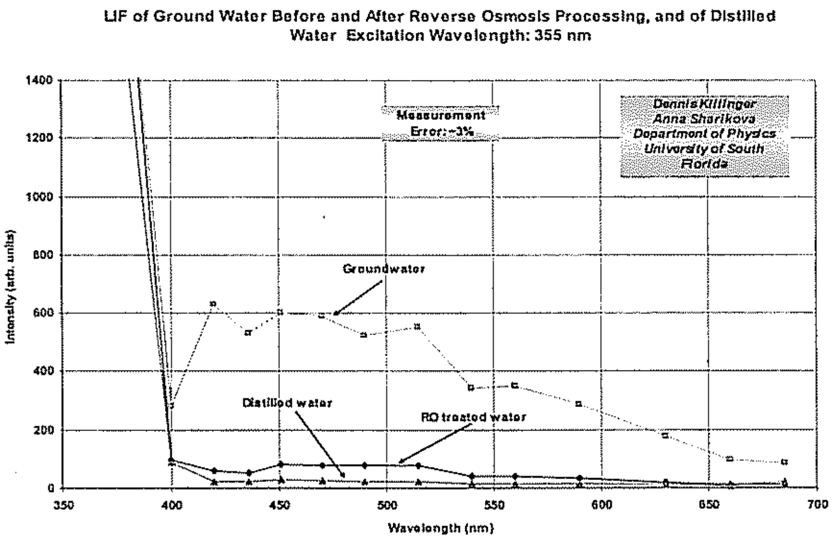

Figure 4: LIF measurements of RO Processed Ground Water using 355 nm laser excitation

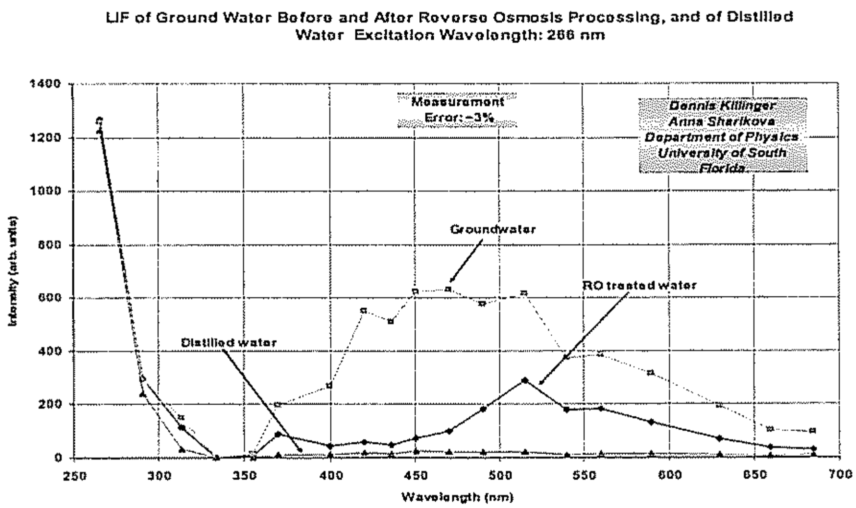

Figure 5: LIF measurements of RO Processed Ground Water using 266 nm laser excitation

As can be seen, the LIF system allows for the detection of the DOCs in water.

We have used the LIF unit to help monitor the water in real time. The LIF system was set-up near some of the RO water processing units we have in an associated water processing lab on campus. Figure 6 shows a photograph of one of the RO water processing units at USF.

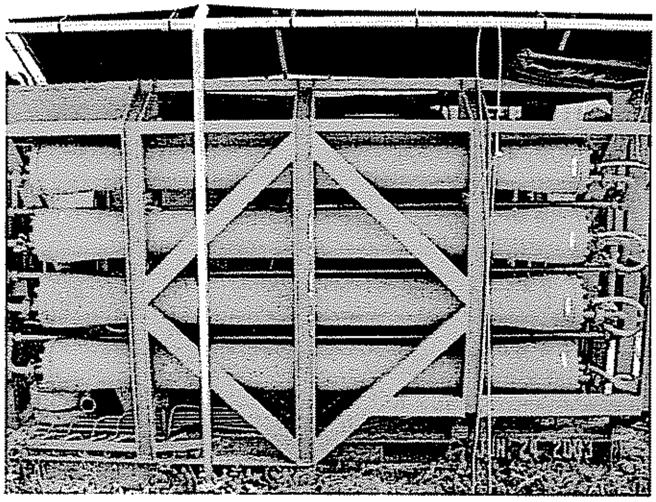

Figure 6: Photo of one of the ROWPU units on campus used for processing water for subsequent analysis by our LIF system.

The initial measurements showed a large spectral feature at the DOC emission wavelengths. We are now conducting further tests in real time to detect different spectral data as the input water quality changes.

It should be added that a considerable effort was also made to modify the pre-existing LIF system including re-writing the LabView instrument controller software, re-aligning the optical system, and incorporating different calibration and background spectral subtraction procedures.

Task 2: Chemical analysis of water samples and fluorescence spectral features:
:

The water used in the RO unit is in the process of being analyzed for total organic content using a Hach DR/4000 instrument. These results will be compared to the LIF results.

We have also started to make preliminary spectral measurements of samples of surrogate chemical agents using Malithion which has a similar chemical structure as VX and GB. For example, Figure 7 shows preliminary LIF spectra of the weak vinegar (0.01M) acid wash water used to clean a ROWPU. We are also studying similar spectra for other trace and toxic chemical species related to the RO process and eventually related to toxic and chemical agent contamination.

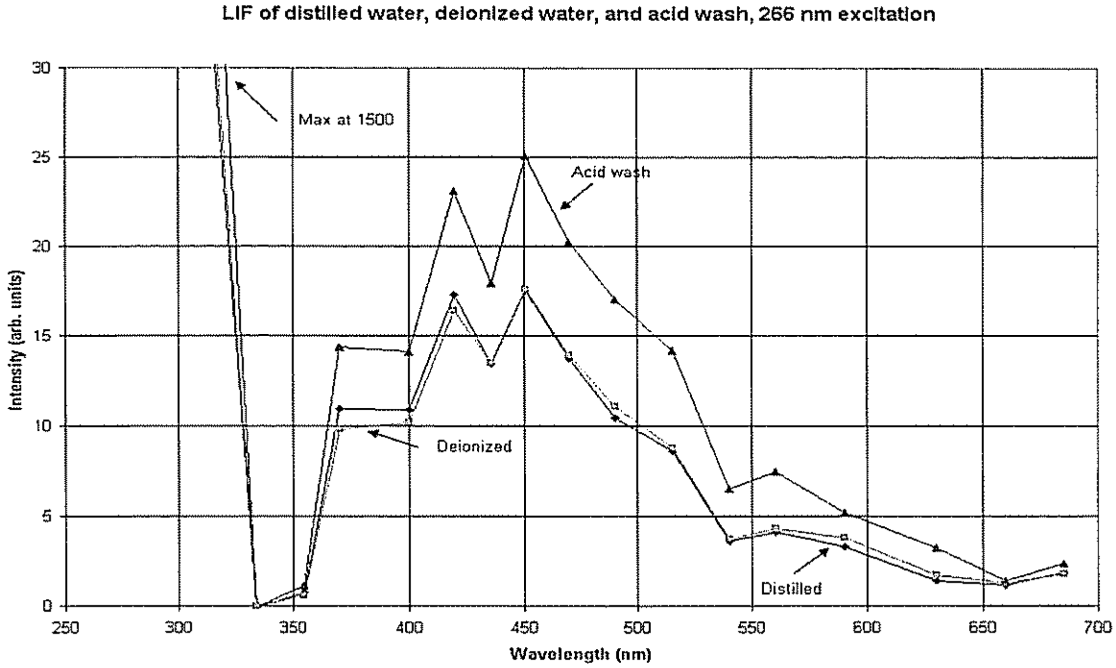

Figure 7: LIF spectra measured for chemical wash used in RO Processing. Note: The intensity scale has been expanded compared to the other LIF spectra usually shown.

Research that is still needed includes a more complete wet-chemical analysis of the water (mass spectroscopy, liquid chromatography) and the comparison of this data to the LIF data.

Task 3: Initial use of deep-UV LEDs for excitation sources for water detection

We studied and demonstrated the first use of deep-uv LEDs for LIF type detection of DOCs and trace species in water. A schematic of our apparatus is shown in Fig. 8

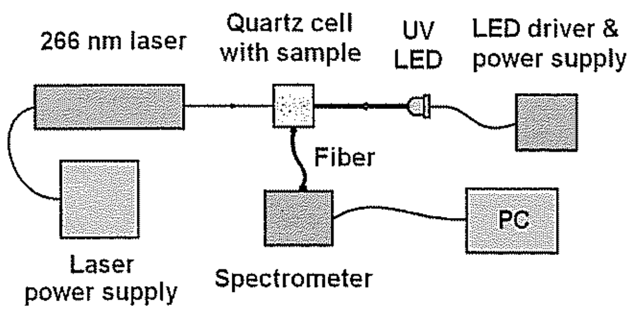

Fig. 8 Schematic of LIF type system using deep-uv LEDs

The initial results were very promising, and the LIF type signal was found to be on the same order of magnitude as that using the UV laser source. Figure 9 shows some of the results.

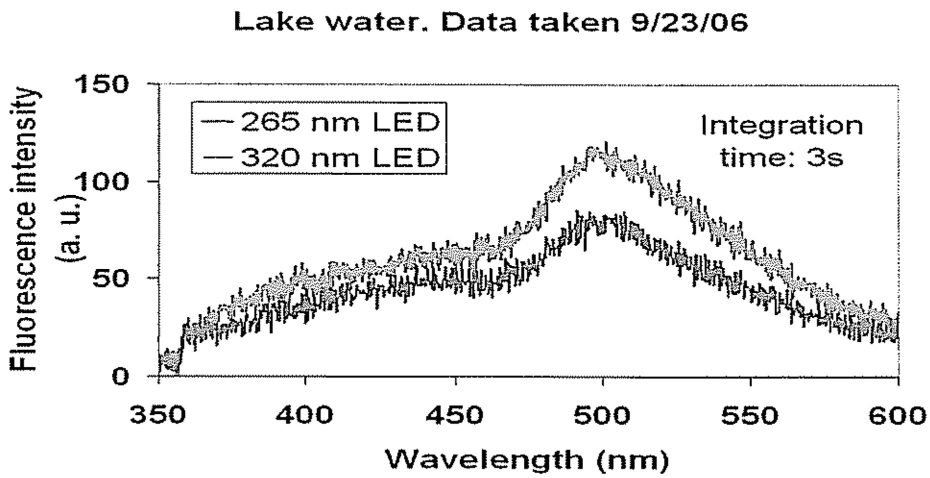

Fig. 9 LIF type emission from water using deep-UV LEDs for excitation

We plan to extend these results and develop a compact LED based LIF system for water monitoring in real-time.

4. Conclusions and Recommendations

The LIF system has been successfully used for the first time to measure trace species in the water stream of a RO processing unit. The levels of DOCs were measured using the actual input/output water flow of the RO water processing system. The sensitivity of the LIF system appears to be very high, in-line with our earlier work showing it to be several orders of magnitude better than conventional spectrofluorometer sensor systems.

We plan to extend these measurements to a wider range of input water contamination conditions and to different chemical agents and toxic species. The system will be used as a real-time sensor to demonstrate its utility as a warning sensor. In addition, the LIF measurements will be substantiated with other water chemical instruments in order to better ascertain the chemicals and concentration limits of the instrument.

5. Papers and technical reports supported (or partially supported) under this grant

A.V. Sharikova and D. K. Killinger, Laser-induced fluorescence studied of water processed by a reverse osmosis purification unit, *Proc. of SPIE* **5994**, 59940B-1–59940B-5 (2005).

LIF Detection of Trace Species in Water Using Different UV Laser Wavelengths, Anna Shatokova and Dennis Killinger, Submitted to International Journal of High Speed Electronics (July, 2006).

Water Monitoring with Laser Fluorescence, Dennis Killinger and Vasanthi Sivaprakasam, Invited Review , Optics and Photonics News, p35, January 2006

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Optics and Photonics: Keystone Technologies for Sensors in Homeland Security, Dennis Killinger, Invited Keynote to US Congressional Research and Development Caucus for Optical Society of America, Oct. 6 2005

LIF detection of trace species in water using different UV laser wavelengths, Anna Sharikova and Dennis Killinger, ISSSR 2006 Conference, Bar Harbor, May 30, 2006.

New spectroscopic methods for stand-off detection of biological and biopolymer weapons, Dennis Killinger, Invited Overview, DTRA Biotech workshop for Advanced Systems and Concepts (ASCO), Ft. Belvoir, June 14, 2006

6. Scientific personnel supported and any advanced degrees

Two graduate students (A. Sharikova and A. Makoui) were supported partially by this grant. Both students are expected to receive their Ph.D. in 2007.

7. Report of Inventions: A provisional patent application has been filed on October 27, 2006 titled "Deep UV LED and laser fluorescence apparatus for monitoring water quality" based partially on this grant. The patent disclosure indicates:

This invention was made with U.S. government support under grant No. W911NF-05-1-0431 awarded by the U.S. Army Research Office, and grant No. N00014-04-1-0555 awarded by the U.S. Office of Naval Research. The U.S. government has certain rights in the invention.

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