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REVIEWS

Optical Multisensor Systems in Analytical Spectroscopy

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Abstract—A review of works in developing optical multisensor systems, a new class of specialized spectroscopic analyzers, is presented. The development and use of such systems for analyzing food products, monitoring of pharmaceutical production processes, in biotechnology, medical diagnostics, and ecology are considered on practical examples.

Keywords: optical spectroscopy, multisensor systems, chemometrics, food analysis, drug analysis, biotechnology, medical diagnostics, ecology

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The demand for chemical analysis is constantly growing in the modern world. This is primarily due to the increasingly stringent standards for product quality, production efficiency [1], and environmental safety. Analytical control deeper penetrates into production activities [2] and daily life [3]. One of the results of this process is the development of instrumental analytics. Modern analytical tasks require the creation of new devices and new methodology. Analysis on the production line or in the field without constant sampling [4] is more often required, and its results should be issued almost instantly, up to tens of measurements per second. Conventional laboratory analysis does not meet these requirements; new approaches are needed, such as specialization, interim analysis, and screening [5].

Optical spectroscopy is considered one of the main instrumental methods in analyzing multicomponent samples [6], which combines information content, nondestructiveness, and high adaptability. The rapid development of optical analysis is based mainly on the achievements of optics and photonics, like new detectors, light sources, light-conducting materials, and the improvement of electronics and methods for analyzing multidimensional data (chemometrics) [7].

In the last two decades, optical spectroscopy has begun to develop into specialized analyzers, initially created for a specific practical problem. These devices, which occupy an intermediate position between photometric sensors and laboratory spectrometers, are called optical multisensor systems (OMSs) [8], operating in various wavelength regions and designed for determining both individual substances and generalized chemical parameters. A few sensor channels are usually used, generally wide, for example, recording the total absorbance in selected spectral ranges. The use of chemometrics compensates the expected lack of selectivity. Methods of mathematical simulation are used both for data analysis and building predictive models and at the stage of creating a multisensor system, in particular, for designing an experiment and optimizing system channels during the development [3, 8].

This review examines the state-of-the-art optical spectroscopy and considers trends in its development towards creating OMSs. The definition of an optical multisensor system is introduced, and its main differences from conventional laboratory spectroscopy are shown. Examples of current OMS and research in this field are given, illustrating their enormous potential in solving various analytical problems.

MODERN DIRECTIONS OF DEVELOPMENT IN OPTICAL SPECTROSCOPY

Laboratory spectroscopy. Optical spectroscopy has historically been focused on laboratory measurements of precollected samples of various compositions. It has evolved as a universal analytical solution, so it was not fully adapted to modern analytical tasks, such as rapid analysis, process monitoring, and field research. The limited bandwidth of laboratory spectroscopy does not meet the continuously growing number of samples and objects requiring analysis [5].

The development of analytical spectroscopy has followed the technical improvement of instruments. The versatility and efficiency of an optical analyzer for quantitative and qualitative analysis are still associated with the expansion of spectral and dynamic ranges, improved resolution, and the automation of measurements. These and other qualities lead to the constant technical complication of spectrometers, increasing

their dimensions and cost. The structural complexity of mass-produced spectrometers is also associated with their standardization, ensuring the identity of data for the same samples. Unsurprisingly, spectroscopy is strongly associated with high-tech laboratory analysis, stationary equipment, and highly trained personnel. Centralized sampling approach can no longer cope with the growing volumes of samples and controlled parameters in various fields of activity, such as quality control of manufactured products, environmental monitoring, and medicine, and with the emergence of new fields and forms of analysis, that is, field and rapid analysis. As a response to these challenges, it was proposed to use a fundamentally new—multisensory—approach to optical spectral analysis [8], which has been actively developing in the last decade, including through the efforts of Russian scientists.

Decentralization and personalization of analysis. The monopoly of centralized laboratory analysis has been seriously shaken by the development of process analytical technology (PAT) and its consolidation in the regulations of the US Food and Drug Administration (FDA) in 2004 [1, 2]. Optical spectroscopy is the flagship method of PAT, with a process analyzer capable of performing continuous online measurements at its core. In this case, the result of an analysis is received by the local operator of the process rather than by an analytical chemist, without sending samples to the laboratory [9].

The tendency that has arisen in production towards the decentralization of analysis penetrates other fields of activity. Optical spectroscopy plays an essential role in the analysis of food, pharmaceutical, and medical samples. However, along with conventional applications, new ones appear, the social and economic need for which can be significantly lower. In other words, chemical analysis is beginning to be applied where it was not used before. This tendency is still at the very beginning of its development. Many possible tasks and applications have not yet been covered by the currently dominant methodology of chemical analysis [5].

Today, there is a growing need in the analysis of various generalized indicators of chemical composition, such as nutritional value [10] and mineralization [11] of agricultural products, authenticity and the presence of counterfeits in food [12, 13] and pharmaceutical production [14], and many others [15]. Optical analysis is beginning to be applied in new fields, such as diagnostics of biological tissue [16], sorting of materials [17], remote analysis using spectral images [18], etc.

The range of test samples expands due to the reduction in the cost of analysis, and the miniaturization and autonomy of devices. Examples of such devices are already available in the field of personal diagnostics, for example, optical pulse oximeters [19]. Work is underway to create and improve individual noninvasive glucometers [20]. In general, we can state a gradual transition of chemical analysis from the expert field to widespread and, in the future, to mass use.

The widespread availability of mobile phones and other devices equipped with a powerful processor, an optical detector, and a built-in camera facilitates analysis personalization. The prototype of a miniature urine creatinine analyzer created at St. Petersburg State University [21] is a convincing illustration of implementing an optical analyzer based on a smartphone. There are other examples of such devices, which were reviewed in [22].

The industrial production of personal analyzers is associated with an inevitable trade-off between price and quality. The development of scientific approaches to multisensor systems and data analysis obtained with their help is becoming increasingly important.

Materials, technical solutions, and research methods. The current status of optical spectroscopy is directly related to creating new fiber-optic materials, probes, light sources, and detectors and the development of methods for obtaining and processing data. Some examples are given below.

The Lighthouse Probe™ (LHP) immersion probe was designed for continuous spectral analysis of processes in the ultraviolet (UV), visible (VIS), and near-infrared (NIR) regions [23]. It is made of pharmaceutical and food-grade certified materials and records online diffuse reflectance spectra of powders and bulk materials such as granulates and pellets[1], including in their manufacturing and processing. The high information content of the spectra is ensured by a full (360°) view of the medium through seven optical windows located around the circumference of the probe. Each of the windows simultaneously serves to irradiate the medium and receive diffusely reflected light transmitted to a remote detector through a fiber optic cable. The LHP automatic cleaning system periodically removes adhered material (Fig. 1).

The working spectral region of optical fibers is expanding due to new light-guiding materials. Modern optical fibers cover almost the entire optical range, including the conventionally "blind" infrared regions. Chalcogenide IR (CIR) fibers invented in Russia, based on arsenic sulfide (As_2S_3), have high transmission in the range of 1.5–6 μm [24], and oxygen-free polycrystalline IR (PIR) fibers from solid solutions of silver halides $AgCl_{1-x}Br_x$ ($0 < x < 1$) [25] have the required transparency in the area of "fingerprints" (3–18 μm), which contains chemical information from many functional groups.

Thanks to new fiber optic materials, attenuated total reflection (ATR) IR probes are increasingly used in PAT to analyze various media. The optical path of

[1] Pellets are a pharmaceutical form, spherical granules with a diameter of about 1 mm, commonly used to fill medicinal capsules.

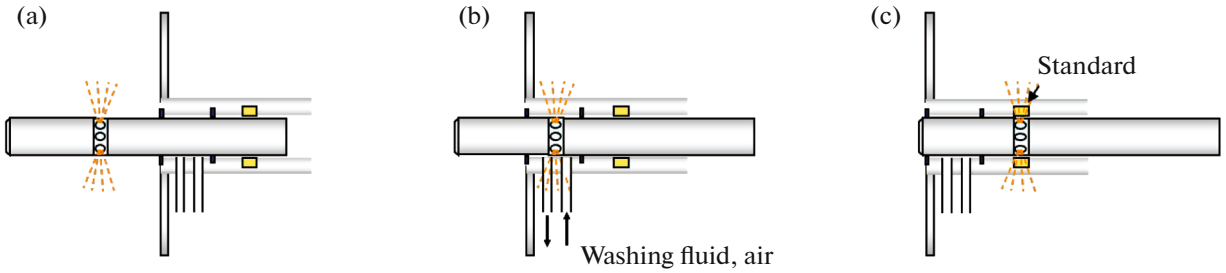

Fig. 1. Principle of operation of an LHP probe: (a) measurement, (b) cleaning and subsequent drying, and (c) calibration.

an ATR measurement is 0.5–2 μm and is determined by the penetration depth of the evanescent field of the used ATR crystal, multiplied by the number of internal reflections determined by its geometry. The relatively short optical path length is often advantageous given the higher (than, for example, in NIR) extinction coefficients of substances in the IR region. The most commonly used ATR cells are made from ZrO_2, ZnSe, Ge, Si, and diamond crystals. Their shape (a cone, prism, hemisphere, polyhedron, etc.) is selected depending on the nature of the sample [26] and the used spectral region. In the last 20 years, some ATR probes for infrared analysis based on CIR and PIR fibers have been developed. These probes coupled with IR spectrometers were successfully tested in solving many analytical problems, including monitoring processes and analyzing biological tissues [27–32].

A real breakthrough in light sources is associated with a significant reduction in the cost and an increase in the capabilities of LEDs, which now cover almost the entire optical spectral region from UV to IR and have intensities of up to dozens of watts (in pulsed mode). Therefore, they are increasingly used in the optical analysis [33]. Being close to monochromatic radiation sources in spectral properties, high-power LEDs can replace lasers for fluorescence excitation [34, p. 342] and even the effect of Raman scattering [35]. The service life of LEDs can be calculated in thousands of hours while maintaining a stable spectrum and emission intensity. This makes them much more practical than lamps conventionally used in spectroscopy. An innovative area of spectroscopic analysis is using a set of LEDs at different operating wavelengths as a source instead of traditional white light, which frees spectrometers from the most expensive components. However, some problems arise in using this approach, in particular, a relatively broad emission spectra of LEDs, their variability and instability, etc. The first examples of research devices using LEDs for spectral analysis [36–38] have shown their advantages as light sources for spectroscopy over conventional lamps. LEDs are highly efficient and possess much higher brightness. However, the development and widespread use of LED analyzers are limited due to the incompleteness of scientific research and the lack of practical experience.

We should note progress made in developing low-cost pyroelectric detectors and miniature high-resolution spectrometers based on them [39–41]. Pyroelectric detectors are based on photosensitive elements covered with a film of pyroelectric material (lead zirconate titanate), which generates a voltage signal when the temperature is changed. Pyroelectric detectors are designed to analyze rather narrow spectral ranges in the NIR and IR regions. A typical example of a microspectrometer is a Fabry-Pérot tunable interferometric sensor (TIS) adjustable over relatively narrow spectral intervals, using microelectromechanical systems (MEMS) technology [42]. For example, a TIS made by InfraTec (Dresden, Germany) [43] consists of moving and stationary mirrors deposited on a film with a thickness of 300 μm. The backs of both mirrors are coated with antireflection layers optimized for a specific spectral range, for example, 8–10 μm. The spectral transmission of such an optical filter is characterized by a narrow-wavelength resonance curve. The maximum transmission at the resonant wavelength can be adjusted electrostatically by changing the distance between the mirrors. The mirrors' quality, reflectivity, and absorption loss determine the TIS resolution; for example, at 50% filter transmission, it is about 200 nm.

The production of mini- and micro-spectrometers for UV-Vis and NIR spectral ranges is developing, and their cost is reduced. This enables the development of OMSs based on them. Qmini microspectrometers (Germany) [44], products of Spectral Engines (Finland) [45], and MicroNIR PAT-U from VIAVI Solutions (Italy) [46] are typical examples of such devices. Because of advances in micromachinery technologies, new areas of mid-IR and near-IR spectroscopy in industrial and field applications appeared.

The approaches to spectral analysis are also changing. A notable trend is a combination of two or more different spectroscopic methods in one analyzer. Combinations of methods are used to cover various aspects of the process in PAT [47–49] or to improve the classification of biological tissues, including in oncological diagnostics [50–52]. This combination is called *complementary*. Suppose a combination of dissimilar spectral data in one model improves analytical

capabilities, for example, the accuracy of determining a component. In that case, we can speak of *a synergic effect* (when the combination works better than each method separately). So far, no generally accepted theoretical justification for synergy in multispectral analysis has been proposed, which would make it possible to obtain a predictable result.

In chemometrics, several efficient algorithms were developed to analyze combined data, including blocks of different methods or stages of a technological process [53–55]. A particular case of combined (or augmented) data is three-way and higher modality data. They are obtained, for example, using two-dimensional fluorescence spectroscopy [56], spatially resolved measurements (as in spectral images [57]), and combined methods [58]. The latter include HPLC with UV detection and thermogravimetric analysis with an IR analyzer. To analyze three-way data, special algorithms are required, such as the unfolding method, which transforms a three-dimensional data array into a two-dimensional one by joining its constituent matrices into one [59]. Three-way data were successfully used for the development of OMSs [3].

Data processing. Real-world spectral data contain a wealth of useful chemical information. Its extraction by mathematical methods is complicated by overlapping analytical signals, scattering, noise, instrument artifacts, and other factors. Therefore, the analysis of complex samples is not complete without chemometrics, which has become an almost mandatory component of modern analytical methods based on optical spectroscopy [7].

The evolution of the instrumental base and methods for analyzing optical spectroscopy data are closely interrelated. The invention of new analytical methods and devices usually stimulates a corresponding mathematical apparatus and software development. A striking example of the reverse effect is a breakthrough in developing NIR spectroscopy, primarily associated with the emergence of the partial least-squares projection algorithm (PLS), a now widely used method of regression analysis. The publication of the PLS algorithm in 1982 [60] and subsequent widespread use in applied research [61], especially for multivariate calibration on spectral data, turned NIR spectroscopy into one of the most demanded tools for quantitative analysis, both laboratory and PAT. Previously, this method was little used in practice because of overlapping bands and an intense background signal.

Regression algorithms, such as PLS and multiple linear regression (MLR), are required to create calibration models in quantitative analysis. Exploratory data analysis methods such as principal component analysis (PCA) [62] and similar projection methods aimed at the in-depth study of the internal data structure in factor space also play an essential role. For samples, this consists in identifying groups and outliers, analyzing relationships (for example, a development curve over time), analyzing statistical influence. The same properties can be studied for variables. In the latter case, the most interesting is the search for the most influential variables and hidden spectral responses [63]. Ultimately, such exploratory data analysis improves understanding of the objects of interest and the analytical method itself. One can create an infinite number of different factor spaces for the same data using known or inventing new projection transformations. The effectiveness of the factor space is ultimately determined by its practicality for the analysis of specific data [4].

Preprocessing of spectra, that is, their modification before analysis is carried out to improve the quality and the information content of the data. In terms of statistics, information is the variance of variables. The purpose of preprocessing is to improve the accuracy of data analysis by removing irrelevant information like noise, background signal (baseline), and uninformative regions of the spectrum while preserving valuable information as much as possible. Preprocessing can also improve the visualization of useful information, for example, in using differentiation or data transformation functions such as linearization. The most commonly used data preprocessing methods are presented in Table 1.

The considered methods are often used in developing the OMSs for preprocessing the initial complete spectral data. However, the possibilities of modifying the OMS data themselves are severely limited by their peculiarities. Because of the small number of variables and the unevenness of the step, only weighting, normalization, and correction of scattering can be applied to them (Table 1), and the SNV and MSC methods are meaningful only when the number of channels is at least three. For a two-channel optical multisensor system, one can use only arithmetic operations with the values on different channels obtained in the same measurement or independent transformation of variables in each of the channels, for example, weighing by the *autoscale* method, that is, dividing each value of a variable by its standard deviation. The selection of the most qualitative and informative data (both objects and variables) constitutes a separate group of preprocessing methods. The selection of variables is essential in developing multisensor systems, and the selection of objects is crucial for the data analysis of working OMSs.

The OMS data have several features that distinguish them from conventional spectra, including a small number of variables, their uneven distribution along the spectral axis, insufficient standardization, and a potentially large volume of measurements. This imposes certain restrictions on the use of data analysis algorithms common in spectroscopy and creates a need in developing new approaches.

The small number of variables in the data matrix and the absence of significant correlations expected

Table 1. Main methods for the preprocessing of optical spectra

Preprocessing	Effects to be eliminated	Algorithms
Weighing	Difference in scales/significance of variables	Autoscaling [64, p. 76]
Normalization	Variable volume of the sample	SNV[a] [65, p. 124]
Scattering correction	"Scattering" effect	MSC[b] [66]
Baseline correction	Background absorption in spectra	PLC[c] [67]
Smoothing	Noise	SG[d] [68], MA[e] [69]
First/second derivatives	Unresolved bands, baseline	SG [68]
Selection of variables and objects	Noninformative variables or objects, outliers	GA[f] [70], iPLS[g] [71], CARS[h] [72]

[a]SNV, standard normal variate; [b]MSC, multiplicative scatter correction; [c]PLC, piecewise linear baseline correction; [d]SG, smoothing and differentiation according to Savitzky–Golay; [e]MA, moving average method; [f]GA, genetic algorithm; [g]iPLS, interval PLS; [h]CARS, competitive adaptive reweighted sampling.

due to optimization make OMS data similar to nonspectral analytical data. The number of variables can also be significantly reduced without a significant loss for the analysis result [73, 74]. Reducing the number of variables in the data does not affect the applicability of PLS regression and most other multivariate calibration algorithms but creates the prerequisites for using the classical method of multiple linear regression, which was widely used before the advent of projection methods [64, p. 125]. Multiple linear regression does not use factor projection, solving the regression equation directly from the data matrix and the concentration vector. According to the available data, MLR on preselected spectral variables gives excellent results [75, 76]. The advantages of the method are simplicity and lower computation load, which can be significant for autonomous sensors using lightweight versions of computers. Because of the small number of variables, the construction of calibration models based on OMS data and the subsequent predictions take less time. This can be a significant factor in analyzing "big data" and online monitoring of fast processes.

OPTICAL MULTISENSOR SYSTEMS

Definition of optical multisensor systems and their distinctive features. The author's previous works systematically introduced the term "optical multisensor system" [3, 8]. Because of their distinctive features described below, OMSs should be distinguished into a separate class of spectrometric devices.

In [8], the following definition was given: "An optical multisensor system is an analytical device that includes a set of two or more optical sensors (sensor channels), optimized for a specific application." The term "sensor" here means a chemical sensor according to the IUPAC nomenclature [77]. The OMS information channels are integrated optical signals in the selected spectral ranges.

The term *multisensor system* first appeared in electrochemistry to describe analyzers of the "electronic nose" type [78] and was firmly entrenched in the works of the "electronic tongue" group of St. Petersburg State University under the leadership of Yu.G. Vlasov [5, 79]. The "electronic tongue" is also based on the optimization of an array of nonspecific sensors (in this case, potentiometric), which have different (cross) sensitivity to the determined components [80]. The conceptual similarity of "electronic tongue" with OMS is obvious, and the differences lie in the physical principle of operation of the sensors used, which justifies the commonality of the terminology.

Introducing a terminologically new spectrometric device is due to conceptual differences between OMS and conventional spectroscopy. The most significant features of OMS are listed below.

Analyzer parameter	Spectrometer	OMS
Analyzer type	Universal	Specialized
Selectivity	High	Low
Use of chemometrics	Desirable	Mandatory

In contrast to universal spectrometers, an optical multisensor system is a specialized analyzer optimized for solving a specific analytical problem. This feature significantly changes the field of applications, opening up possibilities of field, rapid, and online measurements. The OMS optimization consists of using the minimum required number of optical channels on the wavelength ranges selected, taking into account the application.

Unlike spectrometers designed to operate at high resolution [34, p. 91], optical channels of OMS are generally wide. They can be far away from each other or, on the contrary, overlap strongly, so that the term "resolution" itself is not always applicable for them. Generally, the manifestation of selectivity from the sensors constituting the OMS is not expected. Such a goal is not set in creating an analyzer, although a high selectivity of channels to individual sample components is possible. Using only the most informative

spectral intervals avoids non-informative areas and irrelevant responses. The positive effect of integration over broad spectral ranges is manifested in a decrease in the noise level, which also favorably affects the accuracy of the analysis.

The low selectivity of the OMS channels implies multidimensional data analysis methods, such as PLS calibration. The clever use of chemometrics both at the channel optimization and in building a predictive model can fully compensate for the loss of analysis accuracy in switching from a laboratory spectrometer to multisensor systems [81, 82]. On the contrary, the so-called expert approach to the analysis based on someone's personal experience and knowledge to set the number, operating wavelengths, and spectral intervals of OMS channels often turns out to be far from optimal because of the high number of parameters affecting the result [83].

There are also less stringent OMS characteristics that distinguish them from traditional spectrometers. For example, the measurement speed of process spectrometers and OMSs is usually high and amounts to several milliseconds or even microseconds, as in the piecewise sorting of cereal grains "on the fly" [84]. Measurements of OMS analyzers, even of the same type, may differ. The lack of standardization is solved by using *model transfer* methods [85–87], which make corrections either to the data themselves, measured using a standard set of samples, or to the predictive model, which is also one of the tasks of chemometrics. The structural simplification of the OMS decreases the size and cost of the analyzer by tens and hundreds of times and creates prerequisites for the creation of portable and autonomous devices. The availability and miniaturization of OMS analyzers enable the creation of distributed sensor networks that provide the complete control of territories (as in ecology) and complex samples. With the massive use of OMSs, it becomes expedient to use universal (also called *global*) calibration models [88–90], stored "on the cloud," as an alternative to many *local* ones. Chemometric models of a conventional spectrometer are usually included in the software located in a computer connected to the instrument. On the other hand, optical multisensor systems rely on the use of built-in microcomputer technology, which calculates and outputs the measurement results. An essential characteristic of OMS is its high adaptability for a new application through the technical readjustment of the optical channels of the system. A possibility of the modular construction of OMS may paradoxically combine the narrow specialization with the system versatility.

An eye is a unique natural example of an OMS. The multitude of color shades percieved by the eye is generated by only three low-selectivity cross-sensitive optical sensors [91]. The optimization of the sensitivity spectra of individual sensors of the eye for the environment occurred due to evolution; therefore, the perception of color in humans and different animal species is not equal [92].

From the point of view of the proposed terminology, OMS is an "electronic eye."

Optical multisensor systems and single-channel sensors. Single-channel (or simple) photometric sensors are widely used in practice. For example, the colored component of a true solution can be determined by absorption in the visible spectral region, and the suspended component of a colloidal system can be measured by light scattering, as in nephelometry and turbidimetry [34, p. 186]. In the examples given, one wavelength is used, assuming system selectivity for the analyte. To increase selectivity, physical separation or chemical modification of the sample can be used, for example, the conversion of an analyte into a colored complex. Such laboratory sample preparation methods facilitate photometric analysis and are often used in practice. However, they can be tedious and not consistently accurate, especially in analyzing complex mixtures.

Optical information from a single sensor channel may not be sufficient for analyzing complex samples. This main disadvantage of photometry is eliminated by adding additional information channels: the transition from photometry to spectrophotometry. The schematic model in Fig. 2 illustrates the advantage of two-channel measurement for discriminating between two classes of samples. The linear discriminatory model distinguishes between two groups of samples on the plane, although there is no complete separation on each of the individual channels (Fig. 2a). Nonlinear discrimination can be used in a more complex case (Fig. 2b).

An excellent practical example illustrating the advantages of multichannel measurements is the developed optical sensor for the water concentration in powdered materials [93]. This work was based on the intense absorption of water in the region around 1940 nm. A LED radiation at this wavelength was used as a source, and the light diffusely reflected by the powder was captured by a probe and transmitted through a fiber-optic cable to a photometric detector. A calibration model for determining water according to the sensor readings had a rather low accuracy due to random fluctuations in the intensity of the recorded signal associated with the morphological inhomogeneity of the powder surface (scattering effect) [94]. Since the scattering intensity by relatively large particles in the NIR region is practically independent of the wavelength, its differences can be compensated using a second LED channel at 1300 nm. By detecting signals from alternately operating sources and subtracting the second signal from the first, the scattering effect is neutralized by using the second channel as an internal reference measurement (reference-free method). To explain further the principles of OMS development, let us imagine that the absorption of another compo-

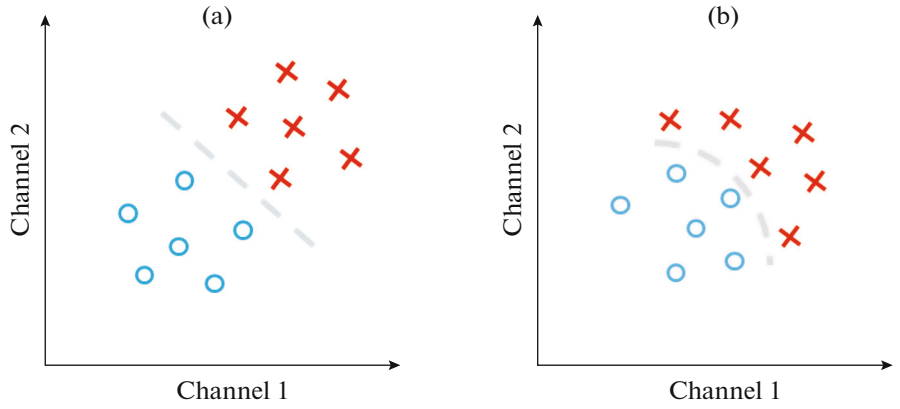

Fig. 2. Schematic illustration of the discriminant analysis of the data of a two-channel multisensor system: (a) linear and (b) nonlinear separation of classes on a plane composed by measurements of two information channels.

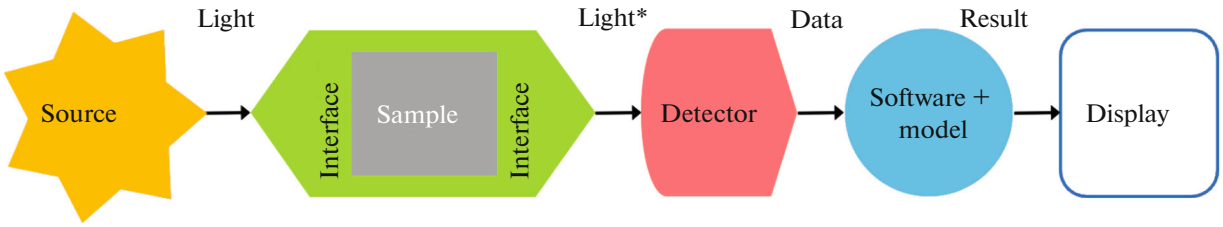

Fig. 3. Diagram of information flow of optical multisensor systems (asterisk denotes transformation).

nent of the mixture with a variable concentration is superimposed on the water absorption band. One more LED must be introduced into the sensor system to compensate for this factor. If the interfering component is unknown, the required optical parameters of the third channel (wavelength and other emission spectrum parameters of the third LED) should be determined experimentally. This can be done without completely separating the mixture using the full spectrum data of an appropriately planned set of samples. However, even with pure spectra of the components of the mixture under study, it is hardly possible to "manually" select the best LEDs for the created multisensor system. The determination of their number and optical characteristics should be the subject of mathematical optimization, approaches to the solution of which were considered in [3, 8].

The use of three or more information channels in the OMS opens up opportunities for applying many chemometrics algorithms, including data preprocessing and the construction of predictive models. The complexity of the OMS is determined precisely by the number of information channels, that is, independent sources of information in the output data, which are further used for mathematical analysis. The technical presence of many optical sensors does not determine the number of OMS channels. For example, of all optical sensors in a system, only one can be used if other sensors are disabled or their responses are averaged. In this case, the analyzer is still single-channel regardless of its technical implementation. Even a high-resolution spectrometer can be used as a simple photometric sensor if it is calibrated to determine concentration from a single wavelength or an integral of the absorption peak.

Architecture and principle of operation of optical multisensor systems. A multisensor system can be described in terms of an *information flow*, as a device for collecting, transmitting, and transforming information [8]. A schematic diagram shown in Fig. 3 is suitable for any spectroscopy method. It is especially useful for illustrating various aspects of the design and use of OMSs.

The original information carrier is electromagnetic radiation of the optical spectrum, emitted by one or several sources. The sources can include devices that convert white light to monochromatic, such as optical filters or a monochromator, or initially emit light in a narrow wavelength region. During the analysis, the source can operate in a continuous or a pulsed mode.

Analytical information appears when the light spectral composition changes as a result of its interaction with a sample. The *measurement interface* is important to ensure the collection of relevant information about the sample. This is a set of optical–

mechanical devices used to convert the luminous flux before and after the sample and give the necessary shape to the sample itself at the time of analysis. Measurement interfaces can be standard or specially designed for a specific analytical task. The interface determines the *measurement geometry* (optical path length, the distance to the sample, measurement angle, and other parameters affecting the propagation of light in the sample) and the method of the delivery of the modified light to the *detector*. The frequently used measurement interfaces are the probe, cuvette, flow cell, and optical window [95]. More specific devices include a goniometer (a device for changing the viewing angle), an integrating sphere, and much more sophisticated devices, such as a spectral camera and a confocal microscope. The analysis can take place both at a contact of the sample with the elements of the measuring interface and remotely.

Standard elements of measurement interfaces include protective windows, lenses, mirrors, ATR crystals, and optical filters. A filter can be installed in front of the sample or after it (in front of the detector) to cut off the unnecessary spectral regions or signals, such as the emission peak of an excitation laser in Raman spectroscopy or luminescence analysis [34, p. 88].

After the detector, the information carrier is changed. Light is first converted into an analog electrical signal, which is then digitized. In Fig. 3, the analog-to-digital converter is conventionally assigned to the detector. The data of the OMS information channels released from the detector become an *analytical signal*.

The final step in the OMS information flow is a prediction, involving the application of a previously created mathematical *model* to a new measurement and transforming an analytical signal into an analysis result. The result can be a concentration value or a generalized chemical indicator, and also the assignment to a class, that is, the final result of qualitative or quantitative analysis. If the purpose of the analysis is to determine the concentration of a component in a sample, a *calibration* model is needed, while a "yes/no" answer results from discriminant analysis. In any case, the predictive model is an indispensable element of the information flow. Chemometric models are digital. That is, the work of an OMS supposes the presence of a computer.

A computer with installed software is the essential element of an OMS. It controls the system and is responsible for predicting and issuing the result. These functions can be built-in or transferred to an external computer connected to the multisensor system via a cable or in a wireless mode. Autonomous OMSs use an embedded computer with its own display, which simultaneously serves to control the device and display the prediction result. In some cases the result can be displayed using color signal lights on the analyzer housing. For example, green means "yes," red means "no," yellow means "questionable," and white means "measurement error."

There are OMS implementations where the data flow diagram (Fig. 3) is simplified. For example, the right side of the circuit after the sample can be replaced by human perception, the eye (analog of a detector) and the brain ("computer"). For example, the fluorescence emission of an excited sample in the visible region indicates the presence of a specific chemical substance, and the intensity of this radiation indicates its concentration. In another version, the source may be absent from the diagram (Fig. 3), and natural, for example, solar radiation, may play its role. Moreover, the light source can itself be a sample; for example, in the spectral analysis of emitting samples, lamps, liquid crystal displays, etc. can be used.

Structural elements of optical multisensor systems. Various structural elements are used in optical spectroscopy as light sources, measurement interfaces, and detectors. The selection of elements in the development of OMSs depends on the nature of the sample, the spectral method used, the optimal measurement geometry, and the specific requirements for the analyzer, such as measurement speed, cost, fit-in, and size. Modern technical elements used for the design of OMSs, the types of software, and the computers used are given in Table 2.

With all their diversity, various radiation sources and detection systems form stable pairs, the technical characteristics of which determine the division of the analyzers into spectral regions and methods, such as UV, Vis, NIR, and IR. Measurement interfaces are more versatile and are often applied to different spectrometers and types of molecular spectroscopy. For example, a quartz cell can be used to record any optical spectra, except for IR.

Modern compact microcomputers are usually applied to store the model and predictions in autonomous OMSs. Microcontrollers equipped with the necessary software are increasingly used to control the device. The predicting software can be installed on a built-in or an external computer and be standard (available commercial product) or proprietary. The latter may be necessary, for example, in creating a highly optimized sensor. An alternative approach to prediction is API, which can simplify the device by transferring all calculations to a remote server ("to the cloud"), but connecting to the model requires access to the Internet.

The list of structural elements in Table. 2 is, of course, not exhaustive. It includes only the main elements used in the practical applications of this work and considered in the publications.

Classification of optical multisensor systems. Optical multisensor systems are diverse and can be based on different design principles. For systematic design, it is helpful to distinguish between device types. The

Table 2. Structural elements of optical multisensor systems

Unit	Structural element
Source	LED [36–38, 93, 96–98], laser diode [99], laser, filter [100, 101], diffraction grating [81], monochromator [99], prism, lamp [95, p. 74]: incandescent [81], halogen [102, 103], deuterium, mercury
Interface	Cuvette [103], transmission probe [81], diffuse reflection (DR) probe [69], attenuated total reflection (ATR) probe [50, 81, 104], replaceable ATR element [81], transmission cell [102], light guide [81, 96, 97, 103, 105, 106], optical window [107], lens, filter [99, 50], aperture [103], integrating sphere [69], goniometer, monochromator [99]
Detector/spectrometer	Photodiode [93, 96], DAD [69, 103], CCD [105], MMS [102], pyroelectric [81], microspectrometer [107], TIS [81]
Software for prediction	Standard, proprietary [96, 107], API
Computer and display	Personal computer, microcomputer [93], microcontroller [96]

CCD, charge-coupled device; DAD, diode-array detector; MMS, monolithic miniature spectrometer; API, application program interface. The references give examples of various structural elements in the current OMSs or systems under development.

OMS classification can be based on specific criteria [3, 8]. The basic physical principles of optical spectroscopy are illustrated in Fig. 4.

From the point of view of the measurement geometry, three main *measurement modes* can be implemented in the OMS, depending on the detection angle with respect to the irradiation flux: transmission (180°), reflection (0°), and scattering (at an angle of 90°, as, for example, in nephelometry, or at a different angle). A separate "reflection" category is represented by the method of attenuated total reflection (ATR), where the properties of the crystal determine the angle of internal reflection. The above terminology is conditional. In each of the above measurement modes, the light flux detected after the interaction with the sample may contain a combination of the effects of absorption, scattering, luminescence, and Raman scattering.

From the point of view of the design, OMSs can be divided into three types, depending on which of the nodes of the information flow (Fig. 3) is responsible for specializing the spectrum analyzer according to its application: source, detector, or software (Table 3).

The LED OMSs (type 1) present one of the most attractive development fields. They combine the simplicity of the design with a wide range of possibilities [33]. Similar designs of OMSs with automatically changeable filters and a broadband light source are implemented, for example, in NDC analyzers (Dayton, United States) [100] and a BioView analyzer equipped with a probe for analyzing processes by two-dimensional fluorescence spectroscopy [101, p. 29]. Instead of LEDs, powerful laser diodes can be used, for example, in fluorescence OMSs [99]. Highly informative and accurate fluorescence and Raman OMSs can be implemented based on tunable lasers, especially if their cost—the main obstacle to the widespread use—will decrease.

Optical multisensor systems of the second type are characterized by specialized detectors in a specific narrow spectral range, which is selected depending on the application. These detectors include miniature pyroelectric detectors [39, 40] for NIR and IR regions,

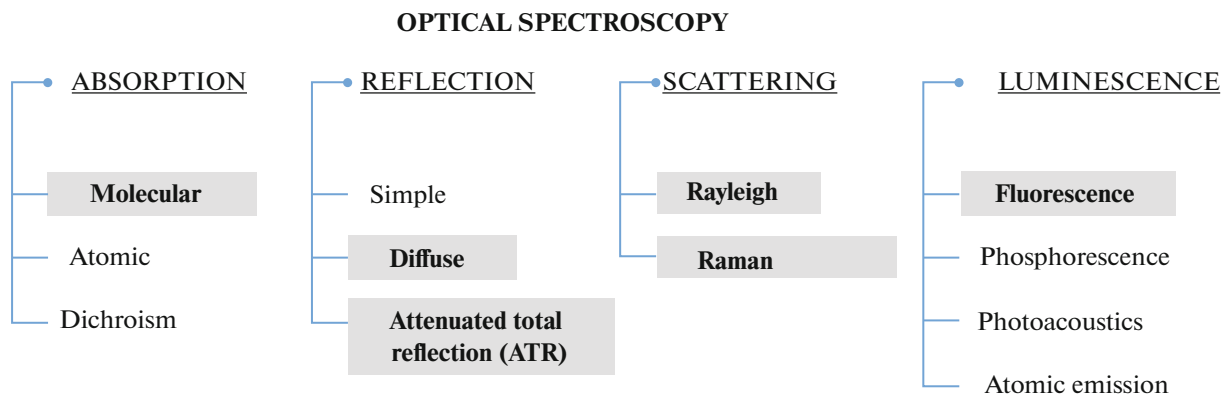

Fig. 4. Physical effects used in optical spectroscopy and (bold font) optical multisensor systems.

Table 3. Classification of optical multisensor systems by the design principle

Type	Specialized unit	Elements and methods of forming channels
1	Source	LEDs, laser diodes, lasers, filters
2	Detector	Pyroelectric detector, CCD, DAD
3	Software	Selection of variables or intervals, averaging

for example, the Fabry-Perót TIS [43]. However, specialized detectors can also be based on an optimized array of DAD or CCD photodiodes with an individually developed method for reading spectral information at the electronics level.

The third type of OMSs is most often used in ready-made mini- and microspectrometers developed for commercial or research purposes. In recent years, there has been an increased interest in manufacturing "democratic" spectroscopic analyzers, mainly for the Vis and NIR regions. Debus et al. [21] showed that a spectrometer made from scrap materials—an old CD, a mirror, and an empty package—can be successfully used to determine creatinine in urine. A smartphone camera is used as a detector and a computer. There are other examples of ready-made household devices, such as a camera or a smartphone, as a basis for improvised spectral analyzers [22, 106]. This approach manifests the request for personalized analysis, noted above. The lack of standardization is the specificity of spectrometers of this type (we will call them simplified spectrometers) and the maximum design lightening due to the rejection of a built-in light source and other elements, which is also typical for process spectrometers. This is true not only for research prototypes but also for commercial brands of higher quality (not so cheap), such as products from RGB Photonics [44] or Spectral Engine [45]. Simplified spectrometers are, in fact, semifinished products, and their use in practical analysis is associated with completing the missing components, such as software for *low-level* data processing (before they are written to the computer memory), which makes up for the lack of standardization, including the unevenness and redundancy of the spectral data collection step. At the stage of low-level data processing, the selection of variables and their averaged intervals takes place, which means that the OMSs of the third type can be specialized (Table 3) by optimizing software for the selected application. A typical example is a sensor for the online determination of water in a powdered food supplement during its production [107].

EXAMPLES OF DEVELOPMENT AND USE OF OPTICAL MULTISENSOR SYSTEMS

This section illustrates the development and applications of OMSs with examples from various practical areas: food and pharmaceutical industries, biotechnology, medical diagnostics, and ecology. The systems presented in [37, 49–51, 69, 81, 96, 99, 102–112] with the participation of the author are at different stages of development (Table 4), based on the principle of simplifying the full-spectrum method due to its specialization and optimization for a selected application.

Determination of the nutritional components of milk. A new method was proposed to determine fat and total protein in milk [97, 102, 103, 105, 106, 108–110]. The method is based on light scattering, observed in the spectral region 400–1100 nm. The experimental results were further used in the development of a LED OMS. The accurate determination of fat and protein in natural non-homogenized milk is due to the ability of the spectral method (in combination with chemometrics) to distinguish low-selective spectral profiles of scattering by colloidal particles of different types and sizes: protein micelles (mainly 80–200 nm) and fat globules (1–15 μm). To substantiate the approach experimentally, a series of studies were carried out with artificial milk samples prepared according to the principles of planning a multicomponent calibration [113, 114]. The natural variability in the size of the fat globules was taken into account by the stepwise ultrasonic homogenization of the samples. Each sample was analyzed first in the initial state and then after two homogenization steps, 10 and 20 s each. Chemometric analysis of full-spectrum data from a laboratory DAD spectrometer proved a fundamental possibility of determining fat and total protein in natural milk with high variability in the size of the suspended particles (Table 5).

A possibility of using LEDs to determine milk fat and protein by the proposed method was demonstrated in a series of preliminary experiments using the analysis of digital images of diffuse spots observed when the milk layer was illuminated at three different wavelengths [106]. Using the algorithm developed [115] for optimizing optical channels, the configuration of the optimal OMS based on LEDs was theoretically calculated. The set of LEDs was optimized for the simultaneous (in the course of one measurement) determination of fat and protein in a sample. The calculated OMS with seven LEDs at the selected wavelengths (Table 5, LED OMS transmission) was comparable to the full-spectrum method in the accuracy of determining milk components.

In a separate experiment, we showed a possibility of analyzing milk in the diffuse reflectance mode and supplementing the spectral resolution with a spatial resolution to increase the accuracy [105]. The spectra were recorded at various distances from the light source irradiating the sample, using a probe with a flat

Table 4. Examples of the development of optical multisensor systems

Industry	Parameter	Sample	Type of analysis	Type[a] of OMS	Reference
Food	Fat and total protein	Natural milk	Online	3	[102]
			Rapid	2	[103, 108]
			Rapid	1	[106]
			Field	1	[97, 105]
		Standardized milk	Field	1	[109]
Pharmacy	Water in powders and other solid pharmaceutical forms	Granules, pellets	Online	2, 3	[49, 69]
		Food supplement	″	3	[107]
	Total coating mass (thickness)	Pellets	″	3	[49]
			″	3	[110]
	Dissolution kinetics		″	3	[111]
Biotechnology	Biomass	Fermentation medium	"	3	[81]
			″	1	[99]
			″	1	[99]
	Ethanol and carbohydrates		″	2	[81]
Medicine	Oncological changes	Biological tissue (kidney)	Rapid	1	[37, 96]
			″	3	[50]
		Rectum	″	3	[51]
Ecology	Oil hydrocarbons	Soil	Field	2	[104, 112]

[a]According to Table 3.

Table 5. Statistics of the multilevel validation of calibration PLS models for various prototypes of optical multisensor systems in the analysis of milk for fat and total protein

Method	NC[a]	LV[b]	Root mean-square error			
			calib[c]	FCV[d]	SCV[e]	TSV[f]
Fat						
Full spectrum[g]	401	5	0.089	0.098	0.102	0.103
LED OMS transmission[h]	7	5	0.088	0.095	0.099	0.090
LED OMS diffuse reflectance (reference-free)[i]	9	5	0.094	0.102	0.104	0.091
Protein						
Full spectrum	401	4	0.040	0.042	0.043	0.040
LED OMS transmission	7	4	0.051	0.054	0.059	0.054
LED OMS diffuse reflectance (reference-free)	7	5	0.065	0.071	0.073	0.072

[a]Number of optical channels; [b]number of latent variables (LVs) in the PLS model; [c]calibration statistics (check on the training set); [d]full cross-validation; [e]cross-validation by segments; test-set validation; [g]measurement with a diode-array spectrometer for transmission in a cell with an optical path length of 4 mm; [h]calculation of LED OMS for transmission; [i]calculation of LED OMS for spatially resolved measurements in diffuse reflectance mode.

working surface and a line of eight light-guide channels brought out onto it. One light guide was connected to a white light source, and the others were connected to a spectral detector. A reference-free method was used to analyze the data, according to which one of the probe channels was used as the internal reference spectrum. The calculation of the LED OMS with the spatial resolution was carried out using augmented data, where the measured spectra of all channels were combined. In this case, each spatial channel could have its own optimal set of LEDs. The use of optical fibers in the diffuse reflectance mode was complicated by the weaker intensities of the detected signals than those in the transmission analy-

sis. However, the method showed an almost equal accuracy (Table 5) as the full-spectrum one because of spatial resolution and reference-free measurements. Optical multisensor systems based on recording diffuse reflectance are in special demand in milk analysis. They are easy to maintain and well suited for field and online analysis.

Global calibration models for the practical determination of fat and total protein were developed using a thousand fresh milk samples collected in the Samara region and adjacent regions over 1 year. The root mean-square error of the determination for both fat and protein was about 0.1% in the concentration ranges 1.55–4.97 and 2.27–4.25%, respectively. In [76, 108], a possibility of transferring models to another spectrometer of the same type using the slope and bias correction method was shown. The loss of accuracy of the transferred model was insignificant [108].

Quality control of pharmaceutical products. Online analysis of solid pharmaceutical forms is one of priority fields for developing OMSs. It includes critically important applications [49, 69, 107, 110, 111], i.e., the determination of the concentration of water or an active pharmaceutical ingredient (API), monitoring the application of a protective polymer coating layer, and the associated prediction of the solubility of the finished product.

In the examples below, a DAD spectrometer equipped with an LHP immersion diffuse reflectance probe (Fig. 1) was used in the NIR region (Table 4) as the main spectral instrument for online measurements in the medium of an ongoing process [23].

Insufficient accuracy in determining the moisture content of powders, granulates, and pellets is one of the problems of the existing methods for online monitoring in pharmaceutical production. The analysis, in this case, is hampered by the high turbulence of the granulation and drying processes in the fluidized bed of the reactor, which ensures the circulation of the suspended particles in the supplied bottom airflow. The rapidly changing density of a virtual sample in the "field of view" of the probe leads to strong fluctuations in the total spectral intensity. As shown in [69], conventional methods for eliminating this effect by the mathematical preprocessing of the spectra (the so-called scattering correction) simultaneously remove useful spectral information, that is, the dependence of light scattering on the material moisture. A high correlation of spectral intensities with the mass fraction of water was observed even at those wavelengths that did not belong to the absorption bands of water.

To improve the accuracy of water determination, calibration models were built for a representative dataset that included 25 process batches, 16303 online spectra, and 301 reference samples taken from the process environment for thermogravimetric analysis. To preserve the most complete information in the data (related to different water concentration), stochastic changes in spectral intensity were eliminated by moving average smoothing along the time axis. This preprocessing improved the quality of the data, avoided information loss during the scattering correction, and decreased the root mean-square error of the prediction of water determination (%, g/100 g) in a wide range of concentrations from the usual 0.3 to 0.1%.

Another pharmaceutical production that requires online control is the application of a protective polymer coating on the pellets, which ensures targeted drug delivery by a delayed release of APIs in the digestive tract. A separate task in analyzing pellet manufacturing processes and developing corresponding OMSs is to predict the release profile of API pellets from the NIR spectra recorded during the process. The dissolution kinetics determines the quality of the product. The planned experiment [111] included 12 process loads with two types of coating material and different conditions. The solubility tests of samples taken from the process medium at different stages of readiness showed that the dependence of the fraction of the released API on time t, regardless of the material and coating thickness, was well described by an equation with two constants m and k, similar to the kinetics of autocatalysis. Parameter m was responsible for the release rate (slope), and k was the delay (induction period), that is,

$$\varphi(t,m,k) = 100k\frac{\exp[(m+k)t]-1}{m+k\exp[(m+k)t]}.$$

Research has shown that m is solely determined by the coating material and can be calculated from the respective process batch data using sequential Bayesian estimation. According to this method of statistical analysis, the data of individual downloads are processed one after the other, and the estimates obtained by nonlinear approximation of the previous download are used as a priori information for the next one. Another constant, k, is closely related to the thickness of the deposited coating (spectrally observed through the total mass of the deposited material) and, therefore, can be determined using calibration on the NIR spectra of the process. Thus, the spectral method was used to predict the drug solubility curve for the first time.

A possibility of determining the thickness of the coating of pellets through their average size was shown in [110]. The thickness was determined by analyzing digital photographs taken in the sample process medium with subsequent PLS calibration on the collected image features. The method can become a basis for the OMS for rapid analysis or can be converted into an online method.

Online monitoring of biotechnological processes. Optical multisensor systems of different types for monitoring the fermentation process of yeast *S. cerevi-*

Table 6. Statistics of the multilevel validation of PLS calibration models for the determination of ethanol, glucose, and fructose from the spectra of test samples taken by various prototypes of IR optical multisensor systems

Analyte	Spectral method	Probe	LV	Root mean-square error		
				calib	FCV	SCV
EG set						
Etanol	FTIR[a]	DATR[b]	2	4.55	5.79	5.10
	GrS[c]	DATR	2	5.18	6.67	5.63
	GrS	LATR[d]	2	7.76	10.58	8.34
	FPI[e]	LATR	2	7.48	9.74	5.75
Glucose	FTIR	DATR	2	5.47	6.66	5.53
	GrS	DATR	2	9.77	11.99	10.87
	GrS	LATR	2	9.12	11.95	11.62
	FPI	LATR	2	8.30	9.87	5.96
FG set						
Fructose	FTIR	DATR	3	0.96	1.14	1.11
	GrS	DATR	3	2.21	3.82	3.71
	GrS	LATR	3	11.07	17.10	16.45
	FPI	LATR	3	2.92	6.64	1.58
Glucose	FTIR	DATR	3	2.35	2.92	1.82
	GrS	DATR	3	3.76	6.76	4.03
	GrS	LATR	3	7.78	14.11	9.30
	FPI	LATR	2	8.03	9.65	10.45

[a]Matrix MF Fourier-transform IR spectrometer (full-spectrum method); [b]ATR probe with a diamond working element; [c]a prototype spectrometer based on a diffraction grating; [d]ATR probe with a working element in the form of a replaceable loop made of polycrystalline fiber; [e]Fabry-Pérot TIS; see also notes to Table 5.

siae were developed based on NIR, IR, and fluorescence spectroscopy [81, 99].

A multisensor IR analyzer for the determination of ethanol, glucose, and fructose [81] was created for online measurements in the attenuated total reflection mode. The development used ATR probes based on PIR fibers with two ATR elements: diamond (DATR) and a replaceable tip with a PIR loop at the end (LATR). In the tested OMS prototypes, two spectrometric techniques were used: a diffraction spectrometer with a PYREOS pyrodetector (GrS) developed in [81] and a Fabry-Pérot TIS (FPI). The TIS was tuned to a relatively narrow spectral range (1150–950 cm^{-1}) in the IR "fingerprint" region, containing the absorption signals of all the components under study. The approach [8] was used to simplify the reference full-spectrum method (FTIR-DATR) by replacing the Fourier-transform spectrometer or diamond probe with more practicable analyzers.

The three created prototypes of IR-OMS were compared using two test sample sets consisted of 25 pairwise mixtures of ethanol–glucose (EG set) and fructose–glucose (FG set). The test sets were mixed in accordance with the diagonal design [113]. A transition from a Fourier-transform spectrometer to a GrS or FPI, as well as the replacement of a diamond probe with an inexpensive and easily replicable LATR, were associated with inevitable losses of spectral resolution and signal quality (Table 6). Nevertheless, the multidimensional models retained a sufficiently acceptable accuracy for several practical applications of monitoring processes in the food industry. Tests in a controlled laboratory bioreactor have confirmed the good online performance of one of the systems (GrS-LATR) in the fermentation process.

The presented results show that chemometrics methods of data analysis and calibration model building in the development of OMSs largely compensate for the decrease in data quality: selectivity, spectral resolution, and other characteristics. The fundamental possibility of creating an IR-OMS for monitoring concentrations of ethanol, glucose, and fructose, typical components of fermentation medium, in the environment of a biotechnological process has been convincingly shown. A possibility of the independent determination of various carbohydrates using OMSs gives an undoubted advantage over the existing single-channel, for example, refractometric analyzers.

Two prototypes of OMSs were developed based on fluorimetry for the online monitoring of *S. cerevisiae*

fermentation [99]. One of typical problems of fluorometric spectral analysis of a fermentation medium is the overlapping of biofluorophore signals over the intense emission band of exciting radiation scattered by the medium. The emphasis of the study is on overcoming this effect by experimental and mathematical means.

The first version shows that the additional emission band observed in online spectra (from the built-in optical sensor) with a maximum at 870 nm noticeably improves the accuracy of biomass prediction compared to using the signal regions of only fluorescence or only the NIR sensor separately. The dependence of the scattering intensity on the concentration of yeast cells makes it possible to distinguish between the increasing fluorescence of intracellular fluorophores and the decreasing fluorescence of similar substances in the composition of the fermentation medium.

To develop a method for the online monitoring of *S. cerevisiae* cultivation using two-dimensional fluorimetry (second option), 39 excitation-emission spectra (EES) were obtained during the process, including fluorescence spectra at 24 excitation wavelengths. Because of the strong dominance of the excitation radiation band in the spectra, the initial data of the process were poorly suited for standard chemometric methods of regression analysis. At the same time, data preprocessing is destructive for a weak fluorescence signal. Therefore, a new algorithm was developed for data analysis that enabled resolving both the trajectory of the process and pure two-dimensional EES of individual fluorophores.

Tests of various optical spectral methods in four fermentation processes of yeast *S. cerevisiae* have proven the promise of creating OMSs based on IR spectroscopy and fluorimetry, including two-dimensional version of the latter method. The maximum extraction of spectral information and the use of exploratory data analysis methods at the development stage are of great significance here.

Optical methods in medical diagnostics. Medical diagnostics is an important field of application of OMSs. In a series of studies [37, 50, 51, 96], prototypes of optical diagnostic analyzers were developed to determine the tumor border in human kidney cancer (permission of the ethical commission EA1/134/12 of the Charité Clinic, Berlin, Germany). Spectral histopathology is a relatively new approach in oncological diagnosis that can decrease the likelihood of error during surgery. In the first example, prototypes of LED OMSs based on NIR spectroscopy were developed, based on rapid alternating irradiation of a sample at several wavelengths, and diffusely reflected light is recorded by a photodiode detector. According to exploratory analysis, we selected four LEDs with central wavelengths near the absorption maxima of water (0.94 and 1.44 μm) and lipids (1.17 μm), known markers of some types of cancer. A LED with a maximum emission at 1.30 μm was intended for scattering correction and served as an internal reference channel following the concept of reference-free measurement (see above). The study aimed to confirm the real possibility of recognizing pathologically altered biological tissue experimentally by the proposed method through spectrally detectable generalized chemical (content of water, lipids, glycogen, and other cancer markers without their quantitative determination) and morphological characteristics with a small number of available clinical samples.

To improve the reliability of the results, the experimental design had several hierarchical levels, including repeated measurements at several sample points. Thus, the resulting measurements reflected the variability of the tissue both within the sample and between them. Discriminant data analysis was carried out by the PLS-DA method, based on the construction of a calibration model, where healthy and cancer tissue samples are coded numerically (0 and 1, respectively), and a new sample is assigned according to the predicted value relative to the 0.5 boundary. The obtained values of the sensitivity, selectivity, and accuracy for the most conservative method of model validation indicate the general suitability of LED NIR-OMS for tumor recognition [37, 96] and the expediency of their further development. The main problem remains the lack of sensitivity caused by a wide variety of tissue of cancer samples, which can be overcome in the future using more representative clinical data. In the course of the development, the optical configuration of the channels (their number and operating wavelengths) and the measurement geometry must be carefully optimized. The information content of the measurement can be increased by expanding the spectral region or by adding other spectroscopic methods.

In the second example, the diagnostic capabilities of fluorescence and IR spectroscopy were investigated, and the efficiency of their combination in one device was examined. To ensure compatibility, the IR spectra (recorded by a Fourier-transform spectrometer with an ATR probe based on a PIR fiber) and fluorescence spectra (excited by a laser at 473 nm and recorded through a diffuse reflectance probe) were recorded in the same marked positions; a total of 31 points on eight available samples were measured. The resulting dataset included 92 pairs of spectra, which were then analyzed separately and together by combining them into one vector along the spectral axis. For analysis, the IR spectra were narrowed down to the most informative (from the point of view of the known biochemistry of the disease) region of 1220–1010 cm^{-1}, and the fluorescence spectra were narrowed down to the region of the observed signal at 490–680 nm. A combinatorial approach was used to find the optimal solution, testing all the best preprocessing methods for individual spectral blocks and their various combinations during the joint data analysis. The exploratory analysis showed a complete sep-

aration of the "cancer" and "normal" classes for the combined data.

In PLS-DA analysis, fluorimetry shows a lower discriminating power than IR spectroscopy. Combining fluorescence spectra with the second derivative of IR spectra with subsequent preprocessing by the SNV method gives a synergic effect. This suggests that the methods considered are responsible for various biomarkers, and because of the small penetration depth, IR spectroscopy predominantly "works" at the cellular level, while the fluorescence signal can come from a depth of several millimeters, carrying additional chemical and morphological information. The result of this study substantiates the feasibility of combining ATR-IR spectroscopy and fluorimetry in one analytical device. In developing a multimodal analyzer, IR and fluorescence spectrometers can be replaced by an OMS.

Environmental monitoring. The final practical example is devoted to developing a rapid method and OMSs for the environmental monitoring of soils to determine total petroleum hydrocarbons (TPH), based on IR measurements through an ATR probe [104, 112]. A preliminary analysis of the IR spectra of a designed series of 57 artificial soil samples prepared by mixing a soil substrate, clay, sand, and dolomite flour made it possible to study the spectral characteristics of soils of various compositions and compare them with the spectra of oil. Based on these data, the spectral region 4000–1700 cm^{-1} and the optimal ATR probe based on a chalcogenide IR fiber with a working crystal element ZrO_2 were selected to quantify TPH.

A calibration series of contaminated samples were prepared by adding oil and water, as the main natural factor affecting the measurement, to 100 g of an artificial soil sample, in a composition close to that typical in the Samara region. During measurements, the probe was brought into close contact with the sample pellet with the crystal completely immersed in it. A training set of 25 samples followed a diagonal scheme [113], in which the concentrations of both components were varied in the range 1–13%. This set was used to build calibration models for TPH and water (%, g/100 g). The best accuracy of the models was achieved by the method of interval optimization [115] using five three-point intervals with averaging without preprocessing for TPH and four individual variables after applying preprocessing methods for the corresponding data, selected as optimal. The root mean-square errors of the prediction were 1.1% for TPH and 0.6% for water.

The main experimental problem of the method is the low overall intensity of the spectra of drier samples and the low precision of respective measurements, which is generally typical for the ATR analysis of solid materials. The proposed techniques for data preprocessing and analysis largely overcome this adverse effect, and the achieved determination errors are acceptable for many applied tasks. The results suggest the further development of OMSs for the field determination of TPH, based on IR spectroscopy in the region 4000–1700 cm^{-1} through a fiber-optic ATR probe. The further increase in the accuracy of the method requires the creation of an improved measurement interface.

CONCLUSIONS

Optical multisensor systems, specialized optical analyzers of low selectivity, represent a new direction in the development of analytical spectroscopy. Because of their practicability features, such as diminutiveness, portability, autonomy, online use, and affordability, OMSs can significantly expand the analytical capabilities of optical spectroscopy in comparison with conventional laboratory analysis. Their planned widespread use for solving various qualitative and quantitative analysis problems in the industry, medicine, and other fields increases the level of analytical control of many vital aspects of human activity. The further development of optical multisensor systems is associated with several scientific, technical, and methodological problems.

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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