

$\delta^{13}\text{C}$ analysis to screen out explosive precursors by using cavity ring down laser spectroscopy^{*}

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Abstract. Characterizing recovered explosives from a bombing or accidents and finding distinctive markers is crucial to clarify the threat and to follow up the emergency. The goal of our work is to design and implement a new analytical platform to analyze isotope ratio of carbon $\delta^{13}\text{C}$ and nitrogen content using a cavity ring down spectroscopy laser spectrometer.

1 Introduction

Characterizing recovered explosives from a bombing or accidents and finding distinctive markers is crucial to clarify the threat and to follow up the emergency. The seat of the blast will certainly contain explosive residues and bits of the device itself may be present; samples of soil, debris and any bits of device from crater will have explosive residue all over it and could reveal the original content of the chemical explosive. Every surface exposed to the blast (including people present at the time of the blast) will have a fingerprint of explosive residues, which can be swabbed or seized depending on the object.

The capability of stable isotope ratios analysis to differentiate the composition of a chemical compound and to mark different origin and processes is well known and could be applied in explosive forensic [1–4].

Same chemical compounds, regardless of their manufacturing (or man-made) process, will exhibit pretty identical chemical composition and sometimes even indistinguishable isotopic C, N and H ratios, but some main additive components of the explosives (as binders and plasticizers) could reveal appreciable difference that could lead to the identification of their origin [5].

The products of an explosion are mainly CO , CO_2 , H_2O , H_2 , NO_x , . . . , gases that immediately mix with the natural atmospheric ones, so the fast sampling and analysis of the accident scene atmosphere could catch instantaneously some specific features that could infer man-made or industrial manufacturing.

Here we want to focus on the discrimination of an explosive using specific isotope ratio of carbon ($^{13}\text{C}/^{12}\text{C}$) and elemental composition (total C and N content) [6, 7]. The capability of stable isotope ratios analysis to differentiate the composition of a chemical compound and to mark different origin and processes is well known in agrifood and materials science and to counterfaction investigations.

The most used methodologies for isotopic light elements ratio implies the use of isotope ratios mass spectrometers that are equipment designed specifically for working in laboratory environment. The goal of our work is to design and implement a new methodology for $\delta^{13}\text{C}$ measurements to be run directly on site using an innovative technique, the cavity ring down laser spectroscopy (CRDS): specifically the carbon dioxide isotope analyzer laser spectrometer (Los Gatos Research, California, US). We designed an interfacial system that could integrate an elemental combustor system with a CRDS laser spectrometer to allow the sampling on site of suspected materials and the analysis of carbon and nitrogen isotope ratios of the component of the explosive.

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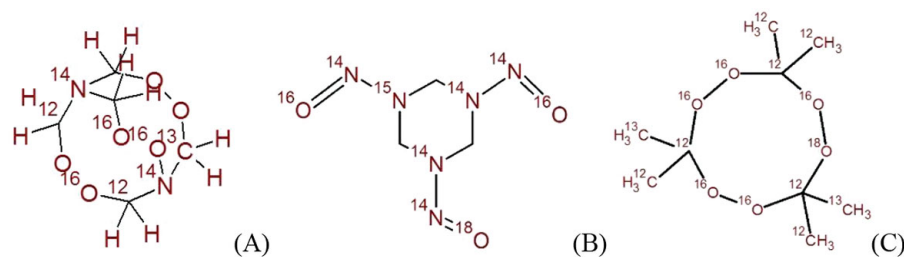


Fig. 1. Images of typical precursor molecules of explosive constituents using Chem Scheck software: (A) hexamethylene triperoxide diamine (HMTD); (B) hexazine trioxide; (C) triacetone triperoxide (TATP).

The proposed instrumental configuration can be used as transportable system to run elemental and isotopic analysis of light elements in working environment and in emergency scenes with fast response time, in order to assess the origin and the manufacturer of the explosive materials or components.

2 Material and methods

2.1 Sample description

Different kind of samples were analyzed: uric acid, fertilizer with equine dejections and two types of nitrate based detergents (detergent_1 was liquid, detergent_2 was solid). We selected these materials, because they contain precursors of explosive constituents.

Figure 1 shows images of typical molecular of explosive constituents obtained by Chem Scheck Software.

2.2 Sample analysis

Elemental analysis of the debris of a blast (weight ≈ 200 mg) can reveal the typical composition of the explosive compounds. We used an elemental combustor (Vario Max Cube, Elementar GmbH, Frankfurt, Germany), based on the Dumas combustion reaction, in order to determine the total carbon and nitrogen content of the samples and its ratio. The elemental combustor is equipped with steel crucibles to avoid the cross-contamination of the samples and to let the recovery of any non-combusted fraction of the sample. The combustion tube was loaded according to manufacturer's specifications with silvered cobaltous/cobaltic oxide, chromium oxide, and quartz wool and operated at 900 °C. The post combustion tube maintained at 900 °C was packed with copper oxide, zinc and quartz wool. The quartz reduction tube, maintained at 830 °C, was packed with reduced copper wire filled between the bottom 40 mm of the tube and the top 30 mm of the tube to maintain a high temperature throughout the copper. Resultant water was removed by an anhydride trap and CO₂ gases were trapped in active charcoal column at 40 °C. Adjustable helium (99.9995% purity) flux was used as carrier. N₂ gases passed through the circuit without being trapped and the thermo-conductivity detector directly measured them. After the N₂ analysis has been completed, the trapping column for CO₂ was heated up to 230 °C to release the adsorbed gas that was then measured by the thermo-conductivity detector.

Samples were analyzed and compared with a reference material consisting of aspartic acid (36% C, 10% N), which was used to calculate the daily factor of the instrument and to normalize C and N data of the sample to a reference sample.

For the $\delta^{13}\text{C}$ analysis a carbon dioxide isotope analyzer (model CCIA-36P, Los Gatos Research Inc., California, USA) CRDS laser spectrometer [8] was used. This technique allows to measure $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, total CO₂ and H₂O in real time with high precision and accuracy and speed of measurement up to 1 Hertz and it is transportable directly on the accident scene. The instrument is based on the off-axis integrated cavity output spectroscopy (OA-ICOS) as absorption cell. OA-ICOS uses a tunable laser source that produces light at a suitable wavelength for interacting with the gas of interest. The laser light enters a highly reflective mirrored cavity, reflecting thousands of times before exiting onto a photodetector (figs. 2 and 3) [8]. This creates an extreme long optical path (many kilometers), increasing sensitivity and producing strong absorptions. This new technique allows a better measure of the absorption line.

The analysis was performed using the sniffer mode of the spectrometer: the samples were put close to the inlet hole and isolated from the surrounding environment (as shown in fig. 4).

In order to measure C/N ratio and C, N, O isotopic ratio subsequently we are designing an innovative connection system that integrates the two techniques: the N₂ and CO₂ fractions produced by the elemental combustor are collected separately and flushed to the inlet of the laser spectrometer to be analyzed. Figure 5 shows the operation mode of the designed integrated system elemental combustor-laser spectrometer.

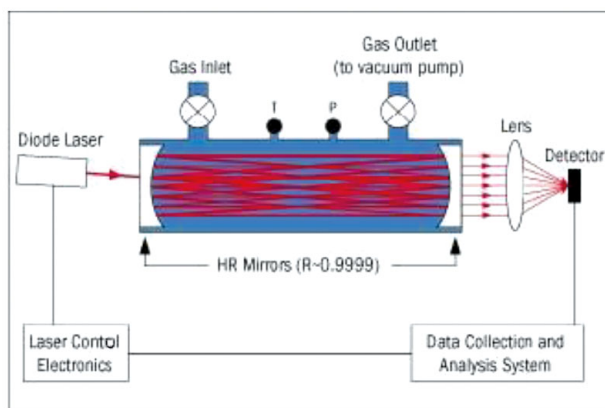


Fig. 2. Off-axis ICOS operation method of the CCIA-36 EP [8].

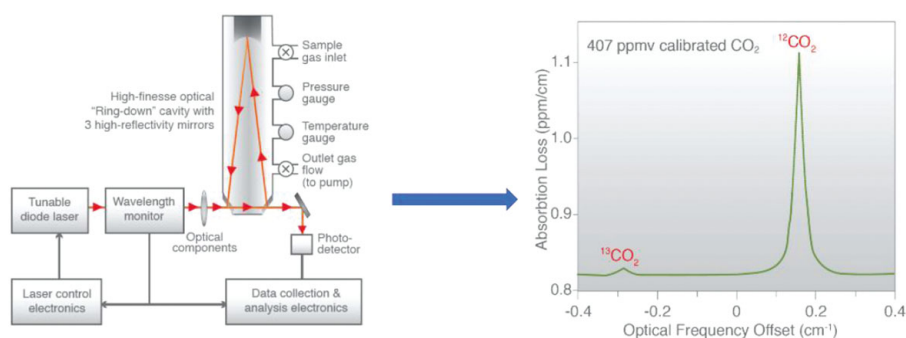


Fig. 3. Schematic of the cavity ring down laser spectroscopy technique and typical absorption spectrum of isotopologues of CO₂, obtained by the carbon dioxide isotope analyzer (model CCIA-36P, Los Gatos Research Inc.) CRDS laser spectrometer.



Fig. 4. An example of analysis using the cavity ring down laser spectroscopy technique: (A) put the sniffer of the spectrometer into the bag; (B) the analysis start; (C) detail of the sniffer into the bag.

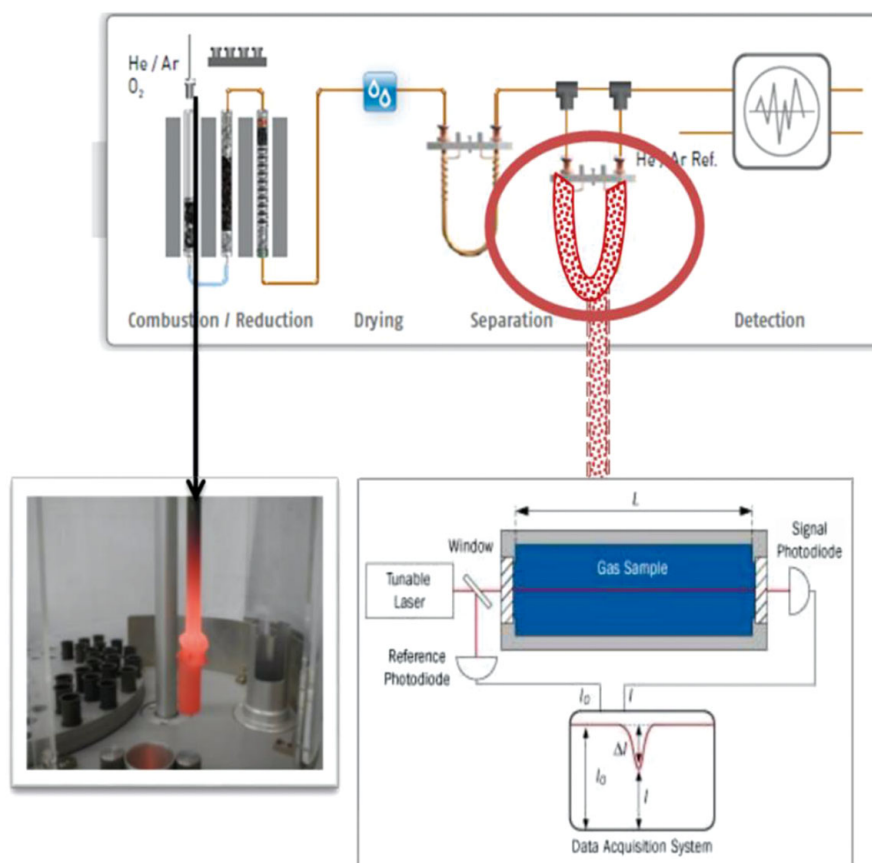


Fig. 5. Schematic of the integrated system elemental combustor-laser spectrometer.

Combining elemental analysis with isotopic laser spectroscopy could be considered a way toward integration of different techniques to be implemented in the accident scene or in an on-site laboratory to support forensic investigation in identifying the manufacture of the explosives that caused the blast.

Stable isotope contents are expressed in “delta” (δ) notation as values in ‰ (per mil), where $\delta = (RA/RStd - 1) \times 103$ (‰) and RA and RStd are the ratios of the rare to abundant isotope (*e.g.*, $^{13}\text{C}/^{12}\text{C}$) in the sample and the standard, respectively. The international standard used for carbon is Vienna Pee Dee Belemnite (VPDB) and the standard for nitrogen is atmospheric N_2 (air).

Samples were analyzed with two different mixtures of certified reference gases containing isotopologues of CO_2 , which were used to normalize sample $\delta^{13}\text{C}$ data to international isotope scales.

3 Results

Table 1 displays the concentrations of carbon (C), nitrogen (N) and $\delta^{13}\text{C}$ for each samples. Uric acid shows the highest concentration of N compared to the other; instead of, fertilizer shows the highest concentration of C.

Figure 6 shows the scatter plot C/N of each samples expressed in percentage. The two detergent samples show low concentrations of nitrogen and carbon too. The solid nitrate detergent (Detergent_2) has the lowest concentration of nitrogen and carbon respect to all the other samples analyzed. On the opposite, uric acid and fertilizer have higher concentrations of the two analyzed elements. Uric acid shows higher concentration of carbon respect to fertilizer, instead of fertilizer has higher concentration of nitrogen respect to uric acid.

Figure 7 shows the $\delta^{13}\text{C}$, expressed in pp_mil (stay for ‰) and, as expected, while CO_2 concentration increase $\delta^{13}\text{C}$ decrease. In fig. 7(A), it is possible to note that $\delta^{13}\text{C}$ of the uric acid is higher than those of fertilizer (minimum value in pp_mil: -120000 uric acid; -60000 fertilizer), but lower than those of the detergents display in fig. 7(B) (minimum value in pp_mil: -1000.000 detergent_1; -800.000 detergent_2). Detergent_1 displays the highest $\delta^{13}\text{C}$ respect to all the other samples analyzed.

Figure 8 shows the concentrations of carbon expressed in ppm compared with the $\delta^{13}\text{C}$ expressed in pp_mil analyzed in each samples collected. It is evident that matching the carbon content with the $\delta^{13}\text{C}$ concentration helps to discriminate the manufacturing origin of the component: the fertilizer is mainly characterized by a higher C content

Table 1. Mean and standard deviation of carbon (C), nitrogen (N) and $\delta^{13}\text{C}$ for each samples.

Sample type	N (%)		C (%)		$\delta^{13}\text{C}$ (‰)	
	Mean	SD	Mean	SD	Mean	SD
Uric acid	57.52	9.02	20.17	0.04	-101.56	3.19
Fertilizer	22.34	2.43	36.73	0.29	-29.08	2.70
Detergent_1	2.15	0.02	5.67	8.70	-1081.10	28.16
Detergent_2	1.01	0.001	2.97	0.15	-259.13	2.36

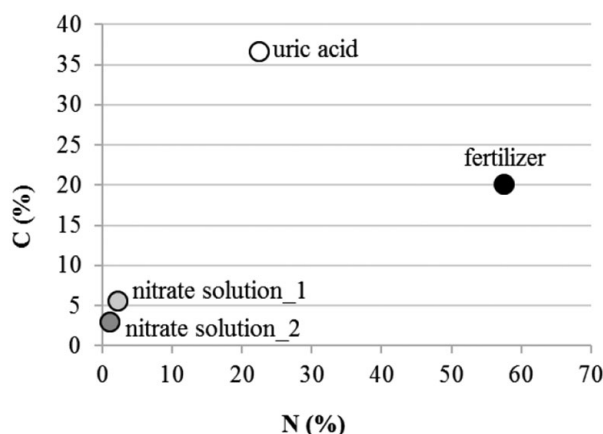


Fig. 6. Scatter plot C/N: uric acid (black spot), fertilizer (white spot), nitrate solution (grey spot).

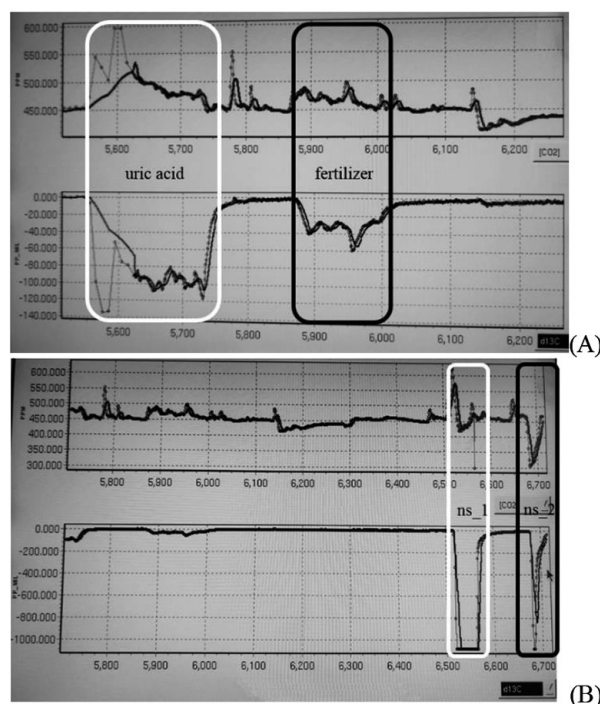


Fig. 7. $\delta^{13}\text{C}$ analyzed by the CRDS laser spectrometer (expressed in pp_mil): (A) uric acid and fertilizer; (B) nitrate solutions.

and a $\delta^{13}\text{C}$ value in the typical range of the primary production, on the other hand the detergent components and the uric acid exhibit a very low $\delta^{13}\text{C}$ concentration indicating they are not based on a metabolic process. Nevertheless, they can still be differentiated according to their C content: the detergents have lower C content compared to the uric acid as they are complex mixtures of different chemical molecules, not carbon based.

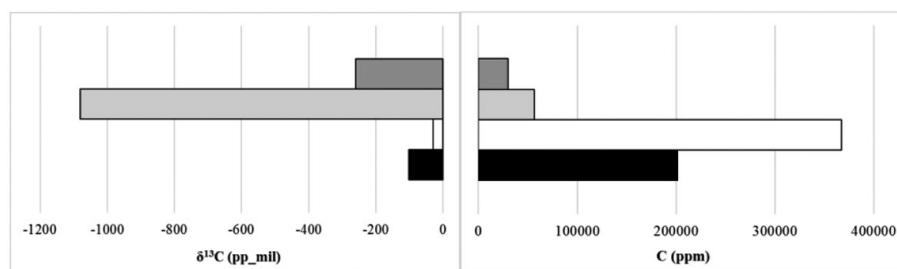


Fig. 8. Concentrations of carbon (C) expressed in ppm compared with the $\delta^{13}\text{C}$ expressed in pp_mil for uric acid (black box), fertilizer (white box), detergent.1 (grey/white box) and detergent.2 (grey/black box).

4 Discussion

The analyses of the nitrogen and carbon concentrations allow discriminating samples with low concentrations of nitrogen and /or carbon to other samples with high concentrations of these two elements. The instrument CN Vario Max Cube is able to analyze macro samples in the gram range with fast response time and the results allow classifying samples based on the content of nitrogen and carbon expressed in percentage.

On the other hand, CRDS laser spectrometer in the sniffer mode points out the presence of samples with different CO_2 and $\delta^{13}\text{C}$ content compared to the ambient air. It was also noted that CO_2 content is strongly affected by any minimal variation within the room (*i.e.*, people going in and out, smokers approaching the equipment, opening the windows), so the results of CO_2 content need to be reviewed with care. On the other side, $\delta^{13}\text{C}$ content varies less strongly against the above mentioned external effects but it gives strong variation when the sensor analyzes different materials. The sniffer mode is efficient and reliable to detect the presence exogenous materials

The use of a comparative two dimensional graph collecting the carbon content and the $\delta^{13}\text{C}$ concentration (*i.e.*, fig. 8) could be used as a fast screening visualization tool, in order to discriminate materials made by primary production compounds and synthetic ones.

5 Conclusions

The proposed instrumental configuration, which provides connection between an elemental combustor (Vario Max Cube, Elementar) and a carbon dioxide isotope analyzer laser spectrometer (CCIA, Los Gatos Research Inc.) allow to characterize samples based on their concentrations of carbon and nitrogen and ratio of carbon $\delta^{13}\text{C}$.

Samples analyzed show that the content of C, N and $\delta^{13}\text{C}$, are distinctive markers characterizing improvised and homemade explosives precursors that could be detected in the bombing accident scene. The sniffer mode of the laser spectrometer has been proved efficient and reliable with very simple preparation of the sample.

The presence of the specific features of C/N ratio and $\delta^{13}\text{C}$, as shown in the article text, in suspected areas could raise the attention to the possible presence of explosive precursors and trigger a more focused investigation.

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