

# A Method of Application of a Mobile Gas-Analysing Facility for the Remote Monitoring of Overall Exhausts of Anthropogenic Gases from Large-Scale Sources

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**Abstract** – Here is shown a possibility to use a method based on the distant measurement of the spatial distribution of pollutant and greenhouse gases in the boundary layer of atmosphere by measured data on their own radiation in the thermal IR spectral region. Using calculated IR spectra of atmospheric radiation, requirements have been established for spectral measuring equipment based on a Fourier-spectrometer for the remote monitoring of the overall exhausts of anthropogenic gases by large-scale sources.

**Keywords:** remote monitoring, pollutant and greenhouse gases, Fourier spectrometry

## 1. INTRODUCTION

In connection with the global climate warming caused, in particular, by the growth of greenhouse gases' concentration in the atmosphere, the Kyoto Protocol has imposed the limitations on the emissions of these gases into the atmosphere. The main gas species has been established that are responsible for the creation of "greenhouse effect", among which the primary one is carbon dioxide, contributing up to 50% of the total exhaust amount, then goes methane (18–20%), and then the rest gases, including nitrous oxide, freons, sulphur tetrafluoride and tropospheric ozone (20–22%). Note that tropospheric ozone brings about 8 to 10% contribution into the greenhouse effect.

The basic source of ozone in the bottom troposphere is NO, formed at burning fuel. NO is oxidized in troposphere up to NO<sub>2</sub> which in turn at photodissociation is a source of ozone.

Since the main anthropogenic sources of air pollution are situated on the earth surface or in its immediate vicinity, the transport of gases and processes connected with the oxidation or reduction of anthropogenic by-products proceed in the boundary atmospheric layer, whose top border is not over 1 km, even at intense day-time mixing. To solve the problem of measurement of gases' contents in the boundary layer, it is suggested that be utilised the radiation of those atmospheric gases whose vibrational-rotational spectral bands are intense enough and fall into the thermal range of spectrum, 4.5–5.5 and 7.5–13.5 μm, which is free from water vapour strong absorption bands. Among the climate-forming gases, those are: CO<sub>2</sub>, O<sub>3</sub> and CH<sub>4</sub>, and also CO, NO<sub>2</sub> and SO<sub>2</sub>, which do not pertain to greenhouse gases, though play an important role in the chemistry of ozone and methane in the troposphere and, to a certain extent, exert influence on the variations in the global concentration of greenhouse gases in the troposphere.

## 2. EQUIPMENT CHARACTERISTICS

Instrumentation for mobile measurement optical facility housed in a minibus vehicle at present is under construction. The facility comprises a multi-channel Fourier-spectrometer (MFS) with a guidance and scanning system through a top hatch of the vehicle, a videospectroradiometer gas viewer (VSR-GV) designed for NO<sub>2</sub> monitoring against diffused sky light in the spectral range of 434–448 nm, positioned on a tripod when brought out of the vehicle, a Notebook PC for controlling the optical instrumentation and for data acquisition and treatment, and an automated meteorological station. The MFS and VSR-GV instruments represent systems for the remote monitoring of exhausts from both local and large-scale sources.

Since the VSR-GV was described earlier (Afonin, 2001), the present paper will only briefly dwell on the MFS apparatus, account for its technical characteristics and specific features of its use.

In connection with the necessity to employ a broad spectral range, to feature high sensitivity and to obtain gas distribution patterns for certain tasks of remote probing a multi-channel Fourier-spectrometer was developed with a photosensitive device comprising 2 cooled strips, each of 14 radiation sensors. The MFS represents a classical Fourier-spectrometer based on a Michelson interferometer with one mobile and one fixed mirrors and an objective lens placed between the interferometer and the radiation detector. On each photodetector element an interference pattern is formed, which is defined by the spectral composition of the radiation coming from the space under investigation that matches the viewing field of each photosensitive element of the radiation detector. Movement of an interferometer mirror is carried out with the help of an electrodynamic drive.

The electric signal of the fringe pattern passes a corresponding amplification path, which consists of a broad-band pre-amplifier and a bandpass amplifier, then via a commutator it comes to a 14-digit analog-to-digit converter and is quantified by the path-length difference with the reference channel signal, which uses a He-Ne laser as a radiation source ( $\lambda=0.6328\mu\text{m}$ ).

Further the information through the interface under the certain program writes in the computer in which files of all 28 interferograms from each detector are formed for their subsequent processing and reception of radiation spectra.

To meet the main requirements in sensitivity put to a Fourier-spectrometer, an original two-spectral photoresistive cooled multi-element photosensor was developed and fabricated from germanium doped with mercury.

The basic technical characteristics of the MFS are listed in Table 1.

Table 1. MFS Basic Technical Characteristics.

Spectral range, $\mu\text{m}$ :	
Channel 1	3.0-5.5
Channel 2	3.0-14.0
Spectral resolution, $\text{cm}^{-1}$	1.0
Light splitter and compensator	KCl
Input pupil diameter, mm	30
Aperture ratio	1:1
Overall viewing field, angular deg.	6
Instant viewing field, mrad	$7 \times 3.5$
Radiation sensor	Ge:Hg
Detectability, $\text{cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$	
Channel 1	$8 \cdot 10^{10}$
Channel 2	$2 \cdot 10^{10}$
Unit sensitive area dimensions, mm	$0.2 \times 0.1$
Interferogram duration, s	4.3
Dynamic range	$10^4$
NESR at the maximum spectral sensitivity, $\text{W}/(\text{m}^2 \cdot \text{sr} \cdot \text{cm}^{-1})$	
Channel 1 at $2082 \text{cm}^{-1}$	$9.3 \cdot 10^{-6}$
Channel 2 at $870 \text{cm}^{-1}$	$3.4 \cdot 10^{-5}$

These photosensors perform high detectability, close to its theoretical limit in each selected spectral range. A specific feature of sensors made of mercury-doped germanium is their low working temperature of about  $\sim 30^\circ\text{K}$ , which demands employing gas cryogenic machines of about 0.35kW power that work on the basis of the Stirling reverse cycle, with a lifetime of  $\sim 2000$  hours.

The spectral characteristic of the shortwave channel 1 is formed by a cooled bandpass filter built in the photodetector on a leukosapphire substrate. To completely eliminate the influence of vibrational disturbance on the spectrometer functioning at the measurement of threshold signals, the photosensitive device allows for an operation mode with the compressor of the gas cryogenic machine turned off. For its implementation in the photodetector design, a cold accumulator is incorporated, which ensures preservation of the sensors' parameters (within 90% of the rating level) at the compressor being turned off for up to 3min, and also a possibility to repeat such a cycle in a period not longer than 50 seconds.

### 2.1. Foundations for the radiometric accuracy of measurements

An effective temperature of the scene under measurement may be considerably lower than the temperature of the equipment ambience, therefore the radiation of the optical elements of the instrument should be considered at the data treatment.

Normally, at radiometric measurements a heated and a cooled black bodies are used, with the help of which at a simultaneous solution of the signal equations, the device's own contribution is well eliminated and the true measured brightness is obtained. There exists a relation between the true brightness spectrum at the device input,  $S^{TR}(\nu)$ , and

the measured spectrum,  $S^{ME}(\nu)$ , expressed by the equation

$$S^{ME}(\nu) = G(\nu) \cdot (S^{TR}(\nu) + S_{ins}(\nu)) \quad (1)$$

where  $\nu$  = the wavenumber in  $\text{cm}^{-1}$

$G(\nu)$  = a complex function of the instrument spectral sensitivity and gain  
 $S_{ins}(\nu)$  = the complex brightness spectrum contributed from the device

Brightness spectra defined by means of a Fourier transform represent complex quantities that depend on the value of error in the determination of the optical path length difference from the point of the zero phase difference. In (Yao, 2002) it was shown that, if the errors of the determination of the zero phase difference point for the case of viewing the scene measured, the cold and the heated black bodies are equal or brought to a same value by means of a special treatment algorithm, then the true spectrum of the scene under measurement (which is equal to the real part of the Fourier transform) can be calculated by the relation

$$R_{SC}(\nu) = \frac{\varepsilon_W \cdot (R_{SC}^{ME}(\nu) - R_C^{ME}(\nu))}{R_W^{ME}(\nu) - R_C^{ME}(\nu)} \cdot B(\nu, T_W) - \frac{\varepsilon_C \cdot (R_{SC}^{ME}(\nu) - R_W^{ME}(\nu))}{R_W^{ME}(\nu) - R_C^{ME}(\nu)} \cdot B(\nu, T_C) \quad (2)$$

where  $B(\nu, T)$  = the Planckian function

Subscripts  $W$  and  $C$  denote the warm and the cold black bodies,  $\varepsilon_W$  and  $\varepsilon_C$  are emission coefficients of these bodies. It has been shown in (Yao, 2002) that, if the errors of the determination of the phase difference at the recording of a viewed scene and the black bodies interferograms are close to zero, the imaginary part of the complex transform is close to zero, too. Using the main equation for the calculation of the brightness spectrum of the measured scene (2), one can execute the analysis of its measurement error caused by the error of the temperature control of the black bodies and the measurement error due to the sensor noises. The latter are characterised by a spectral brightness equivalent to the noise. At the analysis, let us assume that the real parts of the detected radiation spectra of the viewed scene and the black bodies are proportional to the Planckian function at temperatures  $T_S$ ,  $T_W$  and  $T_C$  with a factor of  $|G(\nu)|$ . For convenience of the analysis, we rewrite equation (2) in the following form:

$$R_{SC}(\nu) = A(\nu) \cdot B(\nu, T_W) - C(\nu) \cdot B(\nu, T_C) \quad (3)$$

$$A(\nu) = \frac{B(\nu, T_S) - B(\nu, T_C)}{B(\nu, T_W) - B(\nu, T_C)} \quad (4)$$

$$C(\nu) = \frac{B(\nu, T_S) - B(\nu, T_W)}{B(\nu, T_W) - B(\nu, T_C)} \quad (5)$$

Then, the mean square error of the determination of the viewed scene brightness spectrum, due to the error of the black bodies' temperature determination, will be

$$\Delta R_T(\nu) = \left( (A(\nu) \cdot \frac{dB(\nu, T_W)}{dT} \cdot \sigma T_W)^2 + (C(\nu) \cdot \frac{dB(\nu, T_C)}{dT} \cdot \sigma T_C)^2 \right)^{0.5} \quad (6)$$

where  $\sigma T_W$  and  $\sigma T_C$  are the mean square deviations of the error of the temperature measurement for the warm and cool black bodies, respectively.

The determination errors of the spectrum of the scene under measurement connected with noises in the photoelectronic track can be evaluated with the use of determining the spectral brightness equivalent to the noise, which is expressed through the instrumental parameters by the equation

$$NESR(\nu) = \frac{\sqrt{S_{el}}}{S(\nu) \cdot D^* \cdot \tau \cdot S_{ob} \cdot \Omega \cdot \delta\nu \cdot \sqrt{T_{sc}}} \quad (7)$$

where  $S_{el}$  = the area of the sensitive element  
 $S(\nu)$  = the relative spectral sensitivity  
 $D^*$  = the detectability of the sensor in the maximum sensitivity  
 $\tau$  = the total transmittance of the optical system with the light splitter as a whole  
 $S_{ob}$  = the area of the input pupil  
 $\Omega$  = the solid angle of the viewing field of the sensor unit area  
 $\delta\nu$  = the spectral resolution  
 $T_{sc}$  = the scanning time of the fringe pattern

Differentiating (3) in  $T_S$ ,  $T_W$  and  $T_C$ , one can obtain the mean square error of the viewed scene spectrum evaluation due to the photoelectronic track noise is equal to

$$\Delta R_N(\nu) = \frac{NESR(\nu)}{B(\nu, T_W) - B(\nu, T_C)} [B(\nu, T_W) \cdot \sqrt{1 + (A(\nu) - 1)^2 + A^2(\nu) + B(\nu, T_C)} \cdot \sqrt{1 + (C(\nu) + 1)^2 + C^2(\nu)}] \quad (8)$$

and the total radiometric mean square error is

$$\Delta R(\nu) = \sqrt{\Delta R_N^2(\nu) + \Delta R_T^2(\nu)} \quad (9)$$

The estimations of the radiometric error obtained for the instrumental parameters according to Table 1 allowed making a conclusion that, to realise the required accuracy of measuring atmospheric spectral brightness related to changes in the concentrations of greenhouse gases like ozone and methane, the temperature of calibration black bodies in the range from  $-10^\circ\text{C}$  to  $+40^\circ\text{C}$  must be controlled with a mean square error not more than  $0.02^\circ$ . If the temperature of the cold black body is chosen below  $100^\circ\text{K}$ , which can be achieved on cooling it by liquid nitrogen, the radiometric measurement error will reduce about 2 times and the accuracy of its temperature control can also reduce to an uncertainty of  $\sim 2^\circ$ .

Basing on this study, a system of calibration, guidance and scanning of the monitored scene was made and placed at the MFS entrance, which comprises a two-mirror guidance system and two black bodies. One of the black bodies is kept at an ambient temperature and is controlled by a platinum low-temperature resistance thermometer of TSPN-5V (Russian brand) type and the other is cooled by liquid nitrogen. An increase about 3.7 times in the accuracy of measurements of atmospheric spectral brightness with a multi-channel Fourier-spectrometer can be achieved by averaging measured brightness spectra over 14 channels at a single scanning run of fringe patterns.

### 3. FOUNDATION FOR METHOD OF MEASUREMENT

The MFS technique of the remote monitoring of anthropogenic gases overall exhausts from large-scale sources (like a big metallurgical enterprise or a town) features one specific peculiarity. This peculiarity consists in serial runs of measuring atmospheric spectral brightness in the zenithal direction along the source border line on the windward and leeward sides, extraction of the value of atmospheric spectral brightness change due to anthropogenic gases impact, and the solution of an inverse problem in the determination of gases' contents in the boundary layer for the estimation of the contribution of anthropogenic gases from the source under control.

For the foundation of the measurement method a numerical experiment is needed, which would allow the selection of spectral ranges in the region of the absorption band of the analysed gas. These spectral ranges should be selected so that measurements in them would ensure a maximum sensitivity to variations of this gas contents in the atmosphere at a least possible error introduced to the measurement by the effects of other atmospheric gases present (and interfering). To perform estimations computing, a version of differential method was used, which is based on the analysis of the ratio of atmospheric spectral brightness differences measured in the zenithal direction in clear and in polluted air environments to the mean square sum of the variations of spectral brightnesses contributed by all other gases into the formation of overall radiation in the specified spectral range,

$$\gamma_i(\nu) = \frac{B_i(\nu) - B_0(\nu)}{\left(\sum_j^N (B_j(\nu) - B_0(\nu))^2\right)^{0.5}} \quad (10)$$

where  $\nu$  = a wavenumber,  $\text{cm}^{-1}$

$B_0(\nu)$  = the spectral brightness of clear atmosphere in the zenithal direction calculated by an atmosphere model

$B_i(\nu)$  = the spectral brightnesses of polluted atmosphere, corresponding to the changed (with respect to that at clear air) content of the  $i$ -th gas monitored

$B_j(\nu)$  = the spectral brightnesses of polluted atmosphere, corresponding to the changed content of the  $j$ -th interfering gas

The maximum value  $\gamma_i(\nu)$  in equation (10) corresponds to the highest sensitivity of the method to normalising the value of the  $i$ -th gas contents variation in the boundary layer at the minimum of the contributions from other atmospheric gases' radiation into the observed value of spectral brightness. As follows from the above stated, if in the spectral range under investigation any wavenumbers corresponding to maximal  $\gamma_i(\nu)$  values are found, these wavenumbers should further be used for the restoration of the contents of measured gases in the atmosphere. It also should be expected an achievement of the maximum accuracy in the restoration of the gas contents in the atmosphere that can be provided by this method. Calculations presented in Table 2 were done for the atmospheric model "Medium latitudes, Summer" with the use of FIRE-ARMS software package (Gribanov, 2001).

Table 2. Wavenumbers at Maximum Sensitivity to the Monitored Gas, Spectral Brightness Variations and Coefficient  $\gamma_i(\nu)$ .

Gas	$\nu(\text{cm}^{-1})$	$B_0(\nu)$	$B_i(\nu) - B_0(\nu)$	$\gamma_i(\nu)$
O <sub>3</sub>	1024.75	0.01604	0.000168	1.4
CH <sub>4</sub>	1303.75	0.0398	0.000274	3.9
SO <sub>2</sub>	992.5	0.00508	0.000262	14.5
CO	2169.25	0.000085	0.000015	13.8

The spectral brightnesses are specified in table 2 in  $\text{W}/(\text{m}^2 \cdot \text{sr} \cdot \text{cm}^{-1})$ . As interfering gases, H<sub>2</sub>O vapour, CO<sub>2</sub>, and also monitored gases O<sub>3</sub>, CH<sub>4</sub>, SO<sub>2</sub> and CO were considered. At the calculation, the content variations for all the gases in the boundary layer up to 1 km high were taken equal to 10% of the model value except CO<sub>2</sub>, whose value was taken equal to 1%. The calculation was carried out for a Fourier-spectrometer with an instrumental line-shape Norton-Beer "mean" (Norton, 1976) for HWHM equal to  $0.5\text{cm}^{-1}$ .

The small value of factor  $\gamma_i(\nu)$  for O<sub>3</sub> is caused by influence of CO absorption bands, and for CH<sub>4</sub> by H<sub>2</sub>O vapours that demands to use a content definition method of the gases mixture at the remote sounding.

#### 4. CONCLUSION

The threshold spectral sensitivity of the Fourier-spectrometer is close to variations in spectral brightness at a 1% variation of the average gas concentration in an atmospheric column, which speaks for the possibility of using the developed equipment for the fulfilment of the put tasks concerning greenhouse gases and also for the evaluation of the concentrations of many anthropogenic gases whose radiation spectra are in the range of 4.5–13 $\mu\text{m}$ . When measurements in the zenith direction are necessary, a lack in sensitivity can be compensated at the expense of the accumulation and statistical treatment of fringe patterns of the viewed space region.

The proposed mobile facility for distant measurements allows one to solve a number of ecological problems connected with the determination of the spatial distribution of anthropogenic and greenhouse gases in the near-surface atmosphere, namely:

- determination of anthropogenic and greenhouse gases' contents in the atmospheric boundary layer, including that at the validation of satellite-based measurements;
- evaluation of total exhausts of polluting gases from industrial enterprises, large-scale industrial centres and their transport to neighbouring districts;
- remote determination of the composition and concentration of gases contained in plumages emitted from the chimneys of industrial enterprises and heat power plants.

#### 5. ACKNOWLEDGEMENTS

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