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**Photoinduced Nucleation: A New Technology for the Detection of
Chemical Contaminants**

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Introduction

The detection of substances at ultralow concentrations is a difficult problem with numerous scientific and technical challenges. The vapor-phase concentrations of signature compounds can be very small (part per trillion or smaller) and these species must be detected in ambient air containing unknown concentrations of numerous other components at higher concentrations. We know of no analytical instruments that can detect compounds at these concentrations. This research grant supported the creation and initial development of a new kind of chemical detector; one that can detect species at part per trillion levels because it does not rely on the direct measurement of a species presence; rather, it uses an indirect measurement of the effect of the trace species on the condensation nucleation of a supersaturated vapor. Since this nucleation process is extremely sensitive to the concentrations of certain types of impurities, this nucleation-based detection can be made more sensitive than any current spectroscopic detector.

PIND Process Description

PhotoInduced Nucleation Detection (PIND) consists of illuminating an air stream containing molecules of the substance to be detected (e.g., TNT) with UV light as it flows through a UV transparent cell. Seconds later this stream, which now contains photoproducts, is mixed with a stream that is saturated with a nucleating vapor (e.g., n-butanol). The combined stream then is cooled, thus making the vapor supersaturated. The supersaturated n-butanol vapor condenses onto the photoproducts to form droplets, thus increasing the size of the photoproducts to the point that they are readily detectable by light scattering. The number of droplets counted per second (i.e., the nucleation rate) has a power law relationship to the concentration of the substance in the air stream.

We initially published data¹ showing the detection (*in air*) of extremely small concentrations of TNT and DNT's, as small as 5 parts per trillion (ppt), 10 ppt, and 10 ppt for TNT, 2,4-DNT, and 2,6-DNT, respectively. Sometimes PIND often can provide species-specific identification, i.e., by measuring the nucleation rate as a function of the wavelength of light.¹ Identification occurs when the measured variation in particle counting rate as a function of illumination wavelength exactly matches the substance's vapor-phase UV light absorption spectrum.

Since the last progress report, we have succeeded in obtaining very high detection sensitivities *in ambient air*. The importance of this and how it was accomplished as is explained in the next 3 paragraphs:

Recall that PIND works by nucleating a highly supersaturated vapor (e.g., butanol) on the nuclei formed by the photochemical reaction of molecules of the chemical of interest. *Nuclei* therefore are what are detected, but air contains many nuclei per cubic centimeter(cc). Even after passing through a HEPA filter, there still are more than 1000/cc. Conventionally

¹J. L. Katz, H. Lihavainen, M. M. Rudek, and B. C. Salter, "Photoinduced Nucleation: a Novel Tool for Detecting Molecules in Air at Ultra-low Concentrations", *J. Chem. Phys.*, **112**, 8363 (2000).

operated counting equipment does not detect them because they are smaller than 5nm. However if they are not *almost entirely* removed before the UV irradiation step of the PIND process, it becomes impossible to detect the nuclei formed by photolysis of the *chemical of interest's* molecules because the nucleation they cause can not be distinguished from the nucleation caused by these preexisting nuclei.

The immunity to the pre-existing nuclei in air was accomplished by adding a sorption-desorption process. The sorption-desorption process consists of flowing the air stream containing molecules of the chemical of interest past a surface coated with a polymer. Molecules of the chemical of interest diffuse to and sorb onto the polymer. However, almost all of the preexisting nuclei remain in the air stream and flow out of the sorption section because their larger size (compared to the size of individual molecules of the chemical of interest) causes them to have a much smaller diffusivity. A short duration flow of clean air then is used to remove the remains of the nuclei laden air. The application of a flash of heat to the polymer causes many of the sorbed molecules of chemical of interest to desorb, yet almost all of few preexisting *nuclei* which did diffuse to and sorb onto the polymer during the sorption part of this process remain embedded since the strength of their attachment to the polymer is much stronger than that of the molecules of interest. Thus, the interference would have been caused by the preexisting airborne nuclei is eliminated to such an extent that, even though this research took place in a laboratory whose air is laden with an unusually large number of nuclei, we nonetheless have detected 2,4-DNT in this dirty air at 0.2 ppt.

We wish to note that the incorporation of sorption as the first step of the PIND process has three additional benefits:

The first benefit is that substance *selectivity* can be greatly increased by using polymers specifically designed² to sorb the chemical of interest.

The second benefit is a high degree of "immunity" to interference caused by the presence of high concentrations of other vapors. For example, we attempted to determine the extent of interference by acetone on the detection of 2,4-DNT in ambient air. Ever increasing concentrations of acetone were used with *no* detectable interference. Finally, the highest possible acetone concentration was used, i.e., done by taking the ambient air stream from *inside* an open acetone bottle, a location where the concentration of acetone vapor probably is larger than *ten percent* (i.e., 10^{11} ppt). This acetone laden air stream was flowed both with and without an added small concentration (about 20ppt) of 2,4-DNT over the sorption fiber. When vapors sorbed onto the fiber were desorbed into the PIND device, a signal was observed *only* when DNT had been added to the acetone laded air stream. This result suggests that the addition of sorption-desorption step to the PIND process will enable PIND to operate even in the presence of extremely high concentrations of some contaminants.

The third benefit is amplification of detection sensitivity. There are 2 sources of amplification, time and volume. By making the sorption time long compared to the

²E. J. Houser, T. E. Mlsna, V. K. Nguyen, R. Chung, R. L. Mowery, and R. A. McGill, "Rational materials design of sorbent coatings for chemical of interests: applications with chemical sensors", *Talanta*, **54**, 469 (2001) and references therein.

desorption time, one can increase the concentration being presented to the detector by (almost) the ratio of these two lengths of time. The concentration of chemical of interest molecules presented to the detector also can be increased by making the ratio of the volume of chemical of interest containing air which flowed by the fiber (in the sorption step) large compared to the volume that it is desorbed into.

Figure 1: Schematic of a prototype PIND system.

Output

J. L. Katz, H. Lihavainen, M. M. Rudek, and B. C. Salter, "Photoinduced Nucleation: a Novel Tool for Detecting Molecules in Air at Ultra-low Concentrations", *J. Chem. Phys.*, **112**, 8363 (2000).

Patent No. 6,469,781 "Photoinduced nucleation: a novel tool for detecting molecules in air at ultra-low concentrations"; inventors: Joseph L. Katz, Heikki Lihavainen, Markus Rudek, Brian C. Salter; assignee: U.S. Dept. of Energy and

patent applied for: Case No. S,99-516 "Photo Nucleation Detector", inventors: Joseph L. Katz and Brent A. Johnson; assignee: U.S. Dept of Energy