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SENSORS BASED ON TUNABLE DIODE LASERS AND mid-IR-FIBER OPTICS AND THEIR DIAGNOSTIC APPLICATIONS IN MEDICINE AND ENVIRONMENTAL PROTECTION

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Abstract-The last results on application of tunable diode lasers for medicine diagnostics and atmosphere monitoring are presented. Two apparatus for measurements of CO in atmosphere and simultaneous measurements of CO and CO₂ in expired air are described. The results on incorporation of mid-IR-fibers into the schemes of such systems are reported.

1. Introduction.

Tunable diode laser spectroscopy (TDLs) is now well known as one of the powerful techniques for high sensitive chemical diagnostic. It rising applications for atmosphere pollutions monitoring, sophisticated chemical technologies control and medicine tests demonstrates wide future perspectives of sensors based on TDLs. For recent years the activity of the Diode Laser Spectroscopy Laboratory of the IGPh in this field includes the following directions:

- development, design and field tests of TDL based sensors for atmosphere monitoring of trace gases such as CO, SO₂, NO, freons;
 - application of TDLs for trace amount analysis of BCl₃ and H₂O to check pure materials technologies;
 - diagnostic of gas micro impurities in human exhaled air;
 - development and design of TDL based systems using mid-IR fiber-optic components;
 - hardware and software development of completely automated tunable diode laser system (sensors, analyzers, spectrometers).
- A few most significant results of the investigations are presented below.

2. Trace gases analyzer for atmosphere monitoring.

Several generations of CO-meter for open atmosphere monitoring were developed. A few general ideas have been realized in the various versions. Pulse PbS₂ diode lasers are used to detect absorption spectra of CO. Laser frequency tuning is carried out by laser crystal heating during the current pulse. Two-channel optical schemes are used. In the analytical channel laser radiation is passed through open atmosphere and then turned back by a retroreflector. A receiving telescope collects the radiation to InSb photodetector. The length of the optical path depending on necessary sensitivity usually reaches 200-300 meters. To control stability of laser frequency tuning a reference channel is used. It includes a two-pass cell, a spherical

mirror and second detector. Used PbSSe diode laser and the photodetectors are cooled by liquid nitrogen.

For carbon monoxide detection in atmospheric air, lines belonging to fundamental 1-0 absorption ro-vibrational band at 4.7 microns are used. In this spectral region typical values of CO lines strength and width at atmosphere pressure are $10 \text{ cm}^{-2} \text{ atm}^{-1}$ and 0.10 cm^{-1} , respectively. So the sensitivity to CO of two orders of magnitude less than clean atmosphere content (0.1 ppm) could be obtained without signal storage. Time resolution of the CO-meters was determined by the rate of current pulses and is usually about 0.1 second. Calibration of measured concentrations is carried out by use of three additional reference cells placed into the analytical channel.

Fig.1. Tree years variations of CO in atmosphere at the Kara-Dag National Park (Crimea, Black See).

These CO-meters were installed for long-time continuous operation in regions with different atmosphere pollutions levels. Fig.1 illustrates the data of more than two-years operation of one of them in the Kara-Dag National Park (Crimea, Black See) obtained by S.N.Kotelnikov. The last version of the CO-meter designed in a close cooperation with the Central Bureau for Unique Instrumentation of the Academy of Science of the USSR is completely automated. Special hardware driven by the IBM PC/AT computer supports laser temperature stabilization, control of laser radiation, recording of transmission spectra and calibration of analyzer. Other atmosphere constituents like NO, NO₂, NH₃ etc could be measured in frame of the scheme by TDL replacement.

3. TDL analysis of expired air content.

Medicine diagnostic seems also to be a prosperous field for future applications of TDLs. Due to very high sensitivity and fast response available, common medicine diagnostic techniques in some cases may be forced out by more powerful, sensitive and reliable ones based on TDL application. As well as new advanced methods of diseases diagnostic may be developed on this basis in nearest future.

Our first results on detection of trace gases in human expiration with help of TDL are presented here. Exhaled CO and CO₂ were chosen as investigation objects for the first stage of the study. An above-mentioned CO-analyzer have been modified for this purpose. A compact multi-pass cell was incorporated into the analytical channel of the analyzer. The cell had 25 cm base length and close to 1 liter

volume. More than 100 beam passes were available and so the optical path of more than 25 meters has been achieved. Thus the sensitivity to carbon monoxide in expired air was better than 0.01 ppm.

Concentration of carbon dioxide was measured simultaneously with CO by use of numerous absorption lines belonging to hot ($20^0 0-01^1 0$) or combination ($11^1 0-00^0 0$) ro-vibrational bands laying in the wavenumber region covered by laser. The lines strength in these bands are approximately of 4 orders less than that in fundamental CO band. This distinction was used to compensate essential difference of CO and CO₂ levels in expired air. Sensitivity to CO₂ was better than 0.1% and was enough for our experiments. Thus concentration measurements of both gases in exhaled air may be provided using the same dynamic range of the analyzer.

Exact assignment of analytical lines using carbon monoxide isotopic modifications $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ was carried out. This permitted us direct calculations of gases concentrations with help of line parameters available from data bases, instead of usually used calibration with a set of reference cells. Quite simple and reliable assignment is possible in this case due to: 1) an isotope shift of ro-vibrational band centers; 2) differences in rotational constants for various isotope modifications. As consequence, a view of detected spectra is very specific what allows to determine spectrum region by reciprocal positions and relative intensities of observed lines. Due to detection of spectra without any storage, full measuring time was determined by handling with exhaled air samples.

A few significant results illuminating possible future directions of the investigation were obtained in our first experiments:

1. For nonsmoker persons, expired concentrations of carbon monoxide are slightly higher than that in inhaled air. Surplus CO content reached up to 0.4-0.7 ppm. Specific value depends on the age of person.

2. The surplus CO content in expired air proved to be increased by more than order of magnitude just after intensive physical exercises, eg. jogging.

3. For smokers, pharmacokinetical curve of abundant CO withdrawal from organism could be investigated. CO concentrations in smokers' exhalation depends on quality of cigarettes, rate of smoking and time after last smoking. So smoking status of tested person becomes easy available.

4. Breath-hold simultaneous measurements of CO and CO₂ without preliminary CO loading of human organism show the difference in dependencies of their concentrations in expired air on breath-holding time (see Fig.2). The possibility to

Fig.2. Behaviour of CO and CO₂ concentrations in expired air with increase of breath holding time.

investigate phenomena like molecular pulmonary diffusion through alveolar-capillary membrane and organism's compensation reactions to oxygen shortage in blood seems to become real.

Other trace molecular objects like CH_4 , NH_3 , N_2O , etc., for which TDLs methods of high sensitive detection are already developed in the frames of atmosphere monitoring programs, appear to be perspective also for medicine diagnostic.

4. Mid-IR-fiber accessories for TDLs.

Other hopeful direction of our researches concerns with incorporation of mid-IR fiber-optic elements into the schemes of spectrometers and analyzers based on TDL. It's realizable now due to current progress in IR-fibers technology developed in the ICPH. Now silver halide fibers with optical losses down to 300 dB/km in 7-16 microns spectral region and chalcogenide glass fiber with optical losses down to 200 dB/km in 2-6 microns spectral region are available.

A special unit have been developed for coupling of Pb-salt TDL and IR detectors with IR fibers and their cooling down to liquid helium and nitrogen temperatures. Several TDLs or pairs of TDL and detector may be mounted inside a compact cryostat immersed in a portable deward with cryogenic liquid. Original hardware driven by the IBM PC/AT supports temperature stabilization, control of laser radiation and absorption spectra recording.

In addition several external accessory units with fiber-optics have been developed. A single-pass gas cell, a waveguiding micro-cell with hollow core, and a multi-pass cell with fiber-optic inlet and outlet have been tested using TDL radiation. The different configurations are assigned to solve various analytical tasks arisen. The scheme of multi-pass cell connected with cooling unit by IR fibers is shown in Fig.3. At 25 cm base length of the cell, optical path of more than 25 m has been achieved. Transmission spectra of CO at 4.7 microns, of NO at 5.4 microns and of NH_3 at 10.6 microns have been detected with the cell.

The fiber-optical accessories seem to be useful and perspective when used with TDL. It's due to appearing possibilities to minimize size of TDLs apparatus, to combine laser radiation of different wavenumber in one fiber, and to transport radiation into places difficult of access. Moreover the units proved to be easy in alignment. Such systems hope to be suitable in medicine applications, in design of multi-component analytical apparatus and etc.

Fig.3. The general scheme of TDL based gas analyzer equipped with IR-fiber optics and multi-pass cell.