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# LIDAR DETECTION OF CULTURAL HERITAGE DETERIORATING GASES

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#### Sommario

L'inquinamento dell'aria ha un impatto negativo sul patrimonio culturale. I gas vulcanici contengono forti concentrazioni di biossido di zolfo, uno dei gas più deterioranti per monumenti di marmo. Questo effetto può essere molto importante in città antiche vicine a siti vulcanici. Per questo motivo e per i grandi vantaggi del rilevamento laser, lo sviluppo completo di lidar vulcanici è stato al Laboratorio Diagnostiche e Metrologia (FSN-TECFIS-DIM) dell'Agenzia Nazionale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile (ENEA).

Parole chiave: Patrimonio culturale, telerilevamento laser, lidar ad assorbimento differenziale, rivelazione di gas.

#### Abstract

Air pollution have a negative impact on cultural heritage. Volcanic gases contain strong concentrations of sulfur dioxide, one of the most deteriorating gases for marble monuments. This effect can be very important in ancient cities close to volcanic sites. For this reason and for the great advantages of laser sensing, the thorough development of volcanic lidars has been undertaken at the Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA).

Keywords: Cultural heritage, laser remote sensing, differential absorption lidar, gas detection.

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#### Introduction

Air pollution deteriorates stone, wood, metal and glass<sup>1</sup>. In particular, stone monuments are affected by material loss, surface recession and blackening. One of the most deteriorating gases for marble is sulfur dioxide: this gas can dissolve in the water vapor in atmospheric clouds to form sulfurous acid and sulfuric acid, two components of acid rain, which then falls back corroding buildings and statues. Relevant concentrations of sulfur dioxide, one of the most dangerous gases for marble monuments, have been measured in volcanic gases<sup>2</sup>. This explain why the cultural heritage of historical cities surrounded by volcanic sites it is at high risk of fast degradation.

Ten active volcanos<sup>3</sup> and many dormant volcanos are located in central and Southern Italy. Their craters are often very close to densely populated urban areas. In order to assess the potential risks, Italian Civil Protection National Service (DPC) supports continuous monitoring and restricts the access to dangerous zones. In this framework, the Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) of the Frascati Research Center of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) carries out research on differential absorption lidar (DIAL)<sup>4</sup> of carbon dioxide in volcanic plumes. Carbon dioxide has been chosen because its anomalous release has been shown to anticipate volcanic eruptions<sup>5</sup>. Nevertheless, once modeled or measured the SO<sub>2</sub>/CO<sub>2</sub> ratio by conventional techniques, sulfur dioxide can be accurately retrieved from carbon dioxide.

Two systems are under development: BrIdge voLcanic LIdar (BILLI)<sup>6</sup>, funded by the ERC (European Research Council) project BRIDGE, and VULcamed Lidar (VULLI) funded by the ERDF (European Regional Development Fund) project VULCAMED. The first one is based on injection seeded Nd:YAG laser, double grating dye laser, difference frequency mixing (DFM) and optical parametric amplifier (OPA), and the second one relies on injection seeded Nd:YAG laser and optical parametric oscillator (OPO).

BILLI has been mounted in a small truck and carried out the 3D profiling of the volcanic plume of Pozzuoli Solfatara in October 2014<sup>7</sup>. It is the first time that carbon dioxide in a volcanic plume is retrieved by lidar, although laser remote sensing has already been applied to sound aerosol load<sup>8</sup>, sulfur dioxide<sup>9</sup> and water vapor<sup>10</sup> in volcanic plumes: up to now, to our knowledge, lidar soundings of CO<sub>2</sub> have been performed, but not in volcanic plumes<sup>11</sup>, and differential absorption measurements of volcanic CO<sub>2</sub> have been carried out, but they were not range resolved<sup>12</sup>. VULLI underwent a first test at the end of 2014, is under upgrade at FSN-TECFIS-DIM and it is expected to operate in a volcanic area within 2015. BILLI and VULLI can also be used for the measurement of wind speed<sup>10</sup>, thanks to their ability of aiming the laser beam in different directions. The main specifications of the two DIAL systems are listed on Table 1.

 $CO_2$  absorbs in the 15, 4.2, 2.1 and 1.6 µm bands (in order of decreasing strength)<sup>13</sup>. Unfortunately, in the first two bands viable lasers are not available and atmospheric backscattering is rather low, so the 2.1 and 1.6 µm bands have been suggested for its detection<sup>14</sup>. Nevertheless, the DIAL measurement of  $CO_2$  remains a difficult task because the absorption lines are narrow and weak<sup>15</sup>. As powerful, tunable and narrow-linewidth laser source we chose:

- s powerful, tunable and narrow-linewidth laser source we chose:
  - a dye laser with difference frequency mixing (DFM) and optical parametric amplifier (OPA) for BILLI,
  - an optical parametric oscillator (OPO) for VULLI.

Tm,Ho:YLF and fiber lasers have been discarded<sup>6</sup> mainly for their limited tunability (few tenths of nm) that can prevent to choose the best absorption line<sup>16</sup>.

Table 1. Main specifications of the two DIAL systems.

| DIAL system       |                   | •                      | BILLI                        | VULLI                                     |
|-------------------|-------------------|------------------------|------------------------------|---|
|                   |                   | Pulse energy           |                              | 17 (2014), 25 (2015) mJ                   |
| Transmitter       |                   | Pulse duration         | 8 ns                         | < 6 ns                                    |
|                   |                   | Repetition rate        | 10 Hz                        | 10 Hz                                     |
|                   |                   | Wavelengths            | 1.6, 2.1 μm                  | 1.57–2.08 (2014), 1.5–3.4 (2015) μm       |
|                   |                   | Laser linewidth        | 0.04 cm <sup>-1</sup>        | 0.15 (2014), 0.02 (2015) cm <sup>-1</sup> |
|                   |                   | Beam divergence        | 0.5 mrad                     | 2 (2014), 0.5 (2015) mrad                 |
| Receiver          |                   | Mirror coating         | Al                           | Al  |
|                   |                   | Clear aperture         | 300 mm                       | 300 mm                                    |
|                   |                   | Focal length           | 900 mm                       | 1200 mm                                   |
|                   |                   | Photodiode             | InGaAs PIN                   | InGaAs PIN                                |
|                   |                   | Diameter               | 1 mm                         | 1 mm                                      |
| Detector module   |                   | Responsivity           | 1.2 A W <sup>-1</sup>        | $1.2 \text{ A W}^{-1}$                    |
|                   |                   | Gain                   | $5.1 \times 10^4$ V $A^{-1}$ | $5.1 \times 10^4 \text{ V A}^{-1}$        |
|                   | -                 | Noise equivalent power | 10 pW Hz                     | 10 pW Hz <sup>-1/2</sup>                  |
|                   |                   | Bandwidth              | 0 ÷ 10 MHz                   | 0 ÷ 10 MHz                                |
| Analog-to-digital | converter         | Dynamic range          | 14 bit                       | 14 bit                                    |
| (ADC)             | OC) Sampling rate |                        | $100 \text{ MS s}^{-1}$      | 100 MS s <sup>-1</sup>                    |

#### **BILLI** (BrIdge voLcanic LIdar)

From 13 to 17 October 2014, BILLI measured carbon dioxide inside the volcanic plume of Pozzuoli Solfatara in Contrada Pisciarelli (Campi Flegrei crater area, Naples, Italy)<sup>7</sup>. Lidar retrievals were in good agreement with conventional techniques, yet based on completely independent and significantly different approaches. Each CO<sub>2</sub> profile was obtained averaging 200 lidar returns at 10 Hz, corresponding to a temporal resolution of 20 s. The spatial resolution was 1.5 m. A total plume scan was retrieved combining 20-30 profiles, i.e. in less than 10 minutes.



Figure 1. Left) Location of lidar and plume, and most northern/southern directions of the laser beam during the measurements. Center) Volcanic plume emitted by the Pozzuoli Solfatara in Contrada Pisciarelli. The lidar is mounted in a small truck (inside the white circle). Right) Lidar inside the truck. The laser beam is aimed by two large elliptical mirrors (major axis: 450 mm) mounted in two black boxes (inside the white circle).

BILLI was located at latitude  $40^{\circ}49'46.28"N$  and longitude  $14^{\circ}08'50.51"E$  (Figure 1), and the laser beam scanned typically the heading angles from  $196^{\circ}$  to  $234^{\circ}$  at an elevation from  $0^{\circ}$  to  $18^{\circ}$ . The laser beam was backscattered by the plume and by the rockface (Figure 2). Each lidar return can be divided into two portions, one inside the plume and another outside it, where the  $CO_2$  concentrations equal to the natural background ( $C_0$ =400 ppm). This latter includes two segments, respectively before (length:  $L_1$ ) and after (length:  $L_2$ ) the plume interception. Assuming that inside the plume the  $CO_2$  concentration corresponding to the i-th ADC channel ( $C_i$ ), is proportional to the lidar signal in the i-th ADC channel ( $S_i$ ), the optical depth of the laser path can be written as:

$$OD = \Delta \sigma \left[ C_0 \left( L_1 + L_2 \right) + \Delta R \, k \, \sum_i S_i \right], \tag{1}$$

where  $\Delta \sigma$  is the  $CO_2$  differential absorption cross section and k is the proportionality constant between  $C_i$  and  $S_i$ . The proportionality assumption is very reasonable because the light backscattering is due to aerosol that is dominated by water droplets, and  $H_2O$  and  $CO_2$  are usually proportional in volcanic plumes.

OD can be measured as follows:

$$OD = \ln \left[ \frac{S_R(\lambda_{OFF})/S_L(\lambda_{OFF})}{S_R(\lambda_{ON})/S_L(\lambda_{ON})} \right], \tag{2}$$

where  $S_R$  is the lidar signal from the rockface,  $S_L$  is the signal due to the scattering, inside the laboratory, of some photons of the transmitted laser pulse (this peak gives the exact time of pulse transmission and is proportional to the transmitted energy, thus providing the signal normalization) and  $\lambda_{ON}/\lambda_{OFF}$  is the more/less absorbed wavelength used in the DIAL experiment.

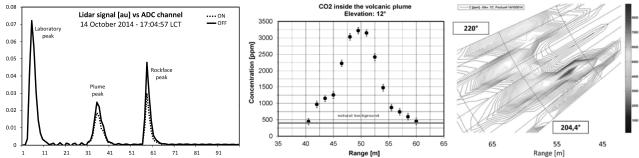


Figure 2. Example of: Left) lidar signal. Center) CO<sub>2</sub> profile. Right) Plume scan (the vent correspond to the grey spot).

Once determined OD, equation (1) can be solved for k, the only remaining unknown, and  $C_i$  can be simply calculated as the product of k and  $S_i$  (Figure 2). Sometimes, the plume was so optically thick that the rockface was not detected. In this case, in equation (2) the signal peak due to the plume was used instead of that due to the rockface, and carbon dioxide was retrieved only before the peak due to the plume, applying equation (1) with  $L_2$ =0.

The measurement error was dominated by inaccuracy in wavelength setting. This is why, back to the Frascati Research Center, we implemented a photo-acoustic cell filled with pure CO<sub>2</sub> at atmospheric pressure and temperature, close to the laser exit, as shown in figure 3. Using new software developed for this application, we are able to change the transmitted wavelength (by moving the stepper motor inside the resonator cavity of the dye laser) and to record the photo-acoustic signal (averaging 10 laser shots, corresponding to 1 s). Once corrected the wavelength for a small shift (0.12 cm<sup>-1</sup>), the agreement between experiment and theory<sup>15</sup> is very good (figure 3).

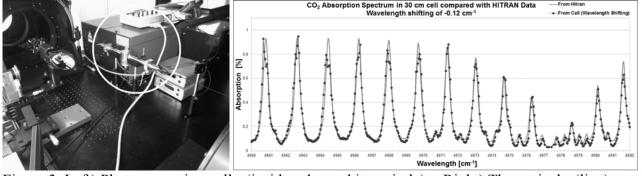


Figure 3. Left) Photo-acoustic cell (inside the white circle). Right) Theoretical (line) and experimental (circles and line) CO<sub>2</sub> absorption spectrum.

### **VULLI (VULcamed Lidar)**

A first version of VULLI has been completed in 2014 (figure 4). It reached the following specifications:

- spectral range 1.57–2.08 μm,
- linewidth 0.15 cm<sup>-1</sup>,
- power 170 mW,
- pulse duration less than 6 ns.

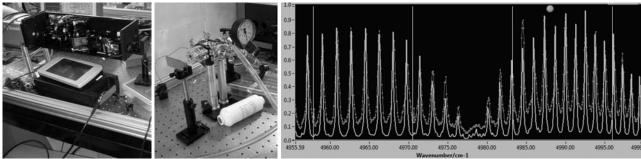


Figure 4. Left) The OPO opened during the test of the laser source of VULLI. Center) Photoacoustic cell. Right) Theoretical (line) and experimental (circles and line) CO<sub>2</sub> absorption spectrum.

The spectral purity of the laser source has been checked with a cell filled with CO<sub>2</sub> (figure 4), equipped with a microphone to record the photo-acoustic absorption spectrum. Theoretical<sup>15</sup> and experimental spectrum are in excellent agreement (figure 4), demonstrating that VULLI is ready to be tested on the field, with the purpose of measuring carbon dioxide in the atmosphere.

Notwithstanding these encouraging result, the system will be upgraded in 2015, in order to reduce even more its linewidth, with the final goal of reaching a linewidth of 0.02 cm<sup>-1</sup> (single longitudinal mode). Other specifications of VULLI will evolve as indicated in Table 1.

#### **Conclusions**

BILLI and VULLI, two differential absorption lidar for 3D profiling of carbon dioxide in volcanic plumes, are under development at the UTAPRAD-DIM laboratory of the Frascati Research Center of ENEA.

Both the laser sources developed for BILLI and VULLI are "single pieces", realized according to our specifications by world leading manufacturers: the great challenge was to realize laser sources transmitting very narrow linewidths and operating in the harsh environment characteristic of volcanic zones. Moreover, they must reach high power and emit nearly simultaneously two wavelengths. The source chosen for BILLI is more conservative: it is more reliable and has a better quality of the laser beam (circular profile, smaller size and lower divergence). On the contrary, the source chosen for VULLI requires still development, but is less complex, large, heavy and expensive. Our strategic choice, effective up to now, was to differentiate the technical approaches, in order to increase the probability of success of our volcanic activity: in fact BILLI carried out the first lidar measurement of carbon dioxide in a volcanic plume and VULLI promises to follow the example of his older brother.

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#### References

- [1] C. Varotsos, C. Tzanis, A. Cracknell, "The enhanced deterioration of the cultural heritage monuments due to air pollution," *Environ. Sci. Pollut. Res.* **16**, 590-592 (2009).
- [2] A. Aiuppa, R. Moretti, C. Federico, G. Giudice, S. Gurrieri, M. Liuzzo, P. Papale, H. Shinohara, M. Valenza, "Forecasting Etna eruptions by realtime observation of volcanic gas composition," *Geology* **35**, 1115-1118, (2007).
- [3] http://vulcani.ingv.it/en/
- [4] L. Fiorani, "Lidar application to litosphere, hydrosphere and atmosphere," in *Progress in Laser and Electro-Optics Research*, V. V. Koslovskiy, ed., 21-75 (Nova, New York, 2010).
- [5] A. Aiuppa, M. Burton, T. Caltabiano, G. Giudice, S. Guerrieri, M. Liuzzo, F. Murè, G. Salerno, "Unusually large magmatic CO<sub>2</sub> gas emissions prior to a basaltic paroxysm," *Geophys. Res. Lett.* **37**, paper L17303 5 pp. (2010).
- [6] L. Fiorani, A. Aiuppa, F. Angelini, R. Borelli, M. Del Franco, D. Murra, M. Pistilli, A. Puiu, S. Santoro, "Lidar sounding of volcanic plumes," *Proc. SPIE* **8894**, paper 7 10 pp. (2013).
- [7] L. Fiorani, S. Santoro, S. Parracino, M. Nuvoli, C. Minopoli, A. Aiuppa, "Volcanic CO<sub>2</sub> detection with a DFM/OPA-based lidar," *Opt. Lett.* **40**, 1034-1036 (2015).
- Early posting: http://www.opticsinfobase.org/ol/upcoming.cfm?page=7
- [8] L. Fiorani, F. Colao, and A. Palucci, "Measurement of Mount Etna plume by CO<sub>2</sub>-laser-based lidar," *Opt. Lett.* **34**, 800-802 (2009).
- [9] P. Weibring, H. Edner, S. Svanberg, G. Cecchi, L. Pantani, R. Ferrara, and T. Caltabiano, "Monitoring of volcanic sulphur dioxide emissions using differential absorption lidar (DIAL), differential optical absorption spectroscopy (DOAS), and correlation spectroscopy (COSPEC)," *Appl. Phys. B* **67**, 419–426 (1998).
- [10] L. Fiorani, F. Colao, A. Palucci, D. Poreh, A. Aiuppa, and G. Giudice, "First-time lidar measurement of water vapor flux in a volcanic plume," *Opt. Comm.* **284**, 1295–1298 (2011).
- [11] G. J. Koch, J. Y. Beyon, F. Gibert, B. W. Barnes, S. Ismail. M. Petros, P. J. Petzar, J. Yu, E. A. Modlin, K. J. Davis, and U. N. Singh, "Side-line tunable laser transmitter for differential absorption lidar measurements of CO<sub>2</sub>: design and application to atmospheric measurements," *Appl. Opt.* 47, 944-956 (2008).
- [12] Queißer M., Burton M., Fiorani L. "Differential absorption lidar for volcanic CO<sub>2</sub> sensing tested in an unstable atmosphere," *Opt. Express* **23**, 6634-6644 (2015).
- [13] P. J. Linstrom and W. G. Mallard, "The NIST Chemistry WebBook: A Chemical Data Resource on the Internet", *J. Chem. Eng. Data* **46**, 1059-1063 (2001).
- [14] R. T. Menzies and D. M. Tratt, "Differential laser absorption spectrometry for global profiling of tropospheric carbon dioxide: selection of optimum sounding frequencies for high-precision measurements," *Appl. Opt.* **42**, 6569-6577 (2003).
- [15] L. S. Rothman, I. E. Gordon, A. Barbe, D. C. Benner, P. F. Bernath, M. Birk, V. Boudon, L. R. Brown, A. Campargue, J.-P. Champion, K. Chance, L. H. Coudert, V. Dana, V. M. Devi, S. Fally, J.-M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W. J. Lafferty, J.-Y. Mandin, S. T. Massie, S. N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi, O. V. Naumenko, A. V. Nikitin, J. Orphal, V. I. Perevalov, A. Perrin, A. Predoi-Cross, C. P. Rinsland, M. Rotger, M. Šimečková, M. A. H. Smith, K. Sung, S. A. Tashkun, J. Tennyson, R. A. Toth, A. C. Vandaele, and J. VanderAuwera, "The HITRAN 2008 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* 110, 533-572 (2009).
- [16] L. Fiorani, W. R. Saleh, M. Burton, A. Puiu, and M. Queißer, "Spectroscopic considerations on DIAL measurement of carbon dioxide in volcanic emissions," *J. Optoelectron. Adv. M.* **15**, 317-325 (2013).

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