TUNABLE LASERS AT THE LASER SPECTROSCOPY GROUP:
SHORT FORM HISTORY FROM THE BEGINNINGS TO DATE

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Abstract. A brief definition of tunable lasers is given. Detailed results on tunable dye lasers
and on tunable diode lasers are presented, as obtained from 1975 – to date. First, the nitrogen pulsed
laser was presented which is used to pump dye lasers: operation, main constructive elements, pulse
time shapes and structure and beam power characteristics. Nitrogen lasers designed and engineered by
the group in the years 70’s – 90’s are also introduced. Secondly, results on dye lasers are presented:
operation, laser cavities/optical resonators, spectral characteristics of the tunable laser radiation
(tunability in the visible and near UV), time structure of the dye laser pulses, beam power evolution
function of working parameters. The dye lasers engineered in-house in the years 70’s – 90’s are
introduced, as well. The main applications developed using dye/tunable lasers are presented for two
main fields: pollution control and biomedicine. Finally, tunable semiconductor lasers studies are
introduced: tunable diode laser systems (emitting in the visible and NIR) mounted in Littrow
extended cavities, beat note detection to measure emitted wavelengths stabilities for two tunable
diode laser systems and the investigation of chaotic dynamics of an external-cavity semiconductor
laser emitting in the regime of low-frequency fluctuations.

Key words: nitrogen pulsed lasers, dye lasers, semiconductor lasers, tunable lasers, laser
spectroscopy, pollution control, laser biomedicine, laser chaos.

1. INTRODUCTION

The tunable lasers have been from the beginning of the laser era a particular
type of optical coherent sources which were developed in direct connection with
the atomic and molecular spectroscopy. In terms of adjustable wavelengths/tunability
one may define two types of tunable lasers:

• Stepwise tunable lasers which are constructed to obtain radiation of more
  wavelengths (one at a time) on the basis of the laser active medium properties. In
  this case the laser optical cavity includes a dispersive element which allows to
  select the desired wavelengths; the stepwise tunability is related to the emission of
  discrete radiation lines of the active medium which are amplified one at a time
function of the dispersive elements position. In the Ar⁺ case, for instance, the active medium emits a mixture of blue-green radiation; introducing a prism at minimum deviation fixed in a constant position with respect to the extraction mirror of the optical cavity one may tune the optical resonator either on 514 nm (green) or on 488 nm (blue) by modifying the incidence angle of the radiation coming from the active medium on the prism.

In the CO₂ laser case the extraction mirror may be replaced by a diffraction grating working in the middle infrared which diffracts the radiation emitted by the active medium back into it, controlling in this way the wavelength of the amplified radiation. Since the CO₂ laser active medium emits a large number of discrete lines there is the possibility to obtain a large number of discrete laser lines in the 10.6 µm region [1].

- Continuously tunable lasers are emitting radiation continuously tunable within a given spectral range. Typical tunable lasers are the dye lasers; in this case the active medium consists of dye molecules in different solvents so that the emission spectrum of the dyes is practically continuous. If the active medium is introduced within an optical cavity which contains a dispersive element one may obtain laser radiation whose wavelength may be tuned continuously within the emission spectral range of the dye. In this way one may cover with laser radiation the visible spectral range (400–800 nm) and even near UV and near IR.

Another continuously tunable laser radiation is emitted by diode lasers for which one may vary the injection current through the laser junction and the temperature within some limits which are compatible with the laser active medium. By varying the two parameters, the emitted wavelength may be practically continuously modified. The tunability spectral range may be widened and the emitted wavelength may be more precisely controlled if the laser diode is introduced within an extended optical cavity of the same type as in the dye laser; in this case the laser active medium is constrained to oscillate at a wavelength controlled by the dispersive element of the extended optical cavity and this wavelength may be finely tuned by changing the diode temperature and the injection current. So, for a given laser diode one may continuously cover more than 50nm spectral range.

In this paper are reported results on the nitrogen laser pumped tunable dye lasers and on tunable semiconductor lasers obtained by the Laser Spectroscopy Group (LSG) from 1975 to date. It has to be observed that the spreading in Romania of the nitrogen pulsed lasers (NPL) and of the tunable dye lasers pumped with NPL originated from this research group.

2. NITROGEN PULSED LASER (NPL)

The molecular nitrogen pulsed laser (NPL) was in 1970’s the most popular UV laser radiation emitter due to its relatively simple construction, good reliability and low cost. The first experimental reports on nitrogen pulsed lasers were made
by Leonard [2], Shipman et al. [3], Shipman and Kolb [4], and the main theoretical problems were first treated by Ali et al. [5] and Shipman [6].

This equipment was also the UV laser mostly studied and utilized by the LSG in its research projects during the 7-th and 8-th decades of the last century.

The active medium is the molecular nitrogen and the excitation is achieved by pulsed, fast, HV discharge through it, which is produced perpendicularly to the optical axis of the resonator. The LSG applied different electrical excitation schemes for the nitrogen lasers, the most effective proving to be the Blumlein excitation and the progressive (Godard) excitation ones (Fig. 1).

![Electric scheme of the N2 laser tube excitation.](image1)

**Fig. 1** – Electric scheme of the N2 laser tube excitation.

Triggering of the electrical discharge to excite the active medium (molecular nitrogen) was done by a thyratron or alternatively by an in-house made spark-gap [7]. The laser channel (laser tube) used was home engineered; the general aspect of such an unit is shown in Fig. 2.

![Molecular Nitrogen laser tube.](image2)

**Fig. 2** – Molecular Nitrogen laser tube.
The electronic energy states diagram of the nitrogen molecule (N$_2$) in the interval of interest for laser emission (second positive band of the nitrogen molecule) is shown in Fig. 3.

The electronic excited states involved in the main laser emission of this laser are C$^3\Pi_u$ and B$^3\Pi_g$ on which the lifetime of the molecule is 40 ns, respectively 6 ns [8]. This fact recommends to obtain a population inversion between the two states using a fast enough discharge in molecular nitrogen gas, the more so as the ratio between the electron excitation cross section for the upper (C$^3\Pi_u$) and lower (B$^3\Pi_g$) laser levels is 1.57 for an optimum electron energy of about 15 eV (obtained in HV discharge at voltages up to 20 kV). Experimentally, this means that a population inversion can be achieved using a very fast discharge which makes it possible to populate the C$^3\Pi_u$ state in less than 1 ns whereas the B$^3\Pi_g$ population is kept low since the lifetime of this level is 6 ns and the population is almost constant in the first 10–20 ns of the discharge. Given the fast discharge through the laser active medium, the nitrogen laser may generate pulsed radiation in two distinctive regimes:

a) Amplified Spontaneous Emission (ASE) regime, in which case the radiation is amplified only by passing one time through the laser tube length, without being necessary to use an optical cavity [9, 10] but a cube corner to totally reflect the beam at one of the heads of the laser tube.
b) Laser Emission regime, acquired by introducing the active medium within an optical resonator with dichroic mirrors optimized for maximum reflection at 337.1 nm; in this case the laser beam is amplified and generated only in ultraviolet at 337.1 nm. The difference between ASE and the laser radiation consists firstly, in the wavelengths of the emitted radiation. Then, the divergence of the laser emission is lower (of the order of 0.1–0.2 mrad) whereas for ASE beam it is of the order of a few mrad. The mode structure of the laser beam is usually single mode, whereas for ASE there is a superposition of intensity distributions which leads to a uniform energy density in the cross section. The laser beam is much more coherent than the ASE beam. The NPL may work at under-atmospheric pressures (between 4 kPa and 9.5 kPa) or at atmospheric pressure or slightly above atmospheric pressure in TEA configuration. In ASE regime and at under-atmospheric pressures, the typical characteristics of the NPL radiation are the following: wavelength of the maximum intensity 337.1 nm, peak power per pulse 1 MW, time length of the pulse 7 ns–20 ns, pulse repetition rate adjustable between 1 Hz and hundreds of Hz [8, 11].

In ASE regime and TEA configuration the beam characteristics are similar to the above mentioned, except the pulse time length which is typically 700 ps and maximum 1 ns. If the optical resonator is used, the spectral distribution of the laser beam contains only the 337.1 nm radiation with a spectral bandwidth of 0.1 nm, the peak power per pulse is 500 kW (typical value) and the pulse duration 10 ns; this variant of NPL construction is suitable for sealed-off lasers, the laser tube lifetime varying function of operating regime, emitted beam characteristics, etc. between 6 months and 2–3 years. Both types of functional regimes were used by the LSG, according to the particular objective aimed – high energy of the pulse for pumping dyes, high spectral brightness as UV light source, high average power, etc.

A comparative study was made on the emission power per pulse of three types of NPL [9]: Blumlein excited, triggered by spark-gap (a) & by thyratron (b), and progressive excitation triggered by spark-gap (c). The power per pulse variation of the laser emission versus operational parameters (filling nitrogen pressure, pulse repetition rate) has shown a maximum value of 175 kW (8 Hz, 50 Torr) for the Blumlein laser triggered by EG&G thyratron, 575 kW (8 Hz, 40 Torr) for the Blumlein laser triggered by spark-gap and 450 kW (3.5 Hz, 30 Torr) for the progressive-excited laser.

The dependence of the pulse power upon nitrogen tube filling pressure or repetition rate gave valuable hints for the operational optimal parameters for lasers of the kind (Fig. 4 a, b).
Fig. 4 – The power per pulse ($P/p$) versus: a) pulse repetition rate, for: □ – 12kV, 30Torr; x – 15kV, 30Torr; ∆ – 12kV, 50Torr; error bar 5%. (b) nitrogen pressure, for: □ – 4Hz, 18kV; x – 4Hz, 18kV; ∆ – 8Hz, 17kV; error bar 5%.

The same type of lasers were comparatively studied regarding the kinetics of the laser pulse build-up versus operational parameters (high-voltage, repetition rate, nitrogen filling pressure) [10] in order to evaluate the constructive and operational features of these lasers (regarded mainly as optical pumping sources for tunable dye lasers) as well as to understand electrical coupling between the excitation source (Blumlein or progressive transmission lines) and the laser channel. For this study a Tektronix 519 oscilloscope and a vacuum photodiode FD125 (Instrument Technology Ltd.) were used. The time development of the laser pulse is closely bound with the instant power generated by the laser – and thereby with the instant effectiveness of the laser. Typical kinetics of a nitrogen laser pulse is depicted in Fig. 5 (a–15 kV, 19 Torr, 10 Hz, Blumlein laser with spark-gap triggering; b–15 kV, 19 Torr, 10 Hz, progressive excitation with spark-gap triggering).

Fig. 5 – NPL pulse time shapes for Blumlein (a) and progressive excitation (b) arrangements of laser tube excitation.

The analysis of the collected data for the studied lasers suggested that, depending of the instant operational parameters, different operational regimes of the excitation of the active medium were installed for each of the three lasers. Also,
the effect of an end-mirror mounted on the laser tube over the pulse evolution was established: the mirror affects but the intensity distribution within laser pulse, not the time duration or the shape of the pulse. Increasing of the high voltage expectedly brings about an increase of the pulse intensity. A time-structure of the laser pulses was signaled, suggesting that actually a superposition of three subsequent pulses occurs, the time span of every pulse being 2.5–3 ns. These pulses may originate from the reflections of the high-voltage electrical exciting waves at the edges of the Blumlein transmission line. One may also notice the functional parameters determining the fastest rise-time of the laser pulse, which is one of the most important factors in pumping dye lasers. The FWHM of the laser pulse approximated 6 ns for the optimum energy emission for every laser type.

Another type of NPL was a transversely pumped TEA laser working at slightly above atmospheric pressure which emits at 337.1 nm laser radiation with the following characteristics: peak power per pulse 150 kW, pulse duration (FTW) 0.7 ns, pulse repetition rate adjustable between 1 pps and 50 pps.

The above presented data constituted valuable conclusions for the improvement of the nitrogen lasers engineered in-house by the LSG, as well as for designing tunable dye lasers pumped by nitrogen pulsed lasers, subsequently developed by the group.

The SLG designed, engineered (laboratory set-up models, up to prototypes) and produced more pulsed nitrogen lasers as presented in Table 1.

Table 1
NPL designed and produced by LSG

<table>
<thead>
<tr>
<th>Laser name</th>
<th>Pulse length (ns)</th>
<th>Max pulse energy (µJ)</th>
<th>N₂ filling pressure (Torr)</th>
<th>Electrical excitation type</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPA750</td>
<td>10</td>
<td>350</td>
<td>30-60</td>
<td>Blumlein</td>
<td>Prototype &amp; production</td>
</tr>
<tr>
<td>NLP 1N</td>
<td>1</td>
<td>150</td>
<td>atm</td>
<td>progressive</td>
<td>Prototype &amp; production</td>
</tr>
<tr>
<td>LPA 77</td>
<td>10</td>
<td>500</td>
<td>30-60</td>
<td>progressive</td>
<td>Prototype &amp; production</td>
</tr>
<tr>
<td>LPA 86</td>
<td>10</td>
<td>250</td>
<td>30-60</td>
<td>Blumlein</td>
<td>Prototype</td>
</tr>
</tbody>
</table>

2. DYE LASERS

The dye lasers have liquid active media which are solutions of different kinds of dyes in various solvents. The mechanism to obtain population inversion in the dye molecules found in solutions is based on the absorption of light beams (uncoherent or coherent) emitted by external optical sources; the process to generate the population inversion through absorption of optical radiation is usually called “optical pumping”.

The first tunable dye lasers were reported by Sorokin and coworkers in 1966 [12-14].
In Fig. 6 the energy level diagram of a typical dye molecule is given, which allows to describe the light absorption and emission processes involved in the laser emission.

The first process in producing laser action is to pump the molecules from the ground state $S_0$ to the first excited state $S_1$. This is followed by a very rapid non-radiative decay to the lower energy sublevels in $S_1$. The typical lifetime of the molecule in the state $S_1$ is a few nanoseconds. Finally, laser action occurs when the molecules make a transition from the lower energy sublevel of $S_1$ to any sublevels in $S_0$. Since there are so many sublevels in $S_0$, there are photons that come from many transitions from $S_1$ and $S_0$ as shown in Fig. 6. This is why dye media can emit along wide spectral ranges of wavelengths. The energy levels of $T_1$ and $T_2$ are involved in the laser action in a destructive way in the sense that they reduce gain and thus stop laser action; a minor part of the molecules make a transition of $S_1 \rightarrow T_1$ even though this is forbidden by the quantum mechanical selection rule, so that the dominating processes are related to the singlet-singlet transitions.

The quantum mechanical selection rule also prohibits the $T_1 \rightarrow S_0$ transition more strictly. This causes the molecules to pile up in the $T_1$ state. However, the transition $T_1 \rightarrow T_2$ is allowed. There has to be a range of frequencies to make this transition occur and that range of frequencies is exactly equal to the laser transition frequencies. So when a photon is emitted by a $S_1 \rightarrow S_0$ transition, it may get absorbed by a $T_1$ state molecule and then that molecule ends up moving to the $T_2$ state.
When this happens, the gain is reduced and the laser action stops. This is the reason why most dye lasers operate in pulses. These pulses are short compared to the time that it takes for the population of $T_1$ to become significant (typically 1 µs) and before the $T_1 \rightarrow T_2$ becomes quite important in stopping the laser pulse build-up.

The mostly used optical pumping sources are lasers; a scheme of a transversely pumped tunable dye laser, which is among the most popular, is shown in Fig. 7 [15, 11] for a Littrow pumping arrangement. The pumping laser must be chosen so that the wavelength of its radiation fits best to the wavelength of the absorption spectrum of the dye molecule in liquid solution.

One of the most convenient lasers to pump a dye laser is a NPL. The radiation produced by the pumping laser is focused (using a spherical – cylindrical lens system, $L$) in the dye solution filled in a quartz cell (Dye cell) and is absorbed according to the scheme shown in Fig. 6; following the absorption, the fluorescence emission takes place so that if a pulsed regime is used, fluorescence pulses appear in a time interval of some ps, the typical time width of the fluorescence pulses being in the range of 10 ns, provided the pumping pulse is shorter than 10 ns.

Due to the fact that in the liquid state, the vibrational-rotational levels of the dye molecule are broadened, the wavelength of the laser radiation may be tuned continuously; this is one of the main advantages of the tunable dye lasers. In order to obtain tunable laser radiation along all the visible spectral range and the adjacent parts of the electromagnetic spectrum (UV down to about 350 nm and near infrared up to about 1.1 µm) one may use successively several dyes [15, 11] which are continuously and sequentially covering this wavelength interval.
Theoretical analysis and modeling of the dye laser operation was a continuous concern for LSG [16]; in order to design efficiently tunable dye lasers it was necessary to develop theoretical models for quantitative description of transversely pumped tunable laser emission. In a rate equation approximation e.g., photon fluxes and temporal structure of the generated pulses were calculated for Amplified Spontaneous Emission case (no cavity) as well as for simple laser cavity (mirror + lens + grating) in the case of a Gaussian pumping pulse with 5 ns FWHM. Reductionist assumptions were made: the pumping energy distribution is uniform throughout the active medium and emission takes place under steady-state conditions. Theoretical data were chosen for the Rhodamine 6G dye (concentration $3 \times 10^{18}$ cm$^{-3}$; refractive index 1.44). Computed results obtained with these models were compared with experimental data measured in conditions chosen to be as close as possible to theoretical assumptions. (Experimental values of the photon fluxes were measured using a calibrated photodiode and by progressively attenuating the pumping pulse with neutral filters. The ASE and laser flux in zero diffraction order were spatially separated by a second grating). The conclusion of running the selected theoretical models is that generated time integrated photon flux dependence of pumping time integrated flux, according to the calculus, is in good agreement with the experimentally measured dependence. This statement is valid in the case of the ASE regime as well as in the case of the Laser Emission regime. For the temporal structure of the dye emission, computations were made for the distance dye cell – grating equaling 60 cm and a time integrated pumping photon flux $Q_p = 2 \times 10^{14}$ photons. As one may notice from Fig. 8, computed and experimental curves are in good agreement, meaning that the rate equation model is suitable to quantitatively describe temporal evolution of the dye laser emission in the uniform pumping approximation. It is also important to note that the model was able to evidence the contraction (shortening) of the pulse generated in the dye as compared with the pumping pulse – phenomenon which was experimentally measured.

The study of the time evolution kinetics of the pulse of a nitrogen laser pumped dye laser proved to be a powerful tool for inferring efficacy of the equipment, as well as of some particular aspects of the operation of the studied lasers. The investigation of the kinetics of dye lasers pumped by different types of NPLs [15] offered beneficial data in further optimization of laboratory set-ups or equipments engineered by LSG. Experimental set-ups in this undertaking included a NPL which was, alternatively, of Blumlein type triggered by spark-gap or a laser with progressive electrical excitation triggered by spark-gap; the tunable pumped dye laser was of Hansch type (telescope × 10 inside cavity, extraction mirror 50%) in which the laser cuvette was alternatively filled with Rhodamine B, Rhodamine
6G and Coumarine at different concentrations. Measurements were made using a vacuum photodiode (Instrument Technology FD125, supplied at 2.8 kV), a high speed oscilloscope (Tektronix 519), as well as lenses, mirrors and neutral filters chosen to properly manipulate laser beams. The wavelength of the laser emission was measured with a monochromator/photomultiplier system. The measurements have shown interesting conclusions in conjunction with the way the dye laser behaves, such as:

- pulse shape of dye laser follows closely the pumping pulse for a focusing arrangement of the pumping pulse which does not generate lasing in dye cell;
- when lasing and laser effect is generated above threshold, time kinetics of the pulse generated in the dye does not follow the pumping pulse, and shows a complex evolution, exhibiting successive peaks, function of pumping arrangement and of the dye cavity configuration (geometrical length, tuning wavelength, etc); these data prefigured ps laser emission by NPLs and dye lasers pumped with them;
- lasing could be generated or not, depending on the concentration of the used dye and on the focusing arrangement. Depending on these parameters, slight time shortening or slight time expansions of the dye pulse in relation to the pumping pulse were observed;
- the presence of the mirror in the dye laser cavity does not influence the time behavior of the generated pulse, while lasing is generated at different focusing arrangements when mirror is in place;

Fig. 8 – Time evolution of the dye laser emission in the uniform pumping approximation.
– the rise time of the dye laser pulse depends on the type of pumping NPL pulse rise time. A 3 ns rise time was observed when pumping the dye with Blumlein NPL while the rise time of the dye pulse was only 1 ns when it was pumped by progressive excitation NPL.

This behavior could be qualitatively and quantitatively explained by taking into account different photo-physical phenomena involved in generation of dye laser radiation at molecular level – e.g. the broadening of the vibrational-rotational energy levels, or the ratio of the effective vibrational temperature and effective rotational temperature during the pumping interval. On the other hand, the increasing of the time interval between the peak of the fluorescence intensity and the laser peak radiation – which was experimentally measured – was explained by the inhomogeneous broadening of the ground state of the dye molecule coupled with the effective rotational temperature evolution.

The above mentioned studies enabled LSG to design and engineer different NPL-pumped-tunable-dye-laser set-ups as shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Dye laser</th>
<th>Pumping NPL</th>
<th>Pulse energy (µJ)</th>
<th>Spectral range covered (nm)</th>
<th>Dyes</th>
<th>SHG capability</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPC 75 LPA 7550</td>
<td>10 – 20</td>
<td>400 - 700</td>
<td>POPOP; 4-MU; Coum; Na-Fl; Rh6G; RhB; Cr-V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPC 77 LPA 77</td>
<td>15 – 35</td>
<td>400 - 700</td>
<td>POPOP; 4-MU; Coum; Na-Fl; Rh6G; RhB; Cr-V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPC 86 LPA 86</td>
<td>18 – 580nm</td>
<td>258.8 – 262.8</td>
<td>POPOP; 4-MU; Coum; Na-Fl; Rh6G; RhB; Cr-V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lab. set-up NPL 1N</td>
<td>5 – 10</td>
<td>400 - 700</td>
<td>POPOP; 4-MU; Coum; Na-Fl; Rh6G; RhB; Cr-V</td>
<td>ADP, 80° ADP, 68° ADP, 60°</td>
<td></td>
</tr>
</tbody>
</table>

The tunable dye laser type LPC 86 is a complex unit including a Blumlein nitrogen pumping laser with its supply unit (nitrogen, HV, trigger pulses), focusing lens system for 337.1 nm, Littrow dye cavity (diffraction grating, telescope x10, extraction mirror) with six indexed, interchangeable dye cuvettes and a Second Harmonic Generation (SHG) unit with three doubling inter-replaceable indexed non-linear crystals and compensating counter-rotating crystal, as depicted in Fig. 9. Grating rotation was controlled by a sine-bar actuated by a stepper motor. The laser operation was controlled by a computer unit.
Fig. 9 – The general scheme of the tunable dye laser type LPC 86: 1 – nitrogen laser unit; 2 – nitrogen laser supply unit; 3 – optical cavity; 4 – optical bench, 5 – frequency doubling unit; 6 – computer assisted unit for laser control.

One interesting solution the LSG has chosen for efficient improving the output of a tunable laser, was to use a dye oscillator-amplifier arrangement pumped by two synchronized TEA nitrogen lasers, as depicted in Fig. 10.

Synchronization was obtained by triggering the two TEA nitrogen lasers from a unique spark-gap. Adjustment of individual operational parameters for every of the two TEA nitrogen lasers ensures the slight de-synchronization necessary in the operation of the dye oscillator-amplifier system. One of the nitrogen-pumped dye cell is provided with a Hansch type laser cavity with Littrow diffraction grating.

The narrow linewidth emission of this tunable laser is optically coupled to the second nitrogen-pumped dye cell, virtually filled with the same dye, where the pulse is amplified. Energy and narrow band of the output pulse enables efficient operation of Second Harmonic Generation in a suitable tailored nonlinear crystal.
3. COMPUTER CONTROLLED DYE LASER SPECTROPHOTOMETER

Relying on the studies on nitrogen lasers and on dye lasers, LSG was able to design and engineer in-house (between 1978 and 1981) a quite sophisticated equipment: a computer controlled dye laser spectrophotometer [17, 11] which uses a tunable dye laser pumped by a NPL in order to generate narrow band tunable laser radiation covering the visible spectral range and some domains in the near-UV (by second harmonic generation in nonlinear crystals). The equipment could be used as a general use spectroscopic optical source or for dedicated purposes such as the detection of traces of pollutants in used water samples.

3.1. SYSTEM STRUCTURE

Fig. 11 shows a detailed block scheme of the tunable laser absorption spectrophotometer, where the light source is a NPL-pumped tunable dye laser. The NPL type LPA 7550 [7] was used. A detailed description of the nitrogen laser electronics and fluids can be found elsewhere [18].
The NPL is used to pump an optical dye cavity which contains, as the active laser medium, several types of dyes introduced successively into it. The dyes are chosen so that the spectral range of the laser radiation obtained using them moves successively in the visible range from 400 to 700 nm.

The laser radiation is introduced into an optical bridge which allows an absorption signal to be obtained for each radiation wavelength. The change of
wavelength is computer controlled, so that at the end of the measuring sequence a real time absorption spectrum is recorded. The same absorption spectrum is recorded in the computer’s memory to make qualitative and quantitative data interpretation by comparison with previously recorded spectra constituting a data library.

3.2. OPTICAL SET-UP

The nitrogen laser radiation is focused inside a dye cell (Fig. 11) using a set of cylindrical lenses; the fluorescence radiation emitted by the dye along the pumping filament is analyzed and amplified in the dye laser optical cavity. The dye cells may be changed by a stepper motor keeping the laser cavity aligned from one dye to another. Each dye cell is provided with a number, in binary code, for computer identification by the cell index unit.

The initial wavelength of the laser radiation emitted by the first dye is indicated by a home-built capacitor transducer which has a TTL compatible output signal. The errors made by this unit in setting the initial wavelength are such that it may be fixed within ±0.2 nm; any other intermediate wavelength obtained using a second stepper motor which acts on the grating's angular position can be calculated using the number of steps counted from the initial position of the grating. The peak power per dye laser pulse is about 10 kW regardless the output wavelength. The spectral bandwidth of the radiation is 10⁻² nm for the arrangement shown in Fig. 11, whereas in standard spectrophotometers the same feature varies with the function of the type of the device, from 10⁻¹ nm to 4 nm. The dye laser radiation power density defined with respect to the spectral bandwidth is 10⁶ W · nm⁻¹.

In the absorption signal processing the power per pulse is important and not the average power, because the information on the absorption process is obtained by measuring at a given time moment the amplitude of the laser pulse for each individual pulse, after passing through the absorption cell.

The excess of light beam energy makes it possible to use a large optical absorption path; this advantage is strengthened by the divergence of the laser beam which is much lower than for standard systems. The small divergence and correspondingly the size of the laser beam spot are kept at the required level using pinholes to eliminate fluorescence background and a long focal distance lens which is mounted paraxially (Fig. 11).

For the absorption signal measurement the radiation is split and introduced into an optical bridge which contains the absorption cell and the corresponding reference cell.

For each pulse, a pair of pulses is formed so that the measured absorption signal and the corresponding reference signal are obtained using laser radiation originating from the same pulse.
Diffusing screens are mounted in front of the photodetectors to avoid detector saturation.

3.3. DYE LASER

The dyes used are introduced in Fig. 12, where the types of solvents and solutions for each case are specified. For each dye, Fig. 12 shows the envelope containing the peaks of the laser lines for all the wavelengths useful in the device.

The computer was programmed to perform three distinct tasks: to sequentially start and stop the system controlling its working parameters, to acquire the data and to make qualitative and quantitative interpretation of them using a data library previously recorded for standard concentrations.

The working parameters controlled by the computer are: the nitrogen pressure inside the laser tube, the dye laser intensity level, the setting of the initial wavelength, the dye cell introduced into the optical cavity.
For the data acquisition the computer asks the operator about the spectral range and number of pulses per wavelength. After the averaged absorption signal is memorized, the computer changes the wavelength, acting on the diffraction grating stepper motor; the operation goes on until the measuring sequence is complete, when a real-time absorption spectrum is recorded and the same spectrum is memorized.

For the qualitative and quantitative analysis of the sample, by comparison with standard data, the computer identifies the compounds using the wavelength of the absorption peaks and finds the concentrations using the intensities of these lines, converting the absorbance into concentrations.

Decisions on the quality of the spectra and analysis are made by the operator.

3.4. DEVICE PERFORMANCES AND EXPERIMENTAL DATA

An important application regards the pollution control, where the device analyses pollutant content of the sample for one or more pollutants at very low concentrations. One class of pollutants which may be analyzed is the pesticides, particularly chlortriazines, among which the most usual are atrasine, propasine and simasine. Usually the chlortriazines exhibit a significant absorption peak in the ultraviolet around 224 nm. To obtain an absorption maximum in the visible, the samples were chemically treated as shown elsewhere [18].

An absorption spectrum of the atrasine derivative is shown in Fig. 13a for atrasine at $10^{-3}$ ppm, which shows the sensitivity of the device in a range of low concentrations.

For computer determination of the triazine concentration in water, a data library is introduced into the computer's memory for concentrations in the range between 1 ppm and $10^{-3}$ ppm using several lengths of absorption and reference cells varying from 10 mm to 750 mm. The number of concentrations used in the data library is chosen in order to minimize the errors which may appear in the data interpretation when interpolation is made. The different lengths of the absorption cells are necessary to keep the strength of the absorption signal below the saturation level of the signal processing unit, regardless of the concentration detected. The quantitative analysis may be made more precise by observing that the absorption maxima are broad so that, at the peak, the signal is quite constant for about 0.5 nm. Recordings of this part of the absorption lines are shown in Fig. 13b; the computer takes into account the constant parts of the curves for quantitative analysis.

The reproducibility of the absorption spectra at each concentration for the same experimental conditions is within 0.4%, so that there exists a strict relation between concentration and absorption peak intensity. This fact makes correct quantitative analysis at low concentrations possible, with respect to the data library, in spite of the over-reading at low concentrations due to the behavior of the atrasine derivative. The over-reading is due to the light scattering at long optical absorption paths, which determines a translation of the absorption signals towards somewhat higher values than real (for data library and current samples as well) with a constant and reproducible quantity over the whole spectral range.
This equipment evidenced the use of a tunable dye laser controlled by a computer in optical spectroscopy as an useful tool in measuring water pollutants.

**4. OTHER APPLICATIONS OF THE TUNABLE DYE LASERS**

The LSG developed more applications of the tunable dye lasers in spectroscopy, biomedicine, monitoring of environment pollutants and, more general, in life sciences which are not the subject of this article and which are generically described in the following.

The applications in spectroscopy were related to the atomic and molecular data measurements for the alkali metals, such as Rb [19].

The applications in biomedicine lead to the design and production of several types of laser medical equipment medically and technically homologated in Romania for ophthalmology (DYCLAS) [20] and dentistry [21, 22] These applications have triggered a basic science research program in biomedicine to clarify within an as large as possible degree the laser beam interaction processes with biomolecular systems.
The tunable dye lasers applications in environment protection were devoted to the measurements of pollutants in air (NO\textsubscript{x}, SO\textsubscript{x}) by absorption, fluorescence and cavity ring down spectroscopy [23, 24], in water (oil and oil components, organofluorated pesticides), and soil (oil, heavy metals) [25-29].

5. TUNABLE SEMICONDUCTOR LASERS

The semiconductor lasers were studied from the point of view of their spectral tunability properties over relatively large spectral ranges, as a potential alternative to the tunable dye lasers. Particular efforts were dedicated to obtain radiation from laser diodes at shorter wavelength, i.e. in nearest IR and visible; in fact the disadvantages of the tunable dye lasers, like large volume, high energy consumption, constructive complexity, etc., are solved in a large extent by the tunable semiconductor lasers.

The LSG reported results on spectral tunability of the laser diodes, with particular emphasis on their capabilities as light sources for spectroscopic applications. A detailed comparison of the tunable semiconductor lasers (TSL) with tunable dye lasers (TDL) and particularly, with nitrogen laser pumped tunable dye lasers is given in [30].

The experimental set-up used to obtain radiation emitted by a laser diode and to measure its wavelength is shown in Fig. 14. The arrangement was made to study different laser diode types, in single mode or multimode operation.

To perform the tunability experiments, the chosen laser diode was introduced in a Littrow extended cavity containing a beam splitter used to extract the laser beam; the beam was sent on an external beam splitter which allowed its further transmission for wavelength measurement and its reflection, for monitoring with one silicon photodiode and for beat-note detection. A second cavity, identical within the experimental limits with the first, but containing another laser diode of the same type, sends the laser beam along the same optical path in order to measure the wavelength of the emitted radiation and to fall on the beat-note detector for frequency comparison using a spectrum analyzer. For accurate wavelength measurements, the laser beam emitted by each external cavity was sent to a lambdameter type LM-10 (NBS), and the measurement was made by comparison with the radiation emitted by a He-Ne-I\textsubscript{2} frequency stabilized laser at 632.99095 nm.

In order to tune the radiation wavelength emitted by a laser diode, the temperature of the diode is varied into a specific range, and for each temperature the forward current is varied with increments which are function of the slope specific to the dependence of the emitted wavelength by the injection current.

In Fig. 15 are shown the tunability spectral ranges at each temperature, resulting the overall capabilities of a STC (LT-50A-03 single spatial mode) laser diode to be tuned.
Fig. 14 – Experimental set-up for laser diodes wavelength measurements.
Over the time, the tunable semiconductor laser became one of the most recommended devices with respect to tunable dye laser for some classes of spectroscopic applications. It is well known that the laser diodes have unpredictable as far as the mode structure, beam power, stability and even divergence is concerned. The theoretical and experimental studies devoted to this kind of problems have shown that even if selected lasers are used as sources of radiation it is always possible to have a chaotic behavior of the laser diode emission implying unpredictable modification of the laser beam structure, variation of the laser beam divergence, beam power modifications and even slight walk-off of the wavelength. This specific behavior of the laser diodes was studied in detail. Of particular interest are the beam power stability and the laser beam mode structure evolution for laser diodes.

In the first studies we reported results regarding the mode structure and laser beam power stability for several laser beams used in low level laser therapy (LLLT) equipment [31]. Other studies have focused on the chaotic properties of the laser diode emission [32-35]. The chaos investigation defined as the study of unstable aperiodic behavior in deterministic nonlinear dynamical systems, becomes more and more present in laser physics studies and this is due to the fact that the laser systems are preponderently nonlinear and now we have the computational power to analyze them. In historical steps, Poincaré first pointed out that no accurate calculation of how three or more bodies move under gravitational interactions for long time into the future can be made, because any tiny imprecision in the initial conditions would grow in time at an enormous rate.

A chaotic evolution is an intrinsic mark of many nonlinear systems. In lasers as well as in nonlinear optical devices, chaos occurs unremittingly. Systems fundamentally simple in mathematical description, or even in construction, show strange and complicated behavior, and may add a new understanding of nonlinear optical interaction phenomena.

The fast development of the technology of semiconductor materials, transformed the laser diode in an usual subject. Very interesting as a physical system and very useful in all kinds of engineering applications, the nonlinear dynamics of these devices was studied especially under external optical feedbacks.

A laser diode shows a rich variety of dynamic phenomena named chaotic dynamics, regardless the emitted wavelength, when subjected to optical feedback from an external reflector [32]. When the radiation emitted by LD is redirected into the laser cavity as feedback from an external reflecting surface, the configuration is known as external-cavity semiconductor laser (ECSL).

Chaotic dynamics of laser diode with external feedback conditions is influenced by some of the intrinsic properties of the lasers. Broad gain spectrum (~5 nm) which allows the excitation of different longitudinal modes of the laser diode cavity, small changes of driving parameters and strong dependence of the active medium refractive index on the excited carrier density or temperature are the most important factors. The amount of the intensity optical feedback greatly influences the system dynamics.
In Fig. 16 is shown the typical scheme of an ECSL system having a diffraction grating as external reflector.

One of the most intensely studied issue on the chaotic dynamics of ECSL is the regime of low-frequency fluctuations (LFF). This is an unstable regime, manifested as a cyclic dropout almost to zero of the output light intensity evidenced when a typical ECSL with weak optical feedback operate slightly above the lasing threshold (Fig. 17).

The time intervals between these dropouts are uncorrelated and depend on the control parameters of the ECSL, having a rate of gradually return to full power of about tens to hundreds of nanoseconds.
The chaotic behavior of an ECSL working in LFF regime can be controlled by different parameters such as injection current, temperature, external cavity length, external feedback, variations in the external cavity length [35].

6. TUNABLE SEMICONDUCTOR LASERS APPLICATIONS

An important area in which the laser diodes were used by LSG is the Low Level Laser Therapy (LLLT). In this respect the group performed studies [36, 37] which were very useful for establishing the appropriate irradiation doses and procedures for LLLT, with particular interest for rheumatology and rehabilitation medicine.

As a general remark, the intensity distribution of the laser beam in transverse section should be for LLLT as uniform as possible, which imposes particular optical processing of the beam for this purpose.

7. CONCLUSIONS

The reported results were based on many in-house components techniques and technologies developed in time by the LSG, from dedicated dyes [38], to mechanical assemblies developed for laser purposes [39–42].

At the same time, the applications area in spectroscopy, environment control and medical applications of tunable lasers was even larger than reported above, as results from references [43–49].

The perspectives in LSG, opened by the already reported data are in line with the current laser spectroscopy evolution, namely: a new approach of the laser spectroscopy studies on micro- and nano-droplets which is related to the lab-on-a-
chip concept, the transfer of the chaotic properties of the laser beams to different kinds of targets, the application of laser techniques in photochemotherapy, the study of optical samples in an integrated spectroscopic approach: absorption, luminescence, Raman, optoacoustic, FTIR, laser assisted microscopy, etc.

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**REFERENCES**