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Laser-based optical techniques for the detection of chemical agents*

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Abstract. Among numerous existing and developing techniques for the detection of air pollution, laser-based optical methods (LBM) are possibly the most promising ones. Unique sensing capabilities of LBM include high speed of analysis, high selectivity, sensitivity and accuracy, low detection limits, and remote detection. This paper gives a brief review of several laser-based systems for optical sensing of gas-phase chemical agents: laser intra-cavity, photoacoustic and laser-induced breakdown spectroscopy, and remote sensing based on differential absorption. For each method, a brief description of the principles of operation is given, and its analytical capabilities are outlined.

1 Introduction

A vapour-phase chemical agent (CA) is any substance in the atmosphere that has adverse effects on living organisms and on the environment. Special cases are chemical warfare agents (CWA), *i.e.* toxic chemicals specifically designed to be used in military applications or as terrorist weapons [1]. Bearing in mind that an adult person consumes $\sim$ 11000 litres of air per day, it is clear that all of these chemical agents can have severe impact on human health. For less toxic chemicals the occurrence of adverse health effects occurs after long-term exposure, while the most toxic agents like CWA can cause instant death.

The importance of air monitoring may be best understood if we recall several incidents that happened over the last three decades. The incident in Bhopal (India) in 1984, where a pesticide facility emitted methyl-isocyanate gas into the air, resulted in over 3000 victims [2]. In the course of the Iraq-Iran War, during 1980–1988, there were indications that chemical weapons were used which caused casualties [3]. In 1995, the incident in the Tokyo subway, when the CWA sarin was used, caused the death of twelve people [4]. Finally, there were indications that CWAs have been used in the ongoing Syrian conflict. All of these examples clearly indicate the importance of rapid detection, identification and monitoring of CAs, in order to prevent or minimize human casualties.

Harmful substances in air must be detected quickly and accurately because their presence is often transient. Besides, the detector sensitivity needs to be below the levels that pose a health risk. A number of methods for CA detection have been developed based on various physicochemical effects and phenomena. They usually include gas chromatography, mass spectrometry, optical spectroscopy and particularly laser-based spectroscopy and detection [5–11]. However, much research is still required in this area to improve selectivity, sensitivity, response time, portability, reliable detection, and capability for operation in unfavourable meteorological conditions.

2 State of the art of the laser-based optical methods for chemical agents detection

Several technologies have been investigated in order to develop a laser-based system for optical sensing of chemical agents [7–11]. Spectroscopy methods for detection of target substances, based on absorption, emission, or scattering of electromagnetic radiation by atoms, molecules, or ions include laser intra-cavity, cavity ring-down, photoacoustic,

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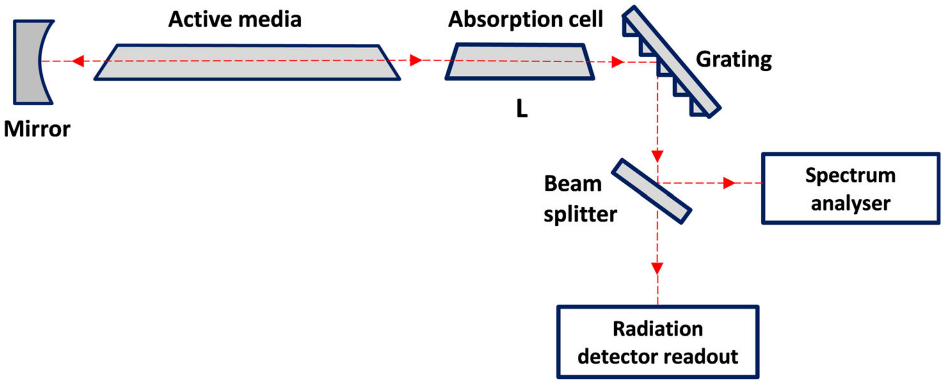


Fig. 1. Schematic view of ILS spectroscopy.

laser-induced fluorescence, Raman spectroscopy, laser-induced breakdown spectroscopy, etc. In relation to non-laser techniques, the main advantages of laser-based methods are high selectivity and high sensitivity (capability to detect threats present only at trace levels, in the range of parts per million by volume, ppmv, to parts per trillion by volume, pptv), real-time response, reliable detection with false alarms at acceptable levels, with *in situ* and stand-off capabilities allowing hazardous substances to be inspected from safe, remote locations. In addition, laser-based methods are environmentally friendly as no chemicals are used thus no chemical waste is produced.

2.1 Laser intra-cavity spectroscopy

Intra-cavity laser spectroscopy (ILS) is an absorption-based technique characterized by high-sensitive and high-speed detection [7,12] that can be used for quantitative analysis of trace concentrations of atomic and molecular species in air. Illustration of the ILS concept is shown in fig. 1. The absorbing cell, length L, along with the absorber is placed inside a laser resonator (cavity). The technique is based on appropriate matching of the laser emission wavelength to the absorption spectrum of the investigated gas. As the effective length/absorption path is a function of the photon life-time inside the resonator, resonator mirrors reflectivity should have the maximum at the wavelength corresponding to the absorption line of the investigated gas. Extraordinarily long effective optical paths can be achieved in an active cavity. Laser operation near the threshold is very sensitive to the changes of the overall gain, therefore the laser output power is proportional to the additional losses inside the cavity due to the presence of absorbing and light scattering species [7,13].

Laser operation (especially single mode) near the threshold introduces difficulties associated with mode competition, which introduces non-linearities, compromising the quantitative use of such method. A solution has been found in using Time Resolved ILS, in which a CW laser is perpetually interrupted in operation, discontinuing thus the mode competition, and using the time period in each cycle while there is linear response of intracavity absorption [7,14]. Various laser systems have been used for ILS, *e.g.* dye, gas, solid state and semiconductor systems. Of special interest are lasers operating in medium infrared (mid-IR), since in this range, particularly between 8 and 12 microns, many extremely toxic substances, like pesticides, insecticides, chemical warfare agents, etc., have high absorption [12,15–17]. Relatively high-efficiency lasers operating in this spectral region are gaseous CO_2 lasers, and semiconductor quantum cascade lasers (QCL). These two complementary laser systems were successfully applied for high-sensitivity ILS detection of numerous compounds in air environment. For example, cw CO_2 laser was used for detection of insecticides (LOD of the order of ppbv) [12] and also for vinyl chloride (LOD $\sim 0.014\,\mathrm{g/l}$), ethylene (LOD $\sim 0.60\,\mathrm{g/l}$) and propylene (LOD $\sim 0.95\,\mathrm{g/l}$) [15], while QCL system was used for detection of carbondioxide (LOD $\sim 40\,\mathrm{ppb}$) [18]. ILS application for detection of insecticides like DDVP, parathion and systox was conducted by application of cw CO_2 laser. In these experiments high sensitivities were obtained, typical LODs were about several ppbv [12].

2.2 Photoacoustic spectroscopy

Photoacoustic (PA) is another laser-based absorption method that can be applied for atmosphere sensing. The method is characterized by extra-high sensitivity and speed of analysis [9,16]. Illustration of the PA concept is shown in fig. 2. The modulated (*e.g.*, chopped) laser radiation is directed toward the PA cell, fig. 2, where an absorber (sample gas) is present. Absorption of the laser radiation induces a series of complex processes, excitation and de-excitation of given species/molecules, heating of the absorber, variation of the pressure and creation of acoustic waves which can be detected by sensitive microphone. The PA signal (S), detected by microphone is proportional to $S = S_m P C \alpha$, where S_m is microphone sensitivity, P is laser power, C is cell factor, and α is gas absorption coefficient [16]. Many compounds were registered by this method, with LOD in ppbv to pptv range, for example, ammonia (LOD $\sim 22\,\mathrm{ppbv}$) [16], and ethylene (LOD $\sim 0.29\,\mathrm{ppbv}$) [9].

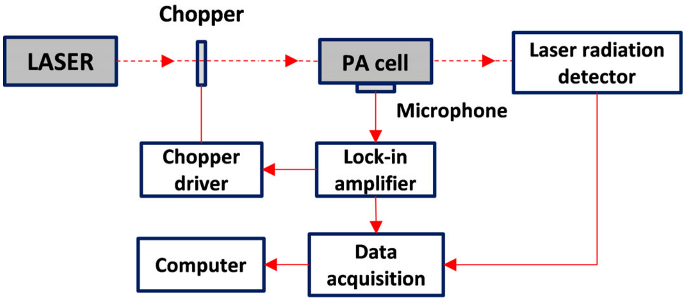


Fig. 2. Setup for photoacustic spectroscopy of gases.

Different laser systems were used for PA technique. However, laser systems emitting radiation in mid-IR (8–12 μm) are especially suitable for detection of chemical warfare agents, like sarin, soman, tabun, VX, etc., as these substances have high absorption coefficient in this spectral region. For instance, VX has two absorption maxima at ~ 9.6 and $\sim 10.5\,\mu$m, which match the emission wavelength of CO_2 and QC lasers [16]. VX absorption at $\sim 9.6\,\mu$m can be attributed to the existence of P-O-C bond inside the VX structure. PA technique based on QCL laser was used for high-sensitivity (20 ppbv) detection of the sarin simulant (DDVP) [19]. An experimental laboratory setup for PA spectroscopy based on cw CO_2 laser was constructed at the Vinca Institute, University of Belgrade [20–24]. The used CO_2 laser was a waveguide system. Numerous compounds were analyzed, like D_2O; H_2S (HTS, HDS); NH_3 (NDH_2, ND_2H); C_2H_4; F-12; CO_2; pesticides, etc. Some of these gases are of high importance for nuclear technology applications. Also, PA spectroscopy was applied for the analysis of different kinds of pesticides. The method was highly sensitive, for example, LOD for malathion pesticide was about 100 ppbv [24]. It should be mentioned that malathion has similar characteristic chemical structures and bonding as some CWAs which intensively absorb IR radiation in the 9–11 μm region.

2.3 Laser-induced breakdown spectroscopy

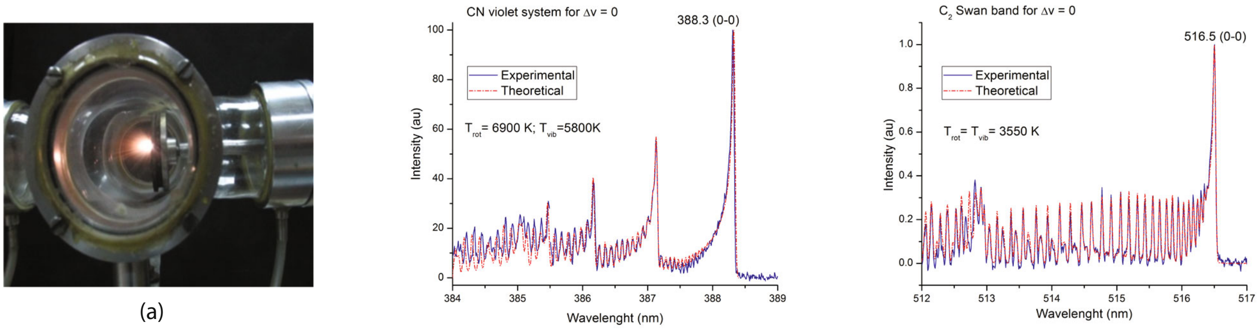
Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses energetic laser pulse as the excitation source. The laser radiation interacts with the material and, if sufficiently high power densities are applied (usually above $10^8\,\mathrm{Wcm}^{-2}$), plasma is created. In plasma, species are excited to emit element specific radiation which is analyzed by a spectrometer. All chemical elements can be identified in any material, solid, liquid, or gas. The method is especially sensitive to the light elements (He, Li, Be, B, C, N, and O) that are difficult for determination by other analytical techniques. Each element in the periodic table is associated with unique LIBS spectral peaks, its spectral signature. By identifying different peaks for the analyzed sample, its chemical composition can be rapidly obtained. LIBS may be used both for *in situ* (point) and remote/stand-off analysis.

LIBS is a promising technique for real-time chemical agent detection [25–27]. It was used for control of air pollution, analyses of aerosols and CWA detection. Analysis of CA is based on identification of characteristic elements and molecules (*e.g.*, C, P, H, N, O, CN, C_2) and estimation of their concentration ratios, or by statistical data processing methods applied to the spectra [25]. Spectral signature of characteristic elements, like F, Cl, P, S and As is used for identification of CWA [26]. For example, sarin (GB) and its simulant (DMMP + fluoroanisole) may be identified by detection of phosphorous and fluorine with an elemental ratio equal to one. Also, LIBS was used for identification of the characteristic elements contained in nerve (P and F) and blister (S and Cl) agents [27]. Detection of CA simulants dispersed in air and adsorbed on a variety of surfaces has also been achieved. For DMMP (sarin simulant) the LOD was evaluated to be $0.060\,\mathrm{mg\,cm}^{-2}$ and $0.60\,\mathrm{mg\,cm}^{-2}$, for cloth and leaf surface, respectively. Evaluation of LOD was based on phosphorus 253.6 nm spectral line. In the same article, LOD for mustard gas simulant (2-chloroethyl-ethyl-sulfide) was estimated to be $5.4\,\mathrm{mg\,cm}^{-2}$, using a chlorine spectral line at 837.6 nm.

Recently, a laboratory LIBS system based on pulsed TEA CO_2 laser was developed, and used for elemental analysis of variety of sample types [28–30]. Currently, applicability of this LIBS system for the analysis of molecular spectra is investigated. The first experiments with graphite target are promising, fig. 3, and present a good base for future applications, *e.g.*, studying of complex organic compounds including hazardous compounds like explosive residues.

2.4 Remote (LIDAR) detection

Laser methods based on different phenomena like, absorption [17,31–34], fluorescence [35] and Raman effect [11], have also been used for remote sensing. As an example, basic principle of operation of a LIDAR (LIght Detection And Ranging) system based on differential absorption, and applied for detection of pollutants in the atmosphere, is briefly described.



(a)

(b)

(c)

Fig. 3. (a) View of plasma created over carbon target inside the chamber. Typical LIBS spectra of (b) CN, and (c) C_2 molecule.

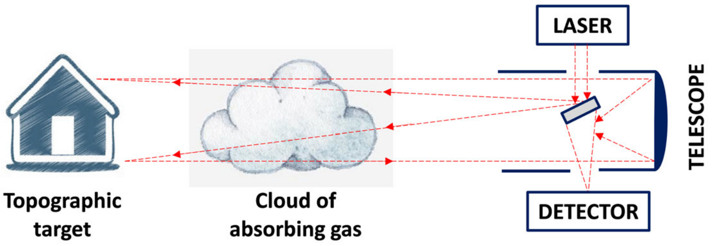


Fig. 4. Schematic view of LIDAR.

As shown in fig. 4, a laser source emits a pulse of light, and as the pulse propagates through the atmosphere, the photons interact with gas molecules and particles along the beam path causing absorption of the laser radiation. The absorption is then detected, and the measured signal is used for determination of chemical concentrations based on differential absorption. Differential absorption LIDAR operates at two wavelengths, one on-resonance and one off-resonance of the molecular absorption of the gas of interest. Because the on-resonance wavelength is more strongly absorbed by the gas, the difference between both signals is proportional to its number density. A concentration (or partial pressure, p) of the absorber (inside the cloud), may be approximated by the equation $p = 0.5\,L\,(\alpha_R - \alpha_N)\ln(I_N/I_R)$, where L is the length of the optical path through polluted air, α represents absorption coefficients at resonant (R) and non-resonant wavelength (N), and I represents laser intensity [31]. Various laser systems have been employed in LIDAR systems, *e.g.* dye laser, Nd:YAG and mid-IR lasers (TEA CO_2 and QCL). Using LIDAR systems, many compounds were detected with LOD estimated at ppbv level, for example, NH_3 (LOD ~ 0.4 ppbv-km), and SF_6 (LOD ~ 0.063 ppbv-km) [34]. A pulsed CO_2 laser LIDAR based on differential absorption is very efficient system for detection of warfare agents. The obtained LODs, at typical distances of 2–3 km, were: Tabun $\sim 62\,\mathrm{mg\,m^{-3}}$; sarin $\sim 45\,\mathrm{mg\,m^{-3}}$; soman $\sim 54\,\mathrm{mg\,m^{-3}}$ and, VX $\sim 147\,\mathrm{mg\,m^{-3}}$ [33]. Another group, using a commercial device [32], reported the following LODs: Tabun $\sim 50\,\mathrm{mg/m^2}$; sarin $\sim 150\,\mathrm{mg\,m^{-2}}$; soman $\sim 120\,\mathrm{mg\,m^{-2}}$ and, VX $\sim 80\,\mathrm{mg\,m^{-2}}$. Experimental LIDAR device based on pulsed TEA CO_2 laser was developed at Institute of Physics, University of Belgrade [31]. The CO_2 laser used had wavelength tuning capability in 9–11 μm spectral range. Resonant laser wavelength used for ethylene was $10.532\,\mu$m, $\alpha_R = 32.17$ (atm cm)$^{-1}$, and non-resonant laser wavelength was $10.611\,\mu$m, $\alpha_N = 1.42$ (atm cm)$^{-1}$. At the distance of several tens of meters from the laser, the absorption chamber with volume of ~ 660 litres along with retro-reflector was situated. The LIDAR used Newtonian telescope and a sensitive detector and it was applied for the analysis of air polluted with ethylene. For the applied laser output energy in the 10 mJ to 15 mJ interval, LOD value was of the order of several ppmv.

3 Conclusion

Review of several, relatively new laser-based methods for detection of chemical agents in air is presented. Laser techniques such as intra-cavity, photoacoustic and laser-induced breakdown spectroscopy, and also LIDAR system based on differential absorption are considered. Extraordinary characteristics of these methods allow their use for identification and monitoring of a wide range of air pollutants including chemical warfare agents. Laser-based optical methods are non-contact and non-destructive, the analysis is fast and highly selective and sensitive, and could be applied for *in situ* or remote detection.

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References

1. A. Ostin, *Chemical Munitions Search and Assessment, Review of analytical methods for the analysis of agents related to dumped chemical weapons for the CHEMSEA project* (European CBRNE Center, Umea, Sweden, 2013).
2. P. Shrivastava, Int. J. Mass Emerg. Disasters **5**, 199 (1987).
3. J. Ali, Nonproliferation Rev. **8**, 43 (2001).
4. T. Okumura, K. Suzuki, A. Fukuda, A. Kohama, N. Takasu, S. Ishimatsu, S. Hinohara, Acad. Emerg. Med. **5**, 613 (1998).
5. M. Mazurek, Z. Witkiewicz, S. Popiel, M. Śliwakowski, J. Chromatogr. A **919**, 133 (2001).
6. D. Profrock, A. Prange, Appl. Spectrosc. **66**, 843 (2012).
7. V.M. Baev, T. Latz, P.E. Toschek, Appl. Phys. B **202**, 171 (1999).
8. K. Lehmann, G. Berden, R. Engeln, *An Introduction to Cavity RingDown Spectroscopy* (Blackwell Publishing, Ltd., Chichester, UK, 2009) `https://doi.org.10.1002/9781444308259`.
9. D.C. Dumitras, S. Banita, A.M. Bratu, R. Cernat, D.C.A. Dutu, C. Matei, M. Patachia, M. Petrus, C. Popa, Infrared Phys. Technol. **53**, 308 (2010).
10. M. Cazorla, G.M. Wolfe, S.A. Bailey, A.K. Swanson, H.L. Arkinson, T.F. Hanisco, Atmos. Meas. Tech. **8**, 541 (2015).
11. S. Almaviva, R. Chirico, M. Nuvoli, A. Palucci, F. Schnürer, W. Schweikert, Talanta **144**, 420 (2015).
12. N. Konjevic, M. Orlov, M. Trtica, Spectrosc. Lett. **10**, 311 (1977).
13. S. Al-Hawat, Opt. Lasers Eng. **46**, 380 (2008).
14. B. Radak, J. Lunine, D. Hunten, G. Atkinson, J. Quant. Spectrosc. Radiat. Transf. **52**, 809 (1994).
15. J.W. Robinson, D. Nettles, Spectrosc. Lett. **11**, 73 (1978).
16. M.E. Webber, M. Pushkarsky, C.K.N. Patel, J. Appl. Phys. **97**, 113101 (2005).
17. P. Geiko, A. Tikhomirov, Opt. Mem. Neural Netw. **20**, 71 (2011).
18. A.V. Muraviev, D.E. Maukonen, C.J. Fredricksen, G. Medhi, R.E. Peale, Appl. Phys. Lett. **103**, 091111 (2013).
19. E.L. Holthoff, D.A. Heaps, P.M. Pellegrino, IEEE Sens. J. **10**, 572 (2010).
20. L.T. Petkovska, B.B. Radak, S.S. Miljanic, S.V. Ribnikar, Infrared Phys. **31**, 303 (1991).
21. L.T. Petkovska, M.S. Trtica, M.M. Stoiljkovic, G.S. Ristic, S.S. Miljanic, J. Quant. Spectrosc. Radiat. Transf. **54**, 509 (1995).
22. L.T. Petkovska, S.S. Miljanic, Infrared Phys. Technol. **38**, 331 (1997).
23. B. Radak, M. Petkovska, M. Trtica, S. Miljanic, L. Petkovska, Anal. Chim. Acta **505**, 67 (2004).
24. D.S. Maravic, M.S. Trtica, S.S. Miljanic, B.B. Radak, Anal. Chim. Acta **555**, 259 (2006).
25. J.L. Gottfried, F.C. De Lucia, C.A. Munson, A.W. Miziolek, Appl. Spectrosc. **62**, 353 (2008).
26. C. Gallou, A. Pailloux, J.L. Lacour, P. Mauchien, J.B. Sirven, E. Vors, E. Bouriah-Coindre, in *Proceedings of the 7th Symposium on CBRNe Threats* (Jyvaskyla, Finland, 2009).
27. A.J. Hartford, R. Sander, G.P. Quigley, L. Radziemski, D. Cremers, in *Proceedings of the Conference on Chemical Defense Research* (Aberdeen USA, 1982) LA–UR–82–3284.
28. M. Trtica, J. Savovic, M. Stoiljkovic, M. Kuzmanovic, M. Momcilovic, J. Ciganovic, S. Zivkovic, in *Proceedings SPIE 9810, International Conference on Atomic and Molecular Pulsed Lasers XII* (2015) `https://doi.org.10.1117/12.2228621`.
29. J. Savovic, M. Stoiljkovic, M. Kuzmanovic, M. Momcilovic, J. Ciganovic, D. Rankovic, S. Zivkovic, M. Trtica, Spectrochim. Acta Part B At. Spectrosc. **118**, 127 (2016).
30. S. Zivkovic, M. Momcilovic, A. Staicu, J. Mutic, M. Trtica, J. Savovic, Spectrochim. Acta Part B At. Spectrosc. **128**, 22 (2017).
31. P. Vujkovic-Cvijin, M. Trtica, N. Konjevic, in *Proceedings of the 22nd Symposium ETAN Mar.* (Zadar, Yugoslavia, 1980) pp. 384–389.
32. *Stand-off detector of Chemical Warfare Agents, Model: DD-CWA*, Technical report (Military Research Institute, Bratislava, Slovak Republic).
33. H. Laszlo, L. Gregory, in *Proceedings IX. Evfolyam 3. Szam* (Budapest, Hungary, 2014).
34. E.R. Murray, Opt. Eng. **17**, 30 (1978).
35. N. Sugimoto, Z. Huang, T. Nishizawa, I. Matsui, B. Tatarov, Opt. Express **20**, 20800 (2012).