

USING LASERS TO MEASURE POLLUTANTS

UDC 53+504.055

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Abstract. *In recent years, a large number of linear and nonlinear laser-based diagnostic techniques for detection of pollutions in different environments have been developed. Applications of laser spectroscopy constitute a vast field, which is difficult to cover comprehensively in a review. Due to that, here are presented only a few spectroscopic methods, chosen to illustrate the power of applied laser spectroscopy in environmental pollution investigation. The paper also gives a brief presentation of main laser spectroscopy methods.*

Key words: *Laser spectroscopy, trace gas detection, optoacoustic spectroscopy*

INTRODUCTION

Lasers have revolutionized spectroscopy, greatly expanding the field of laser spectroscopy in many areas. Immediately after the discovery of the laser (1960), the laser systems were developed for atmospheric studies [1]. The most common principle employed for the detection of environmental pollutants involves the interaction of the trace species with laser light (absorption, scattering). Up to now, various diagnostic methods based on physical process caused by laser light–environmental species [2–6] are developed.

Ideally, detection and monitoring laser based spectroscopic technique should fulfill the following requirements:

- *High selectivity*, for a particular gas species, with no observable cross-response from other species; to measure accurately trace gas concentrations of less than a part per billion;
- *High sensitivity*, to detect a very low concentration, below ppt (parts-per-trillion, 10^{-12});
- Possibility to *detect numerous compounds* with one instrument;
- *Wide dynamic range* to monitor high and low concentrations with a single instrument, in a real-time response that can be linear over more than four decades of concentration;
- *Fast Response*, with measurement speeds of fractions of a second, or signal averaging to achieve still higher sensitivity;
- *Good temporal resolution* for on-line monitoring;
- *Noninvasiveness* and *nondestructiveness*, which do not disturb the sample under analysis.

Laser-based analysis and diagnostics may be classified by a variety criteria such as physical processes caused by interaction of laser radiation with matter, sampling procedure, wavelength region, analytical methods, according to their power-law dependence on external electric field.

In respect to sampling procedure measurements can be performed:

In situ technique, the pollutants are measured directly and in many cases non-destructively. The data is obtained from local space, with less sensitivity, but with real-time monitoring.

Extractive techniques: samples are collected, and then analyzed and processed in laboratory. These techniques has high sensitivity and selectivity. But, sometimes may the contamination problems arise, the data is not obtained in real time and does not allow continuous monitoring.

Remote sensing technique, use of lasers to measure samples at some distance from the laser system. The advantage is the contactless measurement, measurements results give three-dimensional concentration or integrated profile of pollutions.

An important technical criterion of spectroscopic method is the wavelength region used: *visible*, *ultraviolet* (UV), *infrared* (IR) and *microwave spectroscopy*. For species identification IR region is particularly attractive, because the most of main atmospheric molecules (H₂O, CO₂, O₃, CH₄, N₂O, CFCs), have well defined and highly characteristic spectral features in the mid-IR spectral region (the so called fingerprint region) where molecular line intensities are reasonably large.

ABSORPTION-BASED LASER SPECTROSCOPY

The primary process is absorption of photons by atoms or molecules. Hence, *Absorption-based laser spectroscopy* is one of the most widely used analytical tools for detection of a specific molecule and one of the most important techniques for gas sensors in environmental. Direct laser absorption spectroscopy based on the Beer-Lambert absorption law is often used for quantitative measurements. A drawback this technique arise for very weak absorption signals. Traditionally, this problem is surpassed with multi-pass cells [7]. But it is limited by instrument size. High sensitivity can be obtained with other spectroscopic techniques based on the detection of phenomena induced by absorption of light, such as fluorescence in laser induced fluorescence (LIF) [8], ions in resonant enhanced multiphoton ionization (REMPI) [9,10], or pressure changes in optoacoustic spectroscopy (OAS) [11,12]. Another form of laser absorption spectroscopy is Cavity Ring Down Spectroscopy (CRDS) developed by

O'Keefe 1988 [13]. CRDS is based on measurement of changes in relaxation time of a high-finesse optical cavity upon introducing an absorbing species. These techniques permit researchers to obtain an effective optical path length of several kilometers in a very small volume. In CRDS, intensity measurements are replaced with time measurements. CRDS promise very high sensitivity for trace gas detection (Table 1) [14-17].

Table 1. CRDS detection limits

Atmospheric gas	Absorption line wavelength [nm]	Detection range	Theoretical detection limit [pptv]
SO ₂	290	ppt - ppm	20
NO	225	ppt - ppm	20
NO ₂	390	ppt - ppm	100
NO ₃	660	ppt - ppb	10
Cl ₂	310	ppt - ppb	300
O ₃	280	ppt - ppb	200
HONO	350	ppt - ppb	80

LASER REMOTE SENSING

The term "remote sensing" is commonly used to describe a series of techniques for identifying, observing, and measuring an object without coming into direct contact with it. This process involves the detection and measurement of radiation of different wavelengths reflected or emitted from distant sample. The optical interaction of relevance to laser environmental sensing:

- *Absorption*: attenuation of laser radiation when the frequency is matched to the absorption band of given molecules;
- *Fluorescence*: laser radiation matched in frequency to a specific electronic transition of an atom or molecule is absorbed with subsequent emission at lower frequency;
- *Resonance scattering*: laser radiation matched in frequency to that of a specific atomic transition is scattered by a large cross section and observed with no change in frequency;
- *Raman scattering*: laser radiation inelastically scattered from molecules with a frequency shift characteristic for the molecule;
- *Mie scattering* laser radiation elastically scattered from particulates (aerosols or clouds) of sizes comparable to the wavelengths of radiation with no change of frequency;
- *Rayleigh scattering* laser radiation elastically scattered from atoms or molecules with no change of frequency.

A number of remote sensing instruments are used to measure pollutants. Here only a brief description will be given on light detection and ranging (LIDAR) and differential optical absorption spectroscopy (DIAL).

LIDAR (*Light Detection And Ranging*) is a remote sensing technique to study trace constituents, aerosols, atmospheric structure and dynamics, clouds, and also meteorological parameters, such as temperature, humidity and wind velocity. Lidar operates on the same principle as radar, but employs a laser as the radiation source. The laser beam is emitted into the atmosphere and the portion scattered back subsequently detected. Intensity of the backscattered light indicates aerosol number density and sizes, while the time delay indicates the distance between the lidar and scattering particles. There are several main types of lidars (Table 2), which can be operated from ground, trucks, aircraft platforms and spacecraft [17,18].

DIAL (*Differential Absorption Lidar*) has been one of the most popular techniques to study a large of variety of gases. In DIAL measurements are made at two different closely spaced wavelengths. One of them is coinciding with an absorption line of gases under study, transmitted, scattered and the received intensity is attenuated by absorption. The second one is in the wing of this absorption, and measures the density of aerosols and molecules as in standard lidar systems. The difference in intensity of the two return signals can be used to deduce the concentration of investigated molecule (O_3 , CO_2 , CO , CH_4 , H_2O) [18].

Table 2. Ladar systems for different applications

Technique	Cross-section [cm^2]	Application
Rayleigh scattering	$10^{-25} - 10^{-24}$	Density of air molecules, temperatures
Raman scattering	$10^{-25} - 10^{-24}$	CO_2 , H_2O , N_2
Resonance scattering	$10^{-8} - 10^{-6}$	Trace species
Mie scattering	$10^{-6} - 10^{-5}$	Aerosols, smog, dust, cloud
Fluorescence	$10^{-14} - 10^{-12}$	Trace species (Na, K, Li, OH, ...)
Differential Absorption	$10^{-15} - 10^{-14}$	Trace species (CO , H_2O , NO_2 , O_3 , SO_2 , CH_4)

OPTOACOUSTIC SPECTROSCOPY

Optoacoustic spectroscopy (OAS) is based on the optoacoustic (OA) effect, in which acoustic waves result from the absorption of laser radiation by a selected target (samples of any state of aggregation) [3,19–24]. Light absorption results in a transient temperature effect, which then transforms into kinetic energy or pressure variations in the absorbing medium via nonradiative relaxation processes. The origins of OA date back to the discovery of the optoacoustic effect by Alexander Graham Bell in 1880 [25]. The invention of the laser and the development of detection technology of sound enabled the application OA effect in spectroscopy. First trace gas analysis was targeted 1971. by the pioneering work of Kreuzer [25]. He demonstrated that it was possible to detect concentrations of e.g. 10^{-8} (10 parts per billion) of methane in nitrogen, using an intensity-modulated infrared (3 μm) He–Ne laser. OAS is now commonly used for trace gas environmental monitoring [27,28], for non-invasive way to in-vivo monitor various physiological and pathological processes in the human body, as well as for analysis of trace components of human breath [4, 29–32]. Today, OAS has been established as a method of high sensitivity, selectivity and time resolution [2] (Table 3).

The principles of OA spectroscopy can be explained through Figure 1. The sample gas (liquid, solid thin film) located in OA cell (or in free air space), is illuminated by a laser source (continuous or pulsed laser) at wavelength λ . When the wavelength coincides with the absorption wavelength of the target molecule, the photon can be absorbed by the molecule and the molecule is now excited. Excited molecules decay back to their initial state by radiative or nonradiative mechanisms. Nonradiative relaxation converts the internal excitation energy of the molecule into translational energy and the medium is heated. In the absorbing medium transient temperature rise, this then translates into a pressure rise or sound wave.

Table 3. Comparison of detection limits of ammonia for different spectroscopic techniques

Spectroscopic method	Wavelength	Detection limit	Ref.
Optoacoustic spectroscopy	1532 nm	6 ppb	[33]
	10.784 μm	32 ppt	[34]
Cavity enhanced spectroscopy	1532 nm	100 ppb	[35]
Absorption (<i>multi-pass cell</i>)	1532 nm	280 ppb	[36]

The key component of an OA instrument is its sensitivity (detector–cell). For the experimental configuration (Fig. 1) the sensitivity depends on gas pressure p , gas constituents γ , gas temperature T and incident laser energy, E_i . i.e. $S(p, \gamma, T, E_i)$. When measurements are done with the same incident energy and at room temperature, sensitivity can be represented with

$$S(p, \gamma, T, E_i) = S(p, \gamma) .$$

For the elementary model of low absorption and in absence of saturation effects, and if only one kind of molecules is present in a gas sample, then the relationship between OA signal from the microphone p_{OA} , and gas concentration c , is

$$p_{\text{OA}} = S(p, \gamma) \cdot \alpha(\lambda) \cdot c ,$$

where $\alpha(\lambda)$ is the absorption coefficient. Recent value for C_2H_4 is $35 \cdot 10^{-4} \text{ Pa}^{-1} \text{ m}^{-1}$ and for CO_2 is $2 \cdot 10^{-3} \text{ Pa}^{-1} \text{ m}^{-1}$.

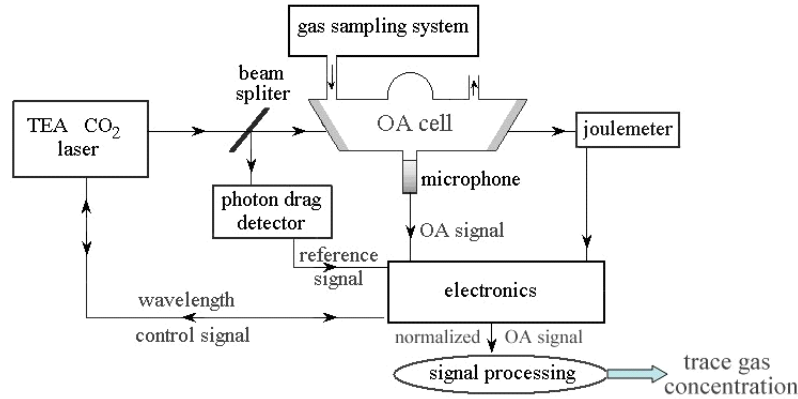


Fig. 1. Experimental arrangement for pulsed OA detector [37,38]: pulsed TEA CO₂ laser (Tachisto 215G, 100mJ per pulse), cylindrical shape OA cell (250 mm long, 25 mm inside diameter), closed with two NaCl Brewster angle windows, A condenser microphone (Bruel and Kjaer 4166)

The sensitivity of the OA detector (Fig. 2) was derived from calibration measurements with a certified mixture of gases: 880 ppm for CO₂ and 39.2 ppm C₂H₄ in synthetic air. These mixtures were diluted to the required concentration levels by a gas sampling system. All measurements were done at room temperature ($T = 300$ K) and with the 10P(14) CO₂ laser line ($\lambda = 10.53$ μm). Incident laser energy of 100 mJ per pulse was found to be appropriate, still avoiding optical saturation.

These results show strong dependence on gas concentration for low concentration range for both gases. This dependence range can be fitted using the least squares method to the equation $S(p, \gamma) = S = A \cdot c^B + D$. The obtained results can be expressed as

$$S_{\text{CO}_2} = 15(7) \cdot 10^2 c^{-1.48(12)} + 9.9(10) \quad 0 < c < 10^3 \text{ ppm}$$

$$S_{\text{C}_2\text{H}_4} = \begin{cases} 0.02(10) \cdot 10^6 \cdot c^{-0.7(10)} + 1.4(24) \cdot 10^6 & 0 < c < 0.3 \text{ ppm} \\ 1.54(9) \cdot 10^6 & 0.3 < c < 1.3 \text{ ppm} \end{cases}$$

The above result for C₂H₄ in high concentration range shows that there is no concentration dependence, and values for S can be described with the so-called cell constant.

The detection limit of the apparatus, defined as the absorbing gas concentration that corresponds to the signal to noise ratio equal to unity, is found by extrapolation from the data, based on the standard deviation of the linear regression analysis. The minimum detectable concentration was found to be: 1.50(8) ppb for C₂H₄ and 17.5(10) ppb for CO₂. These results demonstrate that the pulsed OA spectrometer has significant potentials for trace gas detection in environmental analysis and in non-invasive monitoring of breath tests based on exhaled trace gases.

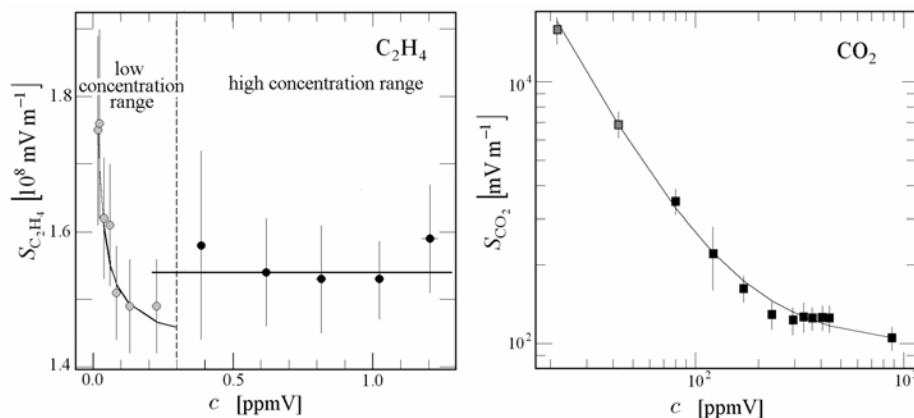


Fig. 2. OA detector sensitivity for C_2H_4 and CO_2 .

NONLINEAR LASER SPECTROSCOPY

In strong light fields various non-linear effects become significant (harmonic generation, multiphoton absorption, induced Raman effects, etc.). Different nonlinear spectroscopy techniques, based on nonlinear optical phenomena in interaction of laser radiation–sample, have been developed [39–43]. Particularly attractive applications are related to obtain information about atmospheric aerosols composition, liquid aerosol, remote detection and identification of bivalents, liquid aerosols. Nonlinear spectroscopy has recently appeared as a very promising method to probe the atmosphere [44]. There are many nonlinear effects that are employed in laser spectroscopy. Among the various laser spectroscopic methods, we here describe briefly the multiphoton spectroscopy and the laser induced breakdown spectroscopy.

Multiphoton spectroscopy

A multiphoton (MP) process is the one that occurs through the simultaneous absorption of two or more photons via virtual states in a medium. In 1931, Goppert-Mayer predicted theoretically that an atom or molecule could absorb two or more photons simultaneously [45]. Observable effect of this phenomenon had to wait a very intense beam radiation–laser. The new kind of spectroscopy to probe those transitions that were forbidden under one-photon excitation could be developed [11, 46,47].

To achieve a two–photon (TP) or multiphoton (MP) process a high photon flux needs to be delivered to the sample. This is possible by ultrashort (fs and ns) pulsed sources. To detect MP processes different techniques are used based on effects occurring in the investigated medium (fluorescence, OA, saturation, ionization, etc.).

One of new attractive applications of MP processes in investigation of aerosol composition is *MultiPhoton Excited Fluorescence* (MPEF) [48,49]. For excitation *in situ* MPEF uses a fs-TW (5 TW, 80 fs, 400 mJ) laser system integrated in a mobile laboratory built in a standard-dimensioned sea container. This mobile laser system includes sending and receiving optics and detection electronics for lidar, and mobility.

Resonant Enhanced MultiPhoton Ionization (REMPI), is being applied to the problem of detecting and identifying specific polychlorinated dioxin and furan below ppt concentration directly in gases. REMPI in combination with Time Of Flight (TOF) Mass Spectrometer (REMPI–TOFMS) is a system which can be used for the detection of a wide variety of compounds in the environment [51] (Table 4).

There are two major reasons which motivate the use of MP excitation: (i) better atmospheric transmission at longer wavelengths and (ii) the possibility of simultaneous size measurement by pump–probe schemes and coherent excitation to improve the detection selectivity.

Table 4. Comparison of sensitivity of REMPI with other spectroscopic methods for molecules NO and NO₂

Spectroscopic method	Molecule	Detection limit	Ref.
REMPI–TOF	NO	10 ppt	[9]
REMPI–TOF	NO	0.5 ppt	[10]
CRDS	NO	212 ppm	[15]
REMPI–TOF	NO ₂	5 ppt	[10]
CRDS	NO ₂	29 ppm	[15]
OA	NO ₂	6.5 ppm	[50]

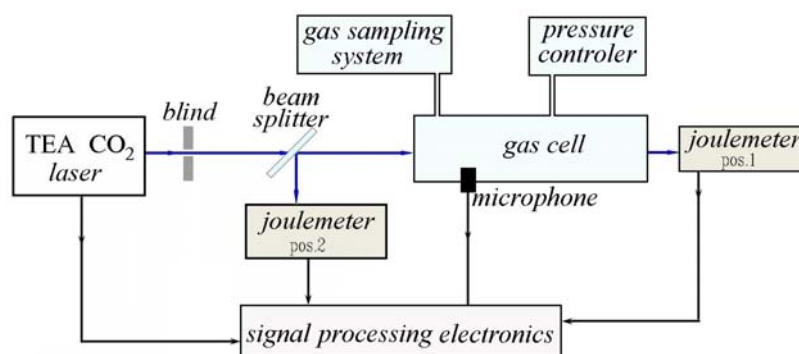


Fig. 3. Simplified block diagram of pulsed OA MP spectrometer

MP processes have been investigated using a number of techniques. In recent years it was widely accepted that the pulsed OA technique is a simple and powerful method to investigate many parameters relevant to MP absorption processes [52,53]. Here we give an outline of the pulsed OA technique [54,55] (Fig. 3). A pulsed TEA CO₂ laser (947.75 cm⁻¹, FWHM 45 ns) was used to excite MP processes in gas mixtures (absorbing gas + non-absorbing gas). The obtained OA signals were measured with a miniature microphone mounted in the OA cell. In order to calibrate the OA system [56], the OA cell was designed to satisfy the criteria for simultaneous use of single–pulse optoacoustic and transmission signals with parallel laser beam measurements. Direct calorimetric determination of the laser energy and the energy absorbed in the cell was performed by a calibrated pyroelectric joulemeter.

Laser Induced Breakdown Spectroscopy

Laser-Induced Breakdown Spectroscopy (LIBS) or often known in literature as *Laser-Induced Plasma Spectroscopy* (LIPS), is a form of spectroscopy in which the interaction of high-intensity laser radiation with matter can lead to generation of a dielectric breakdown through optical absorption. LIBS has proved to be a powerful laser-based analytical technique capable of performing trace element measurements in any kind of solid material [57–59]. Its main characteristics are:

- Minimal or no sample preparation of gases, solids or liquids;
- Measurements are spatially and temporally resolved;
- Real time, semi-quantitative measurement of most elements;
- Detection limits in the order of ppm or better for most elements.

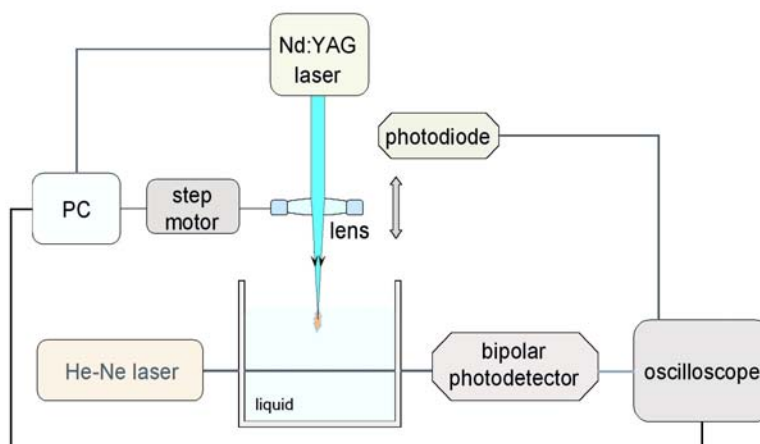


Fig. 4. Experimental setup for LIB in liquids

In every LIPS experiment there is a number of complicated processes that take place, depending on many parameters such as: laser wavelength, pulse shape, duration and intensity, spot size, optical properties of the sample. Several techniques have been used to analyze laser-induced plasma. Here is shortly presented an experimental set-up for LIBS in liquid [60] (Fig. 4), studied within the field of optodynamics [61,62]. Plasma in liquid (aqueous solution CuSO_4 and water) is induced with a Nd:YAG laser beam ($\lambda = 1064 \text{ nm}$), FWHM=10 ns, 180–760 mJ). The laser beam was focused from above through a lens (focal length 100 mm) on the liquid surface and inside the liquid. This leads to sparks of plasma generated in the vicinity of excitation beam focus. The sparks acts as an optodynamic source and were measured by a deflection of a continuous-wave He–Ne laser probe beam, laying parallel to the liquid surface. In liquids it is possible to detect plasma on different depths, thus allowing investigation of different liquid layers. Spatial and temporal resolution can also be obtained (Fig. 5) [63].

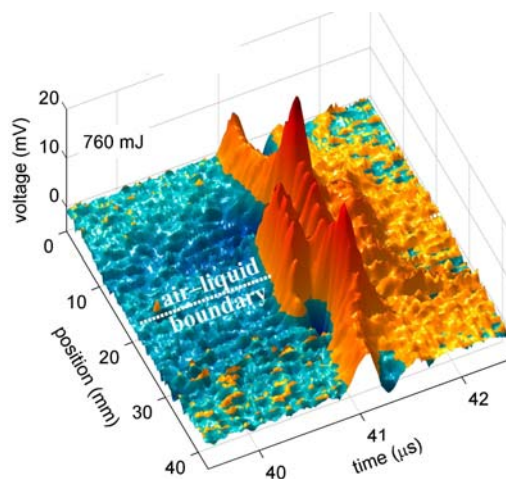


Fig. 5. 3-D representation of waveforms induced in 0.05M aqueous solutions of CuSO_4 at laser energy 760 mJ, for different excitation laser focus positions.

The ability of LIBS to provide microanalysis of bulk samples (solid, liquid, gas, aerosol) in the parts-per-million (ppm) region has been applied in a number of studies [64–66].

CONCLUSION

Laser Spectroscopy continues to develop and expand rapidly. The largest expansion of laser spectroscopy can be seen in its possible and already realized applications to chemical and biological problems and its use in medicine as a diagnostic tool and for therapy, and its contributions to the solutions of environmental problems are remarkable. For all these applications the basic scheme of laser spectroscopy is presented in Fig. 6.

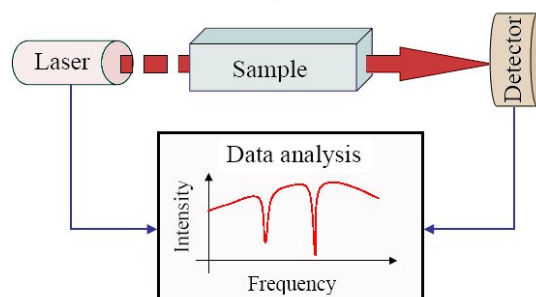


Fig. 6. Basic scheme of laser spectroscopy

Acknowledgments. This work was done as a part of the activities within the frame of 141015 Project of the Ministry of Science and Environmental Protection of the Republic of Serbia, cooperation in science and technology 2004-2005, Slovenia-Serbia & Montenegro and World Year of Physics 2005 activities supported by Serbian and European Physical Society.

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UPOTREBA LASERA ZA ISPITIVANJE POLUTANATA

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Poslednjih godina razvijen je velik broj raznovrsnih instrumenata zasnovanih na laserskim sistemimima. Oni omogućuju da se može pouzdano i u realnom vremenu uraditi monitoring okoline, industrijskih procesa, monitoring bioloških funkcija čoveka, selektivna detekcija molekula u tragovima... Uporedo sa razvojem novih laserskih i detekcionih sistema razvijen je niz linearnih i nelinearnih dijagnostičkih metoda za nedestruktivna merenja koncentracija polutanata u različitim sredinama. Kako je teško pokriti široku primenu lasera u rešavanju problema vezanih za zaštitu čovekove okoline, ovde je dat kratak prikaz, nekih savremenih metoda.