1 Real-time vapor detection of nitroaromatic explosives by catalytic thermal dissociation blue
2 diode laser cavity ring-down spectroscopy

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14 for *Chemical Physics Letters*

15 last revised on: June 21, 2021

16

Abstract

A compact blue diode laser catalytic thermal dissociation cavity ring-down spectrometer (cTD-CRDS) to detect vapors of nitroaromatic explosives is described. The instrument uses heated platinum (IV) oxide catalyst to convert nitroaromatic compounds to NO₂, which is detected at 405 nm. Using the relatively volatile nitrobenzene as a test compound, we show by Fourier Transform Infrared Spectroscopy (FTIR) in off-line experiments that nitroaromatics can be quantitatively converted to NO₂. The cTD-CRDS detection limit was 0.3 parts-per-billion by volume (ppbv) and sufficiently low to allow the detection of a room temperature sample of 2,4,6-trinitrotoluene (TNT) without sample preconcentration.

Highlights

- A catalytic thermal dissociation converter of nitroaromatics to NO₂ was developed.
- Catalytic conversion of nitroaromatics to NO₂ was shown by FTIR to be quantitative.
- A compact blue diode laser cavity ring-down spectrometer (CRDS) was constructed.
- The CRDS was equipped with a catalytic converter and a reference channel.
- Real-time sensing of 2,4,6-trinitrotoluene (TNT) by cTD-CRDS was demonstrated.

Keywords

blue diode laser cavity ring-down spectroscopy, catalytic thermal dissociation, platinum, nitrobenzene, dinitrotoluene, trinitrotoluene, Fourier transform infrared spectroscopy

1. Introduction

The threat of terror attacks on airplanes, trains, and other important infrastructure has led to a strong demand and interest in new devices that can be used for rapid detection of explosives [1-23]. Two complimentary approaches are commonly used at screening check points: bulk and trace detection. In bulk detection, the aim is to find the actual explosive device, for example by X-ray screening or physical searches. Trace detection, on the other hand, seeks to detect residues stemming from the handling of explosive substances and usually involves the detection of the explosive in the gas phase. This can be challenging since the vapor pressures of most explosives at room temperature are small. For example, detection of 2,4,6-trinitrotoluene (TNT) vapor at room temperature requires a detection limit of 10 parts-per-billion by volume (10^{-9} , ppbv), or better [10]. Detection of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX; also known as hexogen and a powerful military explosive), on the other hand, requires a detection limit of 50 parts-per-trillion by volume (10^{-12} , pptv), or better [10]. The majority of passenger security checkpoints currently use commercial instruments based on ion mobility spectrometry [2,6]. Chemiluminescence and gas chromatography coupled to mass spectrometry are also routinely used [1,10]. Due to the high costs and often limited performance of these instruments in terms of selectivity and/or speed, the development of alternative methods continues to be of interest [1].

Several groups have recently utilized cavity ring-down spectroscopy (CRDS) for direct trace detection of vapor explosives. CRDS was invented in the late 1980s [24] and has become a popular tool in absorption experiments requiring high sensitivity, accuracy, and speed [25]. *Todd et al.* [8] described a mid-IR CRDS utilizing an optical parametric oscillator light source and demonstrated a detection limit of 1.2 ppbv for TNT with high specificity. *Usachev et al.* [12] and *Ramos et al.* [13] described UV-CRDS instruments and demonstrated detection of

dinitrobenzene (DNB) and dinitrotoluene (DNT). A disadvantage of UV-CRDS is non-specific detection and interference from other UV-absorbing gases (such as ozone), raising the possibility of frequent "false-alarms". Recently, *Snels et al.* [17] reported selective detection of TNT by near-IR CRDS, but needed to flash heat solid samples to achieve high enough gas-phase concentrations that could be detected.

An alternate approach is to detect explosives indirectly by monitoring their fragments, e.g., the laser-photofragmentation product NO by laser-induced fluorescence (LIF) [20,22,23,26], or the combustion products N₂O and NO by cavity-enhanced spectroscopy in the IR [21] and NO₂ by blue diode laser CRDS [21] or by porous silicon photoluminescence [27].

Our group has developed a blue diode laser thermal dissociation (TD-) CRDS for measurements of nitrogen oxide reservoir species that occur naturally in ambient air [28]. Blue diode laser CRDS is an established, robust, sensitive, and, in ambient air, interference free NO₂ measurement technique [28-30]. In our instrument, organic nitrates (molecular formula RONO₂, where R is an alkyl or peroxyacyl group [28,31]) or nitryl halides [32] are thermally dissociated in a heated quartz inlet and quantified in the form of NO₂ relative to an ambient temperature reference channel with a detection limit of 20 pptv [28]. Many explosives contain one or more nitro functional groups. Some, e.g., ethylene glycol dinitrate (EGDN), pentaerythritol tetranitrate (PETN), or RDX) are alkyl nitrates and are hence, at least in principle, detected by the present TD-CRDS operated at a TD inlet temperature of ~450 °C [31]. Most explosives (e.g., DNB, DNT, TNT, picric acid (PA), or 2,4,6-trinitrophenylnitramine (Tetryl)), however, are nitroaromatic compounds whose activation energies for thermal dissociation to NO₂ are in the range of 270 to 300 kJ mol⁻¹ [33] and substantially higher than those of alkyl nitrates, whose activation energies for thermal dissociation are between 150 and 180 kJ mol⁻¹ [34-36]. Detection

of nitroaromatic explosives by TD-CRDS would require an inlet heated to above 700 °C, which is not practical.

However, the thermal conversion of nitroaromatic compounds to NO₂ can be catalyzed. For example, *Content et al.* [27] reported quantitative yields of NO₂ from oxidation of nitroaromatics in the presence of either PdO or PtO₂ heated to 250 °C, e.g., for oxidation of nitrobenzene (NB):

Here, we show that the vapors of nitroaromatic explosives at room temperature can be detected by catalytic thermal dissociation blue diode laser cavity ring-down spectroscopy (cTD-CRDS). We describe a compact two-channel cTD-CRDS prototype that uses a platinum oxide (PtO₂) catalyst in a heated quartz tube to catalytically convert nitroaromatic compounds to NO₂. We show by FTIR in off-line experiments that conversion of NB to NO₂ is quantitative with this converter. Real-time detection of the nitroaromatic compounds 2,4-DNT and 2,4,6-TNT at ambient pressure and temperature by cTD-CRDS is demonstrated.

2. Experimental

2.1. Construction of catalytic converter

The catalytic converter (Figure 1) was constructed from a 54 cm long, 0.635 cm outer diameter (o.d.), 0.476 cm inner diameter (i.d.) quartz tube in which 0.15 to 0.18 g of catalyst was placed. Two types of catalysts were evaluated: Palladium (5% on alumina, Strem) and Platinum(IV) oxide hydrate (>99.9%, Sigma-Aldrich). The catalyst powder was adsorbed onto quartz wool held in place using an 18 cm long, 0.159 cm o.d. quartz tube which was placed inside the larger one and pushed against a perfluoroalkoxy (PFA) Teflon elbow compression fitting (Entegris Fluid Handling). We chose quartz as, unlike Pyrex or stainless steel, it does not

scrub NO₂ when heated. The converter was heated using 30 American Wire Gauge (AWG) Nichrome wire (~60 Ω) coiled around 24 cm of the quartz tube and held in place by a thermal conductive ceramic adhesive (Resbond 919), in which a K-type thermocouple was embedded. A Teflon filter holder (Cole Parmer) and a 25.4 mm diameter filter (2 μm pore size, Pall Life Sciences) were placed downstream of the converter to prevent contamination of the CRDS or FTIR sample cell with catalyst.

2.2. Determination of NB to NO₂ conversion efficiency using FTIR

To determine the conversion efficiency of nitroaromatic compounds to NO₂, we monitored the conversion of reactants to gas-phase products by FTIR. The FTIR was a Bruker Tensor 27 equipped with a Gemini "Venus" multi-pass gas cell with 6.4 m optical path length, Pyrex cell walls, CaF₂ windows, and internal volume of 0.75 L. The cell pressure was monitored using a pressure transducer (Omegadyne PX419-015A5V) connected to a display (Omega CNi32). The FTIR was operated using Bruker's "Opus" software at a resolution of 0.5 cm⁻¹, in Mertz phase correction mode and Blackman-Harris-3-term apodization. Typically, 16 spectra were averaged. Background spectra were taken after the cell had been flushed with ultrapure ("zero" grade) air (Praxair) for at least 30 min. Concentrations of residual IR absorbing gases in the zero air were below the FTIR's detection limit. The sampling compartment outside the sample cell was continuously flushed by a small flow of N₂, but a small portion of the IR beam (next to the globar source and the DTGS detector) was not kept under a controlled atmosphere. Hence, the background at the dominant atmospheric absorbers (CO₂ and H₂O) drifted slightly following the changes of their concentrations in room air.

Concentrations of gas-phase species were determined using the Beer-Lambert law and infrared absorption cross-sections obtained from the Pacific Northwest National Laboratory (PNNL) vapor phase infrared spectral library (<https://secure2.pnl.gov/nsd/nsd.nsf/Welcome>) [37]. We chose NB (Aldrich, ACS grade, >99%) as a model nitroaromatic compound as it is sufficiently volatile to be quantifiable by FTIR and because the infrared absorption cross-sections of NB are in the PNNL database.

The Beer-Lambert law is, strictly speaking, not obeyed when the FTIR resolution is lower than the width of the absorption lines [38], i.e., for CO₂ and H₂O in this work. We therefore calibrated the FTIR to CO₂ against a commercial Li-COR 7000 CO₂ analyzer by sampling room air diluted with zero air. At either 0.5 or 1.0 cm⁻¹ resolution, the scatter plots were linear ($r > 0.998$), and the slope was 0.178 ± 0.003 (data not shown). We verified in an off-line experiment that the NO₂ mixing ratios measured by FTIR were in quantitative agreement with those observed in parallel by blue diode laser CRDS. Nitroaromatic compounds typically have broad and unresolved absorption features and are hence not affected by this limitation.

NB was placed in a 3-neck trap and eluted with zero air (Figure 2). Typically, the flow rate through the trap, set using MFC 1, was 5.0 standard cubic centimeters per minute (sccm). The trap output was further diluted using a 1.8 standard liters per minute (slpm) zero air dilution flow using MFC 2. This gave a residence time of ~0.3 s in the converter and of ~0.5 min in the absorption cell.

In the experiments shown in Figures 3 and 4, the catalyst was initially operated at near-ambient temperature. The trap was flushed for ~10 min to remove room air, after which the concentration of NB was quantified. Then, the temperature of the converter was increased to ~400 °C, and the production of NO₂, CO₂, and H₂O and the disappearance of NB were

monitored by FTIR. At the end of the experiment, the concentration of NB was measured again to verify that the trap output had not significantly changed during the experiment.

2.3. cTD-CRDS prototype

The cTD-CRDS is a modified version of the compact 2-channel instrument described by *Odame-Ankrah and Osthoff* [39] and has the same external dimensions (53 cm width $\times$ 74 cm depth $\times$ 85 cm height) and optical layout as its predecessor. The main changes from the previous version are: (1) the replacement of the original 662 nm laser and optics with a 405 nm continuous wave (cw) blue diode laser and optics similar to those described by *Paul and Osthoff* [28], (2) the implementation of a non-linear Levenberg-Marquardt (LM) fitting routine, and (3) the addition of a catalytic converter as described in section 2.1 to one of the sample channels. The other sample channel was operated with a quartz tube that did not contain catalyst and was heated to the same temperature as the catalytic converter (250 °C); this channel served as a reference to enable measurement of nitroaromatic by difference.

For this work, we programmed a non-linear LM fitting algorithm to determine the ring-down time constant, τ , by fitting the parameters of an exponential decay equation with a variable offset to the observed ring-down data. The non-linear LM algorithm is computationally expensive but affordable as there are 0.5 s between data transfer steps [39]. We also implemented the discrete Fourier transform algorithms DFT-1 and DFT-5 and the "linear regression of the sum" (LRS) algorithm, graciously supplied and described by *Everest and Atkinson* [40]. With any of the new algorithms, effective laser pulse and data acquisition rates of up to 2.5 kHz with a 1σ precision in the NO₂ mixing ratio as low as ± 0.16 ppbv could be achieved.

A Teflon filter holder (Cole Parmer) containing a 2 μm pore size, 25.4 mm diameter Teflon filter (Pall Life Sciences) was placed between the catalytic converter and the CRDS cell. A second filter and filter holder was placed at the tip of the common inlet. All wetted inlet lines and fittings were constructed from PFA or fluorinated ethylene propylene (FEP) Teflon.

Number densities of NO_2 were calculated using equation (2):

$$N = \frac{R_L}{\sigma} \frac{1}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (2)$$

Here, σ is the NO_2 absorption cross-section at the fixed laser wavelength ($5.8 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ [28]), $R_L = 1.44$ is a correction factor to account for the fact that only a fraction (69%) of the optical path (55 cm) is occupied by sample gas with the remainder occupied by purge gas, c is the speed of light, and τ and τ_0 are ring-down time constants in the presence and absence of NO_2 , respectively. Number densities are converted to mixing ratios using the ideal gas law and are corrected for dilution with purge gas.

2.4. Detection of 1,3-DNB, 2,4-DNT and 2,4,6-TNT by cTD-CRDS

1,3-DNB (97%) and 2,4-DNT (97%) were purchased from Sigma-Aldrich and used as received. 2,4,6-TNT was purchased as 1 mg / 1 mL solutions in 50% methanol / 50% acetonitrile from Accustandard. In offline experiments, we found that the cTD-CRDS was sensitive to acetonitrile which was at least partially converted to NO_2 by the catalyst. We therefore evaporated the solvents using a gentle stream of O_2 overnight to obtain dry, solid samples of TNT for analysis.

In a typical experiment, the nitroaromatic was placed in a 3-neck flask, which was temperature controlled using an external circulating heater, and eluted and diluted with zero air (Figure 2). The flow through the trap (MFC 1) was set to 100 sccm and the dilution flow through MFC 2 to 2.4 slpm. Prior to loading trap with sample, the trap was purged with zero air while the effluent was observed by cTD-CRDS to verify the absence of memory effects from previous experiments. To obtain a stable trap output after loading, it was necessary to keep the trap under flow for several hours prior to analysis and to not modify the trap's bypass valves. Once the trap had been conditioned, it was tee'd into the main inlet, which was flooded with zero air.

In initial experiments (not shown), the cTD-CRDS performance was less reproducible and there was often less efficient conversion of nitroaromatics to NO_2 than had been anticipated on the basis of the FTIR results. This was eventually traced to the fact that the catalyst in the FTIR experiments had been periodically exposed to room air, whereas in the cTD-CRDS experiments, on the other hand, the catalyst was conditioned, over prolonged periods, using (dry) zero air. The catalyst's performance improved considerably once the zero air (used to dilute trap output) was humidified using a bubbler containing deionized water. The bubbler was deployed in all cTD-CRDS experiments shown below.

3. Results

3.1. Catalytic oxidation of nitroaromatic compounds to NO_2

Figure 3 shows FTIR spectra before and after oxidation of NB with PtO_2 catalyst heated to 350 °C. Before the oxidation, the spectrum contains all absorption features expected for NB but also those of trace moisture and CO_2 , likely originating from residual room air eluting from the sample trap. When the catalyst was heated to 350 °C (Figure 3, bottom), there was no evidence

of NB, and only the expected oxidation products, H₂O, CO₂, and NO₂, were observed. This shows that NB had been completely oxidized.

Figure 4 shows a time series of NB and NO₂ mixing ratios, calculated from absorption spectra as shown in Figure 3. The NB mixing ratios were (248±26) ppbv before the catalyst was heated, and (220±12) ppbv after the catalyst had been heated and allowed to cool again (the error indicates the 1σ measurement precision). The NO₂ mixing ratio at catalyst temperatures >250 °C was (245±35) ppbv, consistent with quantitative production of NO₂ (see reaction (1) for the stoichiometry of the reaction). This quantitative ratio was reproduced in several experiments conducted over a period of several months. On the other hand, the measured CO₂ mixing ratios were generally not consistent with the expected stoichiometric ratio of 6:1 and often greater than expected, for reasons that are not clear. As other C containing species (such as CO) were not observed by IR, we speculate that variability in the CO₂ background, which is orders of magnitude higher than the concentration being measured, or perhaps CO₂ produced by oxidation of partially oxidized hydrocarbon residues from preceding experiments contributed to variability in the measured CO₂.

We also evaluated Pd sorbed on alumina with mixed success (data not shown). The IR spectra generally showed less than quantitative yield of NO₂ from NB oxidation, and in some cases revealed the production of NO. Thus, PtO₂ was chosen as the catalyst for the cTD-CRDS.

3.2. Real-time detection of explosives by cTD-CRDS

3.2.1. Detection of 2,4-DNT

Figure 5 shows sample measurements of 2,4-DNT by cTD-CRDS. The source was repeatedly taken offline to determine the baseline ring-down time constants, τ_0 (white underlay). A small

amount of room air was usually observed by the CRDS (as spikes in the data) when the source was connected or disconnected. Nitroaromatic compounds are apparently retained on Teflon surfaces, as indicated from the slow (~15 min) approach to a stable signal when the trap is put inline (shown in gray underlay) or taken offline. The same behavior was observed for 1,3-DNB (not shown) and, to a lesser extent, for 2,4,6-TNT (Figure 6).

2,4-DNT has saturation vapor pressures of 1.8×10^{-5} Torr at 7.0 °C and 7.5×10^{-5} Torr at 17.0 °C [41], which correspond to mixing ratios of 28 ppbv and 120 ppbv, respectively. Flow dilution reduces these concentrations by a factor of 14.0 in our experiments. Assuming that the air flowing through the trap saturates with 2,4-DNT, and 2 molecules of NO₂ are produced from each molecule of 2,4-DNT in the converter, we expect 4.0 ppbv of NO₂ at 7.0 °C and 17 ppbv at 17.0 °C. The data shown in Figure 5 are below those values (2.9 ± 0.2 ppbv at 7.0 °C and 4.2 ± 0.2 ppbv at 17.0 °C). A comparison of observed with expected values for 2,4-DNT, 1,3-DNB, and 2,4,6-TNT is shown in Figure 7 and is discussed further below.

There was an unexpected response in the reference channel (Figure 5, blue) due to absorption by 2,4-DNT, which is slightly yellow in appearance. The reference channel signal implies a 2,4-DNT absorption cross section at 405 nm of $\sim 2.5 \times 10^{-20}$ cm² molecule⁻¹. A similar response in the reference channel was observed for 1,3-DNB (data not shown) and 2,4,6-TNT (see below).

3.2.2. Detection of 2,4,6-TNT

Figure 6 shows a time series of cTD-CRDS demonstrating detection of 2,4,6-TNT. The signal is smaller than for either 1,3-DNB or 2,4-DNT because at the trap temperature in the experiment shown (25.0 °C), 2,4,6-TNT only has a vapor pressure of 6.4×10^{-6} Torr [41]. Assuming equilibration within the trap with the gas flow, this vapor pressure corresponds to a

mixing ratio of 0.88 ppbv after dilution. Following conversion to NO₂, a mixing ratio of 2.7 ppbv is expected, which is greater than observed (1.2 ± 0.1 ppbv). There is also a small response in the reference channel, from which the cross-section of 2,4,6-TNT at 405 nm is estimated as 6.6×10^{-20} cm² molecule⁻¹.

4. Discussion

4.1. Catalytic conversion of nitroaromatic compounds to NO₂

The FTIR results show that NB is quantitatively converted by heated Pt(IV)O₂ to NO₂, at least at the ppmv level. With Pd catalyst, formation of NO was observed, which likely stemmed from reduction of NO₂. We speculate that the alumina support may have contributed to NO formation, as we observed partial loss of NO₂ on aluminum surfaces in off-line experiments. It was concluded that Pd(0) adsorbed on alumina is less suitable than Pt(IV)O₂ for detection of nitroaromatic compounds by cTD-CRDS. The results presented here are consistent with those by *Content et al.* [27], who reported similar performance of Pd and Pt catalyst but had not evaluated the catalyst's performance on alumina support. Further, we found that the presence of trace moisture is needed for efficient catalytic oxidation of nitroaromatic compounds. The dependence of catalyst performance on humidity was not further investigated, since the catalyst performed reproducibly, for several months, once the humidity of the dilution gas was controlled.

When the catalytic converter was coupled to the CRDS and evaluated at up to three orders of magnitude lower sample concentrations than had been used in the FTIR experiments, its performance was less clear, since the nitroaromatic compounds could no longer be directly monitored, and because the product monitored (NO₂) was no longer specific to a particular molecule. Furthermore, 1,3-DNB, 2,4-DNT, and 2,4,6-TNT are much less volatile than NB and

can thus condense within the inlet tubing, leading to significant inlet transmission (e.g., Figure 5) and memory effects. To deliver stable and reproducible concentrations of nitroaromatic compounds under these circumstances, the glass traps containing the explosive under investigation was controlled to temperatures below that of the inlet (i.e., below ambient) to prevent condensation of the eluted explosive. In addition, we found it necessary to purge these glass traps with zero air for extended periods of time (usually overnight) and to keep the sample traps under continuous flow. In this manner, an evaluation of the catalyst's performance under trace conditions became possible (Figure 7). For this evaluation, it was assumed that the zero air passing through the glass trap saturated with the nitroaromatic compound before making its way to the CRDS. However, the accuracy of the saturation vapor pressures is not well constrained as the Clausius-Clapeyron parameters reported in the literature for the compounds tested are fairly uncertain [41,42], with resulting error bars as large as factors of two (error bars were omitted from Figure 7 in the interest of clarity).

Figure 7 shows that the observed NO₂ mixing ratios correlated with the predicted amounts, but were lower than expected from quantitative conversion of the nitroaromatic compounds. For 2,4-DNT, the data suggest that only between 1.5 and 0.5 molecules of NO₂ were generated per molecule. Similar yields were also observed for 1,3-DNB and 2,4,6-TNT (Figure 7). It is unclear whether these results are biased because the trap flow did not achieve saturation vapor pressure or whether the catalyst's performance was reduced. It is highly likely that detection of NO₂ in the CRDS cell itself is quantitative [28,31,32]; however, it is possible that the NO₂ produced from oxidation of the nitroaromatic is partially scrubbed after its catalytic production, for example by reaction of NO₂ with the organic oxidation products (which are highly functionalized). Such scrubbing was not observed when alkyl nitrates were thermally decomposed, which had been

rationalized by the short lifetimes of the organic fragments [31], and would be inconsistent with the (high concentration) FTIR results presented above, but cannot be ruled out at the lower concentrations in the cTD-CRDS experiments where minor reaction pathways may be more dominant. The latter stresses the importance of evaluating the efficiency of catalytic conversion at the concentration levels actually used, rather than relying on results obtained at high concentrations. Fortunately, quantitative conversion to NO₂ is not required for detection of nitroaromatic explosives at a check point.

4.2. Comparison of cTD-CRDS with existing CRDS explosive sensors

While detection of nitroaromatic explosives by detection of their thermal decomposition products is not novel (e.g., [18-21,27]), the combination of catalytic thermal dissociation with CRDS detection of NO₂ presented in this work is new and delivers a faster inherent response (<1 s) and higher sensitivity (<0.5 ppbv, without sample preconcentration) than earlier methods. It is also the first to utilize the visible region of the electromagnetic spectrum for explosives sensing (Table 1). Earlier CRDS instruments have utilized the mid- [8] or near-IR [17], which, unlike the visible region, enables identification of compounds and still achieves sub-ppbv detection limits, in particular when a preconcentrator is used [8]. However, identification of the type of explosives present would only be a secondary objective at a security checkpoint. The UV region has also been utilized [12,13]. UV-CRDS, is slightly more sensitive (detection limits of 0.1 ppbv without preconcentration have been reported [13]) than the other methods. However, it also does not allow differentiation amongst explosives and is more prone to atmospheric interferences than the visible region, e.g., due to absorption by ozone, which is a strong absorber whose concentration is highly variable in ambient air.

332

333 **5. Conclusions**

334 An explosives sensor based upon the catalytic thermal dissociation of nitroaromatic
335 explosives to NO₂ and subsequent detection using blue diode laser CRDS has been described and
336 detection limits of 0.5 ppbv (1 s data) have been demonstrated. Future work will focus on the
337 development of a preconcentrator to further lower the detection limits, improvements of inlet
338 transmission, and evaluation of matrix effects and interferences to make this instrument
339 applicable for real world deployment.

340

341 **Acknowledgments**

342 The authors gratefully acknowledge financial support for this project from the University of
343 Calgary's Research Grant Committee (URGC) and from Canada's Natural Sciences and
344 Engineering Research Council's (NSERC) Discovery program. The authors thank Michael
345 Everest and Dean Atkinson for developing and sharing the Labview code for the DFT-1, DFT-5,
346 and LRS fitting routines, and Ann-Lise Norman for the loan of a Licor-7000 used to calibrate the
347 FTIR for CO₂.

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Figure captions

Fig. 1. Sketch of the quartz catalytic converter.

Fig. 2. Sketch of the sample delivery system. When the FTIR was used, the vent was plugged.

MFC = mass flow controller.

Fig. 3. Catalytic oxidation of nitrobenzene (NB). **(top)** FTIR spectrum prior to oxidation. The lower plot (inverted axis) shows the reference spectra of NB and CO₂ from the PNNL database. **(bottom)** FTIR spectrum observed after catalytic oxidation at 350 °C. The PNNL reference spectra of NO₂, CO₂, and H₂O are shown at the bottom.

Fig. 4. Time series of catalytic oxidation of NB as a function of catalyst temperature (shown on top).

Fig. 5. Detection of 2,4-DNT by cTD-CRDS. The catalyst channel (shown in red) was operated at 350 °C.

Fig. 6. Detection of 2,4,6-TNT by cTD-CRDS. The temperature of the glass trap containing the sample was 25.0°C; the catalyst channel was operated at 350 °C.

Fig. 7. Scatter plot of NO₂ mixing ratios observed by cTD-CRDS against mixing ratios predicted from the saturation vapor pressures of 1,3-DNB, 2,4-DNT, and 2,4,6-TNT.

425 **Table 1.** Comparison of selected CRDS explosive sensors.

Method	Compound(s) detected	Specific	Preconcentration	LOD (3σ)
UV [12]	TNT	No	none	1 ppbv
Mid-IR [8]	TNT, TATP, RDX, PETN, Tetryl	Yes	cold finger without membrane	1.2 ppbv (TNT)
Mid-IR [8]	TNT	Yes	cold finger through membrane	75 pptv
UV [13]	1,2-, 1,3-, 1,4-DNB, 2,4-, 2,6- DNT	No	none	0.1 ppbv
Near-IR [17]	2,4-DNT, 2,6-DNT, TNT	Yes	none	75 ng
Visible [this work]	1,3-DNB, 2,4-DNT, TNT	No	none	0.5 ppbv

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