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Trace Explosives Detection by Cavity Ring-Down Spectroscopy (CRDS)

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 Photo by Sung Lee

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Final report

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Abstract

We built three successive versions of a thermal decomposition cavity ring-down spectrometer and tested their response to explosives. These explosive compound analyzers successfully detected nitroglycerine, 2,4,6-trinitrotoluene (TNT), pentaerythryl tetranitrate, hexahydro-1,3,5-trinitro-*s*-triazine and triacetone triperoxide (TATP). We determined the pathlength and limits of detection for each, with the best limit of detection being 13 parts per trillion (ppt) of TNT. For most of the explosive tests, the peak height was higher than the expected value, meaning that peroxy radical chain propagation was occurring with each of the explosives and not just the peroxide TATP.

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Preface

This study was conducted for the US Army Environmental Quality Technology under the “Environmental Sensors for Explosives” program under PE 633728/Project 03F/Task 19. The technical monitor was Dr. Elizabeth Ferguson.

The work was performed by the ALTI, LLC. At the time of publication, Amber L. Russell was Chief, EPC; Warren P. Lorentz was Chief, EP; and Elizabeth Ferguson was the Technical Director for Installations and Operation Environment. The Deputy Director of ERDC-EL was Dr. Jack Davis, and the Director was Dr. Edmond J. Russo.

COL Teresa A. Schlosser was the Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

This project aimed to optimize and improve an explosives analyzer using thermal decomposition cavity ring-down spectroscopy (TD-CRDS), a method for which a prototype had been completed and tested[1] but required several possible instrumentation upgrades to improve accuracy, precision, and sensitivity, as well as a need for systematic and complete testing of system design. The first upgraded analyzer used a more powerful laser to achieve lower limits of detection and more reliable performance. The second analyzer tested averaging software and proportionate temperature control to show that drift and low-frequency thermal oscillation could be reduced. The third analyzer tested new mirrors with higher reflectivity and led to a more thorough examination of the heater coating and its optimization. So, with each successive generation of the analyzer, we achieved measurable improvements.

1.1 Background

Activated Light Technology Industries (ALTI) LLC was founded by James Hargrove, Ph.D., to commercialize technology developed during and after his dissertation research on TD-CRDS of air pollution at the University of California, Riverside. Recognizing that the existing explosives detection methods such as mass spectroscopy, ion mobility analysis and specially trained dogs have limitations, ALTI LLC developed a new methodology to measure explosive vapors and particles that could prove to be superior.

1.2 Objective

The core goal was to produce and test a consistent, functional system for eventual use in the field. One that could be used to find the explosive compounds used in improvised explosive devices (IEDs) before they can be used to cause harm. The persistence of wide-spread extremism makes the development of this technology critical. All design revisions were in service of this ultimate objective. The TD-CRDS methodology could then be scaled up to provide an effective product.

[1] Szpunar, D. and Hargrove, J. (2013) A 'Smoke and Mirrors' Approach to Remote Explosives Detection. Electronic Military and Defense Annual Resource, 2013 edition

1.3 Approach

To ensure that the effect of each alteration could be observed, changes with each analyzer built were incremental. Individual components were swapped out for parts with greater efficacy for the application. Testing at each stage documented whether the improvements were successful. The assembly process was also refined to reduce errors.

2 Summary

For this ambitious effort to develop a new technology to enhance the existing detection of explosives by TD-CRDS, we upgraded the laser, the electronics, and the mirrors. While we encountered some setbacks, we confidently consider the project a success and plan to address variable sampling situations next.

We began by implementing a purge function and the ability to change optical filter and measurement ranges, and we upgraded the electronics and refined the design to reduce stress on components and prevent them from failing prematurely. A new laser led to increases in signal and some confusion about lower signals until we determined that we needed to broaden the range of the filter to account for the laser variations. Using a short-pass filter in place of the band-pass filter increased the signal by at least a factor of two and, in some cases, eliminated a reduction in laser intensity from the band-pass filter's narrow wavelength range.

We found it most convenient in the laboratory to simultaneously show two data scales: tenths of a part per billion (ppb) as a stable reading and a more sensitive parts-per-trillion (ppt) reading. These two readings make it easier to note improvements in the baseline and to measure the signal-to-noise ratio in the original tenths of a ppb detection level. The more sensitive measurement avoids digitizing the noise and producing a false standard deviation. If the digital resolution is close to the noise level, the digitization artificially reduces the variation in a way that would not distort measurements of explosives but causes the recorded standard deviation to artificially improve.

In our second prototype, we added signal averaging to reduce noise and drift. However, this averaging was not as effective as using a battery as the power supply. Using a battery results in an almost completely flat response after warm-up.

Our third prototype introduced new mirrors. Initially our new configuration yielded no signals, until we realized that the polymer mirror cleaning solution used—the same as that employed by NASA on its gravity-wave interferometers—leaves a slight residue, most likely from the pink dye that kills the signal in a good cavity. (As a side note, we may have built the only system sensitive enough to detect this residue, which could prove

less than a monolayer thick). We reverted to traditional drag wipe cleaning of mirrors and then regained the path lengths that we sought.

As an additional challenge, a small oscillation using the new mirrors remains to be eliminated in the range of 1 to 2 ppb of nitrogen dioxide (NO_2).[1] It is clear that there is not as much random noise, but until we eliminate this systematic error, the new mirrors have yet to show the expected increase in signal-to-noise ratio. The practical ability to measure the path length and use the analyzer for measurements as in the other two analyzers suggests that additional work on optimizing the analyzer will most likely result in the improvements that we seek.

1. For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 265, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

3 Results

3.1 Overview

We set out to build three successive versions of the analyzer, with improvements in each version. The first analyzer used a new laser, leading to an improvement in the signal-to-noise ratio. The second analyzer used proportional temperature control, reducing some of the analyzer drift. The third analyzer used better mirrors, leading to an additional improvement over the first and second versions.

3.2 Analyzer components

3.2.1 Firmware and electronics

We developed several versions of operational firmware for the analyzer prototypes: one set of versions to handle the larger signal from the new lasers and another set to handle the longer path-length mirrors. These mirrors required a longer cycling period for the laser to measure the longer path length accurately. The high-powered lasers required the creation of new electronics, and in the process of implementing that design change, we also eliminated premature component failures.

We also incorporated signal-averaging firmware to minimize drift and low-frequency noise. There are now 10 readings taken per measurement, averaged within each point to reduce any error from sampling over a quarter second. We also found and purchased effective, long-lasting rechargeable batteries for portable use. Battery technology is constantly improving, and any 12-volt battery with sufficient power and a compatible connector will work. It is possible to change the voltage but not trivial. These batteries provided the added benefit of reduced drift and fewer noise spikes during testing. While we are testing these analyzers in the laboratory, we intend them for use in the field.

3.2.2 Features and functionality

We designed a simple yet useful purge function using a solenoid valve to bypass the flow restrictor. This modification clears out the sample cell after peak detection, making running consecutive tests more efficient. This purge function can be coupled with the new zeroing function to readjust

for drift. Additionally, inline flow meters verify the flow rates of gas through sections of the line, for troubleshooting and analysis.

To improve usability, we added colored displays to show the level of explosive response without the need to connect an outside computer. These displays make it easy to demonstrate the analyses to interested third parties, which we did by showcasing the first analyzer.

We converted the second analyzer for use with the wand prototype. As shown in the supplementary photographs, the analyzer picked up a response of 9 ppb from a cotton pad treated with a solution of nitroglycerine. The relatively small response may be partly due to dilution from the bypass flow the wand employs. This smaller response is one area that we hope to optimize for performance as a part of the new project.

3.2.3 Heater

We improved the heater's performance using proportional temperature control to yield consistent temperatures. The early heaters would rise and fall around 5°C–10°C over time to maintain the set temperature range, while the new version consistently holds within <1°C. This greater consistency minimizes data oscillation because of inconsistent temperature.

We also solved an issue with the internal coating of the tubes. Poor application of the coating by the manufacturer caused the analyzer to respond improperly. This improper response seemed partly because of the variability of coating a much longer tube that we then cut to length. We tested three current coatings offered by the manufacturer on the length that we used for each heater, and we identified the optimal coating.

3.2.4 Sample cell

Construction of the sample cell starts with screening the components to assemble them within our set parameters. We used a new ultraviolet-visible (UV-vis) spectrometer to screen mirrors, filters, lasers, and the finished sample cells. While testing our operational parameters, we determined short-pass filters are better than notch filters for use with the new lasers. We also determined that trace levels of dye from a polymer mirror cleaner ruin the new mirrors' reflectivity. This decreased

reflectivity has only been documented by ALTI to our knowledge and becomes a problem only with the longest path-length sample cells.

Our use of this new screening equipment to build a better sample cell improved the path length for the cell used with the third analyzer. The final model has a shorter path length than projected but is still seven times longer than the second model and three times longer than the first.

3.3 Laboratory fixtures

Improvements in the physical environment have also made assembly easier. In the ALTI laboratory space, a laminar airflow hood was installed to reduce dust when assembling the sample cells. With the analyzer as sensitive as it is, even the smallest airborne particle could corrupt the data were it to remain inside the system. We also now use a fume hood, both for safer mixing of chemicals as well as to contain any smoke from initial preparation of the heaters.

3.4 Measurements and data

Five explosives, each representing a common structural category, were successfully measured on all models of the analyzer. Each model passed the explosives challenge. The compounds detected included nitroglycerin (NG), hexahydro-1,3,5-trinitro-*s*-triazine (RDX), 2,4,6-trinitotoluene (TNT), triacetone triperoxide (TATP), and pentaerythritol tetranitrate (PETN). For each of these compounds, linearity measurements were taken, plotting the analyzers' responses to variable concentrations.

Additionally, we confirmed actinite can indeed block pollutants, as we suspected. It filtered significant amounts of ozone and nitrogen oxides while still allowing explosive compounds to pass through. It will improve instrument lifetime, and we expect that lower explosive compound concentrations will be encountered in the field, and less frequent calibration checks will be necessary.

The first analyzer started out with a preliminary limit of detection of 120 ppt of NO_2 and had a path length of 100 m. We optimized this detection limit to 48 ppt and 185 m by the end of the first 6 months. The second analyzer had a path length of 106 m, possibly resulting from ozone (O_3) damage to the coatings and a corresponding larger limit of detection. The shorter path length did not interfere with testing the other improvements

we attempted, so we did not consider it important to fix before moving to the third analyzer with newer and better mirrors.

The third analyzer had a path-length of 694 meters and a noise level of 13 ppt, close to the photon limit of 9 ppt. Eventually, it had a path-length of 937 m and a limit of detection of 9 ppt of TNT that we improved mainly by using better alignment. This most recent result we achieved after the contract period.

A wand inlet, for use when sampling in the field, was successfully constructed with the aid of drawn schematics. After being affixed to an analyzer, this wand was also tested. It functioned as we had predicted, funneling the sample quickly to the analyzer, which is placed in a backpack, while also functioning to relocate the display and feature controls for handheld use.

Measurements of the warm-up time suggested that the first analyzer could warm up in 20 min after switching to a filter that had a lower residency time. We did not consistently achieve this warm-up time, however. The second and third analyzers generally took about an hour to warm up, possibly because with one heater instead of two the analyzer reached an equilibrium temperature later. We predict that a 20 min warm-up may be possible instead of an hour if future analyzers have both heaters and the warm-up rate optimized.

4 Conclusions

All three analyzers are complete and functional. The second and third analyzers need optimization but are still sensitive enough for evaluation of their capabilities. Each analyzer presented its own strengths and challenges. The signal-to-noise ratio is best in the first analyzer: 47 ppt of NO_2. The second analyzer shows more noise at 350 ppt of NO_2, partly because the path length is shorter by a factor of two. We have seen that increasing the path length through adjustments to the laser alignment can dramatically increase the performance, and we expect this improved performance to be possible with the second analyzer. The third analyzer has four times the path length of the second analyzer at 430 m but also produces over a ppb of noise. This problem appears to be a fixable systematic electrical oscillation. There is no visible random noise. This lack of visible random noise leaves room for improvement on the third analyzer, which could lead to a model with both the longest pat-length and the lowest amount of noise. We will be working to address that during the transitional period.

With the actinite scrubber on the inlet, occasional spikes and drift from ambient pollution are reduced or eliminated. Generally, filling the quarter inch (6.36 mm) tubing of the inlet with enough actinite to take up one or two inches (2.5 – 5 cm) of its length will suffice in reducing interference while retaining the response to explosives.

Perhaps the biggest discovery we identified is that radical chain propagation is occurring within the analyzer, not only when measuring TATP but for all the explosives. When breaking down, the explosives each produce radicals that can propagate the conversion of NO to NO_2. From our linearity data on the third analyzer, R^2 is 0.99, but the slope of the trend line is 26, implying a reaction chain length of 26. We needed to perform several linearity tests on each analyzer, possibly because there were variations in the chain length during the separate linearity runs. Alternatively, there may have been a limited amount of NO present since we did not add a separate NO generator to the second or third analyzer because the proportionate temperature control hardware took up too much space. So, if there was insufficient NO in the laboratory's air, it would limit the highest possible readings of the reaction chain length, producing a curved linearity graph. Using smaller interface cards will allow for the inclusion of a dedicated interface card for each of the heaters,

each in communication with the main interface card. We also expect that future designs will be more compact, allowing for NO generators to be included.

The warm-up times for the second and third analyzers proved less than optimal. The first analyzer warmed up in as little as 20 min. Since the second and third analyzers did not contain a NO generator and had better insulation on the converters, the rest of the analyzer compartment heated more slowly and took about an hour to warm up completely, despite the heater reaching temperature in only 10 min. The second and third analyzers did have proportional temperature control, resulting in virtually no drift or slow oscillation after warm-up.

Appendix A: Supplemental Data

Figure 1. Noise measurement close to the photon limit.

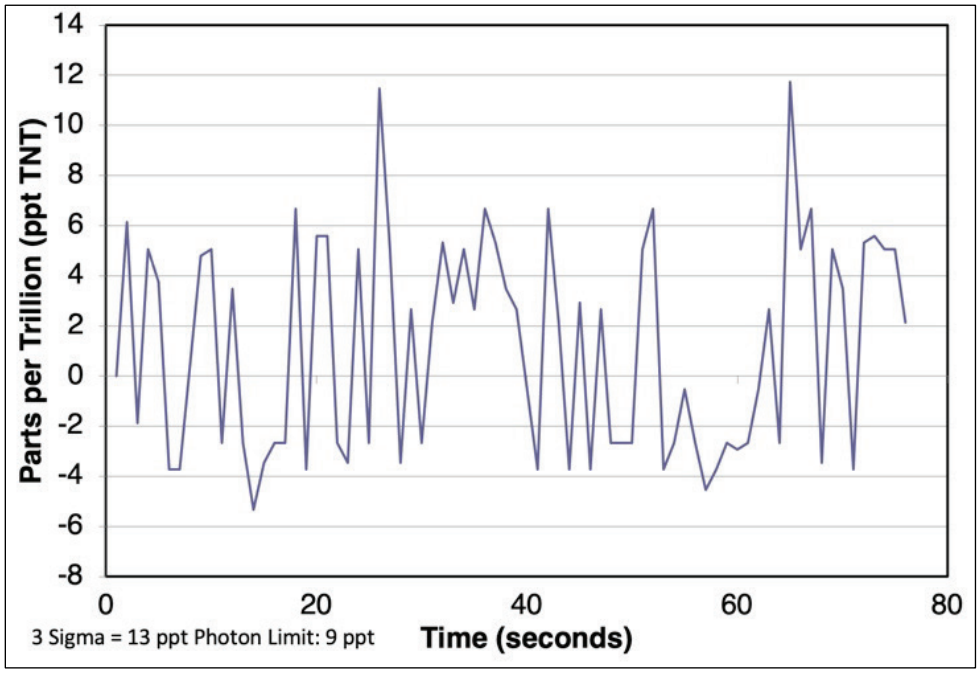


Figure 2. Systemic baseline noise in analyzer V03.

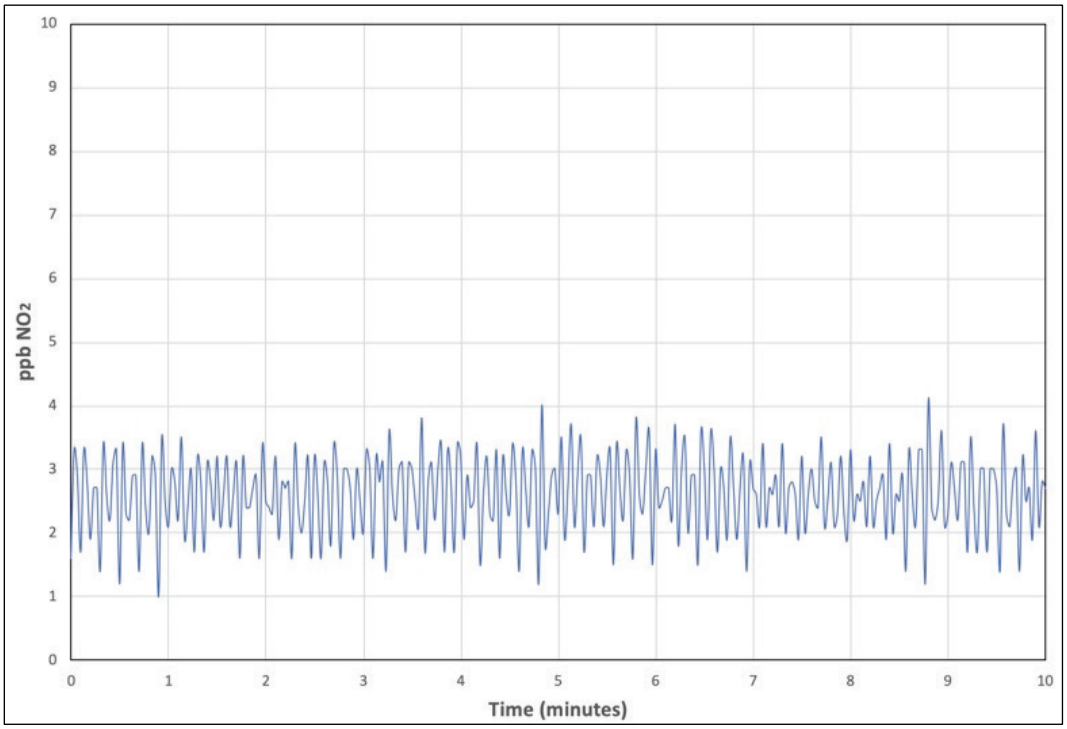


Figure 3. Explosives challenge V01.

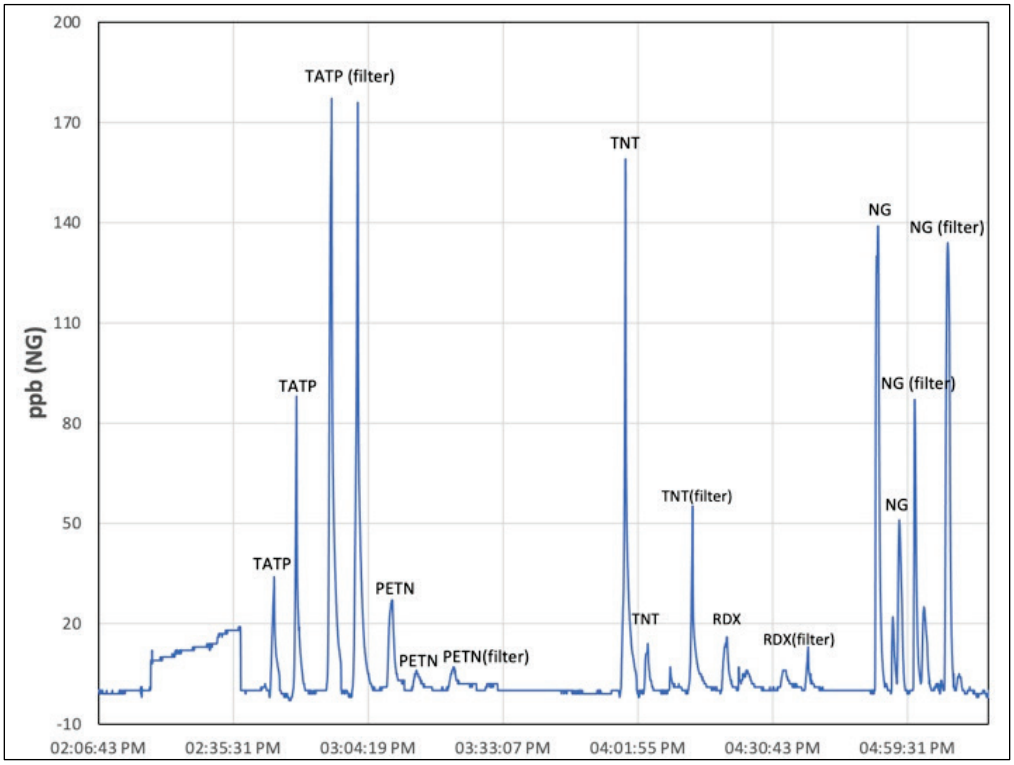


Figure 4. Explosives challenge V02.

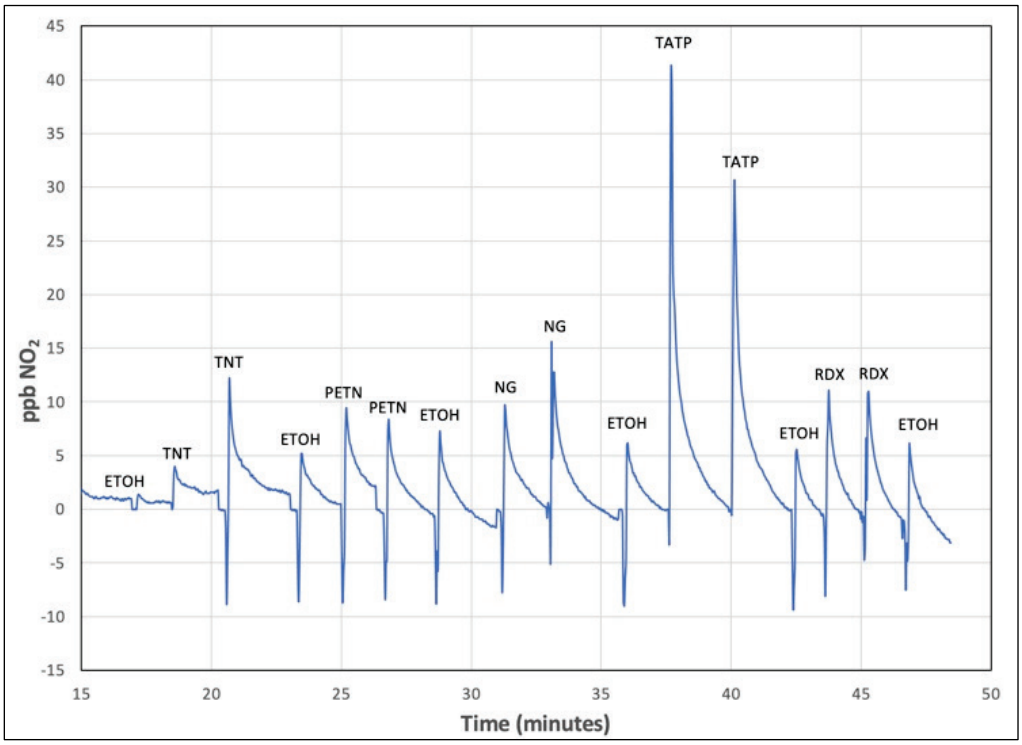


Figure 5. Ozone filter test with and without actinite.

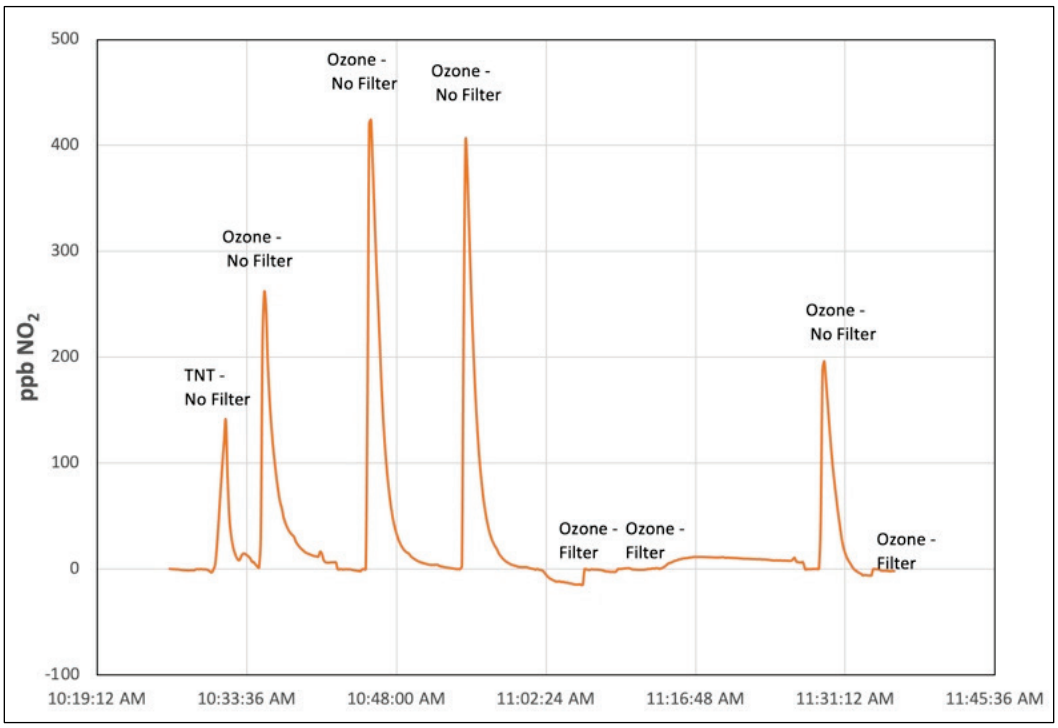


Figure 6. NG linearity test.

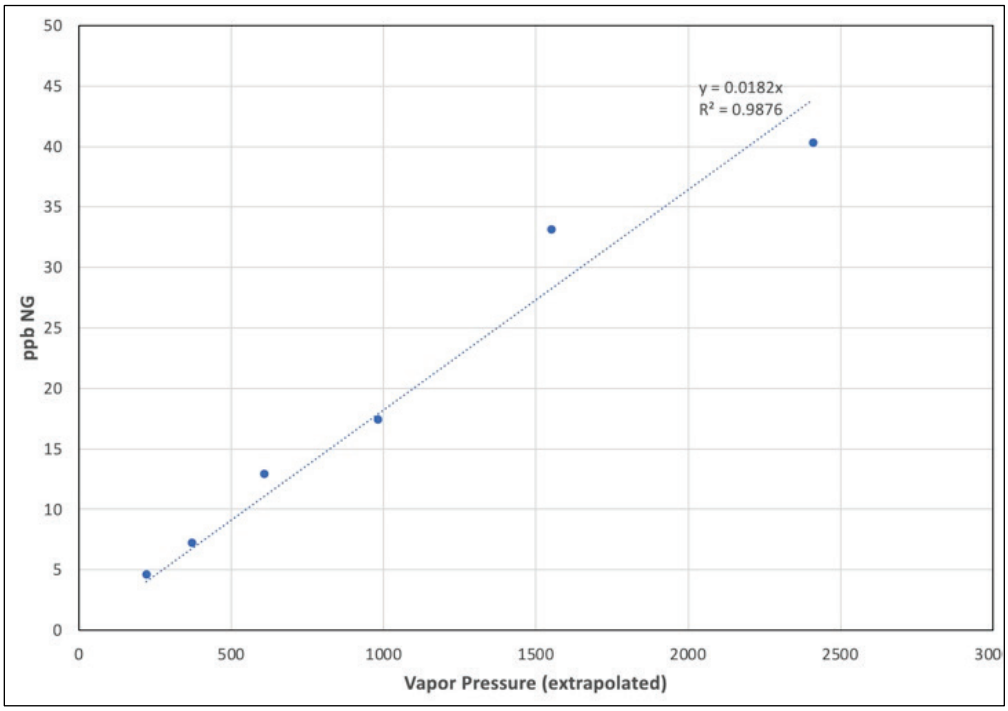


Figure 7. TNT linearity test.

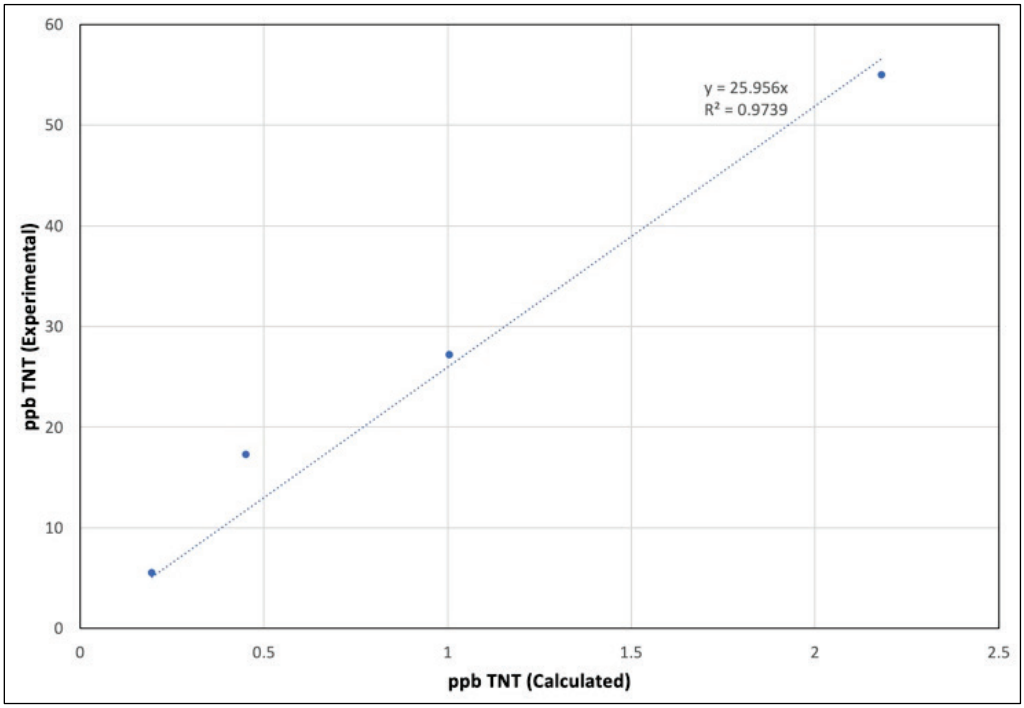


Figure 8. Baseline of analyzer V03.

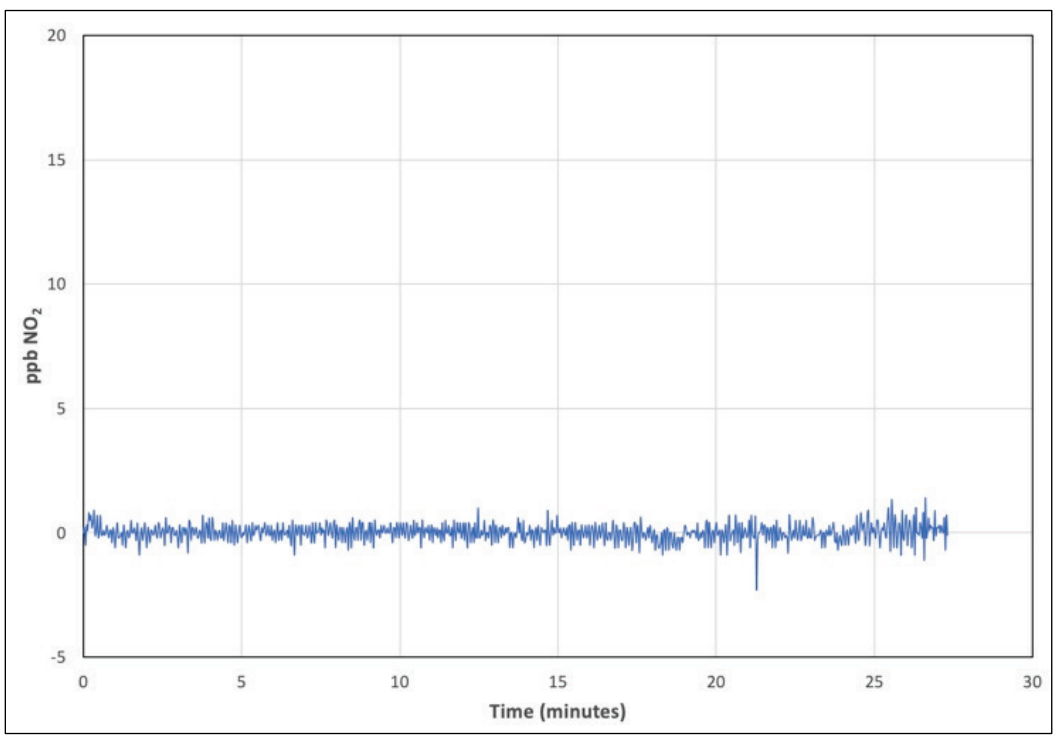
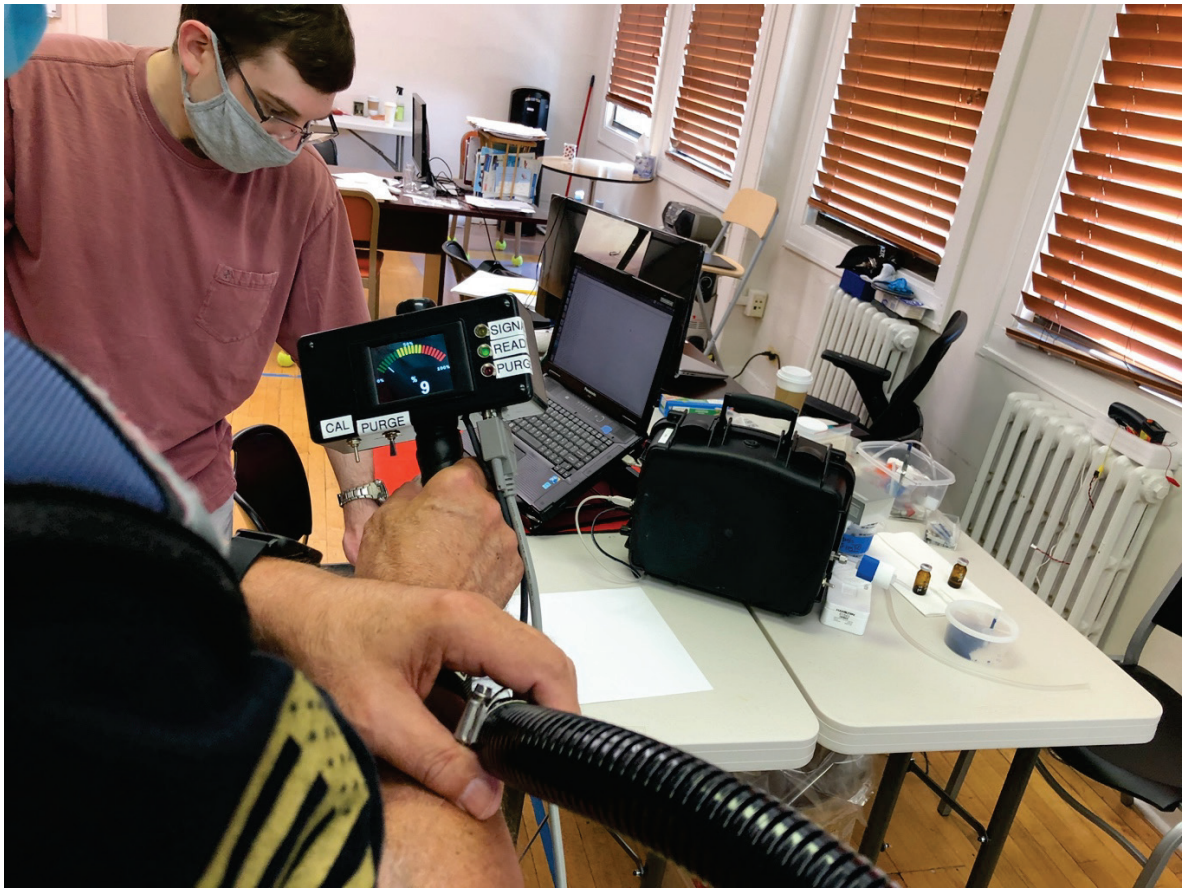


Figure 9. Wand in use.

Figure 10. Wand before screening for explosives.

Figure 11. Successful reading of nitroglycerine after probing for explosive compounds.



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14. ABSTRACT

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