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Comparative Study of Gas-Analyzing Systems Designed for Continuous Monitoring of TPP Emissions

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Abstract—Determining the composition of combustion products is important in terms of both control of emissions into the atmosphere from thermal power plants and optimization of fuel combustion processes in electric power plants. For this purpose, the concentration of oxygen, carbon monoxide, nitrogen, and sulfur oxides in flue gases is monitored; in case of solid fuel combustion, fly ash concentration is monitored as well. According to the new nature conservation law in Russia, all large TPPs shall be equipped with continuous emission monitoring and measurement systems (CEMMS) into the atmosphere. In order to ensure the continuous monitoring of pollutant emissions, direct round-the-clock measurements are conducted with the use of either domestically produced or imported gas analyzers and analysis systems, the operation of which is based on various physicochemical methods and which can be generally used when introducing CEMMS. Depending on the type and purposes of measurement, various kinds of instruments having different features may be used. This article represents a comparative study of gas-analysis systems for measuring the content of polluting substances in exhaust gases based on various physical and physicochemical analysis methods. It lists basic characteristics of the methods commonly applied in the area of gas analysis. It is proven that, considering the necessity of the long-term, continuous operation of gas analyzers for monitoring and measurement of pollutant emissions into the atmosphere, as well as the requirements for reliability and independence from aggressive components and temperature of the gas flow, it is preferable to use optical gas analyzers for the aforementioned purposes. In order to reduce the costs of equipment comprising a CEMMS at a TPP and optimize the combustion processes, electrochemical and thermomagnetic gas analyzers may also be used.

Keywords: boilers, composition of combustion products, gas analyzer, continuous instrumental monitoring, analysis methods, hazardous substances

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During the past 3 years, new nature conservation laws and numerous ecology-oriented legal enactments have been actively developed and adopted in Russia. Their aim is to introduce the available cutting-edge technologies into the industrial and power generating industries. According to [1, 2], implementation of the state policy of nature conservation requires creation and development of a unified automated system of state environmental monitoring, which will have integrated systems of continuous monitoring of emissions from enterprises of the first category, in compliance with Federal Law no. 219-FZ [2–4].

Boilers at TPPs and boiler houses are the largest sources of air pollution emitting nitrogen oxides, sulfur oxides, carbon oxides, and ash into the atmosphere. This is why the primary goal of TPPs is to fit the entire production with systems of continuous monitoring of polluting emissions into the air space.

The composition of flue gases characterizes the process of organic fuel combustion in boilers relative to its efficiency and ecological cleanness and defines the condition of the gas circuit (leaked-in cold air) and reliability of individual heating surfaces (sulfide and sulfur corrosion). Thus, one of the most important tasks during the process of debugging and operation of boiler equipment is accurate determining of the composition of combustion products.

Continuous monitoring of polluting emissions into the atmosphere from TPPs is accomplished using direct gas-analytical measurement of the concentration of various components. The main structural components of a CEMMS at a TPP are gas analyzers and means of measuring the speed, flow, and physical parameters of flue gases: their temperature, pressure, and humidity. For these purposes, both domestic and imported gas analyzers and analysis systems can be

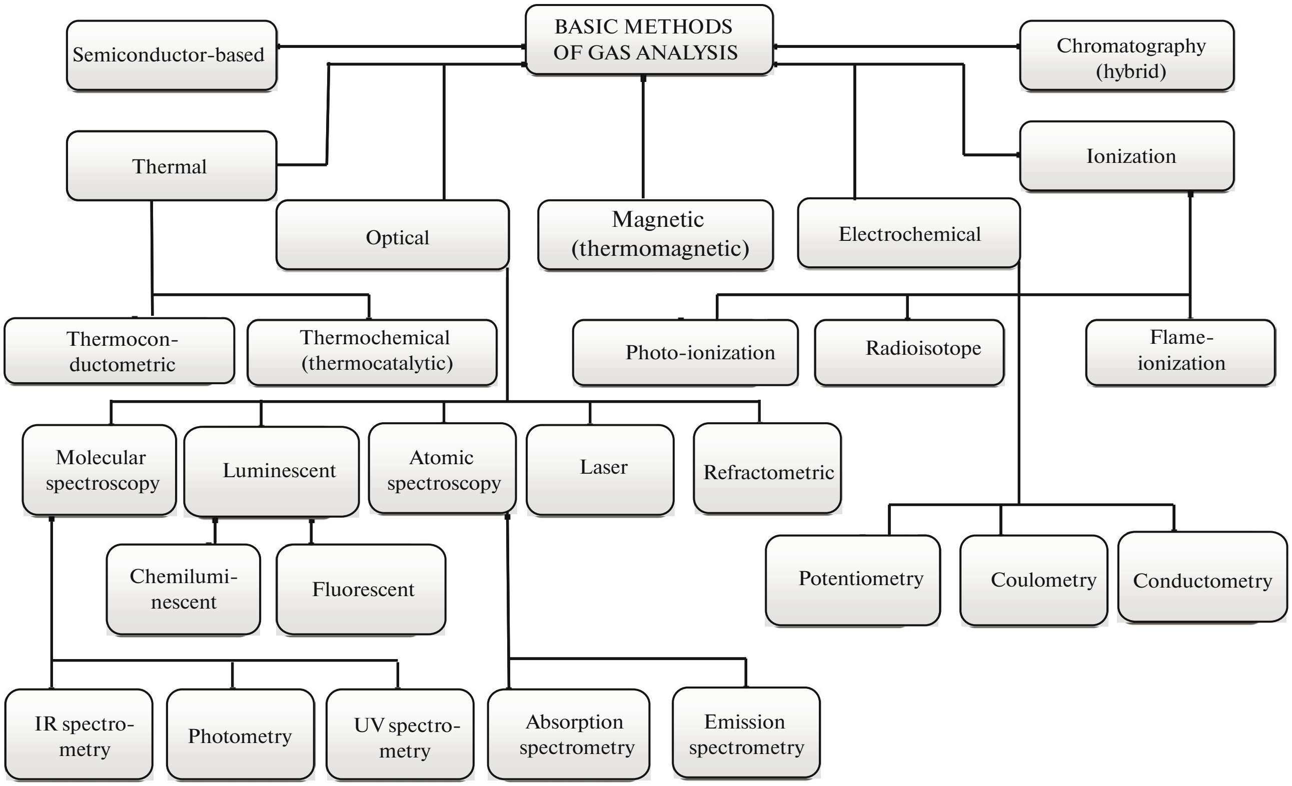

Fig. 1. Basic methods of gas analysis.

currently used. Their operation depends on various physicochemical factors, and they can be used during the process of installing a CEMMS at a TPP. Selection of specific gas analysis systems is associated with considerable difficulties—all of these systems have their own advantages and disadvantages; in order to choose a certain type of such equipment, one has to consider a multitude of different factors and parameters. Such systems can be sample-based and nonsample-based, rely on different analysis methods, measure a specific set of gas impurities, have notable differences in the operating conditions and service capabilities, costs, etc. Consequently, depending on the type and purposes of measurement, instruments of certain types and different features are used. For example, the operating mode of such an instrument can be periodic or continuous (from several hours to several months), its place of installation may be inside or outside of the gas circuit or on a boiler or chimney, it can be executed as stationary or mobile equipment, and the number of measured components and service capabilities may vary.

Below is the comparative study of gas analysis systems for measuring the content of pollutant substances in exhaust gases. The operation of these systems is based on various physical and physicochemical analysis methods: chromatographic, ionization, magnetic, semiconductor-based, electrochemical, thermal, and optical (Fig. 1).

CHROMATOGRAPHIC METHODS

Chromatographic methods of gas analysis are based on dividing a gas mixture through adsorption. For this purpose, the mixture, along with the carrier gas flow, which is fed to the partition column under pressure, flows through a motionless layer of porous adsorbent with an extended surface. Using the electric method, the content of each component emitted from the mixture is measured one by one (Fig. 2) [4].

Physicochemical properties of individual components (A, B, C) contained in the sample are different, so the speeds of their movement through the partition column vary. As the sample goes through the partition column, binary mixtures of each component with the carrier gas are formed. These mixtures are represented by individual bands separated from each other by zones of pure carrier gas. Physical properties of the gas flow leaving the partition column are registered by a detector. The detector allows for quick obtaining of information about the composition of moving binary mixtures and, therefore, about the composition of the whole analyzed mix-

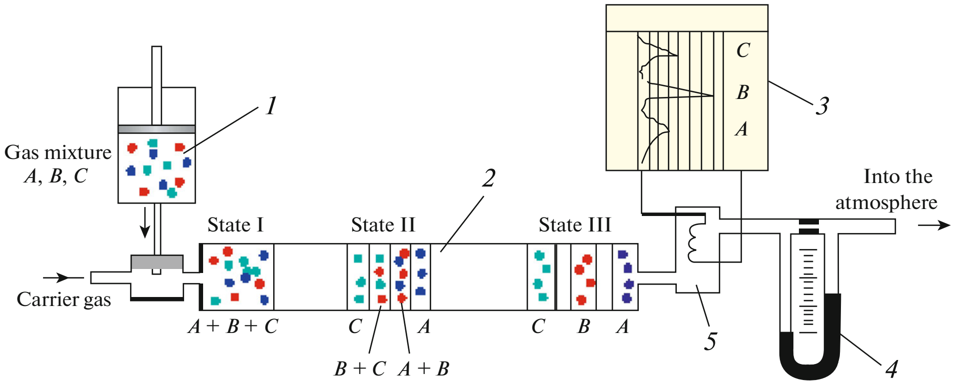

Fig. 2. Principal diagram of a chromatographic gas analyzer. *1*—Dosing unit; *2*—partition column; *3*—potentiometer; *4*—flow meter; *5*—detector.

ture. The outflow of components is recorded in the chromatograph as peaks relative to the base (zero) line, which reflects the detector's signal when pure carrier gas leaves the column (Fig. 3). A chromatogram is the source of qualitative and quantitative information about the analyzed mixture. The quantitative analysis is based on the change of peak heights. The dependence of a peak height on the concentration of an analyzed substance and the time when certain components leave the column are determined in keeping with preliminary calibration, which is carried out for specially prepared control mixtures. Preliminary calibration with the use of control mixtures requires significantly more labor efforts.

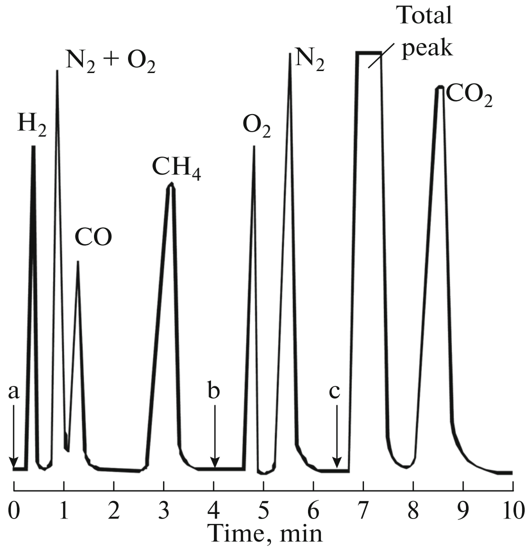

Fig. 3. Example of a chromatogram during analysis. (a, b, c) detector signals transmitted when pure carrier gas leaves the column.

Chromatography is a hybrid method [5] in which two processes are combined: a direct chromatographic partition and measurement of the concentration of analyzed substances in the transport phase on leaving the partition column of the chromatograph with the help of detectors, for which thermal conductivity detectors (catarometers), flame-photometric detectors, flame-ionization detectors, etc. are the most frequently used [6].

The method of gas chromatography has significant disadvantages: poor reproducibility of the results and the lack of appropriate detectors for a reliable quantitative determining of the concentration of nitrogen oxides in combustion products. Currently, due to intense labor efforts required to carry out measurements, chromatographs are very rarely used to determine the composition of combustion products at TPPs. They are usually used when preparing control gas mixtures (CGM), which are applied to calibrate gas analyzers of a sample-based type, and measuring the content of polycyclic aromatic hydrocarbons (PAHs) in laboratory conditions.

IONIZATION METHODS

Ionization methods are based on determining how electric conductivity of ionized gases depends on their composition. All gas analyzers of this type are comprised of an ionization chamber containing electrodes, to which a specific electric potential difference is supplied in the process of analyzing a gas mixture. Ionization gas analyzers include radioisotope analyzers (ionization by β-radiation), photoionization analyzers (ionization by UV-radiation) flame-ionization analyzers (ionization in hydrogen flame), etc. The basic method used for analyzing flue gases is the flame-ionization method. It can be used to determine the composition of hydrocarbons. This method is based on measuring changes in the ionization current obtained when organic substances enter the hydrogen flame. In the absence of organic impurities, the ionization current occurring in pure hydrogen flame is negligibly low. The molecules of organic substances entering the hydrogen flame are easily ionized, causing the flame's electric conductivity to grow rapidly. If such a flame is placed between electrodes to which a constant voltage is applied, ionization current appears between them, is enhanced, and supplied to the registering device.

The flame-ionization method is highly sensitive to organic substances, insensitive to the majority of impurities of nonorganic nature, and possesses a linear characteristic of conversion.

In order to measure the content of a certain substance in a mixture, a combination of several methods is usually used. For example, to determine the composition of methane in a mixture of hydrocarbons, a combination of flame-ionization and thermochemical (capillary chromatography) methods may be applied.

THERMAL METHODS OF GAS ANALYSIS

Thermal methods of gas analysis are based on the dependence of thermal characteristics of the analyzed mixture on its composition. Such methods of analysis include *thermoconductometric* and *thermochemical* methods.

In the case of a thermoconductometric analysis, the dependence of thermal conductivity of the analyzed gas mixture on the concentrations of gases to be determined is analyzed. Detectors used in this situation are not highly selective; they are used only for the analysis of binary mixtures or when thermal conductivity of the measured gas differs significantly from thermal conductivity of other gases.

Thermochemical analysis methods are based on measuring the thermal effect of reactions, accompanied by temperature changes of the sensitive element [7]. In this case, the thermal effect is directly proportional to the concentration of the measured component. Thermal methods also include *thermocatalytic analysis method*, which is based on determining the heat flow occurring during a catalytic reaction of the studied component with an auxiliary substance. In particular, gas analyzers based on the catalytic method are used for continuous monitoring of NO_x and CO in combustion products. In this case, a catalytic reaction of CO oxidation by oxygen in the sensor measuring the content of CO,

$$CO + \frac{1}{2}O_2 \rightarrow CO_2. \qquad (1)$$

In order to determine the concentration of nitrogen dioxides NO_x (NO + NO_x), catalytic reactions of interaction between the studied components with ammonia and oxygen are used:

$$2NO + \frac{1}{2}O_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O; \qquad (2)$$

$$2NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O + \frac{1}{2}O_2. \qquad (3)$$

The given reactions are exothermic (i.e., occur with heat emission), and, thus, the total amount of heat emitted as a result of these chemical reactions in the sensors is directly proportional to the concentrations of NO_x and CO in the studied sample.

The catalytic method allows carrying out measurements with a high level of accuracy (±5% when determining the concentration of NO_x and CO); however, it has a significant disadvantage—it requires the constant supply of ammonia to the sensor of NO_x.

The disadvantages of thermochemical methods are a limited lifespan and a decline in their sensitivity over time. Besides, the presence of certain gases and fumes, such as hydrogen sulfide or alkaline fumes, may "poison" the sensor.

MAGNETIC METHODS

Magnetic methods of gas analysis are based on changing physical properties of a gas mixture under the effect of a magnetic field [8]. Most of the time, gas analyzers that operate on the basis of this method of measurement are used to determine the concentration of oxygen, the paramagnetic susceptibility of which is higher by two orders of magnitude than other gases. The most commonly used gas analyzer to measure the concentration of oxygen is a *thermomagnetic* (*paramagnetic*) *analyzer*, the operation of which is based on thermomagnetic convection.

SEMICONDUCTOR-BASED METHODS

Semiconductor-based methods allow measuring the concentration of hydrogen, oxygen, carbon and nitrogen oxides, and other components by assessing the change in a semiconductor's resistance (e.g., a thin film of zinc oxide on a silicon plate) when interacting with a measured component of the gas mixture [9]. As a rule, the cost of semiconductor-based sensors is low and their design is quite simple; however, they do not have a sufficient selectivity, and the readings depend on the temperature and humidity of a gas medium.

ELECTROCHEMICAL METHODS

Electrochemical methods are based on the dependence of some physical parameter of the process occurring at an electrode or in the interelectrode space of the gas analysis system on the composition of gas entering this system [4]. The method resides in dividing the flow of the studied gas into separate components using membranes, which can allow only one component of the analyzed mixture at the electrolyte (Fig. 4). When implementing all the electrochemical methods, one of the two types of electrochemical sensors is used: either solid electrolyte sensors or electrochemical cells with liquid electrolyte.

Electrochemical methods may be implemented without a reaction at electrodes (*conductometry*) and with electrode reactions, either with no current (*potentiometry*) or with current (*coulometry*) [10].

The operation of conductometric analyzers is based on registering changes in the electric conductivity of a solution, which occur as a result of gas-mixture absorption. The conductometric method does not require sophisticated equipment—the instruments are highly sensitive, quick responding, and compact. This method allows determining the concentration of components in a rather broad range of values by altering the flow of electrolyte and the analyzed mixture. However, one has to keep in mind such disadvantages of this method as low selectivity and long time required to determine the parameters if small concentrations are measured. The given method is mostly used in gas analyzers to measure the concentration of O_2, CO, SO_2, H_2S, NH_3, $COCl_2$, etc.

The coulometric method resides in continuous automatic titration of the substance using a reagent generated electrochemically on one of electrodes in the reaction network. In this case, the current from the electrode reaction serves as a measure of concentration of the studied substance in the reaction medium. The coulometric method is characterized by a high sensitivity and a broad range of measurement values; it does not depend on the temperature and pressure in the gas medium. The main disadvantages of this method are low selectivity and the necessity to replace the electrolyte periodically.

Gas analyzers implementing the potentiometric method can be used to determine the concentration of CO_2, H_2S, HF, NH_3, etc. Potentiometric gas analyzers with a solid electrolyte, which is a ceramic plate of zirconium dioxide ZrO_2, stabilized with calcium monoxide CaO and a thin film of platinum applied on the surface, are used to measure the concentration of oxygen [9]. At a high temperature, the solid electrolyte starts conducting ions of O_2.

A high measurement error in instruments of such a type may be caused by hydrocarbons present in the analyzed mixture. Besides, in order for the solid electrolyte to work efficiently, high temperatures (starting from 500°C) must be maintained. In the meantime, potentiometers show a low response delay and allow carrying out measurements in quite a broad range of substance concentrations.

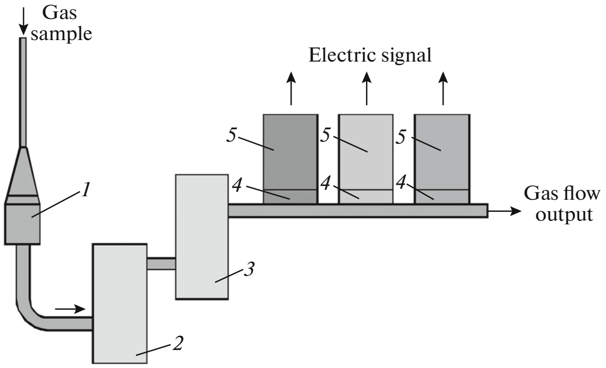

Fig. 4. Principal diagram of an electrochemical gas analyzer. *1*—Sampling probe; *2*—filter; *3*—condensate trap; *4*—membranes; *5*—electrochemical cells.

In general, using electrochemical gas analyzers, one can measure the concentration of several components at the same time, they are rather simple in terms of maintenance, and their cost is low—all these factors define their wide use for gas analysis on Russian sites [4].

One of the disadvantages of such gas analyzers is the possibility of "poisoning" a cell if the concentration of the studied component in the sample exceeds the allowed value (for example, in transition modes of boiler operation), which leads to errors in determining the concentrations in further measurements. This occurs especially frequently with sensors that determine the concentration of carbon dioxide, CO. In order to bring the cell back to normal operation after "poisoning," it must be purged with clean air for an extensive period of time.

OPTICAL METHODS

Optical methods for gas analysis are broken down into the following methods [11]:

(1) *Absorption* (or optical absorption) methods based on the ability of substances to differentially absorb the radiant energy in specific regions of the spectrum; absorption methods of analysis are divided into molecular and atomic-absorption spectroscopy methods depending on the substance composition.

(2) *Refractometric* methods based on the dependence of the refraction coefficient on the substance concentration.

(3) *Luminescent* methods based on the dependence of the substance's luminosity intensity during the absorption of outer energy on the composition of this substance (fluorescence, chemiluminescence).

Atomic spectroscopy is based on the analysis of the spectra of emitted (*emission spectroscopy*) or absorbed substances (*absorption spectroscopy*) after it transits to the atomic state as a result of an exterior high-energy impact.

In order to conduct the atomic-absorption analysis, the analyzed substance must be preliminarily transferred to the atomic state. For this purpose, the temperature of the substance must be equal to several thousands of degrees Celsius. At such a temperature, electrons switch to higher energy levels and emit a quantum of radiant energy hν. The required temperature levels can be achieved using a plasma burner, electric arc, or a high-voltage spark [11]. A spectrometer is used to analyze the spectrum.

The essence of *molecular-absorption* spectral analysis resides in measuring the weakening of light flux caused by the differential absorption by the analyzed gas. Depending on the wavelength of the used electromagnetic radiation, this method is classified in the following order:

(1) *ultraviolet* spectroscopy;

(2) *photocolorimetry* and *spectrophotometry* (visible range);

(3) *infrared* spectroscopy.

Molecular spectroscopy is the simplest method and can be carried out using a spectrophotometer, which measures the absorption of the light flux in the monochromatic light, or a photocolorimeter, which measures the intensity of color of the reaction products. The polychromatic light in photocolorimeters is formed by means of light filters.

Depending on the analyzed components, modern absorption gas analyzers usually use sources of ultraviolet (UV) and infrared (IR) radiation, which is why the methods are often called IR- and UV-spectrometric methods, and the instruments operating on their basis are called optoelectronic gas analyzers.

Currently, two types of optoelectronic gas analyzers are produced: the first one is formed as a system measuring the concentration of a component in a specially selected sample of gases (sample-based method of measurements); the second one has a measurement probe to be installed directly in the gas duct (nonsample-based method—in situ measurements), which allows (in the case where beams pass through the entire gas duct) obtaining a mean value of the function for the concentration across the entire section.

There are multiple options of execution for absorption gas analyzers: single-beam, multibeam, single-channel, multichannel, etc. Despite their high cost, optoelectronic systems are better tailored for hazardous emission monitoring systems due to their features (accuracy, components to determine, ability to operate for a long period of time without maintenance, etc.).

Using infrared gas analyzers, one can perform measurements with a high level of selectivity due to the uniqueness of molecular absorption spectra of various hazardous substances in the analyzed gas mixture. The optic-acoustic method of IR-spectroscopy is widely used; it registers an acoustic wave excited in the gas during a differential absorption of the radiation, modulated by the amplitude, in a resonant optoacoustic cell. The change in the acoustic spectrum of a wave is proportional to the specific absorbed power [12].

A GM series system manufactured by Sick AG (Germany) is an example of a nondispersion gas analyzer, which uses the method of absorption spectrometry in the IR region of the spectrum and correlation by gas filters; it is purposed for determining the concentration of carbon monoxide CO by a noncontact method [4] (Fig. 5).

The transmitter and receiver units are installed at flanges on opposite sides of the gas duct or chimney. The infrared radiation from the source situated in the transmitter unit passes through the studied gas covering a known distance to the receiver, at which a special IR filter is installed, emitting the required part of the spectrum, and then goes to a highly sensitive sensor.

In this situation, the analyzer measures the change in the light flux absorbed by CO molecules in the specific range of wavelengths and compares it with the intensity of the emitted flux. The concentration of CO is determined by the ratio of emitted and absorbed light fluxes. The measurement distance may reach 10 m, which allows installing this instrument crosswise of large gas ducts and chimneys and, thus, measure the mean value of the function for the concentration.

The GM system provides for a high accuracy of measurements, within ±2% of the upper value of the measurement range and (depending on the execution) can operate at a temperature of the studied gas medium up to 400°C. For the purposes of cooling and protecting the optical elements of the transmitter and receiver from pollution, they are to be constantly purged by atmospheric air.

Ultraviolet gas analyzers are less selective compared to IR gas analyzers, since polyatomic gases show a continuous absorption spectrum in the UV region. In this context, such gas analyzers allow for quite accurate measurements for N_2, O_2, CO_2, and water vapors due to the absence of absorption spectrum in the UV range for these substances. Figure 6 shows an example of an SM 8200 series ultraviolet gas analyzer manufactured by Monitor Labs (United States) and purposed for measuring NO and SO_2 in flue gases [13].

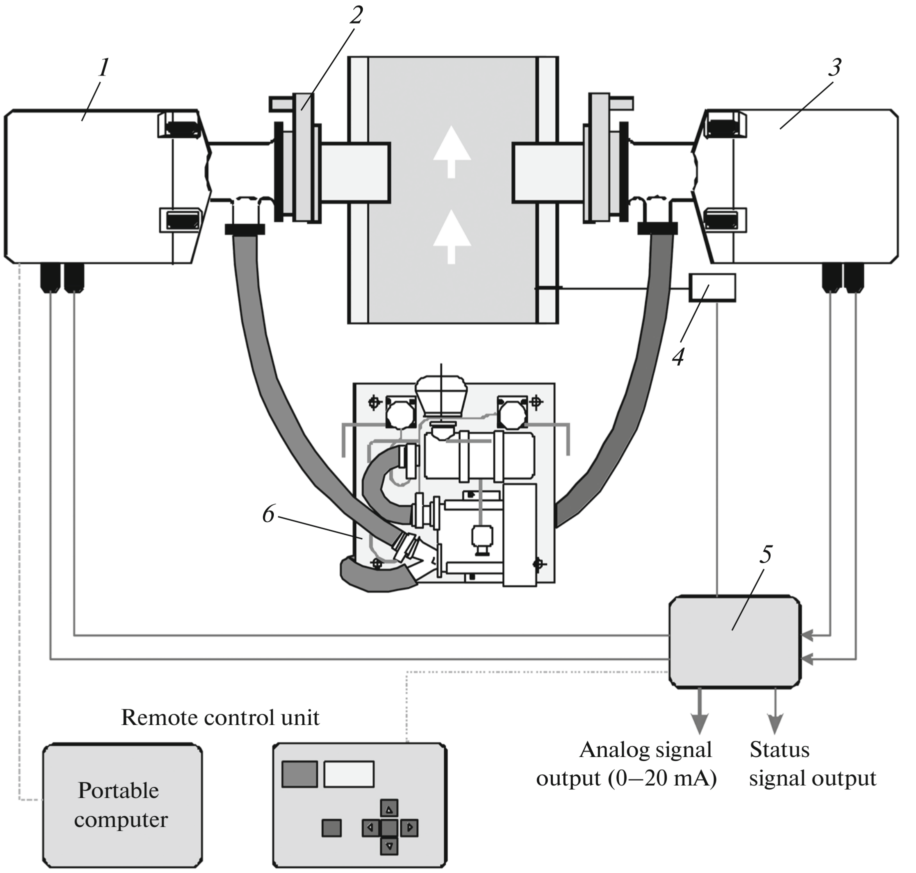

Fig. 5. Principal diagram of a nondispersion IR gas analyzer. *1*—Transmitter unit; *2*—protective closure; *3*—receiver unit; *4*—temperature sensor; *5*—connection node; *6*—purge device.

Ultraviolet radiation from the light source (deuterium arc lamp) passes through the measuring cell situated in the end of the probe. The reflector returns the altered beam to the transmitter/receiver unit where the monochromator distinguished two wavelengths typical for NO and SO_2 for transferring to the detector. The wavelength of each of the two monochromatic beams is modulated relatively to the time by a rotating quartz scanner. As a result, the light flux reaching the detector is modulated by two narrow spectral regions coinciding with the bands of NO and SO_2 absorption. This allows performing direct measurements of the second derivative of the signal and, thus, increasing the signal–noise ratio in comparison with direct absorption methods. The emitted spectra for NO and SO_2 pass through the septum one by one. In order to increase the accuracy of measurements, a temperature stabilization of the optical system is introduced. The measuring cell is made from porous material, which filters the combustion products and protects optical elements from pollution. The cell is periodically cleaned by purging it with compressed air. Similarly, the measuring system can be valuated and calibrated by purging with control gas mixtures. The relative measurement error for SM 8200 is 5%.

Laser methods are usually classified as a separate group; their potential of application is associated with features of laser radiation, such as monochromaticity, directionality, and high energy density. With this method, the absorption is analyzed not along the entire band but at a certain absorption band, which

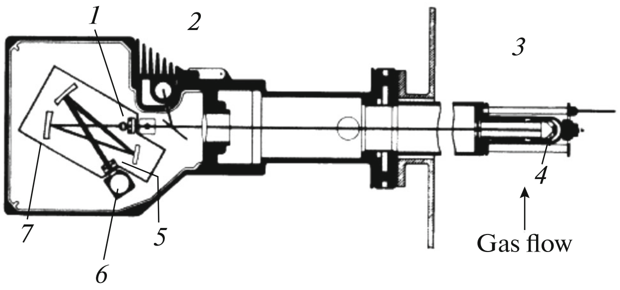

Fig. 6. Principal diagram of an optical gas analyzer. *1*—Scanner; *2*—light source; *3*—measuring cell; *4*—reflector; *5*—septum; *6*—detector; *7*—monochromator.

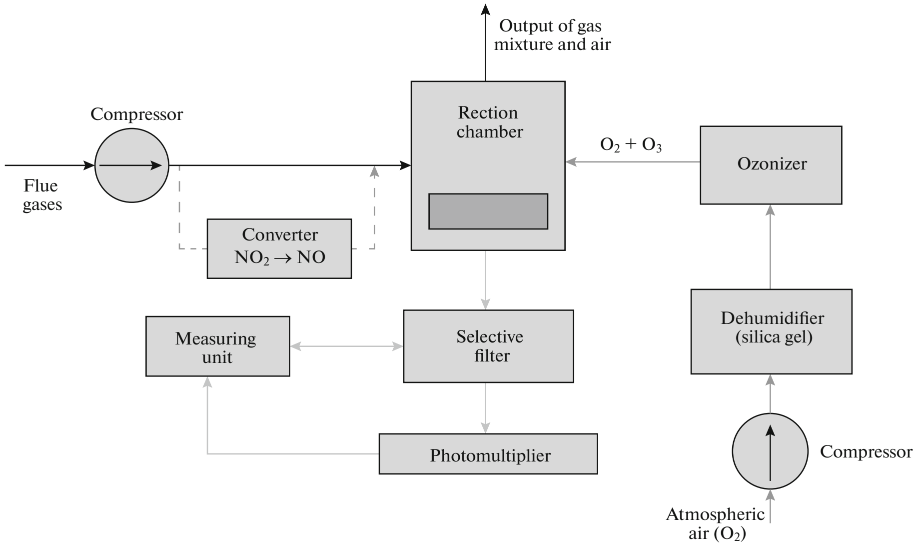

Fig. 7. Principal diagram of a chemiluminescent gas analyzer.

notably raises the selectivity and sensitivity of gas analysis. The concept of laser monitoring is as follows: passing through a gas medium, the impulse of laser radiation interacts with it and leaves a footprint of light, whose diffusion can be described by a certain law, or the loss of energy due to its absorption, or energy absorbed by atoms and molecules and immediately emitted light energy, or frequency of radiation based on the effect of Raman effect.

Laser methods require sophisticated and expensive equipment. Most of the time, they are applied to analyze pollution of the atmospheric air in large spaces. Currently, according to the requirements of Russian nature conservation laws for regions of high industrial impact on the environment, it is planned to carry out the industrial monitoring of atmospheric air quality in the environment, which may require laser methods of monitoring.

Luminescent methods are based on two processes: *chemiluminescence* and *fluorescence.*

Chemiluminescent gas analyzers measure the intensity of luminescence that occurs during a chemical reaction between the studied components and a reagent. The chemical reaction used to determine the concentration is specific to each of the studied substances, which is why the given method must be very sensitive. In the meantime, the presence of other components in the gas mixture may introduce an error in the measurement results [9].

This method is one of the most widely used to monitor nitrogen oxides and is based on the property of NO to emit a quantum of light on interaction with ozone. The reaction of NO oxidation to NO_2 is accompanied by luminescent glow within the range 600–3000 nm of wavelengths, and the maximum value of glow is 1200 nm.

In chemiluminescent gas analyzers, NO reacting with excessive ozone O_3, turns into NO_2, wherein a part of NO_2 molecules is in an excited state:

$$NO + O_3 \rightarrow NO_2^* + O_2. \tag{4}$$

The molecules transitioning to the basis state emit energy—chemiluminescent glow, the intensity of which is proportional to the concentration of nitrogen monoxide NO in the flow of incoming gas:

$$NO_2^* \rightarrow NO_2 + h\nu\uparrow. \tag{5}$$

The chemiluminescent glow is emitted by optic filters, enhanced by a photomultiplier, and goes to the registering instrument (Fig. 7). This method can be also used to determine the concentration of NO_2, restoring it to NO by ammonia NH_3 using special catalysts. The oxidation reaction occurs at a temperature of 300–600°C. If excessive NH_3 is present in the sample, it also oxidizes and turns into NO, which adds error in measuring the concentration of NO_x.

The given method is outstanding due to its high selectivity and accuracy of measurements and was developed especially for monitoring the concentration of nitrogen oxide in exhaust gases from various industrial facilities and in atmospheric air. Chemiluminescent gas analyzers allow performing continuous, highly accurate measurements during an extensive period of time and can be widely used both to control and debug furnace conditions and to perform monitoring.

Table 1. Comparative analysis data on sample-based and nonsample-based gas analyzers

Parameter	Gas analyzers	
	sample-based	nonsample-based
Advantages	Possibility of maintenance for several sampling units at the same time	Best metrology characteristics. Are not susceptible to factors that may act upon the transferred sample
Disadvantages	Additional error associated with a change in the concentration of components and the composition of the transferred sample. A hazard of gathering solid particles, moisture, and aggressive condensed acids in the system	Temperature restrictions (not higher than 400–450°C). High cost. Complicated maintenance and calibration. Influence of increased vibration and climatic factors on measurement results
Area of application	Monitoring the modes of fuel combustion	Continuous automatic monitoring of hazardous emissions into the atmosphere

All instruments that use the chemiluminescent method must be periodically calibrated using specially prepared control mixtures. A relative measurement error in determining the concentration of nitrogen oxide is ±5% of the measured value.

Fluorescent gas analyzers measure the change in the intensity of luminescence under the influence of ultraviolet radiation on the gas mixture. Such gas analyzers are characterized by high sensitivity and selectivity.

In order to measure the concentration of suspended substances (dust) in emissions, optical gas analyzers are also used, which are usually based on molecular spectroscopy and luminescent methods. Choosing this type of gas analyzer is associated with the dependence of the size and shape of dust particles on their optical properties.

In general, optical gas analyzers possess high sensitivity, selectivity, and resistance to overloads; they are durable, highly reliable, and are not affected by corrosion media. Electromagnetic and radiation fields do not influence measurements with such gas analyzers.

Stationary gas analysis systems featuring high accuracy and reliability and allowing for long-term measurements and continuous monitoring the composition of combustion products or changes required to control technological processes are the most expensive instruments. As a rule, manufacturers produce a whole complex of instruments that provide for measurement of all the necessary components. Stationary systems usually have a high level of integration with computing devices and various kinds of software. By the method of gas analysis, such systems can be broken down into sample-based and nonsample-based. They use various methods of gas analysis and have significant differences in operating conditions, service capabilities, cost, etc. The comparative analysis data for sample-based and nonsample-based gas analyzers are given in Table 1.

Sample-based systems comprise devices for taking, preparing, and transferring samples to the gas analyzer. They allow sampling combustion products for analysis from a zone of high temperatures, which is often required in controlling technological processes. They are also used for arbitrary measurements and are present in monitoring systems. As a rule, stationary sample-based gas analysis systems are built on a modular basis; i.e., depending on a defined purpose, they are fitted with various gas analyzers, sample preparation units, equipment for control and calibration, etc. and combine a single computerized gas analysis complex.

When special toggle switches are installed, one gas analysis system may be used to determine the composition of flue gases from several points of sampling.

The operation of nonsample-based systems resides in IR and UV spectrometry methods (optoelectronic methods). Electrochemical cells with a solid electrolyte are also used—they are placed directly at the flow of flue gases. Measuring elements and sensors of these systems have limitations by the temperature of gas flow, which normally must not exceed 400°C.

Although the use of such systems is limited at the place of their installation by the temperature of combustion products, their significant advantages are not only the absence of sampling and sample preparation systems but also the possibility to install such systems in hard-to-reach places and the extensive period of autonomous operation. Thus, they are usually used in systems of monitoring and control of technological

Table 2. Comparative analysis of gas monitoring methods

Methods of gas analysis	Basic principle	Advantages	Disadvantages	Area of application	Gas analyzer examples (manufacturer)
Chromatography (hybrid method)	Numerous separation of components between two phases, carrier gas and solid absorbent; measuring the concentration of emitted components	Versatility. High accuracy	Intense labor efforts. Insufficient reproducibility of the results	Laboratory analysis; periodical and continuous industrial monitoring of combustible (CO, CH_4, etc.) and noncombustible (CO_2, NO, NO_2, etc.) gases	Chromatograph KhROMAT-900 (SPO Analitpribor, Russia); chromatograph MAG, model KS 50.360-000 (OOO NTF BAKS, Russia)
Thermal methods					
Thermoconductometric method	Analysis of the dependence of thermal conductivity of the analyzed gas mixture on the concentrations of gases to be determined	Broad range of measurements Ability to work with chemically inert components	Low selectivity. Ability to analyze basically two-component mixtures. Susceptibility to electromagnetic fields	Continuous monitoring of N_2, H_2, NH_3, SO_2, CO_2, and other components in technological processes	Gas analyzer GAMMA-100 (SPO Analitpribor, Russia); gas analyzer DISK-TK (ZAO ENAL, Russia)
Thermochemical (thermocatalytic) method	Measuring the thermal effect of reactions, which are accompanied by temperature changes of the sensitive element	Quick response. Broad range of substances to control. Low cost	Low resistance to overloads. Short lifespan (2–3 years). Low selectivity	Monitoring exhaust gases for optimizing combustion processes. Annunciators of combustible gases and fumes in the air of the operating zone	Gas analyzer AKVT-03 (SPO Analitpribor, Russia); Gas annunciator IGS-98 (NPP Delta, Russia)
Ionization methods (flame-ionization method)	Measuring the ionization current that occurs in the process of combustion of the analyzed gas mixture in the hydrogen flame	High sensitivity. High selectivity in relation to nonorganic impurities	Low selectivity in relation to organic impurities	Controlling the total concentration of hydrocarbons in the atmosphere. Controlling gas leaks in pipelines	Gas analyzer GAMMA-ET (OOO ETEK, Russia); gas analyzer APXA-370 (HORIBA Ltd, Japan)
Magnetic methods (thermomagnetic method)	Principle of thermomagnetic convection	High accuracy	Can only be used for measuring O_2	All kinds of measurements for oxygen concentration	Gas analyzer DAM (SPO Analitpribor, Russia); gas analyzer GMS 80 (SICK AG, Germany)
Semiconductor-based methods	Measuring the concentration of a gas mixture component by assessing the change in a semiconductor's resistance during interaction with this component	Low cost. Simple design	Dependence on the temperature and humidity of the surrounding environment. Insufficient selectivity	Measuring the content of O_2, CO (incomplete combustion), NO, and other substances in exhaust gases in order to optimize combustion processes. Measuring H_2S and NH_3 in the air of the operating zone	Gas analyzer SIGMA-03.DP (OOO Prompribor-R, Russia); gas analyzer COMTEC 6000 (ENOTEC GmbH, Germany)

Table 2. (Contd.)

Methods of gas analysis	Basic principle	Advantages	Disadvantages	Area of application	Gas analyzer examples (manufacturer)
Electrochemical methods (potentiometric, conductometric, and coulometric methods)	Determining the dependence of a physical parameter of the gas analysis system, which is measured as a result of the process occurring at an electrode or in the interelectrode space on the composition of gas entering it	Possibility of simultaneous measuring of several components. Low cost. Compactness. Simple maintenance	Possibility of "poisoning" the sensor in case of exceeding the maximum concentration of the substance allowed for measuring. Low selectivity. Long time required to acquire readings in case of low concentrations. Rather short lifespan (2–3 years)	All kinds of measurements for SO_2, O_2, NO, NO_2, CO, CO_2, H_2S, NH_3, O_3, and Cl_2	Gas analyzers KADG (ZAO NPF UranSPb, Russia); gas analyzer PEM-4M (Promanalitpribor, Russia)
Optical methods					
Molecular absorption spectroscopy (photocolorimetry, IR and UV spectroscopy, and laser spectroscopy)	Measuring the intensity of differential absorption of the studied light spectrum by gas and fume molecules	High selectivity. Resistance to overloads. Insusceptibility to electromagnetic fields and aggressive media. Ability to transmit the analytical signal across large distances without distortion. Extensive lifespan. Reliability	High cost. Difficult maintenance when installed at great heights	All kinds of measurements for SO_2, NO, NO_2, N_2O, CO, CO_2, CH_4, NH_3, suspended substances, etc.	Gas analyzer PEM-2M (Promanalitpribor, Russia) gas analyzers GM 32, GM 35, GM 700 (SICK AG, Germany)
Luminescent methods	Determining the dependence of the substance's luminosity intensity during the absorption of outer energy on the composition of this substance	High sensitivity. High resistance to overloads. Insusceptibility to electromagnetic fields. Ability to transmit the analytical signal across large distances without distortion. Extensive lifespan. Reliability	Necessity to preliminarily remove water vapors, which influence the measurement results	Continuous automatic monitoring of NO_x concentration in the air of the operation zone and in atmospheric air	Gas analyzer R-310A (ZAO OPTEK, Russia); gas analyzer ET-909 (OOO ETEK, Russia); gas analyzer VA-3000 (HORIBA Ltd, Japan)

processes. At the same time, nonsample-based systems are more expensive.

Table 2 lists basic characteristics of the methods commonly used in the area of gas analysis. As is shown in the table, the majority of methods enable measuring the required amount of substances; however, only a part of the listed methods can be applied in compliance with the CEMMS purposes at TPPs and allow covering the necessary ranges of measuring the concentration of substances. Such methods, which could be fully suitable for monitoring pollutant emissions, may include chromatography, magnetic, electrochemical, and optical methods (Table 3). Besides, in order to optimize the process of combustion, thermal, ionization, and semiconductor-based methods can also be applied (Table 4).

Considering the necessity of the long-term, continuous operation of gas analyzers for monitoring and measurement of hazardous emissions into the atmosphere, as well as the requirements to reliability and independence from aggressive components and temperature of the gas flow, it is preferable to use optical gas analyzers for the these purposes. In order to reduce the costs of equipment, which is part of a CEMMS at

Table 3. Technical parameters of gas analysis systems intended to monitor pollutants emitted as a result of the use of various types of fuel

Parameter	Natural gas	Solid fuel	Liquid fuel
Measured substances	CO, NO, NO_2 (or NO_x)	CO, NO, NO_2 (or NO_x), SO_2, ash	CO, NO, NO_2 (or NO_x), SO_2
Range of measurement:			
CO, mg/m^3:	0–300	0–400	0–300
NO and NO_x, mg/m^3	40–400	200–800 (for bituminous coal) 200–500 (for ligneous coal)	100–500
NO_2, mg/m^3	0–50	0–50	0–50
O_2, %	0–21	0–21	0–21
SO_2, mg/m^3	–	0–1500	0–1500
Ash, mg/m^3	–	50–300	–
Measurement error, %			
CO, NO_x, NO, NO_2, SO_2	±10		
ash (solid particles)	±25		
Maximum allowable temperature of gases, °C	200		
Compliance with best available technologies	Nonsample-based systems, optical methods		

Table 4. Technical parameters of gas analysis systems intended to optimize the processes of combustion of various types of fuel

Parameter	Natural gas	Solid fuel	Liquid fuel
Measured substances	CO, NO_x (or NO), O_2		
Ranges of measurement:			
CO, mg/m^3	0–500	0–500	0–500
NO_x, mg/m^3	50–400	200–800 (for bituminous coal) 200–500 (for ligneous coal)	100–500
O_2, %	0–15	0–21	0–21
Measurement error, %	±10		
Maximum allowable temperature of gases, °C	600		
Compliance with best available technologies	Sample-based systems; thermal, ionization, optical, and paramagnetic methods; in order to reduce the cost of equipment, application of electrochemical methods is allowed		

a TPP and that is intended for optimizing the combustion processes, electrochemical and thermomagnetic gas analyzers may also be used.

CONCLUSIONS

(1) The analysis of modern gas analysis methods showed that most of them generally ensure measuring the content of polluting substances from the list of required substances to monitor. However, the area of their application and covered ranges of measurement are not always consistent with the purposes and goals of a CEMMS at a TPP.

(2) In order to monitor pollutant emissions, chromatography, magnetic, electrochemical, and optical methods can be used.

(3) The most promising gas analyzers are optical ones; if reducing the cost of gas analyzing equipment

is necessary, the use of electromagnetic and electrochemical gas analyzers is possible. In order to monitor and optimize the process of combustion, thermal, ionization, and semiconductor-based methods can also be applied.

(4) In order to measure the concentration of suspended substances (dust) in emissions, it is recommended to use optical gas analyzers, the operation of which is based on molecular spectroscopy and luminescent methods.

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