PHOTONICS TECHNOLOGY OBNINSK
Obninsk, Russia

10779

DIFFERENTIAL OPTICAL ABSORPTION SPECTROMETER

DOAS M1

Brief description

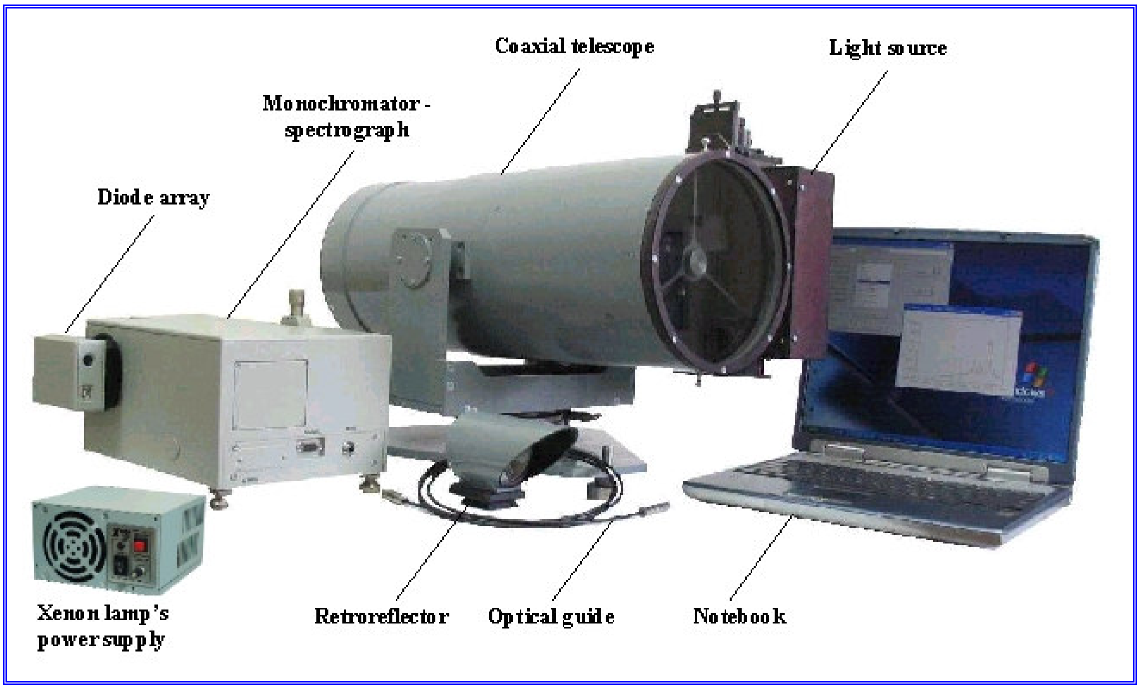


Fig. 1. **DOAS M1 presentation.**

- Device is intended for measurement of trace gases and pollutants (such as **nitrogen dioxide, sulfur dioxide, ozone, nitric oxide, formaldehyde, ammonia, toluene, benzene** and many others) in the atmosphere at a level of milliard volumetric portions, at real time, without air sampling. Time interval for one measurement of one (or several) gas concentration is from 30 s and up to 3 min.

- **COAXIAL TELESCOPE** of a small dimensions has been used for the first time that has been allowed to design the most light at peace DOAS spectrometer (mass of DOAS M1 is not exceeded **32 kg**), which is easy in functioning, foolproof, convenient for mobile system for environmental monitoring and, finally, low-cost.

- A new developed **MONOCHROMATOR** allows measuring concentration of **33 GASES AT ONCE** in broad spectral range (**up to 143 nm**) without additional alignment. The measurements are carried out **AUTOMATICALLY** during long time period (up to 2 months).

INTRODUCTION

Differential optical absorption spectrometer (DOAS) technique is now widely used for measurement of trace gases in the atmosphere. This brochure describes a **TRACE GAS ANALYZERS DOAS M1** developed by **Photonics Technology Obninsk** and featured by low price, flexibility and applicability for tutorial process.

The action of the DOAS is based on the registration of the absorption spectra of the atmosphere and its comparison with data on spectral absorption of the gases to be previously determined.

There are few commercial DOAS instruments now available for control of air pollutant in ambient air. Among them are **OPSIS** (Sweden), **SANOA** (France), **DOAS-2000** (USA) and some others.

The advanced **DOAS M1** spectrometer design differs by the unique optical circuit, simplicity of construction, reliability, and convenience in execution of monitoring and low prices. In the present time **DOAS M1** spectrometer is most precise gear among commercial trace gas analyzers.

In **DOAS M1** spectrometer a **coaxial telescope** is used unlike existing methods. This innovation considerably simplifies operations on execution of trace monitoring and essentially reduces their cost. Other methods of trace exploration use a search-light and a telescope installed on the different ends of a path, that demands separate power supplies, additional peripherals, considerably rises the price of a system and makes it by more composite in usage and alignment.

Designed coaxial telescope is brand new technical creation confirmed by the **Russian Certificate on useful Model** N 9311 with priority from February 20, 1998 and N 16032 with priority from June 09, 2000.

The precision **corner cube reflector** (retroreflector), manufactured from UV grade fused silica is used for return a light in a telescope. Usage of the retroreflector allows doubling a path length. Retroreflector is completely passive and does not demand energy and maintenance.

As a spectrograph and a photodetector in **DOAS M1** spectrometers the modern, reliable, precision and compact photoelectric devices are used: a **monochromator-spectrograph** and a **photodiode array**.

Gas analyzer DOAS M1 is a compact modification of certified gas analyzer **DOAS-4R** (**Certificate RU.C.29.027.A N 10799** is registered in the State Standard of Russian Federation 17.09.2001). Telescope of **DOAS M1** differs by smaller dimensions and accordingly by much smaller mass.

Verification of spectrometers is executed in accordance with "**Manual for Verification DOAS.4901.004.10850053"** each year.

The gas analyzers **DOAS** successfully have passed field-testing on polygons of cities Moscow and Obninsk. Now series of **DOAS** instruments are developed, produced and in operation in Uchta at LUKOIL gas refinery (Russia), in city of Moscow, Belgorod and Obninsk (Russia), Kwangju (South Korea), Tianjin and Xefei (China), Shiraz (Iran).

In summer 2002 a large cycle of simultaneous measurements with help of DOAS-4R (in Obninsk) and Opsis DOAS spectrometer (in Moscow) have been performed. Results have been analyzed and reported at Workshop in Heidelberg [1]. Some results of measurements in period 2002 – 2004 at Obninsk, Iran and China are presented in ***Appendix 2***.

1. DOAS BENEFITS, ADVANTAGES AND APPLICATION

DOAS M1 spectrometers benefits and advantages:

- gas concentration averaged on all atmospheric path is measured that is allowed to calculate mass of pollutants carried by wind through the air path;
- **precise measurements** of gas pollutants concentrations – at a level of milliard volumetric portions;
- **fast measurements** – time of unitary measurement is not more than 3 minutes;
- **continuous measurements in automatic mode** - duration of continuous measurements without of additional adjusting of device is not less one week and up to 2 months);
- ability of **simultaneous measurements of 33 gases** without of additional alignment;
- **no air sampling** and consequent analyses; no disturbances of environment;
- **device is compact and mobile** – total weight of DOAS M1 is not exceeded **32 kg**; it may be used for gas concentration measurements in smoke bonnets and other hard-to-reach volumes;
- **device is simple in operation** and demands minimum maintenance;
- **device is easy in calibration** – gas calibration mixtures are not required. A calibration is carried out with help of a subjoin device unlike other similar spectrometers for which this procedure is at all impossible;
- ability of **long-term measurements** for research of dynamics of an air pollutant level.
- **low-cost** as compared with other similar spectrometers.

DOAS M1 instruments may be used for:

- **control of gas pollutants** in urban territories, highways, cement industry; at fertilizer plants, sulfuric acid plants; at woodworking industry; at incineration plants and smokestacks;
- determination of **pollutant transfer** from plants to the residential districts;
- measurements of **background pollutants**.

Flexible block structure of the devices, simplicity of the process of installation and maintenance and comparatively low price make our systems especially convenient for laboratory study and using in educational process in research Institute, laboratories and University for research of atmospheric gaseous pollution, ultraviolet atmospheric spectroscopy and for tutorial aims.

DOAS M1 spectrometers may be delivered in a various kit:

- for indication of the current pollutants;
- for long-term monitoring of pollutants: in special stationary container or as a mobile module.

2. SPECIFICATIONS

Light path and Measured Gases

- Open-air two-fold pass arrangement and coaxial optical setup is used. Coaxial (transmitting - receiving) telescope with ultraviolet light source, measurement instrumentation unit and data processing system are placed at one end of atmospheric path, and retroreflector is placed at the opposite one. Retroreflector reflects the light to the receiver.
- Atmosphere path length (light path) .... 200 – 750 m
  Note: Term **path length** means a double distance between the telescope and retroreflector.
- The list of the pollutant gases measured by DOAS M1 spectrometer is presented in ***Appendix 1***.

Temporal parameters of measurements

- Time interval for one measurement of one (or several) gas concentration .... not more than 3 min
- Duration of continuous automatic measurements
  (it is depended from operating time of a lamp) .... not less than 1200 hours

Light Source

- Emitter of UV radiation .... arc xenon lamp of high pressure ***XBO 150W/1 10X1***
- Power supply unit .... source of a direct current with the ignition device
- Electrical capacity of consumption .... 150 W
- Operation voltage of a lamp .... not more than 20 V
- Voltage of triggering impulse .... 25 kV
- Operating time of a lamp up to its replacement .... not less than 1200 hours

Coaxial Telescope

- Telescope is used as a collimator of light source radiation and a receiver of the radiation, passed the atmosphere path, simultaneously.
- Main direction of optical axis of a telescope .... horizontal
- Diameter of main spherical mirror .... 195 mm
- Focal length .... 500 mm
- Angular resolution .... 20 ang. s

Biaxial mounting

- Range of elevation angles positioning .... from -5° up to +20° from horizontal
- Range of azimuth angles positioning .... from -15° up to +15°

Retroreflector

- a fused silica corner cube reflector with an accuracy of reflection of radiation .... not less than 15 ang. s

The measurement instrumentation unit

- Number of the signal registration channels 1
- Monochromator-spectrograph and a diode array with 14 bit analog–to-digital converter are used for analysis and registration of radiation spectrum.
- Main monochromator's features:
  - usable wavelength range (~40% eff.) .... 190 – 560 nm
  - wavelength accuracy .... ± 0,18 nm
- Number of image photosensitive elements of a diode array 1024
- Transmission of radiation from the telescope to a monochromator is carried out by a fused silica fiber optical guide.
  Diameter of an optical guide single fiber .... 200 micrometers
- Spectral range of DOAS M1 measurements .... 205-460 nm
- Number of gases measured simultaneously .... up to 33

System data processing

- Special dedicated ***DOAS Software*** is intended for device control, for conduct measurements and for visualizing and processing of measurement data.
- Measurements can be done as in automatic as manual modes (serial and single regimes).
- Measurement's results are displayed on the PC monitor and saved in PC memory.
- Minimal demands to a computer:
  - Pentium II-500 with RAM 128 Mb and hard disk volume of 10 Gb
  - Operation system .... Windows 95/98, Windows NT

Outline dimensions (L×W×H)

- Telescope with the biaxial mounting, the light source and its power supply .... 750×370×350 mm
- Monochromator with a diode array .... 320×230×165 mm
- Retroreflector.. 135×67×72 mm

Weight

- Telescope with the biaxial mounting, the light source and its power supply .... 20.6 kg
- Monochromator-spectrograph with a diode array .... 7.7 kg
- Retroreflector.. 0.3 kg
- Total weight.. not more than 32kg

Site

- The telescope with the light source, control and processing electronics are to be at laboratory condition at air temperature...from +10 up to +35°C
- Retroreflector is to be at open air condition at temperature.. from -40 up to +45°C
- In a working room also the system of air conditioning must be stipulated for avoiding high ozone concentration produced by the working xenon lamp.

Power

- Power supply network .... (220 ±22) V, (50 ± 1) Hz, single phase AC
- Power consumption .... not high than 0.3 kW

3. STRUCTURE

DOAS M1 appearance is demonstrated in Fig. 1, schematic diagraph is shown in Fig. 2.

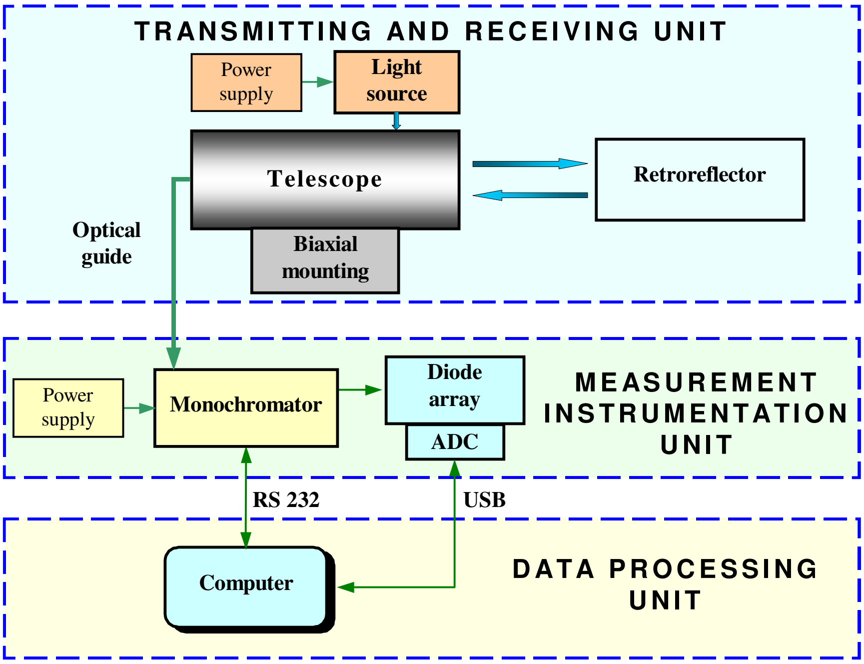


Fig. 2**.** The function chart of **DOAS M1** spectrometers.

DOAS M1 instruments consist of the following main units:

- ***Ultraviolet radiation source*** of the projector type which coincides with a telescope (arc xenon lamp with its power supply unit).
- ***Coaxial telescope*** (which serves as projector and receiver of radiation simultaneously) installed on the ***biaxial mounting*** for tilting in a horizontal and vertical planes.
- ***Retrorerflector*** (corner cube reflector) - for reflection of radiation from the air path remote end to the telescope.
- ***Fused silica fiber optic guide*** (FSFOG) – for transmission of radiation from the telescope to a monochromator.
- ***Monochromator-Spectrograph*** - for decomposition of radiation, incoming from the atmospheric path, in spectrum.
- ***Photodetector (diode array)*** with an ***Analog–to-digital converter*** (ADC) - for registration of spectrum.
- ***IBM PC computer*** and the dedicated ***DOAS Software***, used for control the instrument and conduct measurements, and also for visualizing and to processing the measurement data.
- ***Equipment for device alignment and calibration.***

4. OPERATION PRINCIPLE

4.1. Differential optical absorption spectroscopy technique

Operation principle of DOAS spectrometers developed on the basis ***of differential optical absorption spectroscopy (DOAS)*** technique is based on measurement of absorption by polluting gases in UV spectral range. Spectral device (one of units of DOAS system) allows fixing alterations in spectral distribution of registered radiation, which are caused by absorption of radiation by gas components of atmosphere at passing through the air path between the source and receiver of radiation.

The absorption cross section on the given wavelength is a characteristic property of any species serving by a basis for calculation of the content of gases in investigated environment. This value can be measured in the laboratory and registered in the database of a gear.

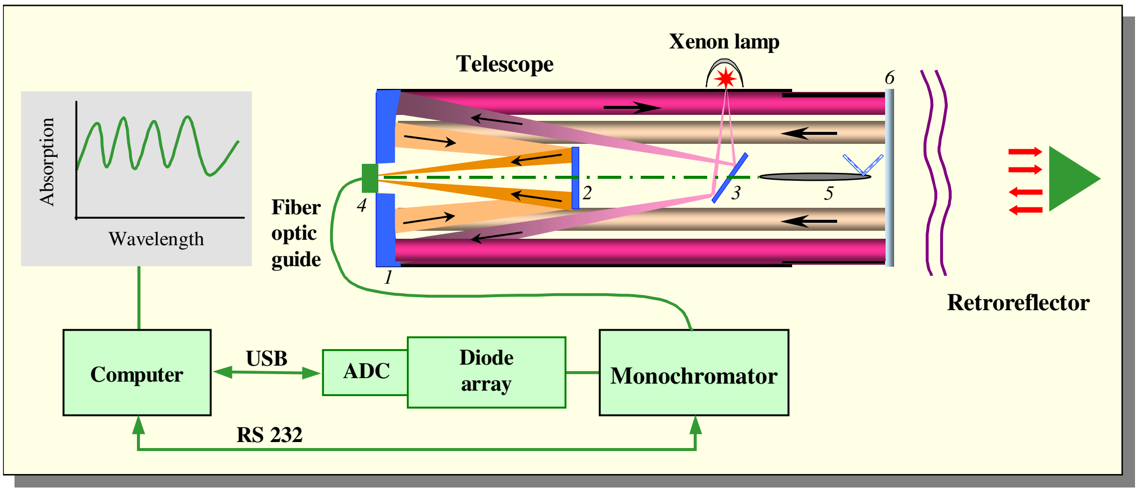
Note, that DOAS procedure can be applied only to those species the absorption spectrum of which contains reasonably narrow absorption structures as bands and absorption lines.

In ***Appendix 1*** the list of gases which has remarkable absorption spectrum and are measured by DOAS M1 are presented. List of gases may be easily extended. Besides the concentration detection limits (of level 3σ) calculated for the DOAS M1 instrument along with the average daily Maximum Concentration Limits (MCL) adapted in Russia are presented.

At producing measurements one of some spectral ranges is chosen from the overall spectral region and spectrum is registered in this range. The least square method provides for simultaneous determination of concentration of all gases having absorption in the selected spectral range.

4.2. Operation principle of DOAS-M1

Optical radiation generated by the light source (a xenon arc lamp) and collimated by a telescope is transmitted to the atmosphere path (Fig. 3). On the remote end of the path a retroreflector is installed, which intercepts a part of radiation and reflects it back. The part of radiation, passed backward, comes in the aperture of the receiving channel of a telescope and is focused on an input window *4* of FSFOG.



1 – main spherical mirror
2 – round flat mirror
3 – turning flat mirror
4 – alignment assemblage of FSFOG entrance window
5 – shutter with a subsidiary retroreflector
6 – protective glass

Fig. 3. Experimental setup for **DOAS M1** spectrometer.

The target end of FSFOG is interfaced directly to an entrance port of the monochromator - spectrograph where light radiation is decomposed in a spectrum. In a plane of the output port of the monochromator a diode array is mounted whose signal is digitized with the help of an analog-to-digital converter (ADC). A digitized signal is transmitted to the computer for further processing.

During processing the spectral distribution of radiation, passed the atmosphere path, is compared to a spectrum of a light source and the variations, stipulated by absorption of radiation by atmospheric gas components, are revealed. Since every gas component has its individual characteristic absorption spectrum, the analysis of spectral changes gives opportunity to identify the absorbing gases and determine its concentration.

5. DESCRIPTION AND OPERATION OF THE MAIN UNITS

Here a function and design of the main units of DOAS spectrometers are described briefly. Their main specifications are listed in Section 2.

5.1. Source of radiation

As an of UV radiation the xenon lamp of high pressure is used which is located in a focal point of an external ring of a main mirror of a telescope.

To insure the safety of operation the xenon lamp is located in a protective box with a special XYZ fine stage (for alignment of a lamp) and a ventilator (for cooling of the working lamp). Box with a xenon lamp is fastened at the telescope's tube side (see Fig. 1). The light of a lamp passes inside of the telescope through a hole of its tube.

Power supply of a xenon lamp is produced by help of an own supply unit (see Fig. 1), which is a source of a direct current ensuring ignition (triggering) of a lamp and maintaining of given stable operating current of a lamp in case of current oscillations voltage from 180 up to 250 V.

5.2. Coaxial telescope

Design and an optical layout of the telescope are shown in Fig. 3.

5.2.1. Design

Telescope case is made from special aluminum alloy. The internal surface of the telescope is covered with a light-absorbing paint.

Main detail of the telescope – a precision spherical mirror *1* is mounted in a back end of a telescope frame. A main spherical mirror and also the round flat mirror *2* and the turning flat mirror *3* are covered by enhanced aluminum. For protection of the telescope's mirror surfaces against pollution and moisture the fused silica flat *6* is used which is fastened at the telescope's entrance end.

Compartment *4* for a FSFOG's input is installed on the back end of the telescope's case and allows for establishing careful alignment for light focusing on the reception aperture of the FSFOG. Moreover a toolbar with changeable filter (for spectral range selection) is mounted at this compartment.

A positioner intended for signal lamp measurement (or an inner calibration) is installed at the telescope tube front part. It is a cylinder attachment with a round shutter *5*, which is turned with help of a twist handle. An additional retroreflector is mounted on the shutter.

By means of pivot bolts the telescope is fastened to biaxial rotary mounting whose four mechanisms provide for as coarse as fine aiming of the telescope on the retroreflector.

5.2.2. Optical scheme of the telescope - transmitting and receiving channels

The main spherical mirror of the telescope is used both in the transmitting and receiving parts of the device.

The transmitting part (projector). As a collimating device necessary for collecting of lamp radiation and forming from it a narrowly directed light beam, the turning flat mirror *3* and the external part of a main spherical mirror *1* of a telescope are used. The collimated hollow beam of arc xenon lamp radiation is transmitted to the atmosphere in the line of the retroreflector located on the remote end of air path.

The receiving part. The inner ring of the main mirror *1* focuses optical radiation reflected by the retroreflector back to the aperture of a telescope. A round flat mirror *2* is used for reflection of light focused to a FSFOG's input *4*.

During measurements at an air path the shutter *5* of the positioner is turned in position not preventing to output of a xenon lamp's light to path (that is parallel to the telescope's optical axis).

5.2.3. Optical layout of the xenon lamp signal measurement

Spectral signal lamp measurements give reference signal for further mathematical treatment of air path measurements data, namely, for calculation of the optical absorption thickness of a pollutant gas and determination of its concentration. With that end in view an inner calibration (signal lamp measurement) is carried out with help of the shutter of the positioner. At that the shutter plane is installed perpendicular to the optical axis (Fig. 4) owing to a part of the lamp's light is directed to FSFOG not passing an air path.

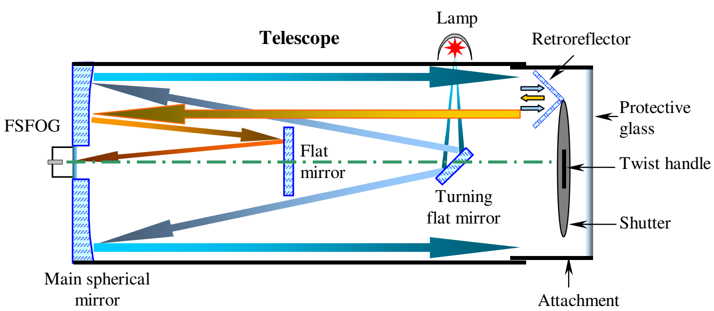


Fig. 4. Optical layout of the lamp signal measurement mode (top view).

`5.3. Retroreflector

The basis of the retroreflector is represented by a fused silica corner cube reflector, which reflects radiation falling on it in the direction of a light source. The angle reflector in the mounting is fastened on any support on the remote end of air path.

5.4. Fused silica fiber optical guide

Fused silica fiber optical guide (FSFOG) is used for transmission of radiation from the telescope to a monochromator. The guide is a silica single fiber in protective polymer envelope with brass caps on end-walls.

5.5. Monochromator

Monochromator-Spectrograph is intended for separation of monochromatic radiation during DOAS M1 spectrometer functioning. It is constructed according to the asymmetrical Czerny-Turner optic configuration.

Alignment assemblage intended for joining of the fiber optic guide to the monochromator and combined adjustment of FSFOG and the monochromator is mounted on the monochromator's entrance slit holder. The lateral exit slit is supplied by an adapter for attachment of the photoreceiver (diode array).

Monochromator-Spectrograph is a fully computer-aided device. The inner controller, managed by a computer via RS 232 Interface cable, is used for turning difraction grating and control of the monochromator's shutter.

Universal network adapter with an exit voltage of direct current of 24 V is used for the monochromator feeding.

5.6. Diode array

Diode array with the electronic unit is used for detection of optical radiation across a broad spectral range. It is mounted on the lateral output port of the monochromator via adapter (see Fig. 1).

The electronic unit of the diode array includes 14 bit analog-to-digital converter (ADC), which digitizes signals from the diode array. PC controls diode array functioning with help of ***DOAS Software*** through an USB Interface Cable.

5.7. System of data processing

System of data processing is intended for processing of signals from the photodetector, visual control of measurements and saving results of processing. This system represents a special dedicated ***DOAS Software*** with comfortable and evident interface. The operator controls the system of data processing in an interactive mode of operation.

DOAS Software provides the following opportunities:

- to set parameters for producing measurements; to start and to stop the measurements and to control the system of registration during work; to process signals and to save the initial data of measurements;
- to process the initial data of measurements with help of special numerical methods (namely to calculate concentrations and of optical depths of gases measured); to present the data of processing as a graphic chart at the PC display; to print the data as a graphic chart; to store results as a text file.

5.8. Equipment for device alignment and calibration

Equipment for device alignment and calibration consists of a mercury lamp (for calibration of the monochromator's wavelength scale), an eye-piece (for preliminary aiming of the telescope to the retroreflector) and some other accessories.

References

1. S.S. Khmelevtsov, V.A. Korshunov, D.I. Busygina, and V.S. Khmelevtsov. DOAS-4R continuous measurements of SO_2, NO_2, CH_2O and O_3 concentration at Obninsk in Summer 2002. Second International DOAS Workshop in Heidelberg, September 2003.

2. U. Platt "Differential optical absorption spectroscopy (DOAS)", in Air Monitoring by Spectroscopic Techniques, M. W. Sigrist, ed., pp. 27-84, Chemical Analyses Series, Vol. 127, 1994, John Wiley & Sons, Inc.

Appendix 1. List of 38 gases, defined with the help of DOAS M1

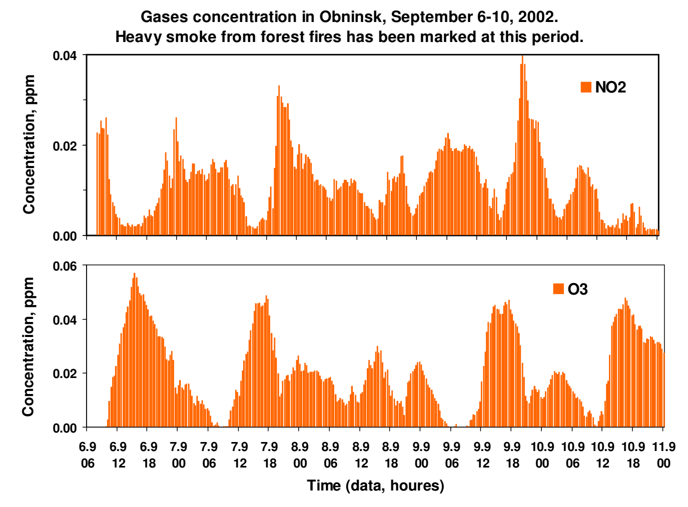
Formula	Gas name	Detection limit, ppb	MCL average daily, ppb
NH3	ammonia		50
NO	nitric oxide		45
NO2	nitrogen dioxide	2.8	20
NOHO	nitrous oxide	1.1	-
SO2	sulfur dioxide	0.8	20
O3	ozone	1.4	14
CH2O	formaldehyde	3.4	2
C6H6	benzene	0.8	30
C7H8	toluene	3.6	150
C6H6O	phenol	0.2	0.7
C7H6O	benzaldehyde	0.5	8 *
C8H10	ethylbenzene	3.8	4
	styrene		0.4
C8H10	o-xylene	8.0	40
	m-xylene	4.0	40
	p-xylene	1.0	40
C7H8O	o-cresol (o-hydroxymethylbenzene)	2.0	6 **
	m-cresol (m-hydroxymethylbenzene)	0.8	4 **
	p-cresol (p-hydroxymethylbenzene)	0.2	4 **
C8H10O	2,3-dimethylphenol	1.2	-
	2,4-dimethylphenol	1.4	-
	2,5-dimethylphenol	1.6	4 **
	2,6-dimethylphenol	2.8	2
	3,4-dimethylphenol	1.2	-
	3,5-dimethylphenol	0.4	-
C9H13O	2,4,6-trimethylphenol	7.4	-
C9H12	1,2,4-trimethylbenzene	3.2	3
	1,3,5-trimethylbenzene	6.0	20 **
C8H8O	o-tolyladehyde (2-methylbenzaldehyde)	0.8	-
	m-tolyladehyde (3-methylbenzaldehyde)	1.0	-
	p-tolyladehyde (4-methylbenzaldehyde)	0.3	-
CS2	carbon disulfide	9.0	2
OClO	chlorine dioxide	0.03	-
IO	iodine oxide	0.2	-
BrO	bromine oxide		-
CH3COCHO	methylglyoxal	0.2	-
CH2C(CH3)CHO	methacrolein	16	-
CH2CHCHCH2	1,3-butadien		400

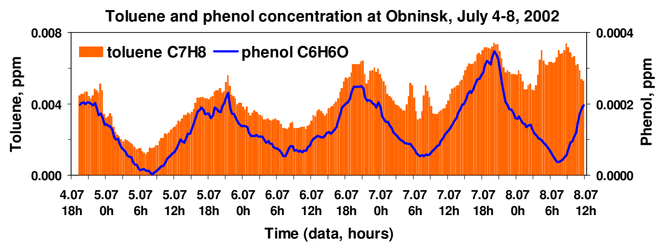
Notes:

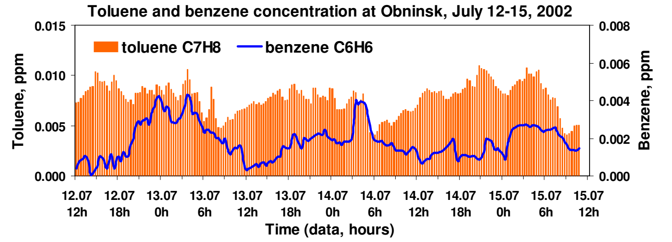
1. MCL - Maximum Concentration Limit.
2. * is denoted MCL p.v. – disposable peak value of MCL. ** is denoted ASLE - approximate secure level of exposure. These values are referred, if MCL daily average values are not specified.
3. Actual noise level for DOAS instrument is accounted at estimates of detection limits. Noise value varies from $2 \cdot 10^{-4}$ up to 10^{-3} depending on wavelength range.
4. The open air path length is taken 450 m.

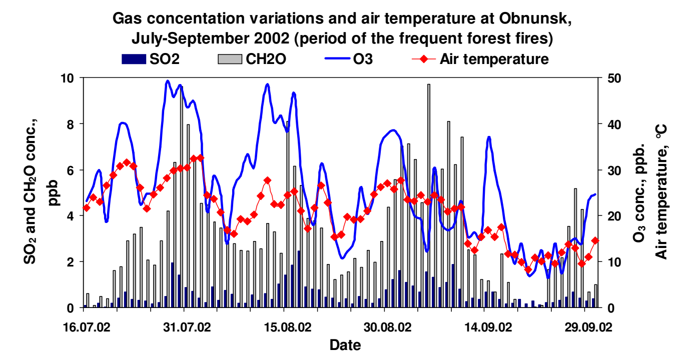
Appendix 2. Some results of gas pollutant measurements

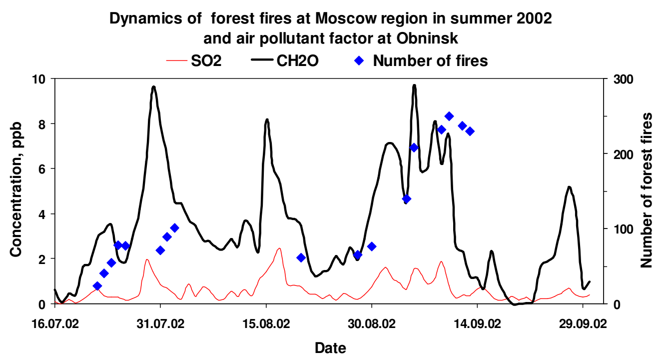
Some samples of results of gas pollutant measurements produced by DOAS spectrometers in Obninsk (Russia), Shiraz (Iran) and Tianjin (China) in 2002-2003 are presented. Also a comparison with data of synchronous measurements of ozone in Moscow by Opsis DOAS spectrometer is performed.

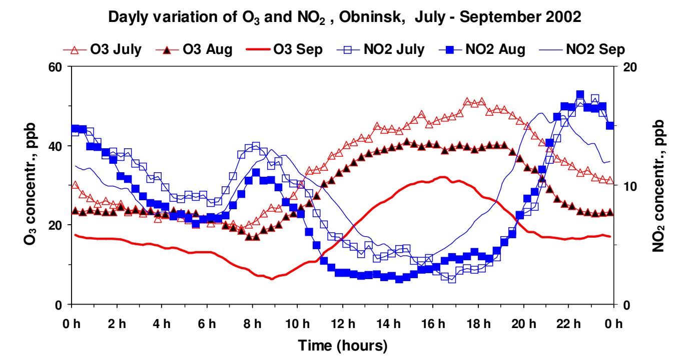


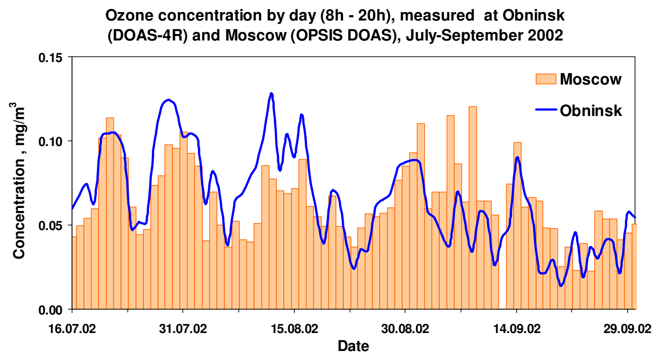


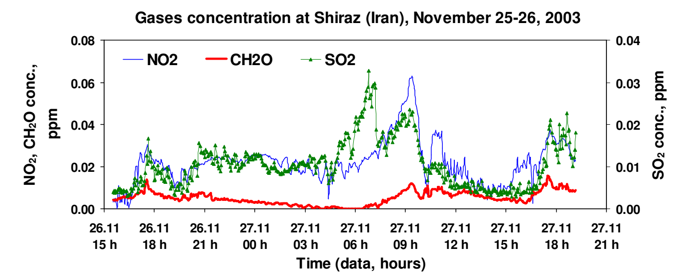


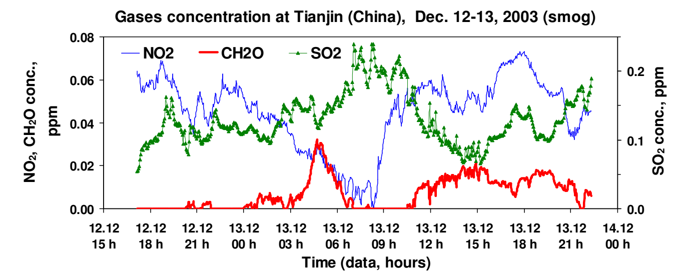












Measured summary absorption spectra together with result of calculation in spectral range 280-360 nm. Obninsk, September 8, 2003.