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Methodology for Assessing the Gas Composition of Soils

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Методика оценки газового состава грунтов

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gas geochemical studies, soil air, soils, methane, carbon dioxide, oxygen, hydrogen, sampling equipment, gas analyzer, methodology, sampling, analysis, engineering and environmental surveys, measurement results, accuracy indicators.

The subject of this work is the development of a methodology for conducting research on the concentrations of methane, carbon dioxide, oxygen and hydrogen in soils and soils in areas of upcoming construction.
The developed methodology, after its certification in accordance with GOST R 8.563-2009, can be used in areas of upcoming construction during engineering surveys, with subsequent adoption of design decisions based on the measurement results.
The purpose of this work is the development and experimental research in laboratory conditions of a methodology for examining a work site.
The main tasks are: analysis of archival and stock materials, normative and technical documentation, published works; development and production of sampling equipment; development of “Methods for measuring the volume fractions of carbon dioxide, methane, oxygen and hydrogen in soil air using portable gas analyzers” in accordance with Appendix B to GOST R 8.563-2009; setting up and conducting experimental studies in laboratory conditions.
Research results:
– the equipment necessary for sampling ground air: a sampling probe with an adjustable sampling depth and a storage pump that allows you to take a sample from depth, accumulate it in a chamber, transfer the sample to a gas analyzer, with the ability to “loop” the air flow and supply air to gas analyzers without a built-in pump;
– a draft methodology “Methodology for measuring the volume fractions of carbon dioxide, methane, oxygen and hydrogen in soil air using portable gas analyzers”;
– an experimental assessment of the method quality indicators (repeatability and intra-laboratory precision) in laboratory conditions;
– conclusions about the need to certify the methodology for compliance with GOST R 8.563-2009 using state standard samples (SSO) in the form of cylinders containing pure gases or gas mixtures with a known concentration of gases.

Ключевые слова:
газогеохимические исследования, грунтовый воздух, грунты, почва, метан, углекислый газ, кислород, водород, пробоотборное оборудование, газоанализатор, методика, отбор проб, анализ, инженерно-экологические изыскания, результат измерений, показатели точности.

Предметом настоящей работы является разработка методики проведения исследований концентрации метана, углекислого газа, кислорода и водорода в почвах и грунтах на участках предстоящей застройки.
Разрабатываемая методика после ее аттестации в соответствии с ГОСТ Р 8.563-2009 может применяться на участках предстоящей застройки при проведении инженерных изысканий, с последующим принятием проектных решений, основанных на результатах измерений.
Целью настоящей работы является разработка и экспериментальные исследования в лабораторных условиях методики обследования участка проведения работ.
Основными задачами, решаемыми при разработке методики, являются: анализ архивных и фондовых материалов, нормативно-технической документации, опубликованных работ; разработка и изготовление пробоотборного оборудования; разработка «Методики выполнения измерений объемных долей диоксида углерода, метана, кислорода и водорода в грунтовом воздухе с использованием портативных газоанализаторов» в соответствии с приложением «Б» к ГОСТ Р 8.563-2009; постановка и проведение экспериментальных исследований в лабораторных условиях.
Результаты исследования:
– разработано оборудование, необходимое для выполнения отбора проб грунтового воздуха: пробоотборный щуп с регулируемой глубиной отбора проб и насос-накопитель, позволяющий отбирать пробу с глубины, накапливать ее в камере, передавать пробу на газоанализатор, с возможностью «закольцовывания» потока воздуха и подачи воздуха на газоанализаторы не имеющие встроенного насоса;
– разработан проект методики «Методика выполнения измерений объемных долей диоксида углерода, метана, кислорода и водорода в грунтовом воздухе с использованием портативных газоанализаторов»;
– в лабораторных условиях проведена экспериментальная оценка показателей качества методики (повторяемость и внутрилабораторная прецизионность);
– сделаны выводы о необходимости проведения аттестации методики на соответствие ГОСТ Р 8.563-2009 с использованием государственных стандартных образцов (ГСО) в виде баллонов, содержащих чистые газы либо газовые смеси с известной концентрацией газов.

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Introduction

Air is an integral part of soils and subsoils. The composition of soil air can vary significantly. Specific soils, such as peat, bulk soils with a high content of household garbage, contain significant amounts of such gases as methane and carbon dioxide.

In industrially developed areas, the presence of saturated and unlimited, polycyclic hydrocarbon gases in soils is possible. The main factor which unites these soils is the high degree of explosion hazard during hot work, the entry of carbon dioxide into the basements of buildings can lead to consequences for human health [1–4].

The main natural source of biogas is soils. Most of the carbon dioxide (up to 2/3) in the soil is formed as a result of the activity of aerobic microorganisms, the rest is formed as a result of the activity of plant roots. Other sources of carbon dioxide delivery from the soil into the atmosphere are insignificant. The most part of the carbon dioxide formed in the soil enters the atmosphere [5–11].

Methane (CH4) in soils is formed as a result of the so-called methane fermentation: the decomposition of organic matter under anaerobic conditions.

In the oxygen-free environment when some organisms use the metabolic products of others bacteria form a complex trophic system. At the same time, bacteria have a narrow specialization in terms of the number of the used substances: some types of bacteria produce organic acids and hydrogen, while others reduce them to methane [5–11].

In 2021, SR 502.1325800.2021 ‘Engineering and Environmental Surveys for Construction’ was approved and put into operation [12, 13]. According to the clauses 5.18.4, 5.18.7 of this document the soil air sampling and analyses should be carried out following the certified methods and be accredited in the established order by laboratories.

According to the Register of certified measurement techniques (methods) (FGIS ‘Arshin’) [14, 15] presented on the website: https://fgis.gost.ru/fundmetrology/registry/16, at the present moment in the Russian Federation there is no single certified technique describing the rules of soil examination by gas component. This fact may lead to the possible errors in the design of buildings and structures which may result in the above-mentioned unfavourable consequences.

Analysis of Archival and Fund Materials, Regulatory and Technical Documentation and Published Works

Gas and geochemical studies are carried out in two stages: studies aimed at identification of gas chemical contamination of the territory and anomalous gas-generating areas in the survey area. Also it is carried out the studies directly at gas-generating sites, detailing of their boundaries and zoning of gas generation in depth. In the course of gas geochemical studies the following field work is carried out: various types of surface gas surveys (borehole, emission), accompanied by sampling of soil air and surface atmosphere air; borehole gas and geochemical studies with layer-by-layer sampling of soil air, soils, and groundwater [16].

The analysis of the published works has shown that measurements are carried out on a grid, with its step varying from 20 to 50 m, and samples are taken from a depth of 0.8 m and deeper [16–26]. As a rule, the authors do not provide sampling methods. At the same time, sampling is the most important stage in gas-geochemical studies, which is confirmed by our experimental studies: at sampling with a gas analyser directly from the borehole the readings of the device increase up to a certain value, after which the gas concentration sharply goes down, apparently, due to the inflow of atmospheric air into the well. Consequently, it was not possible to reliably determine the gas concentration in the soil air without specialised sampling equipment.

Equipment for taking soil air samples is not produced on the territory of the Russian Federation.

To analyze the collected sample we considered portable gas analyzers designed to measure carbon dioxide and methane. On the territory of the Russian Federation this equipment is presented in large quantities. We have considered devices which provide measurements in the range indicated in Table 1. 5.5. of SR 502.1325800.2021 [12].

Development of ‘Methodology for Performing Measurements of Carbon Dioxide, Methane, Oxygen and Hydrogen Volume Fractions in Soil Air by Portable Gas Analysers’

According to the Appendix “B” of State Standard 8.563–2009 “Measurement Techniques (Methods)” [27] the docent for the measurement procedure must contain:

1) the introductory par;
2) requirements for measurement accuracy idicators;
3) requirements for measuring instruments, auxillary devices, materials, reagents;
4) measurement method(s);
5) safety and environmental protection requirements;
6) requirements for the qualification of operators;
7) requirements for the codirions of measurements;
8) preparation for measurements, including requirements for sampling;
9) the procedure for performing measurements;
10) processing of measurement results;
11) registration of measurement results;
12) control of the accuracy of measurement results.

Introduction. The introductory part of the methodolog indicates the purpose of the technique and the scope of its application. Thus, this section contains information about which object is subject to research and where this technique is used. Obviously, the object of study in this case is ground air. The places of work are indicated in the text of the methodology in accordance with the clause 5.18. of SR.502.1325800.2021 [12], namely soil air:

–soil;
– bulk soils with an admixture of construction waste;
–dumps;
– landfills for solid municipal and industrial waste.
– natural organo-mineral and organic soils.

Also, in the introductory part of the methodology, the ranges of measurements and units of measurement are indicated.

Normative references. This section is not provided for by the requirements of Appendix “B” to State Standard 8.563-2009 [27], but it is presented in most measurement methods. This section contains documents establishing requirements for the object of research, requirements for equipment, requirements for safety and environmental protection, etc

Requirements for measurement accuracy indicators.

This section of the methodology establishes requirements for measurement accuracy indicators [28–30], namely:

1) recurrence index – the value of uncertainty or the ascribed characteristic of a random error of the results of a single analysis obtained according to the method under conditions of recurrence;

2) intralaboratory precision index – the value of uncertainty or the ascribed characteristic of random error of the analysis results obtained according to the method under conditions of intralaboratory precision;

3) correctness indicator – the value of the uncertainty of the displacement or the attributed characteristic of systematic error, obtained on the basis of the results of measurements from different laboratories;

4) accuracy indicator – the value of uncertainty or error characteristics established for any result of the analysis obtained in compliance with the requirements and rules of this methodology.

These indicators are evaluated during the certification of the methodology with the participation of several laboratories. At the initial stage of the development of the methodology, these indicators, as a rule, turn out to be unreliable.

Requirements for measuring instruments, auxiliary devices, materials, reagents. The section describes all the equipment necessary for carrying out work according to the method and its technical characteristics. The selection of equipment and materials is the most important stage in the development of a measurement technique, since its characteristics significantly affect the quality and reliability of the analysis results.

To implement the developed methodology, equipment is needed for:

– gathering samples of soil air;

– gas analytical equipment;

–materials and reagents used to implement the developed methodology.

Due to the lack of sampling equipment produced in the Russian Federation it was decided to independently develop a device for sampling soil air.

We have manufactured a flexible sampling probe with a plug installed on it to isolate the well. The sampling probe diagram is shown in Fig. 1.

For the purpose of lifting gas from the depth and extracting samples, we decided to independently develop a pump combined with a storage chamber. As a result, an electric pump was developed, combined with a storage chamber and the possibility of "looping" during sample analysis, which can significantly reduce the volume of soil air sample. The diagram of the storage pump is shown in Fig. 2.

Gas analytical equipment was selected in accordance with the requirements of SP 502.1325800.2021 "Engineering and Environmental Surveys for Construction" [12]. The measurement range of gas analyzers according to Table 5.5 of the above-mentioned document shall be:

– for methane and carbon dioxide – from less than 0.1 to more than 5.0 % vol. fraction;

– for hydrogen – from less than 0.1 to 4.0 % vol. fraction;

– for oxygen – from less than 18.0 %.

For measurements of carbon dioxide and methane gas analyser ‘MAG-6 P-K’ was used. Multi-component gas analyser ‘MAG-6 P-K’ is designed to determine the volume fraction of oxygen, carbon dioxide, methane, mass concentration of carbon monoxide, ammonia, hydrogen sulfide, sulfur dioxide, nitrogen dioxide [31]. The gas analyser can be used in various technological processes in industry, power engineering, agriculture and other branches of economy. The measurement range and the limits of the basic error of the gas analyser are presented in Table 1.

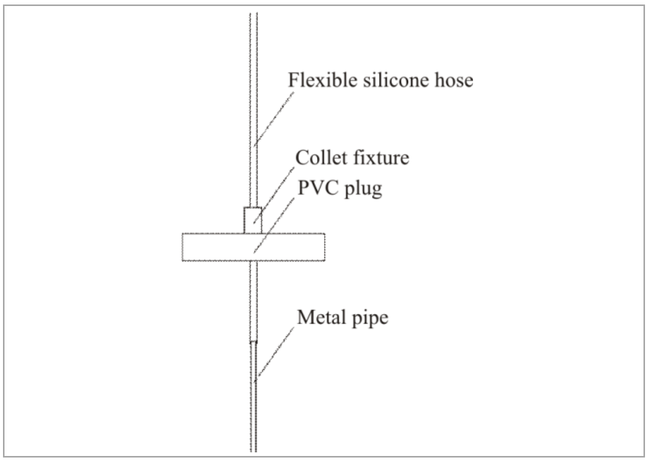

Fig. 1. Sampling Probe Diagram

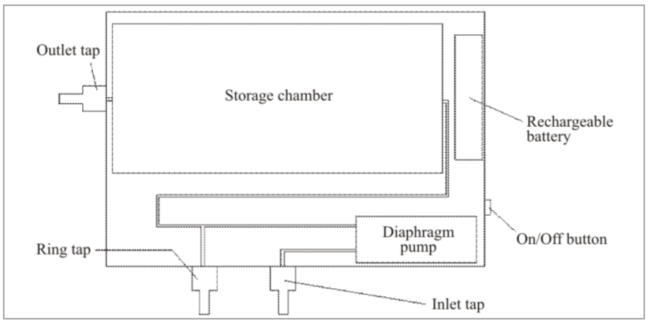

Fig. 2. Schematic diagram of the storage pump

Table 1

Ranges of carbon dioxide and methane measurement by gas analyser MAG-6 P-K

Defined component	Range of measurement, % vol,fr.	Limits of permissible basic error
Carbon dioxide	from 0.0 to 10.0	$\pm$ $(0.1 + 0.05 \cdot C_{BX})$ % vol.fr.
methane	from 0.0 to 2.0 from 2.0 to 5.0	$\pm$ 0.2 % vol.fr. $\pm$ 10 % rel.

Table 2

Ranges of methane, oxygen and hydrogen measurement by the Senson-M gas analyzer

Defined component	Range of measurement, % vol, fr.	Limits of permissible fundamental relative error, %
Oxygen	from 0.1 to 30.0	$\pm$ 15
Methane	from 0.001 to 1 from 1 to 100	$\pm$ 15 $\pm$ 5
Hydrogen	from 0.01 to 4.0	$\pm$ 10

For measurements of methane, oxygen and hydrogen we used the gas analyser ‘Senson-M’ [32]. The gas analyser ‘Senson-M’ is designed for monitoring atmospheric air and process media and has metrological characteristics presented in Table 2.

For the purpose of experimental verification of the possibility of carrying out studies chemical reagents were selected, using which it is possible to obtain sufficiently stable measurement results.

The following factors were evaluated in the selection of reagents:

1. Availability of reagents.
2. The possibility of carrying out the reaction under normal conditions.
3. Minimisation of the nomenclature of reagents.
4. Duration of the reaction.

Based on the above factors, the following chemical reactions were selected [33]:

– accumulation of carbon dioxide was carried out due to the interaction of sodium hydrogen carbonate and hydrochloric acid:

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 \uparrow + H_2O;$$

– The accumulation of methane occurred due to the reaction of hydrochloric acid and aluminum carbide:

$$Al_4C_3 + 12HCl \rightarrow 4AlCl_3 \downarrow + 3CH_4 \uparrow;$$

– The accumulation of oxygen occurred due to the reaction of decomposition of hydrogen peroxide:

$$2H_2O_2 \xrightarrow{MnO_2} H_2O + O_2 \uparrow;$$

– The accumulation of hydrogen occurred due to the reaction of sulfuric acid and zinc:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow.$$

Measurement method(s). This section specifies the methods used in the research. Due to the use of gas-analytical equipment, the method of measurements when carrying out work according to the developed methodology depends on the type of sensor installed in the instrument [31, 32].

Table 3 presents the applied methods of measurements.

Safety and environmental protection requirements. This section specifies the normative documents, compliance with which will lead to safe for human and environment fulfilment of the technique. In the process of working with gas analysers the requirements of safe work with chemical reagents according to State Standard 12.4.021 and State Standard 12.4.007, electrical safety according to State Standard 12.1.009, fire safety according to State Standard 12.1.004 [34–37] are fulfilled.

Requirements for qualification of operators. The requirements for education of operators, requirements for familiarisation with documents related to the safe conduct of work, technical documentation of equipment, etc. are specified.

Requirements for measurement conditions. This section specifies the requirements for environmental conditions, compliance with which will allow to qualitatively perform work on the measurement procedure.

Formation of carbon dioxide and methane depends to a great extent on environmental conditions.

The main source of methane and carbon dioxide in the soil air is anaerobic and aerobic bacteria. Optimal temperatures for microbiological activity are from 30 to 40 °C. At the same time, the range of bacterial activity by temperature is much wider. The activity of some microorganisms does not stop at sub-zero temperatures, and the amount of released gas is significantly reduced [6–8, 38, 39]. In addition, the gas output is significantly reduced when soils freeze.

It was not revealed significant influence of atmospheric pressure and relative air humidity on the activity of microorganisms. The soil is characterised by differences in relative air humidity and pressure depending on the variation of sampling depth.

The depth of groundwater table is also an important condition. This level is the lower boundary of the research.

By reference to the above mentioned the main conditions for measurements are:

– positive air temperature;

– absence of ground freezing;

Table 3

Methods of measurement

Name of substance	Measurement method
Carbon dioxide	Both electrochemical and optical are used
Methane	Both electrochemical and optical are used
Oxygen	Electrochemical
Hydrogen	Electrochemical

– requirements for atmospheric pressure and relative air humidity are set based on the technical characteristics of the equipment used for measurements.

Preparation for measurements, including requirements for sampling. In the process of preparation for the measurements it is necessary to check the performance of the equipment. The equipment check includes:

1. Control of the battery charge of the equipment being used.
2. Control of the tightness of the pump storage chamber.
3. Control for the damage to the gas tubes.
4. Control of gas analysers operability.

Sampling is carried out according to the following algorithm:

1. Layout of the network of measurement points:

– drawing the network of points on the map material;

– marking the position of the points directly at the place of measurement.

2. Borehole drilling (borehole drilling).

Boreholes are drilled to a depth of 0.8 m, boreholes are also drilled to greater depths.

3. Installation of sampling equipment.

Immediately after completion of the borehole (borehole drilling), a sampling probe must be placed in the borehole so that its plug completely covers the borehole mouth.

4. Borehole (well) pumping. After installation of the sampling probe it is necessary to connect the pump-storage device to it and pump the borehole (not less than 2 well volumes).

5. Sampling. After pumping the borehole (well) it is necessary to fill the storage chamber with soil air.

Measurement procedure. Measurements are performed by feeding the analysed sample into the gas analyser. To do this:

– connect the gas analyser to the 'Outlet' tap of the storage pump;

– after stabilisation of readings take data indicated on the display of the gas analyser.

Processing of measurement results. The result of measurements carried out according to the developed method is the arithmetic mean of the results of two parallel (two measurements on the 1st sample) determinations of the concentration of the desired gas X_1 and X_2 [28–30]:

$$X_{cp} = \frac{X_1 + X_2}{2},$$

for which the following condition is true:

$$|X_1 - X_2| \le r,$$

where r – the limit of repetition, the values of which are determined during the certification of the methodology. If $|X_1 - X_2| > r$, two more measurements are carried out, in accordance with the developed methodology the median of X_1 ... X_4 values is taken as the result X_m.

Registration of measurement results. This section specifies the requirements for the provision of

Table 4

Calculation of the required amount of reagents and the expected gas concentrations under the storage hood

Molar mass, g/mol		Used reagent		Expected amount of produced gas		Expected approximate volume of gas under the hood after the reaction, l	Expected approximate volume fraction of the desired gas after the reaction,% of vol. fraction
Of Used reagent	Of produced gas	Weight, g (volume, ml for hydrogen peroxide)	Weight, g (volume, ml for hydrogen peroxide)	Amount of substance, mol	Volume, l		
Sodium bicarbonate 84.007	Carbon dioxide 44.01	0.04	0.0005	0.0005	0.01	2.11	0.5
		0.40	0.0048	0.0048	0.11	2.21	4.9
		0.80	0.0095	0.0095	0.21	2.31	9.3
Aluminum carbide 143.96	Methane 16.04	0.005	0.00003	0.0001	0.002	2.102	0.11
		0.22	0.0015	0.005	0.10	2.20	4.7
		0.48	0.0033	0.010	0.22	2.32	9.7
Hydrogen peroxide 34.02	Oxygen 32	0	0	–	–	0.440	21.9
		5	0.009	0.004	0.101	0.541	25.5
		9	0.0162	0.008	0.181	0.621	28.9
Zinc 65.38	Hydrogen 2.016	The reaction of hydrogen production is not stable and depends on many factors (temperature, concentration of sulfuric acid, etc.). At the same time, it is possible to assess such an indicator as recurrence					

measurement results in the protocols. In the developed methodology, the results of the analysis in the documents providing for their use are in the form of:

$$X_{cp} \pm \Delta,$$

where X_{cp} – arithmetic mean (median) based on the results of two (four) measurements of the volume fraction of the sought gas; Δ – error characteristics.

Control of the accuracy of measurement results.

This section describes methods for operational control of measurements, as well as methods for monitoring the stability of measurement results.

The control methods are based on Part 6 of GOST R ISO 5725-2002 "Accuracy (correctness and precision) of measurement methods and results. The Use of Accuracy Values in Practice" [30].

Operational control is based on checking the acceptability of measurement results, the algorithm described above. The control of the stability of measurement results is based on the control of intra-laboratory precision, as well as the indicators of accuracy and correctness.

Experimental Research in Laboratory Conditions

At the first stage, we calculated the amount (mass and volume) of substances necessary to create a certain concentration of the desired gases, based on the volume of the storage hood of 2.1 liters. The results of calculation are presented in Table 4.

It should be mentioned that the above given concentrations are indicative and cannot be used to determine correctness and accuracy indicators. From a metrological point of view, it is necessary to use state reference materials (SRM) [40–45] to determine the indicators of correctness and accuracy. For the developed methodology it is proposed to use cylinders filled with pure gases, or cylinders with gas mixtures with a known concentration of gases.

At the second stage, we conducted a series of experiments to obtain the desired gases without using a device simulating the emission and accumulation of gases. During the experiments, the production of the desired gases was controlled by gas analyzers.

A silicone hose was attached to the inlet fittings of gas analyzers. The inlet of the hose was located above the utensils used for the experiment. The experiment was considered successful if the concentration of the desired gas was indicated on the display of the gas above its content in the atmospheric air. In order to simulate gas emissions, we proposed a scheme with the installation of a storage hood in a container filled with water. The storage hood was made by 3D printing. The installation scheme is shown in Fig. 3.

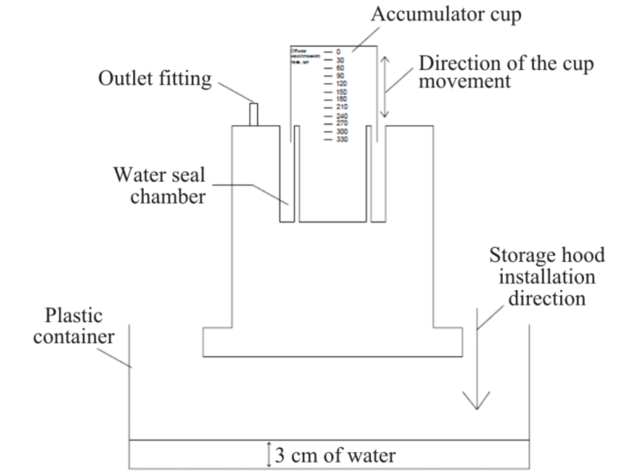

Fig. 3. Storage hood installation diagram

The container with liquid reagents was installed on a stand at least 3 cm high.

Dry reagents were added to the container only after the storage hood with the dismantled storage cup was installed. A perforated metal tube with a closed bottom was used to add dry reagents to the container.

At the end of the reaction, an air sample was taken from under the storage hood.

The selected sample was fed to a gas analyzer and two parallel measurements were carried out, the arithmetic mean of the two measurements was taken as the result.

At the end of the measurements, repeatability and intra-laboratory precision were assessed.

A total of 16 series of measurements were carried out for each substance, with the creation of three different concentrations of the desired gas (except for hydrogen), corresponding to those presented in Table 5. Statistical indicators were calculated in accordance with RMG 76-2014 "Internal quality control of the results of quantitative chemical analysis" and GOST R ISO 5725-6-2002 "Accuracy (correctness and precision) of measurement methods and results" [29, 30]. The results of statistical processing of the data obtained are presented in Table 5.

Table 5

Evaluation of repeatability, intra-laboratory precision Analytical Procedure

Indicator	Concentration	Repeatability rate, % vol. fr.	Reproducibility index, % vol. fr.
Carbon dioxide	0.50	0.11	0.19
	4.90	0.19	1.91
	9.30	0.11	1.07
Methane	0.11	0.03	0.03
	4.66	0.18	0.39
	9.30	0.27	1.27
Oxygen	21.9	0.08	0.10
	25.5	0.14	0.42
	28.9	0.15	0.54
Hydrogen*	–	6.79	–

N o t e : * – The standard deviation of recurrence in relative units (%) was estimated.

At the end of the experimental control the obtained data were analyzed. As a result, the following was noted:

1. It is impossible to fully determine the quality indicators of the methodology at this stage. Repeatability and intra-laboratory precision are calculated approximately.

2. The maximum recurrence rate was 0.27 % vol. fraction and the minimum is 0.03% vol. Fraction. These values are set for the laboratory for the purpose of further operational quality control of the performed measurements. In the process of testing the methodology the maximum repeatability values obtained for each indicator will be used.

3. The results of methane measurements were lower than estimated. This is due to the fact that at least 10 % of aluminum carbide did not react, in addition, the surface of the hydrochloric acid solution was covered with a film which did not allow the gas residues to escape.

Conclusion

Archival, stock and published materials related to the experience of conducting gas geochemical studies are analyzed. The equipment necessary for soil air sampling has been developed and manufactured: a sampling probe with adjustable sampling depth and a storage pump that allows you to take a sample from a depth, accumulate it in a chamber, transfer the sample to a gas analyzer with the ability to "loop" the air flow and supply air to gas analyzers that do not have a built-in pump.

The "Procedure for measuring the volume fractions of carbon dioxide, methane, oxygen and hydrogen in ground air using portable gas analyzers" has been developed in accordance with Appendix "B" of GOST R 8.563-2009 "Measurement Techniques (Methods)".

In laboratory conditions, experimental studies were carried out according to the developed methodology. As a result, there were determined the approximate indicators of repeatability and intralaboratory precision of the results of the analysis of the sought gases volume fraction.

It is required additional certification of the methodology in accordance with GOST R 8.563-2009 for further use in gas and geochemical studies in the areas of future development.

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