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# Analytical Methods in Technological and Environmental Studies

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**Abstract**—The possibilities of modern analytical techniques to solve control problems in high-technology and environmental studies are considered. The first part of the article provides a review of the key concepts of the analytica. The second part is devoted to the problems associated with the analytical software technologies for high-purity substances and evaluation of the detection limits of elements by atomic spectrometry methods. The final part describes the analytical methods used in environmental monitoring. The main attention is paid to the studies that have been intensively conducted at the Research Institute of Chemical Reagents and Special Purity Chemical Substances, starting with 1970s. The institute has preserved traditional approaches and comprehensive research programs until present, even though the range of research topics is not so wide and the problems to be solved are not so ambitious.

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## INTRODUCTION

Modern science-based technologies of the production and processing of high-purity materials are put in the forefront of research and development in many research centers, companies, and universities. Such research is, in essence, basic research, and it calls for revision of traditional approaches to solving science and technology problems. Methods of analytical chemistry, a science developing a general methodology and methods and tools for gaining experimental information on the chemical composition of the matter, as well as methods of analysis of different objects, do not stand aside of these problems. In particular, technologies associated with the production of high-purity substances and materials for micro- and nanoelectronics, optics, and space systems, as well as other high technologies require priority development of methods for analysis of the composition and properties of substances at virtually all stages of production of the final product. Fairly high requirements are also placed on the methods of control of the quality of raw materials and process media, as well as the cleanliness of production facilities. The objects for study are pure and ultrapure organic and inorganic substances, chemical reagents, components of semiconductor structures, process fluids, thin films, and other substances and materials.

When it comes to the environment and environmental safety, we would like to mention the following issues. It is commonly accepted that the present environmental problems are associated with large-scale human activity. The areas of environmental stress or crisis, generated by multifactor, constantly growing human-induced impacts tend to extend far beyond local territories, becoming more and more regional and global.

Especially hazardous are large-scale emissions and effluents of pollutants by industrial enterprises, power plants, motor vehicles, and other technogenic sources, the volume of which has presently reached critical levels. Such pollutants enter the atmosphere, hydrosphere, and lithosphere, where they are accumulated, transformed, and involved in the biogeochemical cycles, thereby inducing irreversible processes at the levels of local ecosystems, region, and the whole globe. As examples we can mention here such regional and global manifestations of the growing environmental impact of human activity as acid rains, ozone holes, and global warming. Here, too, analytical methods play a key role in assessing the environmental situation and making managerial decisions.

## Definition of the Key Concepts of the Analytics

The problems associated with studying the chemical composition of the matter are the subject of analytical chemistry, one of the key component parts of the multifaceted chemical science. Academician Yu.A. Zolotov in his monograph “Analytical Chemistry: Problems and Achievements” [1] gives the following definition of the subject and content of the classical analytical chemistry: “*Analytical chemistry is the science about the methods and tools for chemical analysis of substances. By the methods of analysis are meant, first of all, methods for separation, detection, and determination of the components of analytes, as well as (to a certain degree) methods for studying the chemical structure of compounds.”*

At present, in view of the differentiation of chemical science in itself and increasing role of modern instrumental methods of studying the composition and properties of the matter, the analytical chemistry was proposed to be named *analytics,* thereby setting it aside from chemistry as an independent branch of science. For example, Danzer et al. [2] define analytics as follows: *“Analytics as a science discipline deals with gaining information on materials systems, namely, on the nature and compositions of the components, including information on their spatial structure and local distribution and change in time, as well as with developing procedures for this purpose.”* Such definition of modern analytical chemistry seems quite reasonable, because analytics has acquired a universal character and is based on the achievements of not only chemistry, but also physics, computer science, technics, and technologies. Analytical methods, as a tool for studying the pollutant compositions of vital components of the environment, are gaining more and more significance for solving ever growing environmental problems.

The basic concepts and definitions of analytical chemistry (analytics) can be found in the mentioned monographs, as well as in numerous papers focused on the problems of control in technological and ecological research [3–7]. Among the huge number of foreign monographs dealing with fundamentals and different facets of analytical chemistry we would like to mention the monograph of Skood et al. [8] which by now has went through 5 editions. Special attention should be paid to the book of a prominent German analytical chemist Georg Schwedt [9], which combines brief and intelligible discourse of general principles and basics of modern methods of analytical chemistry and excellent illustrations.

Obviously, to gain insight into the essence of a field of science, one should first of all learn the terminology and understand the meaning and content of the key concepts. Let us consider, in brief, the terminological vocabulary of analytical chemistry. Below we present the recently corrected definitions of the most important concepts and terms, developed by the Scientific Council on Analytical Chemistry of the Russian Academy of Sciences (SCAC RAS) and recommended for practical use [10]. The listed terms and definitions are provided by the comments of the authors of the mentioned recommendations.

*Analytical chemistry (analytics)*: science developing a general methodology, methods and tools for gaining experimental information on the chemical composition of the matter, as well as methods of analysis of different objects.

*Chemical analysis*: gaining information on the chemical composition of the matter, as well as the corresponding field of activity.

*Method of analysis*: sufficiently universal and theoretically substantiated was to gain information on the chemical composition of the matter on the basis of the principle or principles of analysis.

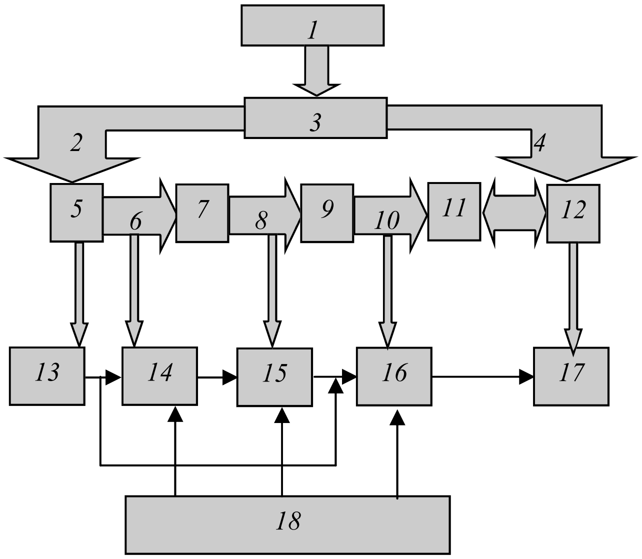
*Procedure of analysis*: detailed description of rules and operations for the determination of the composition of a specific object by means of the chosen methods.

*Principle of analysis*: phenomenon, property, or regularity, which form the basis of the method of analysis.

*Measurement*: gaining information on the value of the analytical signal.

*Analytical control*: verification of conformity of the result of analysis to specified requirements, standards, and conditions.

*Monitoring*: fairly long-term observation of changes in the parameters (composition) of an object or a process and recording these changes with time; more rigorously, tracing changes in the characteristics of an object or a process in the space–time coordinate system.



Analytical process and its relation to the general principle of information processing: (*1*) general task allocation; (*2*) sampling; (*3*) object for study; (*4*) final conclusion; (*5*) sample; (*6*) sample preparation; (*7*) object for measurement; (*8*) masurement; (*9*) measurement data; (*10*) data processing; (*11*) result of analysis; (*12*) analyst; (*13*) information source; (*14*) selection, enhancement; (*15*) coding; (*16*) decoding; (*17*) information receiver; (*18*) information accumulator, processing rules, algorithms.

Further we will consider the notes of the authors of the above project, as reworded by us, and will make some necessary comments.

First and most important comment. The term "chemical analysis" is sometimes related to chemical methods of analysis. However, we do not recommend to do that, because the concept "chemical analysis" has nothing in common with methods of analysis. Chemical analysis can be accomplished by chemical, spectral, nuclear physical, and any other methods. The term "chemical" is used, because we deal here with the detection and quantitation of *chemical particles, elements of molecules,* and *phases*, whatever the method of detection and quantitation. Note that we could not find the term "chemical particles" in the literature.

Second, even more frequent textual discrepancy relates to the words "analysis" and "to analyze." These terms are recommended to relate exclusively to the *object of analysis,* rather than to *detected or measured components*. For example, we can analyze air, alloy, ore, and water. But the word combinations "analysis of dioxins in breast milk" or "analysis of cadmium in soil" are not recommended. The right phrases are "determination of dioxins in breast milk " or "analysis of breast milk for dioxins."

Third, the terms "*analysis*," "*control*," and "*monitoring*" are sometimes considered to mean the same, but they are different and most frequently not interchangeable. *Analysis is a broad-sence term*; analysis is done for different purposes (in principle, purposes are not specified), including control and monitoring. *Control*, as mentioned above, is verification of conformity to specified requirements and conditions. *Monitoring* is recording the parameters of an object, a process, or a phenomenon for a certain or an uncertain period of time. The definition of the term "monitoring" in some Russian environmental documents, including even *making decisions by the results of observations and, what is more, realization of these decisions*, seems *unjustifiably broad.*

Finally, such terms as "*measurement*" and "*to measure*" are recommended to be related exclusively to an *analytical signal*, i.e. to the physical property (parameter) used as the analytical signal. Such properties (parameters) can include emission intensity or optical density, current or potential, etc. These words *are not recommended* to relate to *concentration or quantity*. For example, the prase "measurement of concentration" is not recommended. This is, in particular, associated with the fact that the value of analytical signal is related to the value of concentration by a certain equation (naturally, the equations are different for different methods), which may not be ideal, and its parameters depend on experimental conditions. Measurement of an analytical signal is only one stage of analysis. Thus, the following word combinations are recommended: *object – analysis, components – detection or determination, analytical signal – measurement.*

To conclude this section, we would like to attract attention to one more, fairly interesting comment which was first made in the monograph [2]. The authors point to the fact that, according to the theory of information and measurement systems, *an analytical process* can be presented as a *multistage information processing process* (see figure).

Here let us focus on the main issue: *the sample of an object in study is the main source of information and its material carrier*.

Further on the author of the cited monograph notes that *information* is always associated with a certain *signal* (signals are the states of or processes in material

**Table 1.** Physical detection limits and ranges of analytical methods

| Methods | Classical | High-sensitivity | Ultrahigh-sensitivity | Particle detection |
|---|---|---|---|---|
| Mass[a], g | $10^{-2}$–$10^{-6}$ | $10^{-6}$–$10^{-10}$ | $10^{-10}$–$10^{-14}$ | $10^{-18}$–$10^{-22}$ |
| Number of particles (atoms) | $10^{20}$–$10^{16}$ | $10^{16}$–$10^{12}$ | $10^{12}$–$10^{8}$ | $10^{4}$–1 |

[a] The absolute mass of a chemical element is expressed in grams. The absolute mass of the carbon atom is $1.99 \times 10^{-23}$ g. The Avogadro number ($N_A$) is a natural constant showing the number of atoms, molecules, or other microparticles in 1 mol of a substance, $N_A = 6.023 \times 10^{23}$. For example, 1 g-mol of lead (207 g) contains $6.023 \times 10^{23}$ of atoms, i.e. the mass of one lead atom is $207/N_A = 3.4 \times 10^{-22}$ g, and the mass of one magnesium atom (24 g) is $24/N_A = 0.4 \times 10^{-22}$ g.

systems). In analytical chemistry (analytics), precipitate formation in chemical reactions or changes in the color of solutions or in the intensity (absorption) of emission, and other phenomena are referred to as *signals.* Signals (or a sequence of signals) become *information carriers.* Therewith, an important role belongs to such terms as *principle of analysis, method of analysis,* and *procedure of analysis*. In the framework of the analytical process, the *principle of analysis* determines the *method of measurement* and *coding* in the information chain.

## Brief Review of Analytical Methods

Analysis of the composition of a substance is based on different principles of detection of atomic-molecular, ionic, and other structural elements, methods of identification and interpretation of the analytical information, and producing data on the component and concentration composition with the corresponding metrological characteristics of the measurement results. The central place in this system of intrinsically related system of methods belongs to the principle (method) of detection, which ultimately determines the potential and performance of the entire analytical process.

The prevalence of detection is especially evident in those fields of basic and applied research, where extremely high values of parameters characterizing the qualitative and quantitative composition of substances are required. It should be emphasize that just the demand for solving such challenging problems not only stimulated development but also transformed the methodology of the classical analytical chemistry, thereby contributing much to its progress and establishment as an autonomous field of scientific knowledge with its own methodical, instrumental, and informational base.

In this connection, as already mentioned, the analytical control in high-tech sectors in its strategic goals and tasks, features of methodology, potential, and information load of the involved methods can be related to a basic science studying material systems with extremely low levels of impurities, up to individual microparticles (atoms).

The physical detection limits of the chemical (elemental) composition of substances extend over 20 orders of magnitude and embrace the weight range from $10^{-2}$ to $10^{-22}$ g, which, in its turn, corresponds to the quantities of individual microparticles (atoms, molecules) from $10^{20}$ to 1. The modern physicochemical methods that cover the above detection range can be divided in several groups in terms of their sensitivity limits (Table 1): classical analytical methods ($10^{-2}$–$10^{-10}$ g), high-sensitivity methods ($10^{-10}$–$10^{-14}$ g), ultrahigh-sensitivity methods ($10^{-14}$–$10^{-18}$ g); methods capable of detecting microparticles (atoms, molecules) ($10^{-18}$–$10^{-22}$ g).

The quantities close to the upper detection limit ($10^{-2}$–$10^{-5}$ g) are measured by gravimetric methods. The quantities falling into the medium detection range can be measured by a great variety of physicochemical methods, and the detection limits of about $10^{-8}$–$10^{-10}$ g have presently been achieved for the most part of the elements of the periodic table. For certain elements in fairly simple matrices these values are lower by 2–3 orders of magnitude. The record-breaking low detection limits can presently be achieved in certain favorable conditions and by means of a limited number of methods.

From the viewpoint of the achieved level and potential for further decrease of the decetion limits for chemical elements, the following groups of analytical methods capable of providing high- and ultrahigh-sensitivity detection can be recognized.

In the first group of methods, a methodical approach traditional in classical analytical chemistry is realized, specifically, preconcentration of the analytes followed by instrumental detection.

Even though concentration complicates the analytical procedure, makes it more time-consuming, and not infrequently deteriorates the metrological characteristics of qualitative measurement, this approach, when combined with the above-mentioned instrumental methods, makes possible solution of the principal problems of a high-sensitivity elemental analysis.

It can be stated that the concentration of microquantities of impurities with a sufficiently high concentration factor ($10^2$–$10^4$) and the use for detection of a high-sensitivity method is one of the mainstream of the development of analytical chemistry at present and in foreseeable future.

The second group includes high-sensitivity instrumental methods, and their detection limits can be substantially decreased both by improving the systems of formation and registration of the analytical signal in the framework of the framework of the detection principle (method) in itself and by combining them with the above-mentioned separation and concentration of impurities to be detected.

At present instrumental analytics is a rapidly progressing field of modern analytical chemistry, which makes maximal use of the potential of a wide range of methods of detection of atoms, molecules, ions, and other structural elements of material systems. Among such methods special mentioning should be made of atomic emission spectroscopy (AES) with inductively coupled plasma (ICP) as an ion source. This source has gained wide recognition in high-sensitivity determinations due to the fact that it allows simultaneous multielement analysis and has a wide dynamic range and fairly low levels of spectral matrix interferences.

Inductively coupled plasma has also found application in mass spectrometry (MS), due to which the arsenal of modern analytical methods has been enriched by one more quite sensitive instrumental method of elemental and isotope analysis. At present these methods has entered into practice of analytical and environmental laboratories (centers), they outcompeted a number of known methods and are used to success with solving routine and research tasks.

The high analytical potential of atomic absorption and atomic fluorescence spectrometries with various emission and atomization sources should also be mentioned.

As early as 1970s, a new scientific field associated with the development of high-sensitivity methods of elemental analysis has formed in the framework of classical analytical chemistry. Since then analytical chemistry has been enriched by highly efficient methods and corresponding instrumentation for precision measurements. Among them are ICP–MS, ICP–AES, electron microscopy and X-ray microanalysis, gas and liquid chromatography (GC and LC), GC–MS, etc. It is pertinent to note that the State Research Institute of Chemical Reagents and Special Purity Chemical Substances (IREA) had a prominent place in this research, solving the problems of analytical support of research and engineering development works in the chemistry and chemical engineering of organic and inorganic compounds.

At present this field of analytical chemistry has strongly extended due to the development of its theoretical basis, emergence of new methods of detection of the atomic and molecular composition, as well as fairly high level of systematization and generalization of the great body of data on the analysis of trace impurities in ultrapure substances and materials. An important role here belongs to modern computer technologies, systems for processing and analysis of multidimensional analytical information, automation of procedures associated with sample preparation, standardization, etc.

A kind of a mark of the end of long-term research in the chemistry and technology of deep purification of substances is the exhibition–collection of special purity substances at the Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences. This collection contains more than 600 samples of the most pure simple substances (elements), volatile compounds, and molecular solids. The exhibition is a unique scientific project having no analogs in Russia and abroad in the coverage and completeness of information on the chemistry of special purity substances [11, 12].

Atomic absorption and atomic fluorescence spectrometry (AAS and AFS, respectively), too, are capable of detecting quite low concentrations of chemical elements, up to single atoms (molecules). In this connection it should be specially emphasized that as far back as 1968 the Soviet physicist V.S. Letokhov was the first to put forward the hypothesis that atoms can be polarized and trapped (optical tweezers) under the action of an inhomogeneous field generated by a laser beam [13]. For such trapping to be possible, atoms should be preliminarily strongly slowed down, specifically, cooled down to 1 K, and this can be done by means of laser. To this end, the light beam should be directed counter to the atomic beam, and, therewith, the light radiation frequency is slightly lower that the atomic absorption frequency. Then, due to the Doppler effect, the energy of photons will become equal to the resonance energy, and atoms will begin to absorb photons and then reemit them in random directions; as a result, light pulses will be transmitted to atoms and they will slow down.

At about the same time one of the authors of the present paper (A.Z. Razyapov) under the supervision of Prof. M.S. Chupakhin has performed at the Analytical Department of the IREA theoretical and experimental research aimed at improving the sensitivity of AAS and AFS on the basis of classical (not laser) emission sources and combined electrothermal atomizers. Below we outline the results of this research.

## Evaluation of the Detection Limits of AAS and AFS

First we would like to note that theoretical and experimental evaluation of detection limits in atomic spectroscopic methods goes back a long way. In particular, it was shown as far back 1960–70s that the sensitivity of the atomic emission method is limited by an insufficient efficiency of sample atomization and a short residence time of atoms in the excitation zone. Calculations showed that the minimum intensity emission from ~$10^4$ atoms is detectable only if the sample contains $10^6$ times more particles (atoms). Consequently, the sensitivity of atomic spectroscopic methods can be considerably (by several orders of magnitude) increased by creating conditions that would ensure localization and retention of atoms in their detection zone.

In evaluating the AAS and AES detection limits let us restrict ourselves to graphite furnace–flame combined atomizers as the most promising in terms of localization of atoms in the detection zone. Moreover, a more correct calculation of the detection limits requires accounting for a number of factors, including atom source geometry, processes on the surface and inside the atomizer, etc. Therefore, for simplification and illustrative purposes, we based our calculations in [14, 15] on certain simplifying assumptions.

Thus, in the simplest terms, the registered analytical signal in the atomic absorption and fluorescence methods is proportional to the number of atoms $N(t)$ in their detection zone, which, in its turn, can be presented by the equation:

$$N(t) = N_\Sigma \int_0^t F_a(\tau) F_\Gamma(t-\tau)\, d\tau, \qquad (1)$$

where $N_\Sigma$ is the total number of atoms in the sample; $F_a(\tau)$, atomization function; and $F_\Gamma(t-\tau)$, atom source function.

Let us introduce a parameter that characterizes the efficiency of the use of atoms for forming the analytical signal:

$$\gamma = N(t)/N_\Sigma. \qquad (2)$$

As seen from Eq. (2), the higher $\gamma$, the stronger the analytical signal and, consequently, the sensitivity of measurements. To reach the highest possible sensitivity, one should maximize the $F_a$ and $F_\Gamma$ functions in Eq. (1).

At a given atomic distribution in the detection zone $F$, the equation for the atomization function can be deduced from the atomic balance equation:

$$dF_a = dt = V(t)/N_\Sigma - F_a/\tau, \qquad (3)$$

where $V(t)$ is the rate of arrival of atoms to and $\tau$ is the residence time of atoms in the detection zone.

The $\tau$ value is given by the equation:

$$1/\tau = \sum_{i=1}^{n} 1/\tau_i, \qquad (4)$$

where $\tau_i$ are the residence times dependent on different physicochemical processes in the atomizer.

By solving Eq. (3) under the initial condition $F_a(0) = 0$ we obtain the following function:

$$F_a(t) = e^{-t/\tau} \int_0^t V(\xi) e^{\xi/\tau}\, d\xi. \qquad (5)$$

The concrete value of $F_a$ depends on the form of the $V(t)$ function. For simplicity leat us assume that $V(t) = N_\Sigma/\tau$ in the atomization time $\tau_a$ and $V(t) = 0$ in the other time. Then

$$F_a(t) = \tau/\tau_a(1 - e^{-t/\tau}),\ t \le \tau_a,$$

$$F_a(t) = \tau/\tau_a(e^{-\tau_a/\tau} - 1)e^{-t/\tau},\ t > \tau_a. \qquad (6)$$

The highest value of the atomization function is observed at $t = \tau_a$:

$$F_a^{\max} = \tau/\tau_a(1 - e^{-\tau_a/\tau}). \qquad (7)$$

As seen from Eq. (7), the $F_a^{\max}$ value depends on the ratio of the effective atomization time to the characteristic atom loss time:

$$F_a^{\max} \to 1, \tau_a \le \tau,$$
$$F_a^{\max} \cong \tau/\tau_a << 1, \tau_a >> \tau, \quad (8)$$

The $\tau_a$ value can be decreased by increasing the temperature of the atomizer (about 3000°C for existing atomizers. Another possibility to decrease $\tau_a$ consists in faster local heating of the sample holder.

However, the most radical way to reaching a maximum analytical signal $N(t)$ is to prolong the residence time of atoms ($\tau$) in the detection zone.

Theoretical calculations and experiments with various atomizers, performed by the author and coworker, showed the following. The most efficient way to retain atoms is to use a graphite atomizer placed inside a hollow flame. In this case, the losses of atoms due to oxidation are almost excluded, because excluded is the access of oxygen from the environment. The major losses of atoms inside the flame are associated with their carryover with convective streams (vertical component), as well as a horizontal diffusive blurring.

However, the design of this atomizer does not ensure complete retention of atoms in the detection zone of the flame, because the atom source (graphite furnace) is not spatially separated from the burner. As a result, the flame structure, especially its internal part (detection zone) is perturbed, which favors carryover of atomic vapor from this zone.

Later we proposed an improved design of the atomizing device in which the electrothermal atomizer and the flame are separated from each other so that the atom source is mounted inside a burner with a ring-shaped orifice. Such design allowed us to completely isolate the internal zone of the flame (detection zone) from its surrounding hot gas streams [16].

Thus, we can state that the lowest detection limits in atomic absorption and fluorescence spectrometry can be reached by prolonging the residence time of atoms in the detection zone.

In conclusion, turning back to laser spectroscopy, we would like to emphasize again that the idea that atoms can be localized (cooled or trapped) by a resonant laser field was first put forward and experimentally confirmed by the Russian scientist V.S. Letokhov. Thus, as shown in his monograph [17], the retention time of cold trapped atoms in a vacuum of $10^{-8}$ Pa at a mean atomic thermal velocity of $10^2$ m/s should be about 1 h. Due to this, the entire atomic absorption spectrum can in principle be measured having only one atom. In this connection it is worth noting that the Nobel Prize in Physics 1997 was awarded to a group of foreign scientists for “development of methods to cool and trap atoms with laser light.” It is quite regretful that V.S. Letokhov, a prominent Russian scientist, physicist, and a founder of a new field of science, associated with the methods of laser spectroscopy of atoms and molecules, was not among the nominees of this prize.

## Nonselective Analytical Methods

Nonselective methods of analytical control in production technologies, as a tool for purity control of liquid substances and reagents, as well as a tool for determination of the number and mass concentration of aerosol particles in production facilities and clean rooms occupied a rightful place in the research practice of the IREA. One of the authors of the present paper V.Z. Krasil’shchik was a pioneer in the use of nonselective methods (such as piezomicroweighing of dry residues of various liquids and aerosol air pollutants) for technological purposes. Together with high coworkers, V.Z. Krasil’shchik designed corresponding experimental setups and analyzer instruments and developed procedures for their use in quite a wide range of tasks.

Among such developments, we would like to focus the analyzers of the total mass concentration of aerosol particles in the working zone air of production facilities.

The mass concentrations of aerosol particles in air are traditionally determined by gravimetric methods involving weighing of particles deposited on a filter. The use for this purpose of filtration materials made of various polymer and glass fibers ensures a highly efficient collection of aerosol particles with a wide size distribution. However, gravimetric methods have certain limitations. They work to success if the particle concentrations are fairly high. When the particle concentrations are low, such methods become labor-consuming, because to obtain a representative sample one should aspirate a large volume of air. One more disadvantage of using filters is the necessity of careful temperature and humidity controls. Therefore, for stable and reliable determination of weight gain the filter should be conditioned at definite temperature and humidity before each measurement. Furthermore, gravimetric methods are difficult to be automated.

*Optical methods of* the determination of the mass of particulate matter are based on the measurement of light absorption or reflection by the particles deposited on filters after aspiration of a definite volume of air. This principle underlies the design of automated analyzers, where particles are collected onto a tape sampler which moves, at strictly set time intervals, a certain part of the filter for collecting the aerosol particles of interest. However, in these instruments the attenuation of light intensity by the deposited particle layer depends not only on the mass of the particles, but also is a complicated function of their size, shape, and chemical composition. Moreover, the proportionality of absorption (reflection) and paticle layer mass takes place only when the mass of a deposited aerosol is small and the particles do not overlap with each other. The material of the filter, too, affects the results of analysis. Certain disadvantages are also characteristic of automated continuous flow aerosol mass analyzers which measure light scattering by the particles. The readings of such instruments are proportional to the logarithm of the particle concentration only at constant physicochemical characteristics of the aerosol.

*Automated detectors* for measuring the mass concentration of aerosols by the *attenuation of α and β radiation* through the particle-laden filter are known. The principal functional units of these instruments are the source of radioactive radiation, receiving and recording system, portable pump, and filter transfer device. In these instruments, unlike what is observed in optical analyzers, the absorbance is almost independent of the chemical composition and dispersity of the aerosol. The sensitivity and precision of these can be further improved by enhancing the activity of the radiation source, as well as by using filter materials with a low intrinsic absorbance.

Certain advantages of high-sensitivity measurement of the mass concentrations of aerosols are offered by the method based on the *piezoelectric effect*, specifically, on the dependence of the *intrinsic vibration frequency of a piezoelectric plate* on the mass of a substance deposited on its surface. The detection limit is as low as $n \times 10^{-11}$ g. The method features simple instrumentation and can be implemented in portable analyzers for express control of aerosol air pollutants.

Let us consider in detail the potential of this method. As known, some natural crystals (quartz, tourmaline, etc.) undergo mechanical deformation when exposed to electric field. When an alternating electric field is applied to a piezoelectric plate, it starts to vibrate at a certain frequency. If the frequency of the alternating electric field is close to the intrinsic mechanical vibration frequency of the plate, then the latter, being involved in the positive feedback loop of the generator, forces the latter to generate a frequency equal to this resonance frequency. The intrinsic vibration frequency of the crystalline plate depends on the shear angle of the crystal, the thickness and density of the place, and, consequently, on its mass. The intrinsic vibration frequency decreases with increasing mass of the plate.

The method of a highly sensitive piezoelectric weighing, proposed in late 1950s, is based on the dependence of the intrinsic vibration frequency of a piezoelectric plate on the mass of a substance deposited on its surface. The mass concentration of the particles is given by the following equation:

$$\Delta f = f_1 - f_2 = -A/S\Delta m, \tag{9}$$

where $f_1$ and $f_2$ are the vibration frequencies of the resonator before and after deposition of particles on the plate surface ($\Delta m$); $A = f_0^2/\rho N$, mass sensitivity of the resonator; $r$, density of the piezoplate material; $N$, frequency factor the resonator plate; and $S$, area of the vibrating part of the plate. As the $A$, $N$, and $S$ values are constants for the given plate, the $\Delta f = F(\Delta m)$ function is linear.

At present this method is widely used to determine the thickness of films (up to a few tens of nanometers), in trace analysis, as well as in research on physicochemical phenomena associated with changes in the mass of substances. The suitability of piezo-quartz microweighing for the determination of the mass of aerosol particles was first demonstrated by the example of micrometeorites.

The experimental methods used to deposit particles on the surface of piezo-quartz plates can be divided into two groups: the first includes inertial impaction and the second, electrostatic deposition. Piezo-quartz microweighing of particles deposited by inertial impaction on the thin film of an adhesive substance applied on the plate surface seems more rational, because in this case, first, the possibility of strong adhesion of the particles (especially coarse) to the substrate increases considerably and, second, one can ensure a high degree of localization of the deposited particles in the central, the most sensitive zone of the quartz resonator. Moreover, the sampling process here is much more facile and controllable.

Thus, the brief consideration of the methods of determination of the mass concentration of atmospheric aerosols shows that *gravimetry and piezo-quartz microweighing* allow *direct* determination of particle mass. Optical methods of analysis, instruments with α- and β-radiation sources, and some other methods are, to a certain extent, indirect, because they measure not the mass of aerosol particles but a certain mass-related parameter (reflection, transmission, particle charge, etc.). Furthermore, piezo-quartz microweighing both continuous mass analysis and control of immediate (peak) changes in aerosol concentration up to the measurement of the mass of a single particle (due to its low absolute detection limit, reaching ca. $10^{-11}$ g).

Impressive progress of the methods of measurement of the number concentrations and size distribution of aerosol particles should also be mentioned. Such information is important for complex assessment of the ground-level air pollution. Moreover, knowledge of the number concentration of particles is quite essential for cleanliness assessment of facilities for high-purity production and processing engineering.

## Methods of Environmental Pollution Control

The above-described methods of technological control of the composition of impurities in high-purity substances can also be used in environmental monitoring.

In the very general case, pollutants entering the environment due to natural processes or human activity as gases, vapors, aerosols, and liquid and solid industrial and domestic wastes, are complex mixtures of organic and inorganic compounds. The environmental samples contain both hazardous pollutants and natural background micro- and macrocomponents and have the following properties:

– complex and extremely inhomogeneous total composition;

– wide range of component concentrations;

– as a rule, lack of a priory information on the initial component composition;

– limited “life span,” tendency for aging and transformation;

– each sample is, to some extent, unique and reflect the state of the environment in real time.

Studying such complicated objects require much larger volumes and higher level of theoretical and experimental work, and trace analysis of toxic and extremely toxic compounds is much more demanding to instrumentation and methodology in terms of the choice of detection technique and development of rational protocols and algorithms of sample treatment and analysis. The problems of sampling and metrological support are of primary importance in this field.

From the metrological viewpoint, environmental pollution control generally is a complex scientific research involving complicated multifactorial experiments not infrequently using unique instrumental equipment.

In terms of management, special attention should be paid to stationary (automated) monitoring stations and mobile laboratories which provide express information on increased pollutant levels with simultaneous sampling in any site of a territory under control.

One of the authors of the present paper (A.Z. Razyapov) proposed to establish a new applied science and define it *geoecometrics* [18]. Geoecometrics is a field of knowledge about measurements in ecology, which would focus on the development of the *methodology and principles of measurements*, *entire range of methods of environmental measurements, as well as technical means (systems) used for these purposes.*

Modern methods of environmental measurements, used for detection, identification, and determination of the component and concentration composition of pollutants in environmental matrices can be divided in three independent while interrelated, to a certain extent, groups [18]:

– *laboratory methods* involving *taking samples* and study (*analysis*) of an object to be controlled in *a specialized laboratory*;

– *express (or field) methods* realized by means of *mobile instruments on-site*;

– *remote sensing methods* based on the *principle of direct measurements*, when an instrument (measurement complex) is located *at a certain distance from an object to be controlled.*

The most representative is the group of laboratory methods [19] which are presently used in the overwhelming majority of studies involving detection, identification, and quantitation of pollutants in the environment. As already mentioned, virtually the entire arsenal of analytical methods, which allows the detection of various pollutants in the atmospheric air, aqueous media, and soils, is employed in such studies.

The list of environmental pollutants which are subject to control includes a variety of organic and inorganic compounds. First of all we would like to focus on the group of *biophylic elements,* such as vital elements which are divided into *macrobiogenic* (H, C, N, O, Cl, Br, S, P, Na, K, Mg, Ca) and *microbiogenic* elements (V, Mn, Fe, Co, Cu, Zn, B, Si, Mo, F).

Of chemical elements, mercury, chlorine, and radioactive elements (thorium, uranium, and radon) are considered hazardous for human health and the environment. The group of *simple compounds* belonging to hazardous pollutants includes *carbon monoxide, sulfur oxides, nitrogen, gaseous fluorides (HF), chlorides (HCl)*, etc. Most hazardous pollutants are organic and inorganic compounds of anthropogenic (technogenic) origin and some of them are *xenobiotics*.

Environmental pollutants are regulated by means of maximum allowable concentrations (MACs). In the Russian Federation such standards have been established for about 100 substances in air, 1440 in aqueous media, and more than 100 in soils. At the same time, one of the important parameters in sanitary regulation is toxicity. *Toxicity* (from Greek *toxikon,* i.e. poison) is defined as the ability of a substance to disturb the physiological processes in human body, which, in its turn, may cause disease or death. The degree of toxicity is characterized by a *dose, i.e. the quantity of a substance per animal or human unit weight* that causes a definite toxic effect. Obviously, the lower is the dose, the higher is toxicity. According to the data of the World Health Organization (WHO), of about *500000 of organic and inorganic substances used in industry and household activities, more than 40000 are hazardous to human health and about 12000 are toxic.*

An attempt to form a list of priority pollutants to be controlled at different levels, as well as to develop the Global Environment Monitoring System (GEMS), was undertook as far back as mid-1980s at the first International (intergovernmental) Meeting on Monitoring, based on the following criteria:

– threat of actual or potential effects on climate, ecosystems, and human health;

– tendency for degradation in the environment or accumulation in food chains or human body;

– possibility of chemical transformation in physical or biological systems so that the resulting substances are more toxic;

– mobility in natural media;

– concentration trends in the environment and human body;

– frequency, levels, and magnitudes of exposure;

– possibility of detection and quantitation in various natural media;

– significance for assessing the state of the environment;

– suitability, because of the distribution in the biosphere, for constant regional and global monitoring.

In terms of toxicity to living organisms and plants, metals were ranked as [18]:

Hg > Cu > Zn > Ni > Pb > Cd > Cr > Sn > Fe > Mn > Al (to animals and humans), Ag > Hg > Cu > Pb > Cd > Al > Zn > Ni > Cr > Co > Mn > Sr (to fish), and Hg > Pb > Cu > Cd > Cr > Ni > Zn (to plants).

Particular risk to humans and the environment comes from persistent organic pollutants (POPs) [20]. There compounds are highly toxic and can accumulate in the environment and living organisms. The list in the Stockholm Convention signed by 110 States (including Russia) initially included twelve POPs: aldrin, endrin, chlordane, mirex, dieldrin, DDT, hexachlorobenzene, toxaphenes, heptachlor; polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs). In 2003 this list was extended to 28 by including alkyl derivatives of lead, tin, and mercury, polyaromatic hydrocarbons (PAH), chlorinated arenes, chlorinated paraffins, and phthalates.

In 1990s the European Commission published a list of substances subject, according to the WHO recommendations, to obligatory monitoring in urban air. This list includes carbon monoxide, sulfur dioxide, nitrogen dioxide, total particulate matter (TPM), particulate matter with a diameter equal or smaller than 10 μm ($PM_{10}$), lead, ozone, benzene, cadmium, arsenic, nickel, mercury, and polyaromatic hydrocarbons (benzopyrene).

About at the same time a regulatory document containing a list of pollutants to monitor in the emissions of metallurgical facilities, thermal power stations, and waste incinerators was developed and adopted. Table 2 presents this list for waste incinerators.

**Table 2.** Pollutants and their allowable levels in waste incinerator emissions, mg/m$^3$

| Pollutant | Daily mean concentration | 30-min mean concentration |
|---|---|---|
| Total dust | 10 | 30 |
| Total organic matter | 10 | 20 |
| Gaseous chlorine compounds | 10 | 60 |
| Gaseous fluorine compounds | 1 | 4 |
| Sulfur dioxide | 50 | 200 |
| Total nitrogen dioxides | 200 | 400 |
| Heavy metals[a] (15) | 0.05 | 0.05 |
| Dioxins and furans | $10^{-7}$ | $10^{-7}$ |

[a] Lead, cadmium, mercury, chromiun, zinc, manganese, cobalt, nickel, arsenic, etc.

There are also substances related to greenhouse gases, which, according to the Kyoto Protocol, should be monitored at their emission sites. The same relates to ozone-depleting substances whose emissions are regulated by the Montreal Protocol (divided into 4 groups: A, B, C, and D).

Let us restrict ourselves to the consideration of atmospheric aerosols. First of all let us focus on the following fact. The present environmental monitoring systems in the Russian Federation deal with a fairly wide range of pollutants. However, as to the aerosol component of atmospheric pollutants, they allow determination of only total mass concentration of particulate matter. At the same time, the greatest health impact is associated with micron and submicron particles. Therefore, according to the WHO recommendations, over the past years the air quality monitoring services in some towns of the USA and Europe, along with monitoring of the total mass concentration of aerosols, have started to monitor PM$_{10}$.

We initiated research on such particles together with the Moscow Department for Environmental Management and Protection.

Below we present the concentrations of finely dispersed particles in the atmospheric air, measured in different districts of Moscow with direct participation of one of the authors of the present paper (A.Z. Razyapov). The measurements were performed using an AIR METRICS miniVOL sampler (USA). It was found that the concentrations of PM$_{10}$ in different administrative districts of Moscow varies from 0.120 to 0.254 mg/m$^3$ (Table 3).

**Table 3.** PM$_{10}$ levels in different administrative districts (AD) of Moscow, mg/m$^3$

| Southern AD | Central AD | Eastern AD | Southeastern AD |
|---|---|---|---|
| 0.120 | 0.170 | 0.143 | 0.190 |
| 0.170 | 0.253 | 0.180 | 0.171 |
| 0.160 | 0.190 | 0.180 | 0.191 |
| 0.143 | 0.160 | 0.190 | 0.202 |
| 0.182 | 0.140 | – | 0.254 |
| 0.143 | 0.190 | – | 0.180 |

As seem from Table 3, the mass concentrations of PM$_{10}$ is lower than the maximum allowable single concentration (MAC$_s$) of particulate matter (0.5 mg/m$^3$), however these values proved to be slightly higher than the maximum allowable daily mean concentration (MAC$_{dm}$) of 0.15 mg/m$^3$.

Table 4 lists the concentrations of heavy metals in the PM$_{10}$ samples taken in an industrial district with an intense traffic. Moreover, such samples also contained iron, manganese, chromium, aluminum, *benzopyrene* (0.2–0.8 ng/m$^3$), and other pollutants.

We also estimated daily mean concentrations of TPM, PM10, and a diameter equal or smaller than 2.5 μm (PM$_{2.5}$) by taking samples concurrently with three AIR METRICS miniVOL instruments. Table 5 lists the resulting data.

The AIR METRICS miniVOL system includes a portable pump, calibrated flow meter, programmable

**Table 4.** Concentrations of heavy metals in PM$_{10}$ samples

| Metal | Concentration, mg/m$^3$ | MAC$_{dm}$ in the atmosphere, mg/m$^3$ |
|---|---|---|
| Lead[a] | 0.0001 | 0.0010 |
| Cadmium | 0.0003 | 0.0003 |
| Copper | 0.0020 | 0.0020 |
| Zinc[a] | 0.0050 | 0.0050 |
| Nickel | 0.0010 | 0.0010 |

[a] MAC$_s$.

timer, and a holder for a standard 47-mm aerosol filter. The system is also equipped with a unit for temperature compesation, which allows the flow rate to be maintained constant within ±5 % in the temperature range from 0 to 40°C.

Power supply of the sampler is provided by a battery pack which can be fairly quickly recharged with the included charger.

The impactor provides preseparation of aerosol particles entering the sampler. The filter in this system collects particles larger than 10 μm, when operated in a one-cascade mode and particles larger 2.5 μm, when operated in a two-cascade mode. For particles of the desired size to be collected, it is necessary to maintain a constant flow rate through the inlet (5 L/min for the model in hand).

MiniVol samplers allow continuous 24-h sampling of particles of different sizes at a rate of 5 L/min (6–7 $m^3$ a day). The instruments are easy to operate and can be used to monitor aerosol pollution of air basin in Moscow. The $PM_{10}$ samples can also be used to determine different chemical elements, including heavy metals.

To introduce the monitoring of finely dispersed aerosol particles into practice, further research with the use of MiniVol samplers at stationary monitoring stations is required. This equipment was also be used for estimating aerosol emissions of major industrial enterprises by sampling air in their buffer zones and residential districts adjacent to these enterprises. At present the impact of one or another enterprise is estimated by taking 20–30-min samples and comparing the obtained data against the $MAC_s$.

The results of such research can present interest for assessment of pollutant transfer within local urban area, including the contribution of transboundary transfer of pollutants from remote sources. The latter are primarily power stations, metallurgical and metalworking facilities, incineration plants, and other powerful industrial sources of aerosol emissions.

Field (on-site) methods of chemical analysis allow real-time monitoring of atmospheric air, surface waters, and soils by means of mobile analyzers.

The monitored substances and parameters are as follows: mercury, carbon monoxide and dioxide, total hydrocarbons, oil products (in soil and water), heavy metals (chromium. manganese, lead, iron, etc.), as well as meteorological parameters, pH, and radioactivity. In what follows we consider the most efficient portable field analyzers.

**Table 5.** Concentrations of particulate matter, $mg/m^3$

| Total PM | $PM_{10}$ | $PM_{2.5}$ |
|---|---|---|
| 0.027 | 0.021 | 0.012 |
| 0.016 | 0.012 | 0.007 |
| 0.043 | 0.025 | 0.021 |

The universal instrument UKR-1 MTs measures mercury in air, natural and waste waters, drinking water, food products, soils, grounds, and wastes. The principle of measurements is atomic absorption; two measurement modes are available: direct measurements and measurements with preliminary accumulation of mercury vapor on a gold collector (sorbent). In the analysis of water and solutions, chemical reduction of mercury is applied ("cold vapor" method), and in the case of soil and solid mineral wastes, thermal sublimation.

Ecoprobe-5 (Czech) is a unique portable instrument with infrared and photoionization detectors for express analysis of underlying terrain emissions for hydrocarbons, methane, and carbon dioxide. The instrument is also capable of measuring oxygen and the soil temperature at the land piece in focus.

The metal, soil, and ore analyzers Delta Standart, Delta Classic DC-2000, and Delta Premium (USA) are among the best portable X-ray fluorescence analyzers. They allow determination of a wide range of chemical elements (including biogenic elements, noble metals, etc.): Mg, Al, Si, P, S, Cl, Ar, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ta, W, Re, Os, Ir, Au, Hg, Tl, Pb, Bi, Po, At, Fr, Ra, Ac, Th, Pa, U, Np, and Pu in ores, alloys, industrial wastes, soils, etc.

The third group of analytical methods in environmental studies includes remote sensing methods. The potential of remote sensing (RS) in solving research and applied tasks of the environmental science, studying global natural resources of the Earth, and meeting demands of different branches of industry and power engineering is quite high [20–24]. These methods allow one to promptly identify the type and features of an object in satellite images, assess the state of the object, trace the dynamics of negative natural pro-

**Table 6.** Objects for remote sensing and expected results

| Monitoring object | Solved tasks |
|---|---|
| World Ocean | Detection of vortices and streams, distribution and concentration assessment of phytoplankton and inorganic suspensions, detection of oil spills |
| Volcanos | Monitong of gas, ash, and magma outbursts |
| Space and near-Earth space | Earth's limb and space debris imaging, monitoring of ozone layer, tomography of the upper atmosphere |
| Main pipelines | Control of pipelines, identification of microcracks and cracks, control of ground dynamics |
| Oil terminals | Control of tank filling, shell deformations, and oil spills (including underground tanks) |
| Megapolices | Detection of current and peak pollutant emissions and their sources |

cesses and phenomena, and, based on this multidimensional information, make appropriate managerial decisions. The range of tasks which can be solved by means of remote sensing is therefore very wide (Table 6).

Let us focus on two quite important fields of application of RS methods for solving global environmental problems.

First of all this is the detection of oil spills on the surface of the World Ocean and monitoring of their propagation by means of airborne radar images. In this connection, it is appropriate to remind here the recent environmental disaster associated with a huge oil spill caused by an explosion at the BP oil rig in the Gulf of Mexico. Oil pollution of marine and oceanic waters is highly dangerous for the flora and fauna of the World Ocean. To reduce this risk, it is necessary to have a real-time information on the location and dynamics of an oil spill for taking appropriate measures for preventing such situations, for example, alleged oil dumping on cleaning of tanker vessels, as well as for removing of already spilled oil.

The second is the *monitoring of volcanos and volcanic* a*ctivity*, for example, observation of different phases of volcanic eruptions in the IR spectral range with continuous monitoring of gas, ash, and magma outbursts. Here we would like to remind the Eyjafjallajokull volcano eruption in Island on April 14, 2010. A huge plume of volcanic ash reached the Northern Europe coast. Within a day the ash cloud reached the Moscow Region. The eruption paralized air transport: more 5000 flights were cancelled both within Europe and in many other coutries.

Laser remote sensors allow monitoring gaseous pollutants, the mass concentrations and distribution of aerosol particles in the atmosphere, as well as water and snow pollution. As mentioned above, sensing equipment is set up in aerospace (satellites, aircrafts, helicopters) and motor vehicles. The promise of laser spectroscopic remote sensing methods can hardly be overestimated, taking into account that these methods have already found wide use in global and regional environmental monitoring systems. Fairly many examples of the use of such equipment at monitoring stations in large cities and industrial centers for tracing the dynamics of pollution and emissions of powerful stationary sources and motor transport.

Remote monitoring of atmospheric pollution is performed by means of *open-path gas analyzers*. Their operation principle is based on the differential optical absorption spectroscopy (DOAS) which measures absorption by atmospheric gases in the UV spectral region. The spectometer incorporated in the gas analyzer detects changes in the spectral distribution of the radiation, caused by absorption by the gaseous components of the air sample, as the radiation makes the path between the source and receiver The measured absorption spectra allow identification and quantitation of gaseous pollutants.

The principle of operation of open-path gas detectors is as follows. Radiation from a light source (xenon lamp) is directed through the atmospheric region of interest along a chosen optical path. The reflector located at the opposite end of the path directs part of the light beam back, and it is registered by the spectral detection system. The processing system compares this spectrum with the source spectrum, thereby revealing changes caused by the absorption of the gaseous components of the atmosphere. The potential application fields of open-path gas analyzers are:

– background monitoring of atmospheric air;

– control of transboundary pollutant transfer within local territories;

– control of general air pollution and emission sources in cities and industrial centers.

The domestic open-path gas analyzer DOAS-M1 was developed at the Obninsk Photonics company (Obninsk, Kaluga Region) [25]. Table 7 lists the compounds which can be detected by means of DOAS–M1 and their detection limits.

Among foreign open-path DOAS analyzers we would like to mention OPSIS (Sweden), DOAS–2000 (USA), and SANOA (France). It should be noted that the OPSIS instruments are set up in Moscow and St. Petersburg (in the capital, for example, along the 3rd Transport Circle, at the Gagarin Square, and near the Bekket Pond). These systems allow automated 24-h monitoring of carbon, sulfur, and nitrogen oxides, ozone, phenol, styrene, formaldehyde, benzene, toluene, etc.

Laser sensing is based on the following processes involved in the interaction of laser radiation with the matter:

– Rayleigh and Mie scattering;

– Raman and resonance scattering;

– absorption and fluorescence.

Remote sensing of atmospheric pollution holds much promise, especially at industrial urban territories with a high concentration of industrial emission sources and motor traffic.

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