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CALIBRATION OF GAS ANALYSIS DEVICES WITH OPEN CUVETTE

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Summary. *Gas analysis devices are measuring instruments and require periodic confirmation of their metrological parameters. This paper deals with methods of metrological support of measurements of absorption remote devices (with open cuvette). The design of the device where the operating and calibration cuvettes (with calibration gas mixture) are alternately (if necessary) placed on the optical path of the device, with the same optical elements. is proposed. This method of calibration and verification allows you to do without the use of CGM, which greatly simplifies calibration and verification of the gas analyzer at the workplace. In addition, the method reduces the calibration and verification error, since in the calibration mode the light flux passes along the same optical path as in the measurement mode, while the light flux and the degree of contamination of the optical elements by selective and non-selective components of the analyzed mixture remain unchanged.*

Key words: *gas analyzer, calibration, radiation, calibration interval, open cuvette.*

Introduction. Absorption instruments for gas analysis usually contain working cuvette through which the gas sample, pre-cleaned and brought to normal parameters (pressure, temperature, humidity, etc.) is pumped. The metrological support of the measure is realized by means of reference (verification) gas mixtures that are passed through the working cuvette. There is also another type of device – device with open cuvette (remote), which can contain open operating cuvette outside the device itself. The metrological support for this type of instrument is different.

Gas analysis devices, especially toxic and explosive ones, are usually measuring instruments. Therefore, it is very important to ensure their metrological parameters. For this purpose, their metrological certification, which is costly procedure is conducted and it is usually carried out by metrological centers. Often there is the need of independent checking of the device performance and its adjustment, and there is a significant number of methods for their calibration, for example, partial darkening of the operating channel, introduction of the sealed cuvette with certain concentration of the measured gas into the operating channel, etc. [1–4]. However, all of them have certain disadvantages both in terms of significant error and the possibility of their implementation.

Analysis of the available investigation results. An interesting method of adjustment was also proposed by the authors in paper [5]. Another modification of calibration methods proposed by the authors of [6, 7] is that when the temperature of the radiation source changes, its radiation spectrum also changes, namely, it shifts to the infrared area (with temperature decrease). Therefore, for infrared two-channel single-beam device, where the channels are significantly separated along the wavelength, the intensity ratio of the operating and support channels changes, and is equivalent to the introduction of the analyzed gas into the operating channel. The basic work is comprehensive work on the main standards for trace gas analyzers [8], which also contains the basics of calibration. Paper [9] describes the use of sensor device based on thermobattery with micro-machines for the analysis of natural gas and its calibration. Paper [10] describes systematic approach

to the metrological support of gas analytical measurements within the range of microconcentrations (trace analysis) using dynamic and static control means.

Another area is the development of devices for calibrating gas analyzers. For example, paper [11] describes static gas mixing device for preparing control gas mixtures during calibration and verification of automatic gas analyzers. The paper describes how the device operates and provides formulas for calculating the volume concentration. However, despite a significant amount of investigations, the number of papers dealing with this problem is limited. At the same time, there are alternative methods. For example, Gas Institute of the National Academy of Sciences of Ukraine has installed 6890N gas chromatograph produced by Agilent Company (USA) for collective use by employees of scientific institutions. This device makes it possible to identify chemical compounds and determine their amount in mixtures of gases and liquids in the wide range of concentrations – from micro impurities to 100%. However, even this method has limitations related to hardware design and cost.

Special attention should be paid to the Order from 22.05.2023 No. 118 «On the adoption of national standards» issued by the State Enterprise «Ukrainian Scientific-Research and Training Center for Standardization, Certification and Quality», which adopted national standards with effect from March 01, 2024 [12].

Theoretical part. As a rule the sample preparation system in gas analysis instruments ensures favorable operation mode of the device and its long-term operation. However, it does not always guarantee the reliability of the sample, especially when the system is polluted: one part of the analyzed gas dissolves in water and is removed from the sample with condensate, while another part is adsorbed on the system walls, enters into chemical reactions with other components of the sample, or changes its physical state when the sample parameters change. In addition, sampling in many cases disturbs the analyzed medium, changes its composition, etc.

In devices with open operating cuvette, analyzed gas medium enters the cuvette by natural diffusion. The advantages of this method of analysis are as follows:
- absense of disturbance of the analyzed medium, no change in its composition;
- absence of consumption of the investigated gas medium;
- measurements are carried out at the location of the investigated gas medium without changing its parameters (pressure, temperature, composition).

These advantages play a decisive role in the investigation of the gas medium in isolated volumes (for example, gas medium in gas-filled installations), as well as in cases where the conditions of gas medium existence are significantly different from the operating ones. To prevent substances from entering the open cuvette that could pollute it, it is usually protected by metal-ceramic cap or another dust filter.

The class of remote gas analysis devices can be defined as devices for qualitative or quantitative analysis of the composition of ambient air when control device and investigated gas medium are spatially separated.

Remote devices are used to solve the following tasks:
- control of specific types of source;
- study of pollutant transfer and diffusion;
- control of the reliability of local measurements, since the level of pollution in local area can differ significantly from the integral level of pollution in the controlled area;
- investigation of the the area while creating optimal network of local control points;
- control for the development and verification of pollutant transfer models;
- measurement of the height of the mixing layer in the air pool;
- control of the pollutants transfer from urban and industrial areas;
- identification of new sources of pollution.

The advantages of remote devices which enable to obtain three-dimensional information about pollution in relation to local ones include. The advantages of remote devices that allow obtaining three-dimensional information about pollution compared to local ones include:

- absence of disturbance in the control of emissions from the source, which is due, in particular, to the possibility of conducting covert inspections of emission concentrations;
- integral measurements along the route, which make it possible to obtain spatial scales of measurement results comparable to the scales of model predictions;
- the ability to carry out three-dimensional measurements, including the distribution of pollutants by height, which has great influence on the spectrum and intensity of solar radiation falling on the Earth's surface;
- the ability to conduct preliminary control of pollution in the area;
- the ability to measure over large geographical areas, indicating economic efficiency of such devices.

Depending on the nature of the radiation sources used, remote devices can be divided into the following types:

- passive gas analysis devices;
- active devices.

Passive devices are used as the source of radiation, direct or scattered solar radiation, radiation emitted by the Earth's surface. Analyzing the interaction of this radiation with the investigated gas medium, information about the concentration of the substances is obtained. Radiation of the analyzed components of the gas medium itself can also be used as radiation source if it is heated (for example, when determining the gas components in the burning natural gas flare). Due to the absence of radiation source in these devices, their weight, dimensions, and power consumption are negligible and they can be portable.

Devices with open gas cuvette are widely used for measurements directly in the flues of thermal power plants and industrial enterprises. Gas mixture in the flue is in conditions that differ from normal ones (temperature, pressure), so when using sampling device, the concentration of the mixture should be recalculated to real conditions. In addition, at high temperatures and certain pressures, there are gases in the flue that subsequently, when these parameters change, are deoxidized (for example, NO turns into NO_2), so open cuvette makes it possible to obtain real gas concentration values.

Short route method is often used to establish readings. In this case, reflector is installed in front of the open cuvette and the radiation returns to the gas analyzer without passing through the open cuvette [2, 3]. This method of setting zero readings has large error, since the light flux passes through different optical path and does not take into account the adsorption on the optical elements of the open cuvette by selective and non-selective (for example, dust) components of the analyzed gas mixture. Also, additional errors arise due to the shift of the operating point on the volt/watt characteristic of the photo-receiving device, which is usually non-linear and requires change in the gain coefficients of the registration system (when the «short path» is turned on, the amount of light flux changes significantly). In addition, it does not allow us to establish the upper limit of the measurement range [13]. If in this case the cuvette is also used for calibration (setting the limits of the measurement range), then the consumption of the calibration gas mixture (CGM) is significant due to the need to purge it with zero CGM before setting zero and after calibration, as well as CGM for setting the upper value of the measurement range.

Experimental part. In order to reduce calibration and verification error and reduce CGM consumption, we propose to change the length of the operating cuvette to its zero value during calibration and set zero readings of the gas analyzer [14]. At the same time, during calibration, after setting zero readings, the length of the calibration cuvette should change from zero to the set value and the upper value of the measurement range should be set. The calibration cuvette is sealed and filled with CGM.
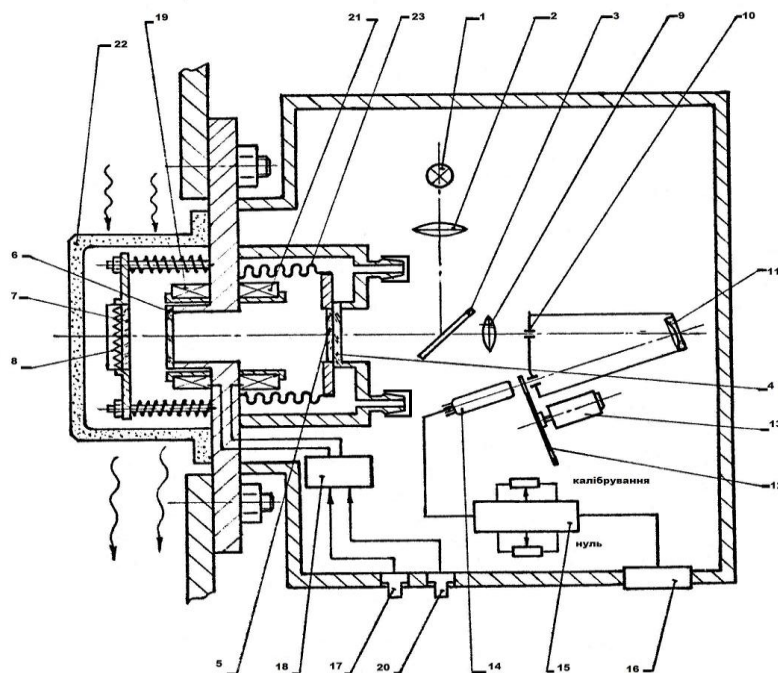
Figure 1. The design of the gas analyzer with open operating and sealed calibration cuvettes, which change their lengths during the calibration and verification process. The gas analyzer consists of radiation source 1, collimator 2, light-splitting mirror 3, windows 4, 5 calibration cuvette filled with CGM, windows 6, 7 operting cuvette, reflector 8, lens 9, input slit of monochromator 10, diffraction grating 11, output slit 12, which is scanned and installed on the drive 13, photoelectronic multiplier (FEM) 14, registration system 15, indicator 16, zero button 17, power supply unit 18, electromagnet 19 of the operating cuvette, calibration buttons 20, electromagnet 21 of the calibration cuvette, metal-ceramic cap 22, bellow 23

The radiation from source 1 is formed into parallel light flux by collimator 2, is reflected from the light-splitting mirror 3 and directed through the calibration cuvette formed by mirrors 4, 5 and filled with CGM into the open operating cuvette, formed by mirrors 6, 7, returns back to the operating and calibration cuvettes due to cataphot reflector 8, passes through mirror 3, is focused by lens 9 on the entrance slit 10 of the monochromator, and is reflected from the diffraction grating 11. Grating 11 decomposes the radiation that has passed through the operating and calibration cuvettes along wavelengths in its focal plane. The radiation spectrum is scanned by exit slit 12, which is the disk with uniformly applied slits in the direction of its radii. Exit slit 12 is rotated uniformly by drive 13. The light flux passing through he exit slit 12 is modulated with the frequency equal to the product of the disk rotation frequency, the number of slits on the disk, and the number of periods of the structure of the analyzed gas in the scanned spectral region. The light flux modulated in this way is detected by light detector 14, the signal is processed by the registration system 15 according to the given algorithm, and the measurement results are displayed on indicator 16. In measurement mode, gas analyzer is installed on the flange of the flue, and its operating cuvette is inside the flue. To prevent contamination of windows 6,7 of the operating cuvette, metal-ceramic cap 22 is used. The analyzed gas mixture enters the cuvette by diffusion through the walls of cap 22. The length of the calibration cuvette is zero (windows 4.5 are pressed together by bellow 23).

In the calibration or verification mode of the gas analyzer, zero button 17 is pressed. At the same time, power supply 18 supplies voltage to electromagnet 19, which attracts window frame 7 together with reflector 8.

The length of the operating cuvette becomes zero. Next, zero potentiometer of the registration system sets zero readings of indicator 16. Then, calibration button 20 is pressed. At the same time, the supply voltage is supplied from unit 18 to electromagnet 21, which attracts window frame 5 mounted on bellow 23. The length of the calibration cuvette filled with CGM takes the specified value. To prevent pressure changes in the calibration cuvette, the membrane

can be provided (not shown in Fig. 1). Then, using the calibration potentiometer of registration system 15, set indicator 16 to the value of CGM concentration specified in its passport. This completes calibration. Buttons 17, 20 are turned off, electromagnets 19, 21 are de-energized, and the lengths of the operating and calibration cuvettes are restored to their original values by the return springs and bellow (the length of the operating cuvette is equal to the set value, the calibration cuvette is zero). Gas analyzer is ready for measurements.

Conclusions. The proposed method of calibration and verification makes it possible to operate without CGM application, which greatly simplifies the calibration and verification of the gas analyzer at the workplace. Indeed, if CGM preparation technology is violated, it can change its concentration over time (especially in the case of aggressive gases and vapors, as well as those prone to adsorption and condensation). Selectively absorbing films or gases in sealed cuvettes can change their optical properties, and the absorption of light flux also depends on their installation in the gas analyzer. The parameters of modern electronic components are more stable over time.

In addition, this method reduces calibration and verification error, since in the calibration mode the light flux passes along the same optical path as in the measurement mode, while the light flux and the degree of contamination of the optical elements by selective and non-selective components of the analyzed mixture remain unchanged.

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КАЛІБРУВАННЯ ПРИЛАДІВ ГАЗОВОГО АНАЛІЗУ З ВІДКРИТОЮ КЮВЕТОЮ

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Резюме. З огляду на поширення газових приладів у промисловості, медицині, дослідницьких лабораторіях та інших сферах методи їх калібрування та повірки залишаються важливими для забезпечення точності й надійності вимірювань. Для забезпечення якості їх метрологічних параметрів періодично проводиться їх метрологічна атестація, яка є затратною процедурою і проводять її, зазвичай, метрологічні центри. Часто виникає необхідність самостійної перевірки працездатності приладу та його налаштування, причому існує значна кількість методів їх калібрування. Однак усі вони мають певні недоліки як з точки зору значної похибки, так і можливості їх реалізації. Розглянуто методи метрологічного забезпечення вимірів абсорбційних дистанційних приладів (з відкритою кюветою), які широко використовуються при проведенні вимірів безпосередньо в газоходах теплових електростанцій, на промислових підприємствах тощо. Однією з переваг приладів з відкритою кюветою є можливість легко змінювати зразки для аналізу та проводити їх очищення та підготовку без необхідності розбирання кювети. Автори пропонують конструкція приладу, в якому робоча й повірочна кювети (з повірочною газовою сумішшю) почергово (при необхідності) розміщуються на оптичному шляху приладу, причому використовуються одні й ті ж оптичні елементи. Даний спосіб калібрування й повірки дозволяє обійтися без застосування ПГС, що істотно спрощує калібрування й повірку газоаналізатора на робочому місці. Крім того, спосіб дозволяє зменшити похибку калібрування й повірки, оскільки у режимі калібрування світловий потік проходить по тому ж оптичному шляху, що й у режимі вимірів, при цьому залишається без змін величина світлового потоку й ступінь забруднення оптичних елементів селективними й неселективними компонентами аналізованої суміші. До того ж, з урахуванням швидкого розвитку технологій, постійного вдосконалення аналітичних методів та зростаючої уваги до якості результатів вимірювань, нові методи калібрування мають потенціал для впровадження в практику для покращення точності й надійності газового аналізу.

Ключові слова: газоаналізатор, калібрування, випромінювання, міжповірочний інтервал, відкрита кювета.