

EXPERIMENTAL STUDIES OF THE CARBON DIOXIDE IN THE ATMOSPHERE OVER NORTHERN SEAS AND ATLANTIC OCEAN

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The commercially available GIAM-15 gas analyzer was improved to make the calibration unattended and to automate measurements and data processing. The results of field measurements of CO₂ concentration in the atmosphere made with this analyzer from aboard the research ship Akademik Mstislav Keldysh during its 37th expedition are presented.

Monitoring of the CO₂ concentration in the atmosphere becomes more and more urgent due to the greenhouse effect. The data obtained up to date¹ show that the CO₂ concentration in the atmosphere can significantly vary in space and time. Unattended measurements of CO₂ background concentrations in the atmosphere are the problem to be solved taking into account the fact that the structure of the CO₂ concentration fields is poorly studied especially in hard-to-reach areas such as continents, mountain areas, Arctic Ocean.

The International Biospheric-Geographic Program (IBGP) provides for conducting complex studies of the global atmosphere-ocean gas exchange, including the study of CO₂ concentration dynamics and the biosphere-atmosphere-ocean exchange by CO₂.

In this paper we describe the instrumentation and some results of the CO₂ concentration measurements made from aboard the research ship *Akademik Mstislav Keldysh* in August-October 1995.

The URAS, UNOR, LIRA, and similar gas analyzers are usually used to measure the CO₂ background concentration at monitoring stations. The GIAM-15 gas analyzer we use belongs to the same class of devices. Devices of this class have, in our opinion, some disadvantages connected with the necessary regular zero adjustment and calibration. This means, first, that each analyzer must necessarily have the balloons with at least two reference gases; "zero" gas, and the CO₂ in N₂ mixture (gas reference). In addition, the complex multistage procedure of calibration must be performed every time.² Moreover, the zero adjustment and the calibration require, in accordance with the devices' descriptions, a attendance of an operator and the manual fine adjustment of zero and the device gain factor from its readings and the concentrations of reference gases.

In order to avoid the operator attendance and to automate the measurement, calibration, and data processing, the electronic circuit of the GIAM-15 gas analyzer has been modified, additional ADCs and a

microcontroller have been introduced together with a computer. The software has been developed including the programs for calibration, automated concentration measurement, and preliminary data processing. This software provides the following possibilities:

- to measure and to compute the calibration constants;
- to turn on, at a given time, the pump which pumps the air through the gas analyzer;
- to receive the data from the gas analyzer via the microcontroller;
- to compute the value of concentration;
- to store the concentration value and the measurement time in a file;
- to conduct the next measurement series in a preset period.

The photoacoustic method of gas analysis based on IR absorption measurements³ is implemented in the gas analyzer.

The device is designed by the differential optical scheme. The IR radiation is incident onto two optical channels: working and reference. Both fluxes are alternatively chopped with a chopper. In the working channel, the radiation flux comes through the working cell to one of the beam-receiving cylinders of the measuring chamber. In the reference channel, the radiation flux comes through the reference cell to another beam-receiving cylinder of the measuring chamber. The analyzed gas mixture continuously circulates through the working cell, whereas the reference cell is filled with the nitrogen which is inactive in the infrared.

The condenser microphone placed in the measuring chamber filled with the N₂-CO₂ mixture serves as a IR receiver providing the selectivity of the analysis. Pressure and temperature oscillations, arising in the gas filling the IR receiver under the exposure to radiation flux, are received with the condenser microphone.

If the IR radiation fluxes coming to the beam-receiving cylinders of the measuring chamber are equal, i.e. there is no component to be measured in the gas

analyzed, the diaphragm of the condenser microphone, which responds to the sum of pressures arising in the beam-receiving cylinders, will be at rest.

If the IR radiation flux, coming to one of the beam-receiving cylinders, is smaller than another one (due to absorption, in the working cell, of the portion of radiation corresponding to the CO₂ absorption spectrum), then in the measuring chamber the variable component of gas pressure change will appear, whose value will depend on the absorption in the working cell.

The oscillations of the condenser microphone in the measuring chamber are transduced into the alternating voltage which, after preamplification and synchronous detection, is measured and transferred to a computer via a microcontroller.

The amplitude of condenser microphone's membrane oscillations depends on the CO₂ concentration in the mixture analyzed and can be presented in the form:

$$P = K_{v_r}(\Phi_0 - \Phi) = K_{v_r}\Phi_0(1 - \exp(-A_v l c)) = K_{v_r}\Phi_0((A_v l)c - 1/2 (A_v l)^2 c^2), \quad A_v l c \ll 1, \quad (1)$$

where K_{v_r} is the integral sensitivity of the radiation receiver; Φ_0 and Φ are the radiation fluxes having passed respectively the reference and working cells; c and A_v are the concentration and the absorption function of the analyzed gas; l is the length of the working cell.

The signal U measured after preamplification and synchronous detection can be presented as

$$U = D + K(Ac - 1/2 A^2 c^2), \quad (2)$$

where D is the zero drift of the optical and electronic channels; $K = K_{am} K_{v_r} \Phi_0$; K_{am} is the linear transfer ratio of the electronic channel; $A = A_v l$; and the concentration of the analyzed gas is

$$c = [KA - \sqrt{(KA)^2 - 2KA^2(U - D)}] / (KA^2). \quad (3)$$

The values of calibration constants D , K , and A needed to compute c can be obtained by recording the signals U_0 , U_1 , and U_2 when using the reference mixtures with given concentrations of the gas analyzed, namely, $c = 0$, $c_1 = 0.5c_{max}$, $c_2 = 0.9c_{max}$, and by solving the system of equations (2). It should be noted that the constants D and K can vary during the operation and should be measured at least once during 24 hours of the device operation. For their further determination it is sufficient to use only two calibration mixtures ($c = 0$ and $c = (0.5-0.9)c_{max}$). As to the constant $A = A_v l$, it should be determined only once

since it is equal to the product of two constants: the absorption function of the gas analyzed and the length of the working cell. (The above technique can be used, generally speaking, independently to find the absorption function of molecules with the use of the spectrophotometric technique with broadband sources.)

The background CO₂ concentrations and that near natural and anthropogenic sources of CO₂ were measured during the expedition of the research vessel *Akademik Mstislav Keldysh*. The map of the expedition is shown in Fig. 1. The CO₂ concentration was measured continuously, in an hour interval, throughout the expedition. The influence of the vessel's exhaust pipe was avoided due to accurate choice of a place for air sampling and excluding the exhaust in concentration measurements. The air was sampled at a height of 15 m above the sea level. The measurement results are shown in Fig. 2 and 3. Figure 2 shows the CO₂ concentration along the vessel route, every point corresponds to the daily average value of the CO₂ concentration. Figure 3 shows the diurnal run of the CO₂ concentration, averaged for some days, in the port cities of Rotterdam, Halifax, Copenhagen and in Atlantic Ocean (41°44'N, 49°57'W). Near natural and anthropogenic sources and sinks of CO₂, its diurnal behavior is characterized by usual elevation of concentration in dark period and reduction in light period that is also typical for land measurements⁴ as well as by significant day-to-day variability, while under conditions close to the background ones the CO₂ concentration in the atmosphere remains stable.



FIG. 1. The route of 37th expedition of the research vessel *Akademik Mstislav Keldysh*: Copenhagen (1), Halifax (2), "Titanic" 41°44'N, 49°57'W (3), Rotterdam (4).

In conclusion we would like to note the stable operation of the device during three month of continuous functioning under field conditions, the undoubted conveniences of modifications in the design of the gas analyzer and the software developed.

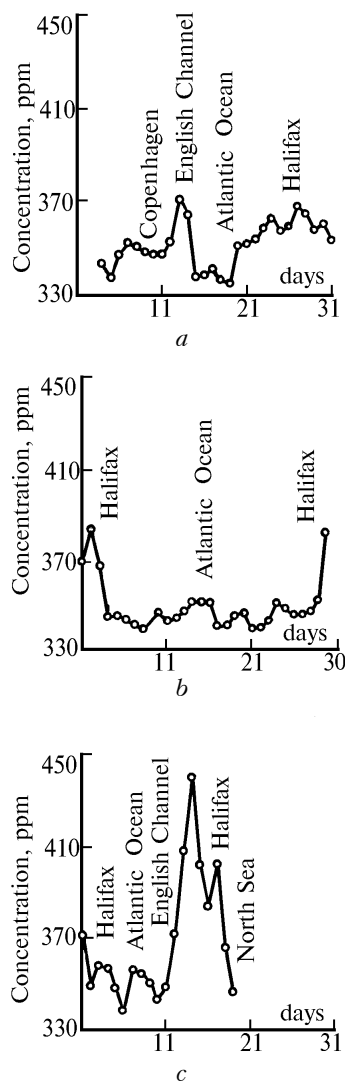


FIG. 2. Diurnal average CO₂ concentration during the expedition: August (a), September (b), and October (c).

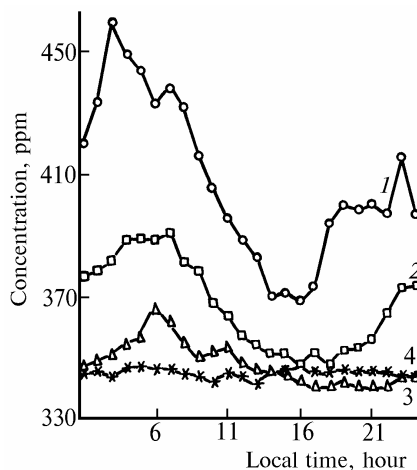


FIG. 3. Diurnal behavior of the CO₂ concentration in the port cities and in Atlantic Ocean: Rotterdam (1), Halifax (2), Copenhagen (3), Atlantic Ocean, 41°44'N, 49°57'W (4).

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